Process Analyzers

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Process Analyzers

Section A—Process Analyzer Considerations

A.1 Scope

Process monitors that measure and transmit information about chemical composition, physical properties, or chemical properties are known as *process analyzer systems.* Many of these systems were first developed for laboratory analysis. Today they are primarily used as continuous on-line analyzers.

A process monitoring system usually requires a sample conditioning system, a process analyzer, and one or more data output devices. Properly designed systems also require overall considerations as to calibration, utilities, sample disposal, safety, and systems packaging.

Process analyzers measure chemical concentrations or physical or chemical properties that can be used as control variables instead of relying on indirect physical parameters, such as pressure, temperature, and inferred data from computer models. Process analyzer systems can provide a significant economic return when incorporated into process optimization and advanced control loops or when used for product quality control.

This section will address the generic design factors that must be taken into consideration in the design and implementation of all analyzer applications.

Chapter 1 provides general information to be considered in the design of analyzer systems.

Chapter 2 describes the requirement for analyzer system data management.

Chapter 3 provides information on analyzer calibration and validation.

Chapter 4 provides an overview of analyzer sample system design considerations.

Chapter 5 describes the benefits of pre-packaging analyzer systems versus field construction methods.

Chapter 6 provides information on the installation and maintenance of analyzer systems.

Chapter 7 provides information on safety in the design of analyzer systems.

1 Analyzer Selection Design Requirements

1.1 Economic Considerations

Analyzer systems can improve product quality, increase the yields of products with higher economic value, increase product throughput and output, and reduce energy costs.

Process analyzer systems should be considered for product quality control when frequent and rapid measurements are required because of fast and substantial variations in process stream quality.

If an analyzer system is to be installed to improve operational efficiency of a process unit, the installation should be justifiable from an economic standpoint. Increased profit from improved efficiency combined with decrease in off-spec material produced must be weighed against the cost of installing, operating, and maintaining the system.

1.2 Environmental and Safety Considerations

Today, environmental standards are becoming more stringent. The use of analyzers for safety or environmental monitoring should be considered in compliance with the regulations of the agencies specifying such monitoring and documentation requirements.

Process analyzers are used to detect hazardous plant conditions and for monitoring government-mandated requirements concerning pollutants in ambient air, stack emissions, risk mitigation, equipment, personnel protection, and effluent streams.

1.3 Technical Considerations

Several technical criteria should be considered when specifying a process analyzer. These are often summarized in a data sheet, and most often would include the following information.

a) *Measured variable*: The variable of interest could be a pure element (such as O_2, H_2, or N_2), an inorganic compound (such as CO, NO_2 or H_2SO_4), an organic compound or group (such as CH_4, C_{6+} or TOC), a chemical property (such as pH, ORP, or electrolytic conductivity), or a physical property (such as specific gravity, opacity or vapor pressure).

b) *Measurement range*: The range of measurement includes a lower limit (not always zero), and upper limit and the unit of measurement. When the unit of measurement is percent, ppm or ppb, the measurement basis should be included (i.e. mole %, weight ppm, etc.)

c) *Measurement purpose*: It is important to establish the analyzer purpose, such as process monitoring, process control, quality control, safety, regulatory compliance, etc. in order to make a proper analyzer selection.

d) *Complete Stream Composition*: Provide expected sample stream composition of all components in the stream. This should include the minimum and maximum concentrations, toxic and corrosive properties. This information will be used to maximize the analyzer's capability to function properly during startup, upset process conditions, and to properly design sample conditioning systems. Provide all operational parameters at the sample point (pressure, temperature, and flow) including the minimum, maximum, and design values. This information will be used to determine the sample extraction probe design or in situ interface, when required.

e) *Application method:* First a determination must be made regarding whether a physical or chemical property or a composition analyzer is required. Then a determination must be made on the specific measurement method (such as infrared spectraphotometry, gas chromatograph, chemiluminescence, etc.). Such method is typically selected for a particular measurement or analysis according to process experience.

f) *Repeatability and accuracy:* The design of all analyzer applications should consider accuracy and high/low limits of detection. Emphasis is usually placed on analyzer stability and repeatability of the measurement. The capability of the analyzer must match the requirements of the analysis required.

g) *Analyzer Availability:* A goal of 95 % or greater on-stream factor of on-line availability is generally desired. Analyzers exhibiting less than 95 % are generally not considered reliable by operations. Analyzers should operate at 98 % or greater availability for use in closed loop control applications. Analyzer availability is defined as the percentage of time the analyzer is operating reliably, relative to process operations. Reliability of the analyzer system, commitment of maintenance personnel, and ease of maintenance contribute to Analyzer Availability.

h) *Overall system response time:* This is the total time required to take a representative sample, transport, condition, analyze the sample, and transmit the measurement results.

i) *Sample conditioning:* The location of the sample tap in the process is important to obtain a representative sample. Ensure that the process conditions are a single phase (100 % liquid or gaseous) at the sample tap. A sample conditioning system must extract, transport and deliver a representative, contaminant-free, single phase sample to the analyzer, conditioned for pressure, temperature and flow. One method of sample conditioning is to provide a sample probe.

j) *Sample Probe*: The sample probe provides primary particulate rejection through kinetic energy. This is accomplished by the process fluid velocity and prevents pipeline “wall creep” debris from entering the sample transport tubing. Thus the sample probe is an essential component of the sample system. See 4.3.3 for additional information on sample probes.

k) *Installation:* Consideration must be given to area electrical classification, protection from the environment, ambient temperature variation effects, ease of availability for maintenance, cylinder storage and replacement accessibility, and sample disposal requirements. The location of sample taps and fast loop requirements should be evaluated when determining analyzer shelter placement.

l) *Maintenance:* Maintenance requirements including frequency, and resources should be considered early in the design phase.

m) *Operating costs:* These should include the cost of utilities, consumables, spare parts, labor, and maintenance.

n) *Safety:* Personnel shall be protected from hazardous conditions associated with analyzer systems. These include toxic, explosive, chemical, electrical, and mechanical hazards.

o) *Training*: Training of operations and maintenance personnel is necessary to ensure the analyzer functions as designed throughout its life cycle.

p) *Environmental requirements:* If an analyzer is required for regulatory monitoring the analyzer must comply with all applicable regulations.

2 System Data Management Requirements

2.1 General

Data transmission is an important consideration in the analyzer system design. Three types of transmissions are common: analog transmission, digital transmission, and discrete.

2.2 Analog Transmission

The electronic output signal from the analyzer is a voltage or current proportional to the measured parameters in the stream. The most common analog signal is 4-20 mA DC. Analog signal loops may be powered from the analyzer (4-wire transmitter) or from the receiving device (2-wire transmitter). A few analyzer manufacturers use the 0-4 mA range of a 4-20 mA signal to transmit special alarms for diagnostic information.

2.3 Digital Transmission

Analyzer communication via a direct serial link is a means of transmitting measurement and status information. Analyzers equipped with one or more serial ports can be interfaced to networks and/or devices such as a printer, central processor unit, personal computer, host computer, or basic process control system (BPCS). Serial ports are also capable of two-way communications. The data messages communicated are not limited to concentration values and may include such things as alarms, system status, data validation or calibration commands, program commands, and diagnostic maintenance routines such as reconstructed chromatograms for process gas chromatographs.

Analyzer status information available through a serial port can include data validation status and hardware status information that can be used by the BPCS for implementing process control strategies.

Typical alarms for data validation are as follows:

a) tolerance against calibration check (validation) drift;

b) excessive change of data output;

c) excessive baseline noise and drift;

d) peak drift for gas chromatographs;

e) communication failure;

f) EPROM error;

g) optical integrity for photometers/spectrometers.

Typical alarms for analyzer system status information include the following:

a) loss of sample flow;

b) loss of utilities;

c) hardware failure;

d) loss of pressurization;

e) loss of power;

f) temperature inside shelter;

g) toxic/LEL inside shelter;

h) oxygen deficiency in shelter.

For multi-analyzer distributed systems, each analyzer produces output data completely independent of any central programmer or central computer system, data highways are used for transmitting analytical data and analyzer status information. Data highways allow many analyzers to communicate through one network to a central location. A distributed system typically may also contain a central operator station for analyzer management and maintenance. Such communication requires simple installation of only two to four wires for linking all the analyzers in the system. Precautions must be made to protect this highway path from the risk of damage or failure so all communications and control will not be lost. For example, if a redundant highway is available, each path should be routed in different physical paths.

Figure 2-1 represents a general multi-analyzer distributed system with typical highway links. Most highway systems then link to a BPCS through a common gateway with a standard communication protocol. The analyzer communication interface connecting to a host device must be coordinated between equipment suppliers to assure compatibility. The communication may require writing a driver program to collect and format the data so as to be compatible with the host device.

Remote links incorporated into analyzer highway systems can include a modem link for remote factory maintenance support.

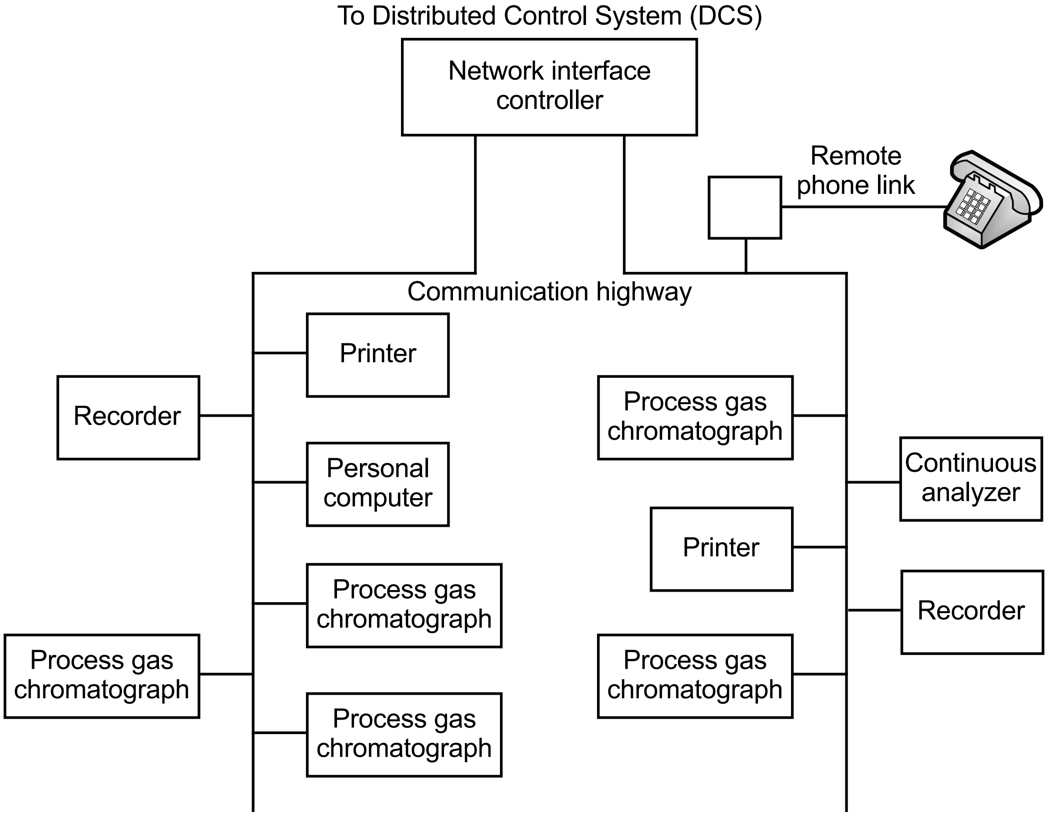


Figure 2-1—Multi-analyzer Distributed System

2.4 Discrete Transmission

Discrete contacts may be available to transmit status information such as validity, analyzer integrity and alarms. Such contacts carry a design rating that must be compatible with the voltage and current to be applied in the loop (i.e. 24V DC, 1 amp). Most often voltage for a discrete signal loop is provided from the receiving device rather than from the analyzer (dry contacts). Both the contact rating and the source of loop power should be determined in advance to ensure loop functionality.

2.5 Other Types of Protocols

Other types of protocols provide diagnostics and additional alarm signals not usually available through analog or discreet outputs. Refer to the different suppliers for their specific capabilities.

3 Analyzer System Calibration and Validation

3.1 General

To determine whether an analyzer is performing properly, it should be checked against calibration/validation samples.

3.2 Calibration

3.2.1 General

Calibration is an important part of the startup, as well as the continuing operation of a process stream analyzer. Depending upon the type of analyzer, its history, and how critical its analysis may be, calibration can be an occasional or routine check to see if the analyzer is operating within acceptable limits.

This section discusses only general methods of calibration because the types of analyzers are too numerous and varied to give specific details for each. The manufacturer's instruction manuals are usually detailed enough to determine the preferred method for calibrating a particular analyzer.

3.2.1.1 Purpose of Calibration

Before an analyzer is shipped from the manufacturing facility, it is operationally tested by the manufacturer to demonstrate performance to design specifications. This calibration data can then be used as a reference for future operational and performance analyzer checks.

It is recommended that an owner or owner's representative witness calibration during inspection at the manufacturer's facility and also during commissioning. Calibration will also be required after a maintenance shutdown or after replacement of parts in the sensing mechanism (such as light or power sources, detector elements, or columns, in the case of a chromatograph). Process plant operators may also request a check as part of plant operations.

Quite often calibration is only verification rather than an update or change in the analyzer's calibration factor(s). Apparent disagreements between analyzer and laboratory results are sometimes due to differences between sampling or measurement techniques between the off-line and on-line data. When comparing lab analysis to process analyzer data wrong time stamping and failure to consider test method reproducibility and analyzer repeatability are common mistakes. Historical records may be used to understand the differences and to indicate whether disagreement is an actual error or not (see 3.2.3.5). Statistical Quality Control techniques may be employed to determine if the analyzer should be re-calibrated or merely validated (i.e. calibration components are measured, but the factors are not updated).

3.2.1.2 Personnel

In most plants, an analyzer maintenance specialist is responsible for the validity and accuracy of the measurement. Refer to Chapter 6 for the qualifications of calibration and commissioning personnel.

An understanding of the sample's chemistry and the analyzer's measuring method will help in procuring suitable standards and in calibrating the device. Laboratory personnel involved in preparing or analyzing calibration standards should understand the principle or technique used in the process analyzer.

Familiarity with measurement units with each type of analyzer [such as mole percent, liquid volume percent or PPM (v/v)] is important for performing a successful calibration.

The analyzer maintenance specialist should understand the process analyzer's theory of operation. This can be useful in deciding whether a change in results is due to component failure or aging.

The specialist should also understand the operation of the sample system associated with the analyzer, since problems with calibration can be caused by problems of the sample system itself.

3.2.2 Standards for Calibration

3.2.2.1 Sources for Standards

Sources for calibration should be certified and traceable to standards provided by the National Institute of Standards and Technology (NIST), or other governmental laboratories that provide traceable certified standards.

A source for calibration information is a laboratory analysis of samples taken from the identified process stream. To avoid possible errors, the container utilized for lab analysis should be used for the process calibration check, thereby maintaining the uniformity of the media. The lab analysis should be made on more than one analyzer where possible. Lab results should then be averaged and the variation in results should be within the test method reproducibility.

Multiple samples and laboratory analyses, plus knowledge of the laboratory's confidence factor are needed to translate the analysis to a standard value. Differences between the laboratory analytical method and the process analyzer's analytical method may result in different measurement data. The confidence factor will indicate if the results are reasonable. The traceable standard should be used as a baseline.

A process line sample calibration uses laboratory analyses of plant samples drawn during steady-state operation. Analyzer readings are noted and then used to make new settings if significant differences are detected. Daily (or routine) laboratory results are used to plot trends for comparison with those of the process analyzer; however, the analyzer may have inherent drift tendencies that must be corrected for on a more frequent basis to achieve the highest accuracy.

A reference sample can be either a retained process stream taken during normal or desirable operation, as described above, or a synthetic blend prepared, analyzed, and certified by a commercial supplier. The synthetic standard may be necessary for materials that react with other ingredients when left standing, or when cooled, or to allow calibration of a material that polymerizes or decomposes with time. "Pure" compounds (gas or liquid) can be used to set the "span" or full-scale reading for some analyzers just as pure air or nitrogen can be used to obtain a zero setting. The retained process stream can serve as an inexpensive "secondary standard" to verify analyzer operation, using the expensive and complex synthetic blend only when required to resolve response issues or full calibration. On occasion process samples can be hazardous and alternative safer calibration fluids can be found. For example, safer fluids are with similar physical properties or chemical composition without the hazardous fluid.

3.2.2.2 Equipment for Calibration

Cylinders containing the calibration standard are often stored at the analyzer location. Some provision should be made for protecting the cylinders from the elements and from tampering. Records of the standard's analysis should be filed for future use since tags or stencil markings on the cylinders can fade or become illegible. Temperature-sensitive samples vapor or liquid, must be stored and used under their design conditions.

Maintain proper records of Certificate of Analysis for all standards used for calibration/validation of process analyzers. These standards must be replaced or recertified upon the expiration of the Certificate of Analysis. Proper storage and connection of calibration standards should be considered in design.

Regulators should be reserved for "standard" service to minimize contamination errors. Tools required to connect and disconnect standard sources should be a part of the operating supplies. Thermometers, pressure gages, flow-measuring devices, and other tools are often needed to verify calibration.

A facility may prepare "check" standards on-site. Additional equipment required includes absolute pressure gages, vacuum pumps, cylinders of "pure" gases to make gas blends, and containers of "pure" liquids to make liquid mixtures.

A supply of small cylinders to transport pressurized samples to a laboratory for checking can be useful for off-line verification.

3.2.3 Calibration Procedures

If service work that can change the output signal of an analyzer is to be performed, the operations personnel should be notified. If the analyzer is used for process control then steps must be taken to switch the controller to manual mode or hold mode.

All calibration procedures should be well documented in a written step-by-step form to ensure repeatability between technicians.

3.2.3.1 “Automatic” Calibration Systems

If the analyzer system is automated to the extent that it periodically (daily or weekly) checks its output reading against a standard, personnel servicing the analyzer may be required only to check the flow rate or pressure gage readings or to verify the operation of solenoid valves. Programmed limit values can be used to alert the user to abnormal readings.

A semiautomatic system allows the service person or process operator to check or update analyzer readings. Again, sample pressure or flow should be checked visually or by the programmed limits.

A preliminary check of the standard(s) should include details such as the age, pressure, or volume remaining and the ambient temperature.

3.2.3.2 Zero/Span Calibration Systems

Some analyzers are calibrated by adjusting the output readings of a fluid containing none of the components of interest (zero) and then adjusting the output readings to match another fluid containing a high-scale amount of the component (span). The high scale value is typically about 80 % of full scale. For such analyzers, the following calibration procedures are recommended.

a) Turn off the process sample to the analyzer.

b) Turn on and adjust the flow of the zero standard.

c) When readings stabilize, make adjustments if necessary.

d) Turn off the zero standard.

e) Turn on and adjust the flow of the span standard.

f) When readings stabilize, make adjustments if necessary.

g) Turn off the span standard, and turn on the process stream flow.

Several iterations will be required if the zero and span adjustments are interactive. Double Block and Bleed valves can be used to improve isolation of process fluids when introducing calibration fluids to prevent cross contamination.

3.2.3.3 Complex Analyzer Systems

In more complex analyzer systems, standards containing one or more components of interest are introduced to set or verify factors. For such analyzers, the following calibration procedures are recommended.

a) Set the analyzer controls to calibration or manual mode, and suspend process values normally at existing values.

b) Turn off the process sample to the analyzer.

c) Turn on and adjust the flow of the standard. (If the calibration mode computes new factors, compare the new factor with the old factor.)

d) Run multiple analyses if output values differ from the standard value to confirm signal values are within the acceptable repeatability range.

e) Verify error values and if percent of the maximum error is exceeded, then adjust factor settings or enter new data to the control device.

f) Turn off the standard and turn on the process stream flow.

g) Restore the suspended values with the new process value readings.

Caution—Before updating the value of the latest factor or changing the analyzer calibration, consider the quality of the standard and the calibration history of the analyzer. Some standards can change with age. A laboratory calibration, especially for blended standards, is recommended at least every 3 months.

3.2.3.4 Alternative Forms of Calibration Check

In analyzer systems where the standard comes from a known process sample, the standard is introduced when the system is in a normal mode (except that the output is off-line). Readings are compared with the known values of the components or quality of interest. For such analyzers, the following calibration procedures are recommended.

a) Shut off plant sample flow.

b) Turn on the standard and adjust the flow.

c) When the analyzer readings stabilize, compare readings with the known values.

d) Make adjustments.

e) Rerun the standard to verify the new settings.

f) Turn off the standard and turn on the plant sample.

g) Put the analyzer system back in operation.

3.2.3.5 Calibration History

A schedule of routine calibration checking should be set up as a part of the analyzer's maintenance procedures. Records of monthly, weekly, or even daily checks serve to increase the user's confidence in the analyzer, as well as to alert the technician to signs of impending analyzer failures. A well designed analyzer system may show no change between periodic calibration checks. The checks then serve as a verification of the equipment's stability. In the case of an analyzer malfunction, the calibration procedure becomes a part of troubleshooting, either by showing an analyzer fault or directing attention to other components, such as the sample system or recorder. The frequency of these checks may vary depending upon the criticality of the measurement. Small process analysis errors can result in large economic losses. The calibration frequency depends on the process criticality and frequency of analyzer failures.

A maintenance history can be brief or extensive but as a minimum should include a log of repair, component replacement, calibration, and consumables replacement, complete with dates and technicians' names for each entry.

Many users set up individual folders for each analyzer as a means of storing these documents. Some have established computer programs for accumulating maintenance history and costs and for scheduling preventive maintenance.

3.2.4 Calibration Criteria

3.2.4.1 Accuracy

The main reason for calibrating an analyzer is to ensure that the analyzer provides an accurate result. In most cases, accuracy is limited by the standard analysis or laboratory results. If an analyzer is calibrated to an erroneous standard, the output is in error even though it may be useful for following changes in the process. The cost of achieving a certain degree of accuracy may be a limiting factor. If high accuracy is required, repeated analyses of standards, verification through parallel lab analyses, and cross-checks with the process operation are important parts of the analyzer maintenance program. The user must establish acceptable calibration accuracy criteria.

3.2.4.2 Repeatability and Reproducibility

The repeatability of a process analyzer is its ability to give the same reading, using the same method on identical test material under the same conditions. Repeatability can be stated as the difference between successive results.

Reproducibility is the closeness of agreement between independent results with the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories, and/or after different intervals of time).

3.2.4.3 Linearity

A sample standard is necessary for each calibration point. Analyzers that inherently have poor linearity will require multiple calibration points. In addition to zero and span standards, intermediate concentrations may be required to establish a “curve-fit” of detector response to concentration.

Although not a typical specification, linearity has an impact on accuracy which is typically quoted as ± % of reading. Linearity error problems usually are minimized if the analyzer can be calibrated at a value close to the normal process concentration.

3.3 Validation

Validation is confirming the analyzer readings using known samples without adjusting factors.

Fully automated systems using Statistical Quality Control (SQC) methods to flag performance issues provides validation.

Where the repeatability of the analyzer is closer than the reproducibility of the reference laboratory test, calibration/ validation samples should be multi-tested to reduce the standard error of the mean.

Detailed information on the validation of analyzers can be found in ASTM D-3764, *Standard Practice for Validation of Process Analyzers*.

Process analyzers can be installed with remote validation capability. A substantial amount of maintenance time is spent validating analyzers because of a request by operations, often with no analyzer problem. Designing the sample system with remote validation capability (e.g. from BPCS) can save in valuable maintenance personnel hours. Validation “Pass”, “Fail”, and “validation request denied” (e.g. low validation fluid flow) flags can be activated to inform the operator of the analyzer condition.

Validation results should be evaluated to determine the frequency of future validations. Too many validations are a waste of maintenance time, and too few validations can lead to excessive analyzer errors. Manufacturer recommendations should be considered.

4 Sample Conditioning

4.1 General

Sample conditioning systems are comprised of all the components necessary to extract a representative sample and to transport and condition it for measurement by the analyzer. The design of the total sample conditioning system must be engineered for each specific application.

The sample conditioning system assemblies are sometimes complex (actually small chemical processes with control systems) and if poorly designed may be often the least reliable segment of an analyzer system.

It is important that all factors that influence an overall system and the operation of an analyzer be given thorough consideration. Such factors as unknown process conditions, process upsets, and contaminants can lead to poor designs.

4.2 Functions of a Sample System

The functions performed by the sample conditioning system as the interface between the process and the process analyzer include the following:

a) Taking and delivering a representative sample from the process.

b) Transporting the sample from the sample tap to the analyzer and from the analyzer to the spent sample recovery system or process return point to reduce the sample transport time.

c) Conditioning the sample by controlling the pressure, temperature and flow rate. Filtering and phase maintenance of the sample are also addressed in order to make the sample compatible with the process analyzer.

d) Sample-stream switching and calibration/validation switching into the analyzer.

e) Control of dew/bubble point.

f) Design incorporates capability for ease of maintenance, cleaning, or (when needed) flushing the entire system.

4.3 Design Factors

4.3.1 Sample Stream Composition

The complete stream composition of all the components and contaminants must be considered. Some contaminants, such as solids or entrained liquids in a gaseous stream, may have to be removed in order to deliver a single phase sample to the analyzer. The process conditions and range of all components during normal and especially abnormal conditions (such as startup, shutdown, rate change, and so forth) must be considered for the analyzer application and sample system design.

4.3.2 Sample Point Location

The following factors should be considered in determining the optimum sample point location.

a) Locate the sample tap in the process stream where a representative sample can be withdrawn.

b) It is important to locate the sample tap such that corrective action may best be achieved in the process. Locations downstream of large vessels or accumulators should be avoided due to an increase in lag time that is introduced by the significant volume increase.

c) Locate the analyzer as near as practical to the sample point to minimize sample transport time while allowing easy access for maintenance.

d) Location should be considered to offer significant differential pressure if the sample is returned to the process. If possible, avoid sample fast loops around process control valves due to the possibility of the valve being fully open and loss of differential pressure across the valve. If this must be used ensure that the CV of the valve is such that when fully open there is sufficient differential pressure to give required minimum fast loop flow. Sample and return points around control valves present two problems: the sample bypasses the valve when it should be closed and there is little or no sample bypass flow when the control valve is wide open.

e) Locate the sample tap for ease of access for cleaning and maintenance. Sample taps should be located such that cherry pickers or ladders are not required to reach them.

f) Locate the sample point where the process reaction or mixing is stable, and avoid sample point location where mixed phases may exist.

g) Locate the sample tap on the top or side of horizontal process lines, and horizontally in vertical process lines to minimize poor sampling. See Figure 4-1.

h) Consideration should be given to the use of single or double process isolation valves in the sample line for high pressure or toxic service.

4.3.3 Sample Probes

4.3.3.1 General

Sample probes should be used because they provide a more representative sample due to the higher flow rates away from process pipe walls.

NOTE For small diameter lines, the line may be swaged up to 3 in. with a spool piece to allow a probe to be inserted.

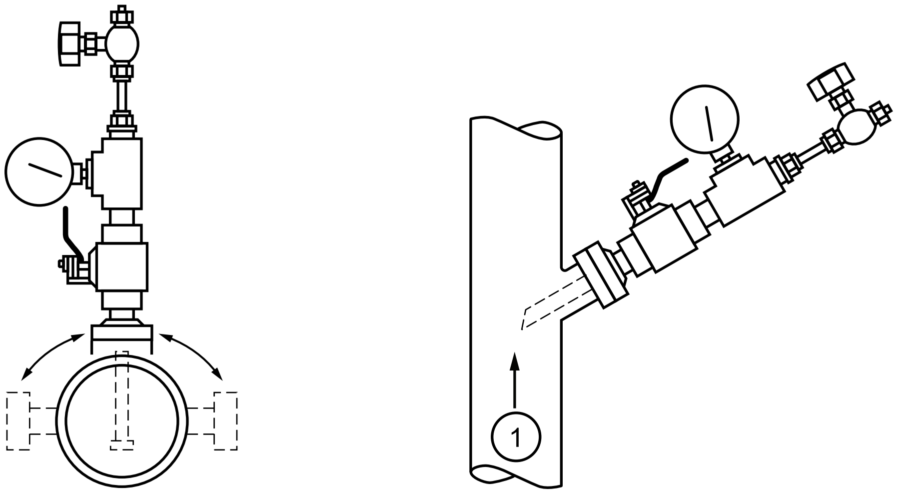
A benefit of the use of sample probes (with extraction near center of pipe) significantly reduces contamination from the inner pipe wall and act as a first stage of filtration and conditioning. Process stream stresses can be significant due to high velocity flow; therefore, stress calculations should be performed on probes and incorporated into design considerations. Corrosive service or high temperatures may require special alloys or materials. Flanged thermowells are often used as sample probes by merely cutting the end off at a 45 degree angle. The probe inlet should face downstream to minimize particulate matter in the extracted sample. Flow direction should be stamped or engraved on any directional probe to minimize errors in installation and reinsertion.

4.3.3.2 Extractive probe: (See Figure 4-2.) Extractive probes are typically made of short lengths of stainless steel or tube, $^3/_8$ in. or $^1/_2$ in. outside diameter and used at temperatures up to approximately 1000 °F (540 °C). Removable insertion probes should have a mechanical restraining device to prevent the probe from blowing out when the packing gland is loosened. To prevent probe damage, all sampling probes should have a means of indicating when the probe is pulled out past the process isolation valve. Extractive probes are not recommended in toxic service. Vibration calculations should be made to ensure the probe design is sufficient to prevent the probe from breaking off inside the pipe, where loss of the mechanical restraining device can cause injury to analyzer technician.

4.3.3.3 Fixed probe: (See Figure 4-3.) Fixed probes cannot be removed from service without interrupting the process. They have the advantage of being less prone to environmental leaks than extractive probes. The minimum bore diameter of a single fixed probe internal diameter is $^3/_8$ inch. For clean service only $^1/_4$ in. ID may be used, $^3/_8$ in. ID or greater for all else.

4.3.3.4 Multiport sample averaging probes: (See Figure 4-4.) Multiport sample averaging probes are used to obtain a sample whose composition is an average of that existing across the entire duct. Averaging is not normally attempted in ducts under 2 ft in diameter. Multiple probe sample averaging is frequently used in flues and stacks of large boilers and heaters in which stratification may be a problem or where required by compliance regulations. The preferred insertion length L and the maximum number of entry holes may be obtained from Figure 4-4.

4.3.3.5 Filter probes: Filter probes are generally used in gas streams such as combustion applications when the stream contains significant quantities of particulate material. The filter materials used are primarily sintered or woven stainless steel and various ceramics. These probes must always be located in the process duct in a manner that minimizes their exposure to particulate matter, or else frequent cleaning will be required. Locating the probe inside and just downstream of a bend, **or** adding baffles just upstream of the probe minimizes the probe exposure (see Figure 4-5).



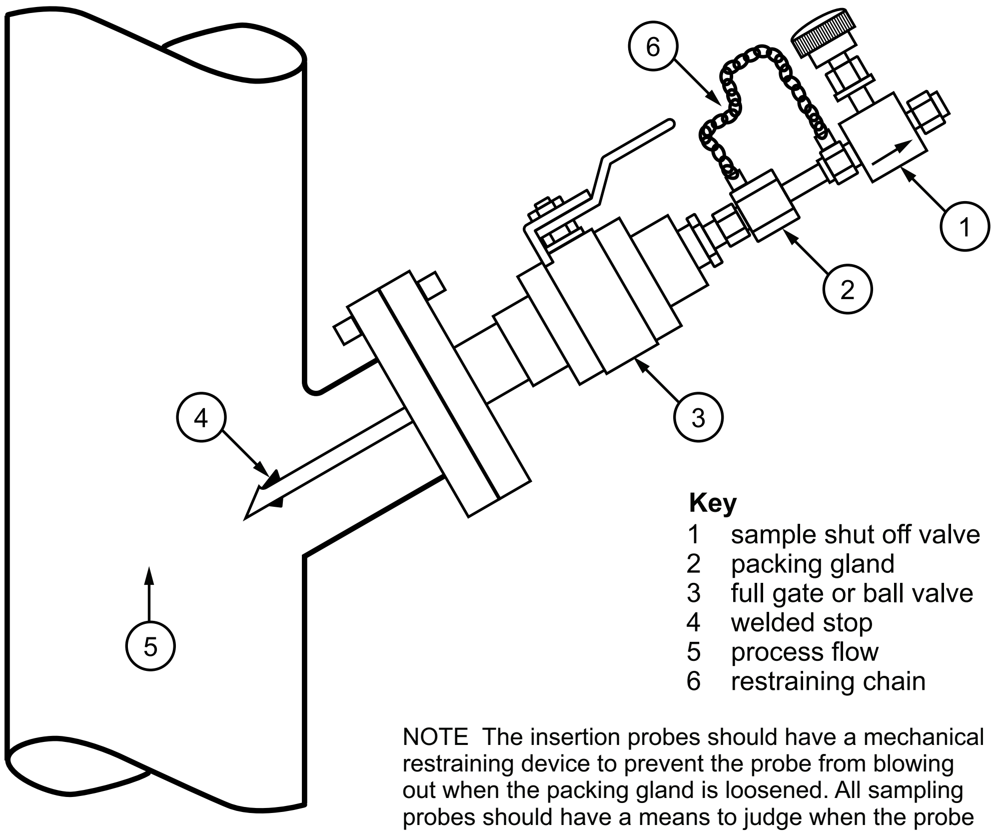
Acceptable sampling
point locations from
a horizontal line

Preferred sampling
on a vertical line

Key

1 flow

Figure 4-1—Acceptable Sampling Areas



Key

1 sample shut off valve
2 packing gland
3 full gate or ball valve
4 welded stop
5 process flow
6 restraining chain

NOTE The insertion probes should have a mechanical restraining device to prevent the probe from blowing out when the packing gland is loosened. All sampling probes should have a means to judge when the probe is pulled out past the valve to prevent probe damage.

Figure 4-2—Insertion Sample Open Probe

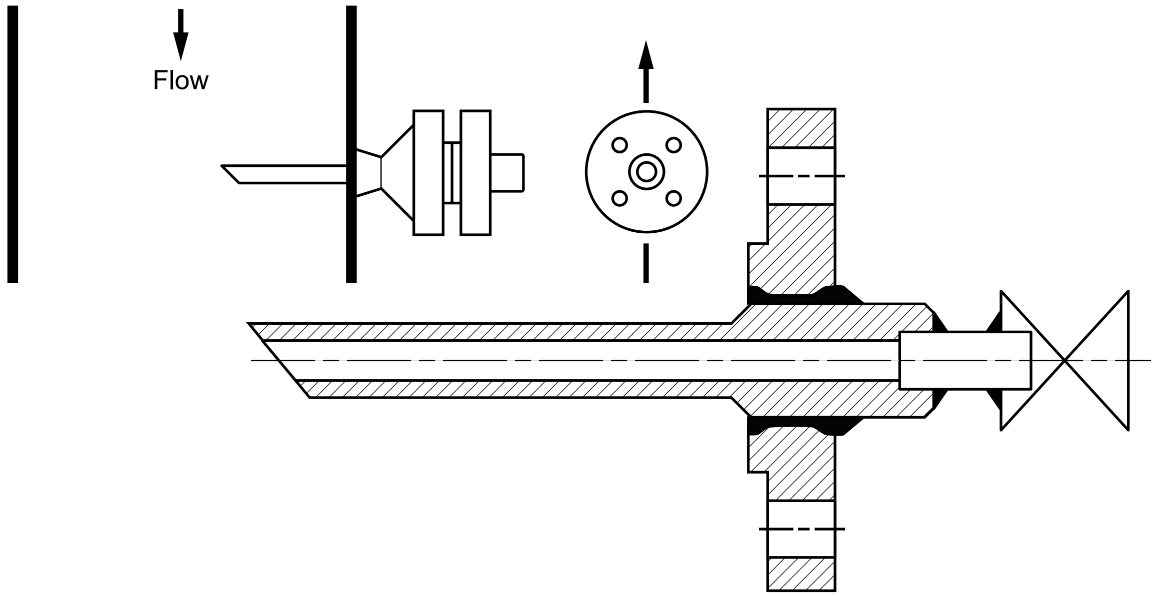
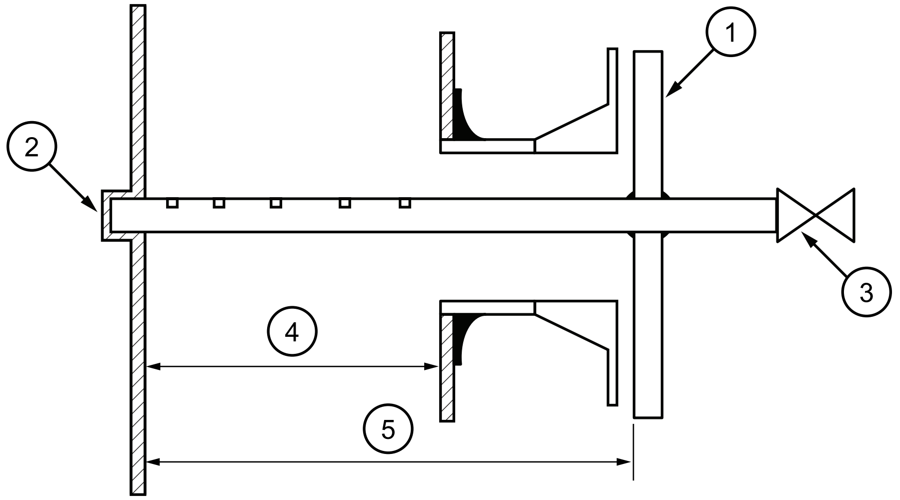


Figure 4-3—Fixed Sample Probe Open Flow Design

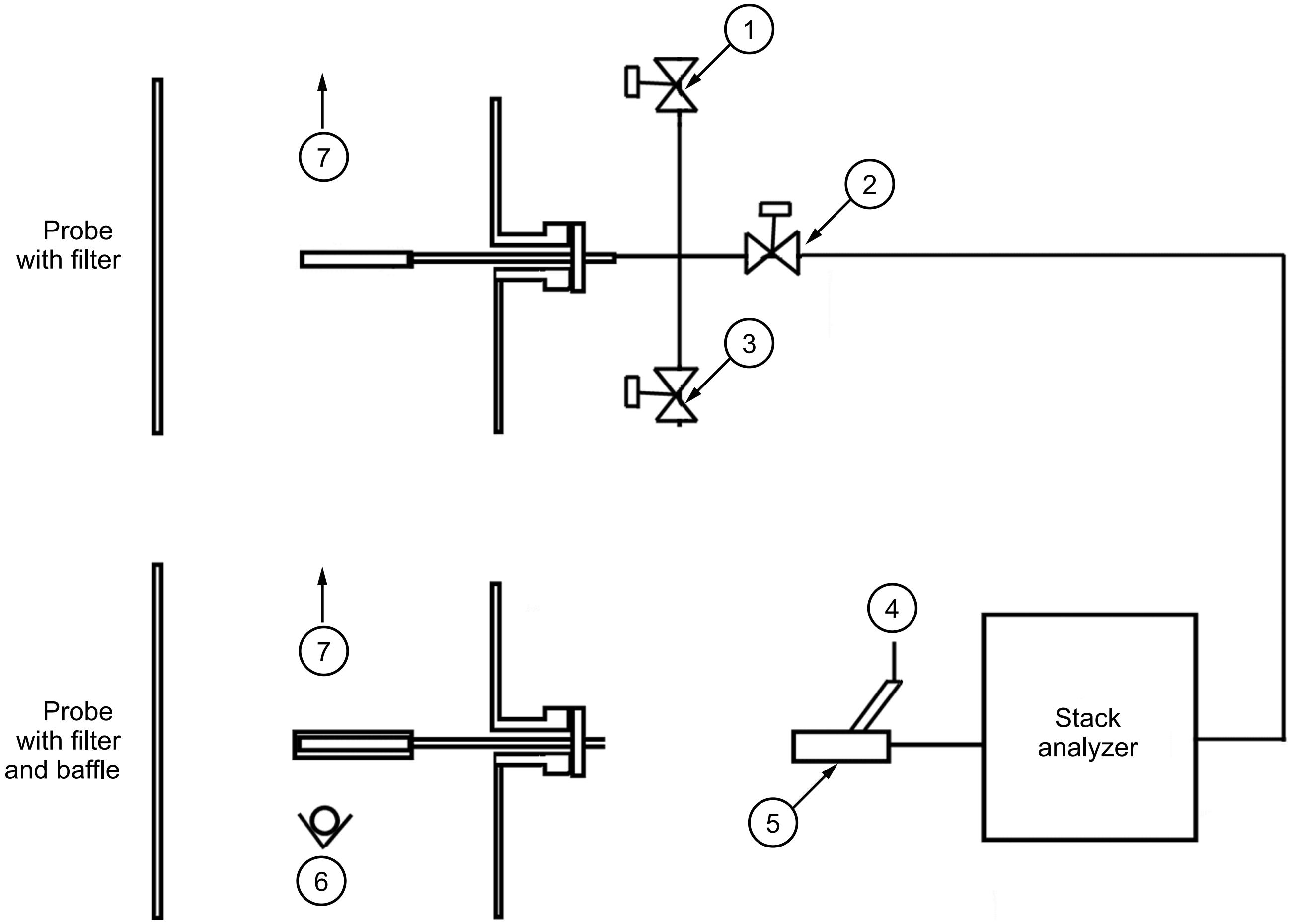


Duct area (ft^2)	No. of points	Location of entry holes as fraction of diameter measured from inner wall at sample point
<2	2	0.146, 0.854
2-8	4	0.062, 0.250, 0.750, 0.938
8-12	6	0.044, 0.147, 0.294, 0.706, 0.853, 0.956
12-16	8	0.033, 0.105, 0.195, 0.321, 0.679, 0.805, 0.895, 0.967
16-24	10	0.019, 0.076, 0.153, 0.217, 0.361, 0.639, 0.783, 0.847, 0.924, 0.981

Key

1	1 ½ in. to 2 in. NB flange
2	for longer probes, support as required
3	ball or gate valve (straight-through valve)
4	stack diameter
5	probe length

Figure 4-4—Multiport Sampling Probe for Flue Gas Analysis



Key

1 steam (for backflushing)
2 sample (to analyzer)
3 nitrogen (for backflushing)
4 nitrogen or air
5 eductor
6 front view of baffle
7 flow

Figure 4-5—Filter Probes

A filter probe must always be operated at a temperature well above the dew point temperature of the stream in which the probe is inserted. Filter probes can be cleaned by removal of the probe from service; however, a more common method is a *blow-back* system, which introduces air, nitrogen, or steam into the sample line to blow back through the filter in the reverse direction. This may be done manually when the sample flow begins to drop to unacceptable levels or automatically at preset intervals. To improve effectiveness filter blowback design should incorporate accumulative blow back gas tanks close to the probe to maximize mechanical shock to the filter. The blowback should be pulsed (e.g. a 1 second pulse with a 5 second air pressure recovery) with up to 5 pulses. This again maximizes shock and reduces the cooling effect on the probe from continual air flow. The sample transport line should be isolated on blowback. If the blow back gas is pulsed and does not drop the sample gas below the dew point temperature, then the blowback gas does not need to be heated.

NOTE Blow-back gas must be compatible with the process stream.

4.3.4 Sample Tap Primary Conditioning

Installation of primary conditioning systems at the sample tap typically allows for more reliable operation of extremely difficult samples that cannot be transported easily to a remote sample conditioning system.

Pyrolysis furnace effluents, regenerator gas from FCCU and reformers or other hot gases with condensable material, particulate matter, and catalyst fines are examples requiring primary sample conditioning in order to maintain a reliable continuous sample draw-off without plugging. A filter reflux column is mounted directly on the process line shut-off valve. The sample is cooled, and the condensable material reflux washes down the solids back into the process line, with a clean saturated sample coming out of the top of the column to the analyzer. Depending on the amount of condensable material available in the sample, steam can be added to the bottom of the column to provide additional condensable material to the reflux and to dilute the acids formed in the process (see Figure 4-6).

Remote pressure let-down and vaporizer regulator stations are another type of primary conditioning system. These stations must be mounted near the sample tap to flash liquid samples and reduce lag times by controlling the sample pressure before transport to the analyzer location. Insulation of a heated enclosure may be required on these installations if the sample dewpoint temperature cannot be maintained.

4.3.5 Sampling Time Dynamics and Transportation Lag Times

In installations where the analyzer and sample system must be located at some distance from the sample point, the sample transport time must be considered. The sample transport time is defined as the time required to transport the sample from the tip of the sample probe to the analyzer inlet.

The total measurement response time is defined as the sample transport time plus the analyzer response time. The analyzer response time for continuous analyzers is often expressed as a T80 or T90 value, designating the time required for an analyzer output signal to achieve 80 % or 90 % of the final measured value from a process step change. For discontinuous analyzers, the cycle time would substitute for the analyzer response time.

A convenient means for reducing the sample transport time is the use of a fast loop connecting process line, sample conditioning system, (commonly located outside the analyzer shelter), and a low pressure return point.

In some applications a lower return pressure may not be found. In this instance either a sample pump can be installed or a sweep stream system can be used (a fast flow by passing the analyzer). A sweep stream sample can be returned into a collection tank (liquids) for pumping back to the process or to flare (gases) for disposal. (see Figure 4-7).

The sample transport time, or lag time, is a function of the sample line length inside line diameter, line pressure (for vapor samples), and sample flow rate. The sample transport time can be calculated by dividing the total volume in the sample line by the average flow rate as described in the following equations.

$$^{t}lag\ (\text{liquid}) = \frac{(V)(L)}{\text{Flow rate}} \tag{1}$$

$$^{t}lag\ (\text{vapor}) = \frac{(V)(L)}{F_s}\ \frac{(P1 + 14.7)}{P2}\ \frac{(520)}{460 + T} \tag{2}$$

where

^{t}lag is the sample transport time in minutes;

$P1$ is the pressure in sample volume whose lag time is to be calculated, in psig;

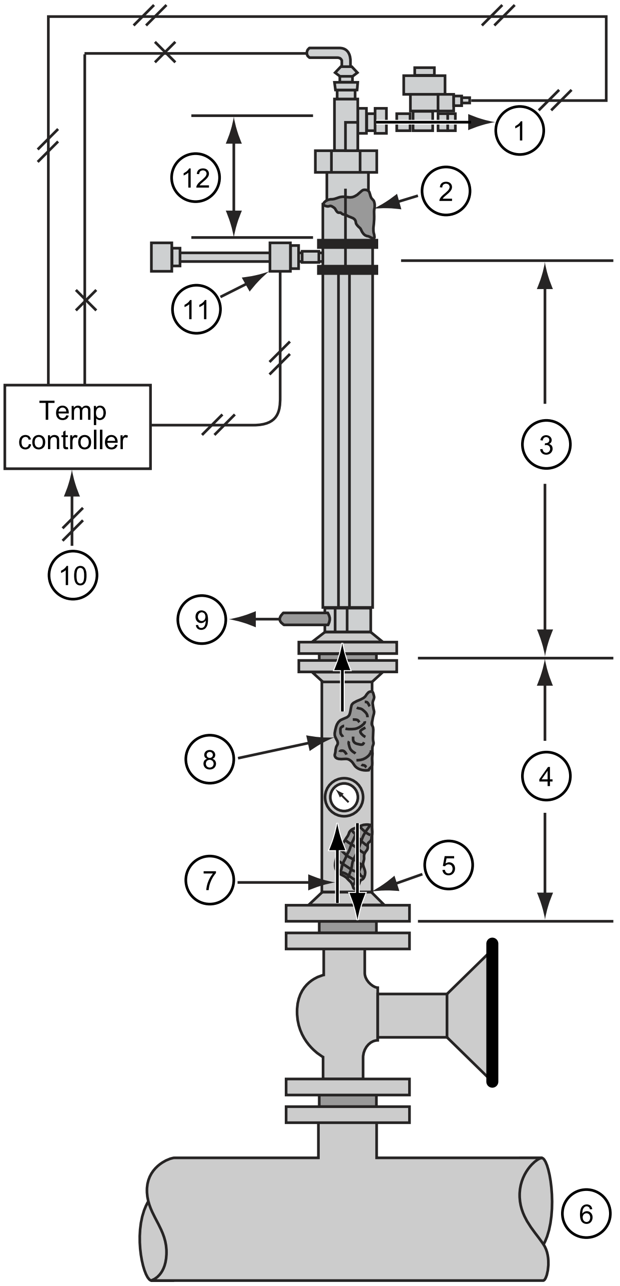
$P2$ is the pressure at point of flow measurement in psig;

V is the tubing volume in cc/ft;

L is the total line length in ft;

F_s is the flow rate in cc/min at standard conditions, (14.7 psia, 60 °F);

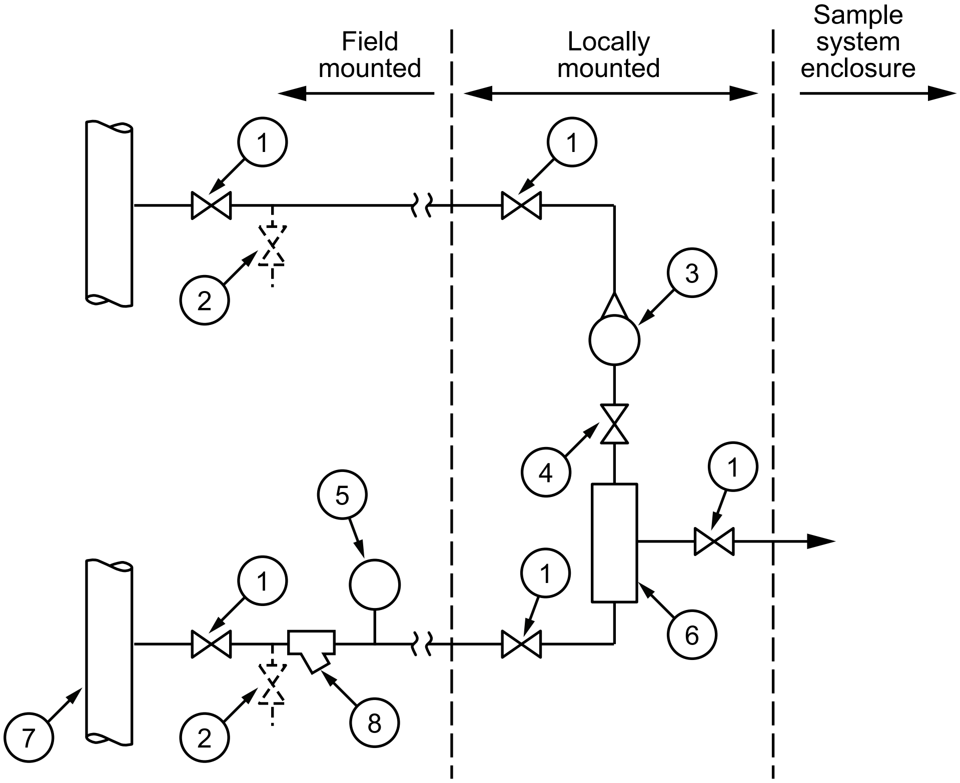
T is the temperature in °F.



Key

1	sample to analyzer	7	sample
2	coalescer	8	reflux action
3	cooling section	9	warm coolant exhaust
4	filter reflex section	10	instrument air supply
5	condensibles	11	vortex cooling tube
6	process line	12	conditioning

Figure 4-6—Pyrolysis Gas Sample Conditioner



Key

1	block valve	5	pressure gauge
2	bleed valve (optional)	6	by-pass filter
3	flow indicator	7	process line
4	needle valve	8	strainer

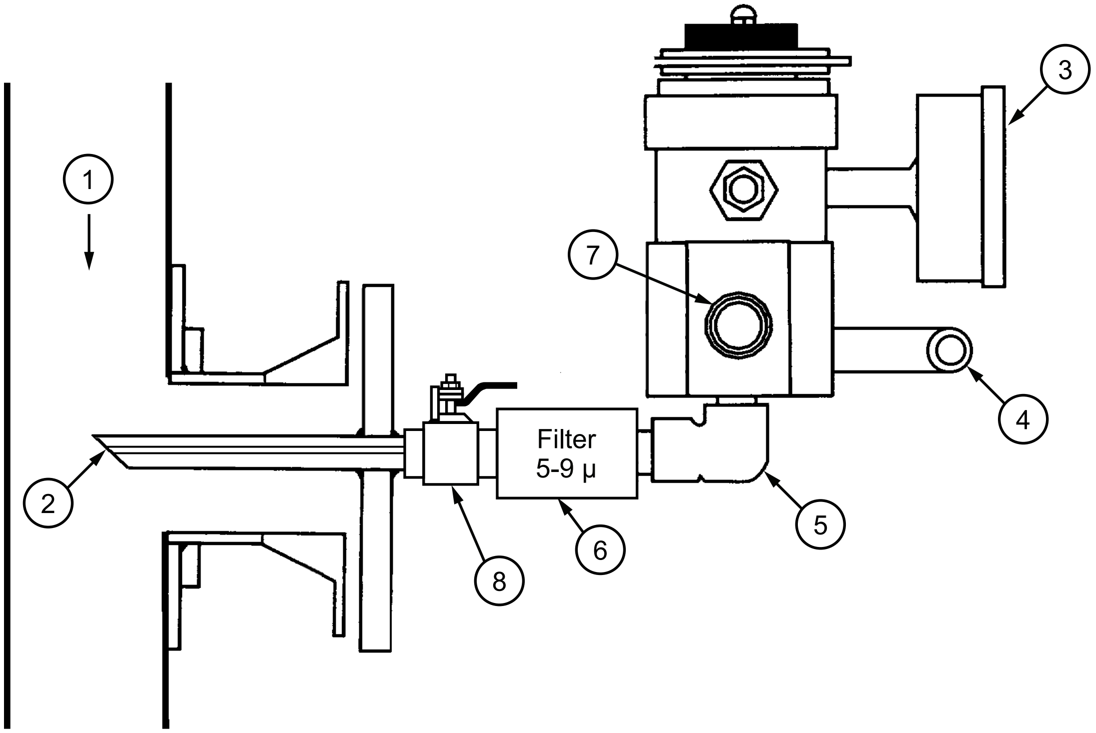
Figure 4-7—Fast Loop Sampling System

Following the ideal gas law, volume varies directly with absolute temperature and inversely with absolute pressure for a fixed quantity of gas. Since gas analyzers are normally vented to atmospheric pressure for stability, the simplest method for determining sample transport lag time is to relate the total gas volume in the system to standard conditions of temperature and pressure (STP). Thus, for any part of a vapor system, the volume at STP can be determined according to Equation 2.

4.3.6 Vaporizing Liquid Samples—Lag Time Considerations

Vaporizing a liquid sample can contribute to a severe lag time because of the expansion effect of a hydrocarbon liquid changing into a vapor. Typically light hydrocarbons can have a vapor expansion of 600 to 1, which results in 1 cubic centimeter (cc) of liquid forming approximately 600 cc of vapor. Since vapor speed loops may flow as little as 2000 cc/min., a representative sample of liquid would not be adequately purged, and partial vaporization might occur if the liquid volume flow is not sized properly for the vapor flow rate.

In high pressure applications, it may be advisable to use a sample probe with an internal diameter of approximately $^1/_8$ in. to avoid the large dead volume of modified thermowells. It is also advisable to minimize the dead volume between the sample probe and the vaporizing regulator (see Figure 4-8). Figure 4-9 illustrates a design of a low pressure sample probe and vaporizer that reduces the liquid dead volume.



Key

1 flow
2 ⅛ in. ID
3 pressure gauge
4 sample tube outlet to analyzer
5 low volume pipe elbow
6 low volume filter
7 vaporizing regulator steam in/out
½ in. OD in/out flow-through design
8 manually operated isolation valve

Figure 4-8—Liquid Vaporization Sample Probe and Regulator Section (High-temperature/Pressure Applications)

4.3.7 Sample Transport Line—General Considerations

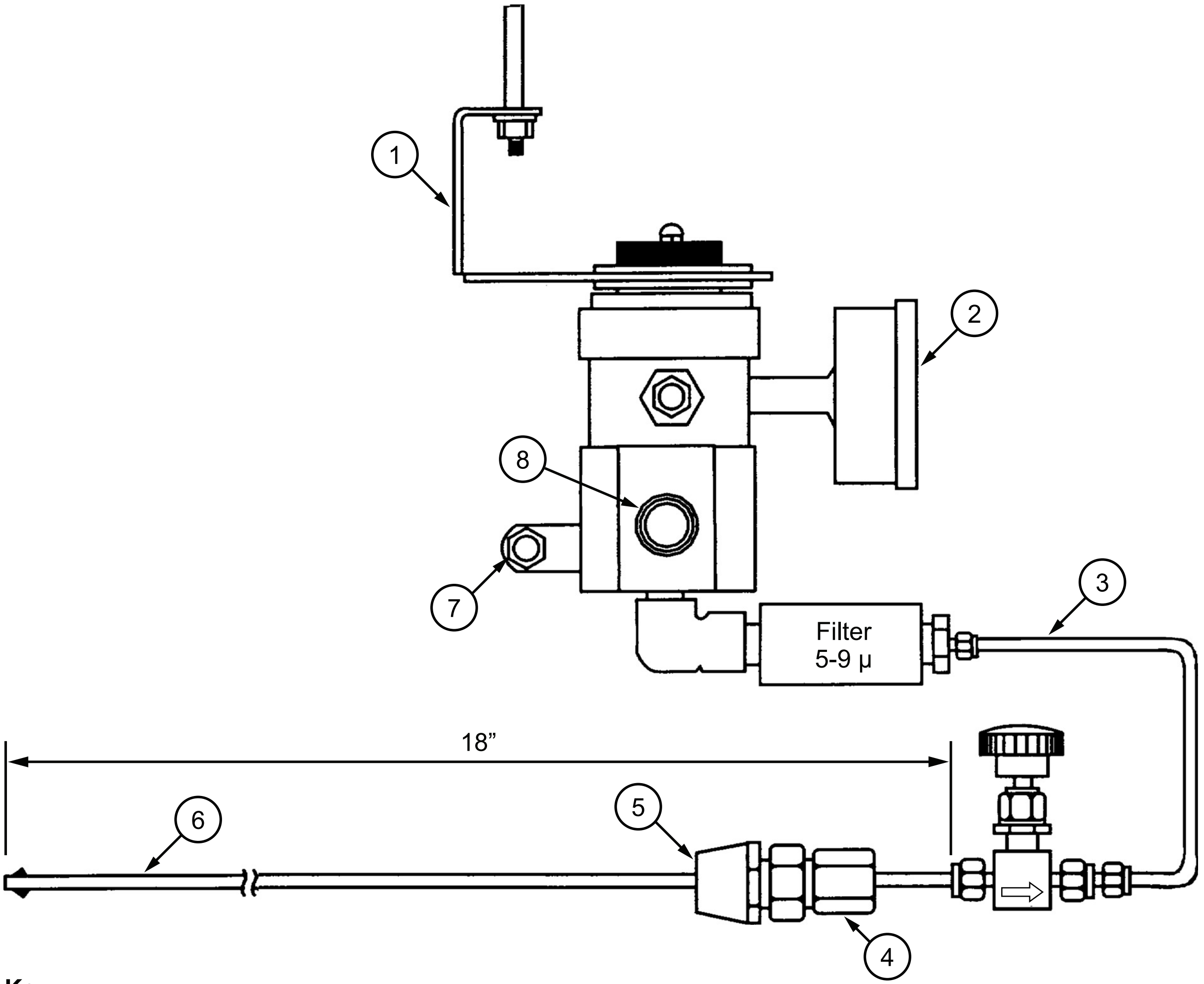
4.3.7.1 Tubing runs are recommended because of metallurgy, smaller internal volume, less entrainment due to abrupt bends, and ease of installation. Piping runs are sometimes required for long speed loops (e.g., >300 ft) to minimize lag times.

Specification of tubing should consider corrosion allowances. The materials used to manufacture the tubing can be very important, especially in high or low temperature installation and where certain chemicals can cause stress cracking. Seamless tubing is often selected to eliminate stress cracking in the tubing longitudinal welds. Continuous drawn tubing bundles reduce the likelihood of sample line leaks as the use of compression fittings is minimized. Tubing bundles can be purchased insulated or traced and insulated which reduces installation costs. Continuous tubing runs must be used for sub-atmospheric pressure applications.

4.3.7.2 Keep samples lines as short as possible to minimize transport lag time.

4.3.7.3 Use the smallest diameter line available to ensure a representative single phase sample that is consistent with the required flow rate and the available pressure drop. Sample supply and return lines of $^{1}/_{4}$-in. O.D., with a 0.035-in. wall are common for many vapor phase transport lines. Liquid sample lines are often $^{3}/_{8}$-in. or $^{1}/_{2}$-in. O.D. due to higher pressure drops.

4.3.7.4 Provide sufficient pressure to maintain adequate velocities. Typical linear flow velocities are 5 ft/sec to 10 ft/sec (~2 m/sec to 4 m/sec) for liquids and 20 ft/sec to 40 ft/sec (~7 m/sec to 15 m/sec) for gases.



Key

1 mounting bracket
2 pressure gauge
3 ⅛ in. stainless steel tubing
4 packing gland mount into process gate valve
5 stainless steel bushing 1 in. x ¼ in. NPT
6 ¼ in. stainless steel tube 0.065 in. (1.7 mm) wall
7 sample ¼ in. tube outlet
8 vaporizing regulator steam in/out ½ in. OD tube (front and rear, flow-through design)

Figure 4-9—Liquid Vaporization Sample Probe and Regulator Section (Low-pressure Applications)

4.3.7.5 Use indicators (flow, pressure, temperature) and check-valves as necessary to ensure that sample flow is adequate and in the proper direction.

4.3.7.6 The sizing of sample transport lines will be influenced by a number of factors as follows.

a) The process sample phase (whether liquid or vapor), dew point, bubble point, density, and viscosity may all influence the calculations of lag time and pressure drop. For relatively low flow and short line lengths, the pressure drop should not be significant; however, at a high flow or long line length, the pressure drop may become an important factor in the system design, especially for liquids. Although the specific gravity of a gas or liquid does not affect the lag time calculation, specific gravity must be considered when specifying flow control and indicating devices. Tables are available relating flow rate to pressure drop for different sample line diameters. Table 4-1 provides examples of pressure drops at various flow rates for gases and Table 4-2 provides examples for liquids. Table 4-3 illustrates the relationship between sample line velocity and pressure drop. Table 4-4 provides a comparison of pressure drops at various flow rates for various liquids, and Table 4-5 provides a similar comparison for common gases.

Table 4-1—Darcy Pressure Drops vs. Line Size per 100 ft Sample Line—Gas Samples

Sample Line Size/Type	Friction Factor (unitless)	Wall Thickness (in.)	Sample Line ID (in.)	Darcy Head Loss (ft)	Methane Density (lb/ft^3)	Methane d/p (psi)	CO_2 Density (lb/ft^3)	CO_2 d/p (psi)	Butane Density (lb/ft^3)	Butane d/p (psi)
1/8 in. Tube	0.035	0.028	0.069	9.417	0.042	0.0027	0.116	0.0076	0.153	0.0100
	0.035	0.035	0.055	11.815	↓	0.0034	↓	0.0095	↓	0.0126
1/4 in. Tube	0.028	0.028	0.194	2.680		0.0008		0.0022		0.0028
	0.028	0.035	0.180	2.888		0.0008		0.0023		0.0031
	0.028	0.049	0.152	3.420		0.0010		0.0028		0.0036
	0.028	0.065	0.120	4.332		0.0013		0.0035		0.0046
3/8 in. Tube	0.025	0.035	0.305	1.522		0.0004		0.0012		0.0016
	0.025	0.049	0.277	1.676		0.0005		0.0013		0.0018
	0.025	0.065	0.245	1.894		0.0006		0.0015		0.0020
1/2 in. Tube	0.022	0.035	0.430	0.950		0.0003		0.0008		0.0010
	0.022	0.049	0.402	1.016		0.0003		0.0008		0.0011
	0.022	0.065	0.370	1.104		0.0003		0.0009		0.0012
	0.022	0.083	0.334	1.223		0.0004		0.0010		0.0013
1/8 in. P (40)	0.027	0.088	0.364	1.377		0.0004		0.0011		0.0015
Sch 80	0.027	0.119	0.302	1.660		0.0005		0.0013		0.0018
3/4 in. P (40)	0.025	0.113	0.824	0.563		0.0002		0.0005		0.0006
Sch 80	0.025	0.154	0.742	0.626		0.0002		0.0005		0.0007
1 in. P (40)	0.023	0.133	1.049	0.407		0.0001		0.0003		0.0004
Sch 80	0.025	0.179	0.957	0.485		0.0001		0.0004		0.0005

$$\text{Darcy Friction Head Loss} = \frac{(\text{Frict.Fact})(\text{Line Length})(\text{Square of Line Velocity})}{(2)(\text{Gravity Constant})(\text{Line ID})}$$

$$\text{Units} = \frac{(\text{ft})(\text{ft}^2/\text{sec}^2)}{(\text{ft}/\text{sec}^2)(\text{ft})} = \text{ft}$$

Pressure Drop = (Friction Head Loss)(Density)

Units = $(\text{lb}/\text{ft}^2)(\text{ft}^2/144\ \text{in.}^2)$ = psi

Gravity Constant = 32.1725 ft/sec^2

Flow Velocity = 1 ft/sec

Table 4-2—Darcy Pressure Drops vs. Line Size per 100 ft Sample Line—Liquid Samples

Sample Line Size/Type	Friction Factor (unitless)	Wall Thickness (in.)	Sample Line ID (in.)	Darcy Head Loss (ft)	Pentane Density (lb/ft^3)	Pentane d/p (psi)	Benzene Density (lb/ft^3)	Benzene d/p (psi)	Octane Density (lb/ft^3)	Octane d/p (psi)
$^1/_8$ in. Tube	0.035	0.028	0.069	9.460	39.357	2.586	55.168	3.624	44.079	2.896
	0.035	0.035	0.055	11.868	↓	3.244	↓	4.547	↓	3.633
$^1/_4$ in. Tube	0.028	0.028	0.194	2.692	↓	0.736	↓	1.031	↓	0.824
	0.028	0.035	0.180	2.901	↓	0.793	↓	1.111	↓	0.888
	0.028	0.049	0.152	3.435	↓	0.939	↓	1.316	↓	1.052
	0.028	0.065	0.120	4.352	↓	1.189	↓	1.667	↓	1.332
$^3/_8$ in. Tube	0.025	0.035	0.035	13.321	↓	3.641	↓	5.103	↓	4.078
	0.025	0.049	0.377	1.237	↓	0.338	↓	0.474	↓	0.379
	0.025	0.065	0.245	1.903	↓	0.520	↓	0.729	↓	0.583
$^1/_2$ in. Tube	0.022	0.035	0.430	0.954	↓	0.261	↓	0.366	↓	0.292
	0.022	0.049	0.402	1.021	↓	0.279	↓	0.391	↓	0.312
	0.022	0.065	0.370	1.109	↓	0.303	↓	0.425	↓	0.339
	0.022	0.083	0.334	1.228	↓	0.336	↓	0.471	↓	0.376
$^1/_8$ in. P (40)	0.027	0.088	0.364	1.383	↓	0.378	↓	0.530	↓	0.423
Sch 80	0.027	0.119	0.302	1.667	↓	0.456	↓	0.639	↓	0.510
$^3/_4$ in. P (40)	0.025	0.113	0.824	0.566	↓	0.155	↓	0.217	↓	0.173
Sch 80	0.025	0.154	0.742	0.628	↓	0.172	↓	0.241	↓	0.192
1 in. P (40)	0.023	0.133	1.049	0.409	↓	0.112	↓	0.157	↓	0.125
Sch 80	0.025	0.179	0.957	0.487	↓	0.133	↓	0.187	↓	0.149

$$\text{Darcy Friction Head Loss} = \frac{\text{(Frict.Fact)(Line Length)(Square of Line Velocity)}}{\text{(2)(Gravity Constant)(Line ID)}}$$

$$\text{Units} = \frac{(\text{ft})(\text{ft}^2/\text{sec}^2)}{(\text{ft}/\text{sec}^2)(\text{ft})} = \text{ft}$$

$$\text{Pressure Drop} = \text{(Friction Head Loss)(Density)}$$

$$\text{Units} = (\text{lb}/\text{ft}^2)(\text{ft}^2/144\ \text{in.}^2) = \text{psi}$$

Gravity Constant = 32.1725 ft/sec^2

Flow Velocity = 1 ft/sec

Table 4-3—Liquid Pressure Drops vs. Different Flow Velocities for a 100 ft Sample Line

Sample Line Size/Type	**Friction Factor (unitless)**	**Wall Thickness (in.)**	**Sample Line ID (in.)**	**Flow Velocity (ft/sec)**	**Darcy Head Loss (ft)**	**Propane Density (lb/ft^3)**	**Propane d/p (psi)**	**Butane Density (lb/ft^3)**	**Butane d/p (psi)**	**Hexane Density (lb/ft^3)**	**Hexane d/p (psi)**
$^1/_8$ in. Tube	0.035	0.028	0.069	1	9.460	31.616	2.077	36.422	2.393	41.412	2.721
				2	37.839		8.308		9.571		10.882
				3	85.139		18.693		21.534		24.485
				4	151.358		33.231		38.283		43.528
				5	236.497		51.924		59.817		68.013
$^1/_4$ in. Tube	0.028	0.035	0.180	1	2.901		0.637		0.734		0.834
				2	11.604		2.548		2.935		3.337
				3	26.109		5.732		6.604		7.509
				4	46.416		10.191		11.740		13.349
				5	72.526		15.923		18.344		20.857
$^3/_8$ in. Tube	0.025	0.035	0.305	1	1.529		0.336		0.387		0.440
				2	6.115		1.342		1.547		1.758
				3	13.758		3.021		3.480		3.957
				4	2.038		0.447		0.516		0.586
				5	38.216		8.391		9.666		10.990
$^1/_2$ in. Tube	0.022	0.035	0.430	1	0.954		0.209		0.241		0.274
				2	3.817		0.838		0.965		1.098
				3	8.587		1.885		2.172		2.470
				4	15.267		3.352		3.861		4.390
				5	23.854	↓	5.237	↓	6.033	↓	6.860

$$\text{Darcy Friction Head Loss} = \frac{(\text{Frict.Fact})(\text{Line Length})(\text{Square of Line Velocity})}{(2)(\text{Gravity Constant})(\text{Line ID})}$$

$$\text{Units} = \frac{(\text{ft})(\text{ft}^2/\text{sec.}^2)}{(\text{ft}/\text{sec.}^2)(\text{ft})} = \text{ft}$$

$$\text{Pressure Drop} = (\text{Friction Head Loss})(\text{Density})$$

$$\text{Units} = (\text{lb}/\text{ft}^2)(\text{ft}^2/144\ \text{in.}^2) = \text{psi}$$

Gravity Constant = 32.1725 ft/sec.^2

Flow Velocity = 1 ft/sec.

Table 4-4—Comparison of Pressure Drops in PSI for Various Liquids vs. Common Line Sizes

Liquid Sample	Density (lb/ft^3)	$^{1}/_{8}$ in. Tube ID = 0.055 in. FF = 0.035	$^{1}/_{4}$ in. Tube ID = 0.180 in. FF = 0.028	$^{3}/_{8}$ in. Tube ID = 0.305 in. FF = 0.025	$^{1}/_{2}$ in. Tube ID = 0.430 in. FF = 0.022
Acetonitrile	48.832	4.025	0.984	0.518	0.324
Acetic Acid	65.495	5.398	1.319	0.695	0.434
Benzaldehyde	65.021	5.359	1.310	0.690	0.431
Benzene	55.096	4.541	1.110	0.585	0.365
Bunker Fuel	63.304	5.217	1.275	0.672	0.419
1,3 Butadiene	42.202	3.478	0.850	0.448	0.280
Butane	37.532	3.093	0.756	0.398	0.249
Chloroform	92.971	7.662	1.873	0.987	0.616
Carbonyl Sulfide	78.835	6.497	1.588	0.837	0.522
Carbon Tetrachloride	80.722	6.653	1.626	0.857	0.535
Cyclohexane	48.602	4.006	0.979	0.516	0.322
DMF	59.227	4.881	1.193	0.629	0.392
Ethanol	49.382	4.070	0.995	0.524	0.327
Ethyl Ether	44.513	3.669	0.897	0.473	0.295
Fuel #3	56.062	4.620	1.129	0.595	0.371
Fuel #6	61.992	5.109	1.249	0.658	0.411
Gasoline	42.140	3.473	0.849	0.447	0.279
Heptane	42.683	3.518	0.860	0.453	0.283
Hexane	41.663	3.434	0.839	0.442	0.276
HCL (40 %)	74.916	6.174	1.509	0.795	0.496
H_2SO_4 (87 %)	112.374	9.261	2.264	1.193	0.745
Isohexanes	41.203	3.396	0.830	0.437	0.273
Isopentane	39.000	3.214	0.786	0.414	0.258
Isopropyl Ether	45.205	3.726	0.911	0.480	0.300
Kerosine	51.192	4.219	1.031	0.543	0.339
Methanol	49.400	4.071	0.995	0.524	0.327
MTBE	46.261	3.813	0.932	0.491	0.307
Naphtha	41.516	3.422	0.836	0.441	0.275
Nonane	44.799	3.692	0.903	0.476	0.297
Oil (–10 API)	72.731	5.994	1.465	0.772	0.482
Oil (10 API)	62.430	5.145	1.258	0.663	0.414
Oil (30 API)	54.688	4.507	1.102	0.581	0.362
Oil (50 API)	49.195	4.054	0.991	0.522	0.326
Pentane	39.093	3.222	0.788	0.415	0.259
Petroleum Ether	39.955	3.293	0.805	0.424	0.265
Phenol	66.937	5.517	1.349	0.711	0.444
Propanol-1	50.175	4.135	1.011	0.533	0.332
SAE 30 Lube	56.062	4.620	1.129	0.595	0.371
Sea Water	63.991	5.274	1.289	0.679	0.424
Toluene	54.121	4.460	1.090	0.575	0.359
Turpentine	54.314	4.476	1.094	0.577	0.360
Water	62.430	5.145	1.258	0.663	0.414
Xylene-O	54.951	4.529	1.107	0.583	0.364

Gravity Constant = 32.1725 $ft/sec.^2$

Flow Velocity = 1 ft/sec

100 ft Sample Lines

Table 4-5—Comparison of Pressure Drops in PSI for Various Gases vs. Common Line Sizes

Liquid Sample	Density (lb/ft^3)	$^1/_8$ in. Tube ID = 0.055 in. FF = 0.035	$^1/_4$ in. Tube ID = 0.180 in. FF = 0.028	$^3/_8$ in. Tube ID = 0.305 in. FF = 0.025	$^1/_2$ in. Tube ID = 0.430 in. FF = 0.022
Acetylene	0.0686	0.0057	0.0014	0.0007	0.0005
Air (70°F)	0.0752	0.8925	0.2182	0.1150	0.0718
Ammonia	0.0449	0.5329	0.1303	0.0686	0.0428
Butane (120 °F)	0.1557	1.8478	0.4517	0.2380	0.1486
Butylene (120 °F)	0.1502	1.7826	0.4357	0.2296	0.1433
Carbon Dioxide	0.1236	1.4669	0.3586	0.1889	0.1179
Carbon Monoxide	0.0780	0.9257	0.2263	0.1192	0.0744
Chlorine	0.1873	2.2228	0.5434	0.2863	0.1787
Ethane	0.0793	0.9411	0.2301	0.1212	0.0757
Ethylene	0.0734	0.8711	0.2129	0.1122	0.0700
Freon	0.3406	4.0422	0.9881	0.5207	0.3250
Helium	0.0104	0.1234	0.0302	0.0159	0.0099
Hydrogen	0.0052	0.0617	0.0151	0.0079	0.0050
Natural Gas	0.0503	0.5970	0.1459	0.0769	0.0480
Neon	0.0524	0.6219	0.1520	0.0801	0.0500
Nitrogen	0.0732	0.8687	0.2124	0.1119	0.0698
NO	0.0779	0.9245	0.2260	0.1191	0.0743
NO$_2$	0.1143	1.3565	0.3316	0.1747	0.1091
Oxygen	0.0832	0.9874	0.2414	0.1272	0.0794
Pentane (120 °C)	0.1874	2.2240	0.5437	0.2865	0.1788
Propylene	0.1093	1.2972	0.3171	0.1671	0.1043
Propane	0.1176	1.3957	0.3412	0.1798	0.1122
SO$_2$	0.1705	2.0235	0.4946	0.2606	0.1627

Gravity Constant = 32.1725 ft/sec.^{2}

Flow Velocity = 1 ft/sec

100 ft Sample Lines

b) The flow rate, pressure, and sample temperature requirements of the analyzer as configured for the analysis must be considered. In the case of multi-stream analyzers, dead volume of the system and adequate flushing of the previous streams must be considered to minimize cross contamination and to deliver a representative sample.

c) Sample conditioning elements contribute to pressure drop and lag time, and must be considered in calculating the overall sample line pressure drop. A common way to do this is to consider each element as contributing a pressure drop equal to some equivalent length of tube and adding all these equivalent lengths to the above calculated straight run length from the sample tap to the analyzer. Even pipe and tubing elbows and bends contribute to the sample line pressure drop. Table 4-6 illustrates the equivalent ft of straight run tubing equal to a bend or elbow that should be added to the sample line length for pressure drop calculations.

The purge time of each element is dependent on the individual volumes and is calculated as the time necessary for a minimum of three volumes of the sample stream to flow through the element.

Table 4-6—Equivalent Feet of Straight Run Tubing

Tubing OD (in.)	90° Elbow (ft)	90° Bend (ft)	180° Bend (ft)	45° Bend (ft)	Tee Branch (ft)
0.25 in.	1	0.5	1	0.5	1
$^3/_8$ in.	1.5	0.5	1	0.5	1.5
0.5 in.	2	5.5	1	0.5	2
$^5/_8$ in.	2.5	1	2	0.5	2.5
0.75 in.	3	1	2	0.5	3
1 in.	4.5	1	2	0.5	4.5

d) Consideration of operating pressure at the sample tap and of how much pressure can be used to supply driving power for the sample line is important. For example, even with a high sample point pressure, there may be some minimum pressure, above which the sample must be maintained at the analyzer in order to avoid problems such as bubble formation or premature flashing of the sample. Pressure at the process point is very important since this consideration partly determines the pressure drop that is available to drive the sample to the analyzer. Also very important is the pressure at the process return point. Calculation of the available differential pressure determines whether a continuous return line is feasible (with or without a sample pump) or if the sample must be returned to an approved disposal system.

The flow velocity in a sample line is related to the pressure drop in the line by the Darcy equation below.

$$h_L = (fLV^2)/(2Dg) = 0.1863\ (fLV^2)/(d)$$

where

h_L is the friction head loss;

f is the friction factor of the line material;

L is the length of the line;

V is the linear flow velocity;

g is the acceleration due to gravity;

d is the internal diameter of the line in inches;

D is the internal diameter of the line in feet.

And, since $\Delta P = ph_L$, then the sample line pressure drop may be calculated by the following equation.

$$DP = 0.001294\, fLpV^2/d$$

Friction factors are a function of the material of the sample line. Friction factors for several common sizes of sample lines are given in Table 4-7.

e) Flow in a sample line must be turbulent to ensure that it is well-mixed and representative of the process. Mixing generally isn't an issue with gaseous samples, but laminar or poorly mixed liquid sample flows can result in data that is not representative of the process dynamics. An estimation of sample mixing may be obtained by calculating the Reynolds Number of the sample flow. The Reynolds Number is a dimensionless number that is based on the

Table 4-7—Friction Factors for Sample Lines

Line Type	Line Size	Friction Factor
Tubing	$^3/_4$ in.	0.018
Tubing	$^1/_2$ in.	0.022
Tubing	$^1/_4$ in.	0.028
Tubing	$^1/_8$ in.	0.035
Schedule 80 Pipe	1 in.	0.0225
Schedule 80 Pipe	$^3/_4$ in.	0.0245
Schedule 80 Pipe	$^1/_2$ in.	0.026
Schedule 80 Pipe	$^1/_4$ in.	0.032

internal diameter of the line, the linear flow velocity, the density and dynamic viscosity of the gas or liquid by the following equation:

$$Re = 123.9\ (dVp)/(\mu)$$

where

Re is the Reynolds Number, a dimensionless number;

d is the internal diameter of the line, in inches;

V is the linear flow velocity, in ft/sec.;

p is the density, in lb/ft^3;

μ is the dynamic viscosity, in centipoise.

Sample flows with Reynolds Numbers greater than 4000 are considered to be turbulent. Flows with values less than 2000 are considered to be laminar (poorly mixed, or “plug flow”). Sample flow with values between 2000 and 4000 are considered to be transitional or partially mixed.

Since the viscosity and density of a process stream are known, it is a common practice to calculate the Reynolds Numbers of the common sample line sizes at various linear velocities. A calculation of the Reynolds Number allows a determination to be made of the minimum linear velocity required for turbulent flow (for example, the typical $^1/_4$ in. tubing with a standard wall thickness of 0.035 in. has an internal diameter of 0.18 in.).

As an example, water has a viscosity of 0.692 cP at 100 °F, and a density of 62.43 lb/ft^3. If the sample line length were 300 ft and the minimum lag time allowed were two minutes (120 seconds), what would the Reynolds Number be for a $^1/_4$ in. stainless steel line with a wall thickness of 0.035 in.?

$$Re = 123.9\ (0.18\text{ in.} \times 2.5 \times 62.43)/(0.692) = 5030$$
$$\text{(turbulent flow)}$$

f) In addition to ensuring turbulent flow in the sample line, provisions must often be made to maintain the temperature above a dew point so that a single phase sample is provided to the analyzer. In such cases, the sample lines must be heat-traced. Sample composition can be affected if the lines are heated or cooled excessively. Improper heating of the lines (especially when analyzing for trace amounts) can result in the tendency of some components adsorbing into the walls of the tube and changing the sample composition during its transport from the sample tap to the analyzer. Manufactured pre-insulated, pre-traced tubing bundles are recommended.

4.3.7.7 Sample line routing, is an important factor for proper operation. Sample line accessibility should be considered for maintenance. Sharp bends or kinks in the lines should be avoided. To minimize potential for leakage, avoid using an excessive number of fittings. Welded tubing joints may be used to avoid leakage. The sample lines should be sloped continuously downwards or upwards (depending on the application) to the analyzer to avoid pocketing. Pre-insulated tubing bundles should be run in a cable tray to eliminate low spots in the lines. The minimum bend radius for pre-insulated bundles can be obtained from the manufacturer. When installing insulated heated sample lines, it is important to make sure that the insulation covers the entire length of the transport tubing as even short segments of exposed transport tubing can result in cooling of the sample to ambient temperatures.

4.3.7.8 When low concentrations of "sticky molecule" measurements are required (e.g., sulphur compounds, moisture etc) the measurand can attach to roughness sites in the sample tubing causing slow reaction to change in the measurement both from increasing and decreasing values. In addition memory effect is dependent on temperature therefore increase in temperature can cause the attached measurand to be released. This is known as diurnal effect. Dependant on the measurand, its concentration and the sample transport line length, tubing with reduced roughness factors (e.g. electro polished/silica glass lined) can be selected to reduce memory effect. The diurnal effect is also seen in pressure reducing regulators due to the Joule-Thompson effect. This can be mitigated by using heated or vaporizing regulators to maintain temperature. Sample lines can be heat traced to reduce diurnal effects. This consideration is only significant in low ppm measurements.

4.3.8 Multi-stream Switching

Single stream/single analyzer configurations are recommended. Multi-stream versions are more complex and have a greater chance of failure, which means a loss of analysis on all streams.

There are several factors that should be considered when designing multi-stream switching systems:

a) Separate conditioning equipment for each stream.

b) Provisions for venting between switching valves to prevent contamination.

c) Cross contamination due to mechanical failure (leakage) or failure to properly purge the stream previously analyzed. Sample streams of high concentration may not be sufficiently flushed causing contamination of very low concentration streams.

d) The relative concentrations of the components in each stream.

A typical Double Block-and-Bleed (DBB), multi-stream sample system designed to minimize cross contamination and reduce dead volumes is illustrated in Figure 4-10. During operation the internal volumes between the valves of the unselected streams are vented to a low pressure destination that allows for a leakage path out of the system and not into the other sample streams. The vent from a DBB valve should be fitted with a sight flow indicator in order to determine if the primary valve has failed.

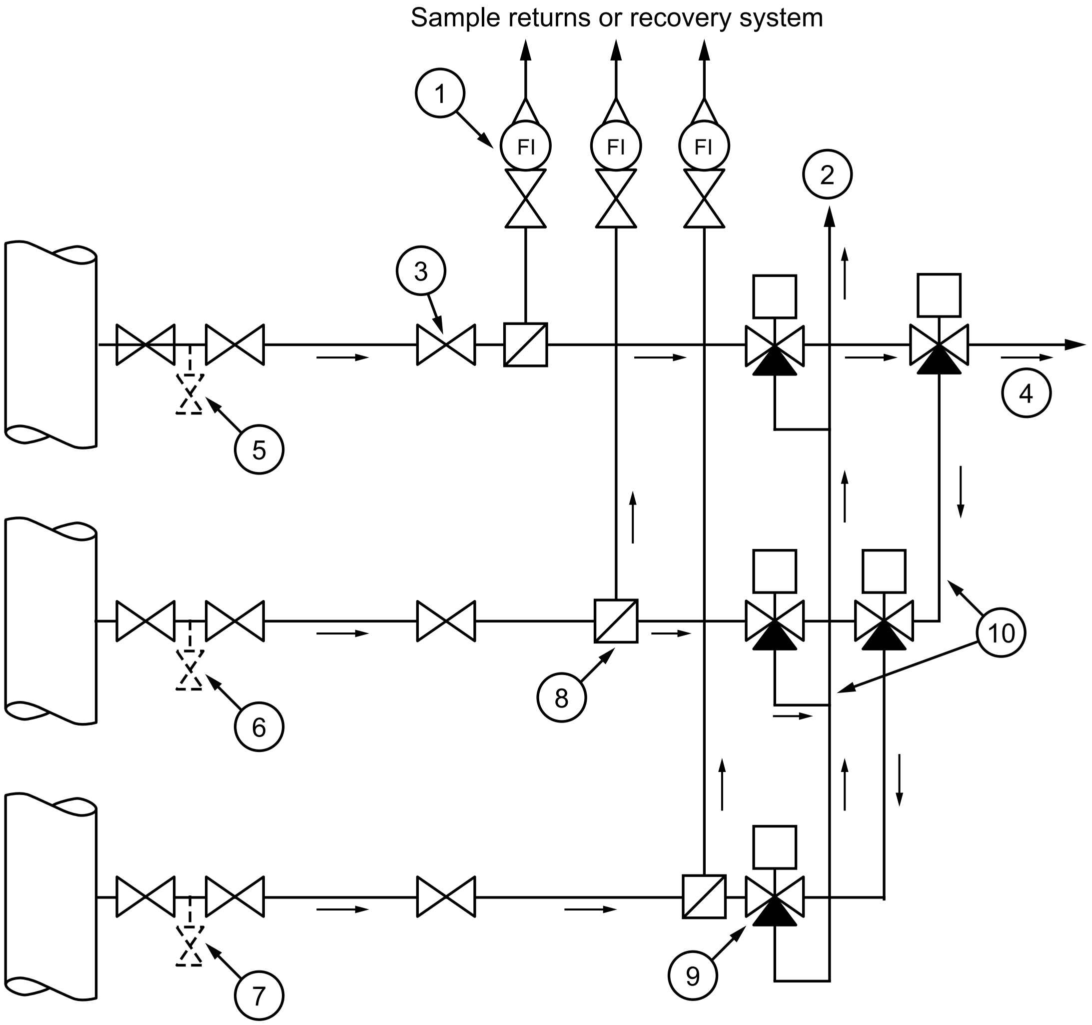
4.3.9 Sample Disposal

The circulating sample should be returned to the process at lower pressure using a speed loop system.

When a sample return point does not exist in the process it is necessary to choose whether to discard the sample to the flare system/closed sewer system or provide a means of pumping the sample back into the process. Discarding of hydrocarbon samples to the atmosphere or an open sewer system must be minimized and is often prohibited for environmental reasons. Sample disposal systems are used when the sample is too valuable or too hazardous to discard. Figure 4-11 illustrates a type of liquid sample recovery system.

4.3.10 Laboratory Sample Taps

Manual sample taps should be installed in a manner that allows lab samples to be taken easily to verify the on-line analyzer readings. Locate laboratory sample points so that they do not interfere with analyzer performance. Lab sample capture may be needed in sample cylinders. When this is necessary adequate cylinder flushing is required and the cylinder should have self sealing connection fittings, isolating valves and anti hydraulicing devices (liquid samples). Operating procedures should include "top off" (ensuing vapor space in liquid sample cylinder). Cylinder design should include provision for vapor space.



Key

1	flow meters
2	atm. pressure vent
3	shut-off valve
4	stream 1 to analyzer
5	stream 1
6	stream 2
7	stream 3
8	by-pass filters
9	3-way actuated valves
10	dead legs bleeding to atmosphere pressure vent

Figure 4-10—Stream Select System with Double Block-and-Bleed

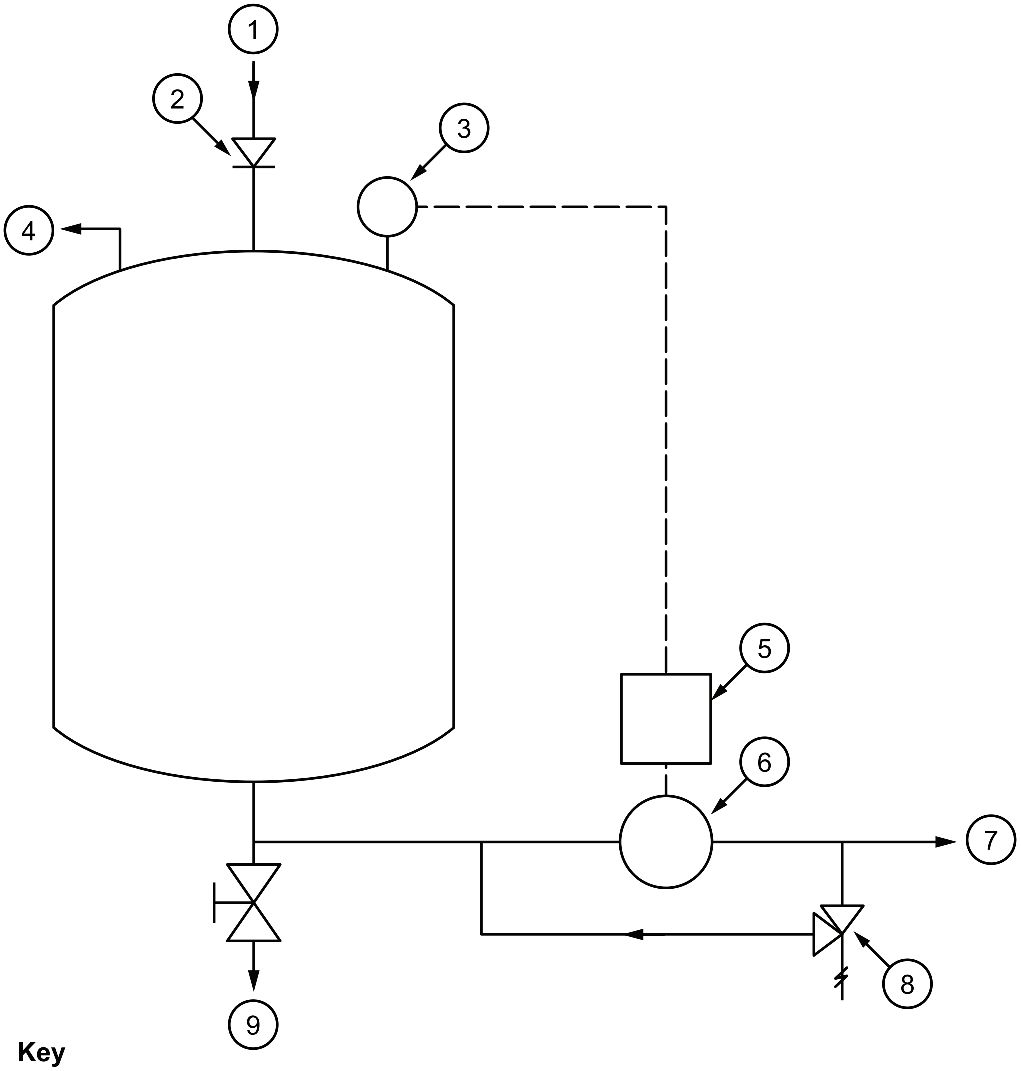
5 Prepackaged Systems

5.1 General

A systems approach is generally considered whenever a packaged system can be a single analyzer with a sample system, or multiple analyzers consolidated into a common enclosure A complete system is typically supplied by a single packaged systems supplier (PSS).The PSS has general responsibility for:

a) analyzers and materials including 3rd party suppliers;

b) suitability of the analyzer for the application;



Key

1	sample in	5	motor
2	check valve	6	pump
3	level switch	7	sample out to process
4	vent	8	relief valve
		9	drain

Figure 4-11—Liquid Sample Recovery System

c) design of the total packaged system;

d) assembly of multiple analyzers into common enclosures;

e) installation design requirements of the analyzer, shelter/enclosures, sample systems, and sample transport system;

f) complete system calibration, and factory acceptance testing;

g) requirements for routine testing and maintenance;

h) site acceptance testing, startup, and commissioning;

i) analyzer system training.

5.2 Advantages of Pre-Packaged Systems

It is recommended that the analyzer system be an engineered prefabricated package complete with analyzers, sample conditioning and calibration system(s) piped and wired in a self-contained unit.

Advantages include the following.

a) Construction is independent of weather and labor conditions at the site.

b) The system is designed and built by specialists familiar with the requirements.

c) The system can be fully tested under simulated operating conditions before shipment.

d) The complete system components and analyzers are warranted by the PSS.

e) The complete analyzer system training is available from the PSS.

f) Cost effective.

5.3 Total Systems Approach

To ensure successful analyzer performance and installation, a total system engineering approach should be followed.

a) Basic requirements should be completely specified with a thorough review of measurement types, analysis requirements, stream composition and stream conditions. The process requirements, site location, maintenance requirements, code compliance, and regulations should be specified completely.

b) Analyzer specification and performance testing requirements should be completely described.

c) Installation and enclosure specifications should also include additional support equipment, calibration requirements and facilities, and suitable spares capability.

d) Documentation requirements that include operation manuals, detailed drawing packages, tagging requirements, bill-of-materials lists, and spare part lists are mandatory.

e) A “Kick off” meeting should held to agree with the work scope and design details.

f) Identify schedules and milestone payments.

g) It is important to identify the purpose of the analyzer (control, monitoring, safety, environmental compliance, etc.) for proper analyzer selection system design.

6 Maintenance, Training, Installation, Inspection, Testing, and Startup Requirements

6.1 Maintenance

6.1.1 Organization

An analyzer maintenance organization may range from one mechanic working part time on analyzers in a general maintenance group to a fairly large group of engineers, technicians, and mechanics with full-time analyzer maintenance responsibility. The size of the group is largely dependent on the number and complexity of analyzers installed in the plant, as well as the attitude of that plant’s management toward analyzer maintenance. Most refineries and plants contain a sufficient number of analyzers to justify at least one full-time person assigned to this task.

An analyzer maintenance group can be structured and function successfully in the refinery organization as part of maintenance, engineering, or operations departments, or the laboratory; however, the analyzer maintenance group must maintain liaison and communication with the other departments if maximum benefits are to be realized from using analyzers.

Some of the specific communication needs of the analyzer maintenance group are:

a) With the maintenance department to schedule other craft work required in analyzer systems and to schedule and plan work and provide for training.

b) With the instrument engineering department to learn of new applications planned, to feed back advantages or disadvantages of particular analyzer system installations and to jointly develop maintenance strategies.

c) With the operations department to learn problems, to schedule and plan maintenance work, to assist operating personnel in the use and understanding of the analyzers, and to receive feedback regarding the advantages and disadvantages of particular analyzer installations.

d) With the laboratory to develop calibration techniques and obtain standards and to develop and maintain laboratory testing as necessary to back-up plant analyzers.

Often the most effective analyzer maintenance groups are those in which there is direct involvement of professionally trained people: instrument engineers, process engineers, and laboratory chemists. They can be very helpful in training, reviewing the efficacy of existing analyzers, and assisting in developing an overall maintenance strategy.

Some plants hire outside specialists for analyzer maintenance. This method may not be as effective as using plant personnel if the specialists are called in only for emergency work; however, it can be satisfactory if preventive maintenance is scheduled where needed or if the specialists report to the plant each day. In this case, they function as regular plant personnel.

6.1.2 Personnel

Special skills are required of analyzer maintenance personnel because most analyzers are complex and difficult to maintain. Therefore, the tendency is to assign more talented people to analyzers. It is desirable that these persons have a good background in the maintenance of conventional instruments, a basic knowledge of chemistry and piping, and a comprehensive understanding of electronics, including digital circuitry and microprocessors. They also require knowledge of refinery processes and laboratory methods.

The classification of analyzer maintenance personnel often is different at various locations. Some use hourly employees, some use staff personnel called technicians or inspectors, some use engineers, and some use various combinations of these groups. Any of these classes of maintenance personnel can be effective if they possess the proper skills. Training is the key. Training of maintenance personnel is discussed in 6.2.

Manpower requirements for maintenance of specific instruments, control valves, and analyzers have been determined by International Society of Automation (ISA) Maintenance Management Division through a survey of its members. Published results for maintaining analyzers are listed in Table 6-1.

NOTE For comparison purposes, differential pressure type flow transmitters required a mean of 6 and a range of 4 to 8 work hours per year.

6.1.3 Facilities

6.1.3.1 General

Maintenance facilities required for analyzers include a shop, adequate facilities for storing appropriate records (including maintenance instructions), necessary test and training equipment, and hand and power tools.

Table 6-1—Analyzer Maintenance in Manhours per Year

Analyzer	Mean	Range	Standard Deviation
Boiling point	80	85 to 74	4.82
Carbon dioxide	21	25 to 18	2.10
chromatograph, gas	145	170 to 130	2.50
Combustibles	50	61 to 44	3.74
Density (displacement)	34	40 to 29	3.16
Density (radiation)	40	49 to 33	4.00
Infrared	76	94 to 62	5.69
Oxygen	38	42 to 35	2.30
pH	29	40 to 20	6.21
Refractive index	40	49 to 33	6.32
Ultraviolet	59	78 to 42	6.00

Ideal shop facilities for analyzers are somewhat different than those required for conventional instruments. Many analyzers constitute a system that includes sampling components, sensors, a transmitter, a control unit, and receiver devices for display and/or alarm and control. Calibration facilities may be included in the total analyzer system. The shop should be designed to handle such complete systems for actual operation of most types of analyzers with representative samples. This requires that the shop be designed for the safe introduction, circulation, and disposal of sample fluids and equipped with the required utilities.

An electronics test and repair area is needed because most analyzers are electronic in nature. This area should be housed in a clean, temperature-controlled room separate from valve or other major equipment repair areas and isolated from the calibration facility. Frequently used parts and components should be readily available. An area is often provided for continuous operation of “Hot Spares” (full or parts of analyzers supplied with electrical power) in order to insure serviceability. Hot spares are also used as diagnostic or fault finding tools.

6.1.3.2 Maintenance Documentation

Appropriate records and documentation are an important part of the facilities required for effective analyzer maintenance. A dedicated information package, often referred to as a “loop folder” is recommended for each analyzer to facilitate repairs and troubleshooting by personnel that may not be familiar with the application.

A typical “loop folder” should contain the following information:

a) sample system diagram (including the fast loop sample and return points);

b) loop diagram (signal(s));

c) a simplified P&ID diagram;

d) all associated prints (electrical, piping, plot plan sample and return points, etc.);

e) original analyzer specification sheets;

f) original vendor literature concerning normal operation and maintenance;

g) calibration standard certification sheets;

h) diagnostic chromatograms indicating the failure of a column or a switching valve (for gas chromatographs);

i) chromatograms (calibration standard and startup runs on each stream [for gas chromatographs]);

j) analyzer startup procedures (such as setting flows, pressures, etc.);

k) procedures for calibration of output devices to recorders or the control system;

l) spare parts lists (especially those that are not stocked in the warehouse);

m) maintenance history log (unless a separate maintenance logbook is kept).

6.1.4 Techniques

6.1.4.1 General

Analyzer maintenance techniques can be preventive maintenance or emergency/breakdown maintenance in nature. Preventive maintenance is designed to prevent breakdowns, whereas emergency maintenance is performed following some problem that appears in the analyzer system. An effective preventative maintenance program substantially decreases analyzer downtime and reduces work orders for equipment failure.

6.1.4.2 Preventive Maintenance

Preventive maintenance is designed to:

a. ensure the integrity of measurement;

b. minimize breakdowns;

c. reduce overall costs.

Often the preventive technique is little more than a series of frequent inspections with minor adjustments performed as necessary. This “mothering” of the analyzer system may be necessitated by the replacement schedule of consumables such as reagents, carrier gases, and calibration standards. More often the inspection is performed to assure that the sampling system is functioning properly and other components in the analyzer loop are operational. The inspection may or may not include a calibration of the analyzer (see Chapter 3).

Preventive maintenance of analyzer systems in many respects is similar to the overview provided by operators of their process units. Indeed the overview of the analyzer system, which often resembles a miniature process, may be the responsibility of the operator.

Other duties performed during preventive maintenance include cleaning, back-flushing, blowing down, and component replacement. The frequency of this work should be based on the manufacturer’s recommendations and the actual maintenance history of the analyzer.

Frequency of performing preventive maintenance may also be governed by the importance of the analyzer in the process. Assuring integrity of analyzer performance may be more valuable on those analyzers in closed loop control than those used just to provide operator information.

6.1.4.3 Emergency Maintenance

Emergency maintenance may be the most cost-effective technique for some analyzers. Under this system the analyzer is operated without preventive work until a failure occurs. This technique could be best for analyzers:

1) that seldom fail;

2) that have spares readily available, ensuring a short out of-service period;

3) where a satisfactory backup can be utilized during breakdown (such as laboratory testing);

4) where the loss of the analyzer information during the repair period can be tolerated.

6.1.4.4 Selecting a Maintenance Schedule

Each analyzer application should be evaluated carefully in determining the best maintenance technique. Preventive maintenance does not assure freedom from all breakdowns, but if performed properly should minimize failures.

Being prepared is important in coping with analyzer failures. Frequently it is important to minimize the out-of-service period, which can be accomplished by utilizing four key items in preparedness:

1) well-trained maintenance personnel;

2) manufacturer's maintenance instructions;

3) proper documentation, including the maintenance history of the analyzer;

4) an adequate supply of consumables and replacement parts, including subassemblies and entire units to permit repair by replacement, when that technique is appropriate.

6.1.5 Troubleshooting

Most maintenance requirements for analyzers involve the sample systems. The failure of the sample system to deliver a clean representative sample from the point of measurement to the analyzer is the most frequent problem. The sample problem can result in three different failure symptoms: plugs in the sample line components, damage to the analyzer, or inaccuracies in the measurement.

If the service experience of a given analyzer system shows repeated maintenance calls as a result of sample problems, then the sample system should be redesigned. Correction may include a better sample tap location, shorter lines, correcting sample velocity, improving temperature gradients, or better filters (see Chapter 4 for further comments). Automated sample systems may be employed, (e.g., using filter switching when plugging starts to occur). This enables maintenance to schedule a filter change. Automated sample systems are gaining popularity with the advent of INSA/ISA 76.00.02-2002 "modular component interfaces for surface mount", and NeSSI™ (New Sampling/ Sensor Initiative) modular sample systems. These use modular design for valves, flow devices relief valves, filters and a number of other devices. Sample system diagnostic data can be transmitted to maintenance in order to correct problems before failure occurs. An increasing number of analyzers are now available that mount directly into the modular system.

Maintenance requirements for analyzers that are not caused by sample system problems can be categorized as follows.

1) Consumables—Many analyzers require reagents, carrier gases, calibration standard samples, or other supplies, which may have become depleted.

2) Utilities—Electric power, instrument air, cooling water, steam, or other utilities are required for analyzers. Utilities must be closely regulated for proper operation.

3) Environment—Many analyzers will not function properly in harsh environments. The ambient temperature cannot be too cold or too hot (see manufacturer's recommendations). Contaminants, such as moisture or corrosive chemicals, may cause problems, particularly with electronics.

4) Mechanical moving parts—Pumps (particularly peristaltic type), valves, relays, and other components that have moving parts are subject to failure or misoperation.

5) Nonmoving parts—Failures can be caused by electronic components or burned out or inoperative sensors.

6) Misapplication—Some applications overextend the ability of the analyzer to make the required determination. For example, a low signal-to-noise ratio can result in many service calls.

7) Lack of understanding—Many users do not understand the meaning of the analyzer reading or the limitations of the analyzer as applied. This is often true with inferred measurements. In these cases the analyzer may be functioning properly, but the maintenance man's job is to educate the user.

8) Troubleshooting with Lab samples: When comparing process and lab analyzer results the reproducibility of the test method is often neglected. The two measurements may give different results but are both within the test method reproducibility, therefore are both correct.

6.2 Training

6.2.1 Training Needs

Training of personnel involved with analyzers can be divided into two general categories: application and maintenance. Professionally trained personnel (engineers, chemists, and others) are generally responsible for the application of analyzers to the processes. Highly skilled specialists (technicians, inspectors, or instrument mechanics) are usually, but not exclusively, responsible for maintenance. Therefore, the training needs for effective analyzer applications are directed toward professionals and the training for analyzer maintenance toward specialists.

Professionals should keep their general background skills updated in mathematics, chemistry, physics, electronics, hydraulics, computer science, refinery processes, and other areas, which may be required for a thorough understanding of the operating principles of analyzers and their sampling systems. This generalized training can be achieved by a combination of job experience, self-study, night school, short courses, seminars, and other means that are beyond the scope of this publication. Additionally, specialized training on particular types of analyzer systems is necessary. This application-oriented training should focus on the capabilities and limitations of specific analyzers and on the experiences of others using analyzers in particular process applications.

Training personnel for analyzer maintenance is quite different from application training. Maintenance training must include general background updating of the personnel as well as specific training on analyzers. It is not effective to teach troubleshooting of chromatographs if the maintenance person has no knowledge of electronics and physical chemistry. Thus the background knowledge listed above, which professional personnel possess, often must be taught to specialists assigned to analyzer maintenance.

6.2.2 Selecting Trainees

It is important to choose the right people to train for application and maintenance of analyzers. The need for training is usually apparent but training the right people at the right time is also important. One general rule to follow is to choose those people to train who will be assigned responsibility in that area following the training. Training is expensive and can be wasteful. Nearly all knowledge gained will be forgotten if it is not used promptly. This is particularly important in maintenance training for specific equipment.

When choosing people for assignment to analyzer maintenance, care should be taken to select those with the most interest and best background and characteristics to be effective in this work. Usually this means selecting some of the more advanced people who already possess, or can be trained to develop, the special skills required for analyzer maintenance.

6.2.3 Types of Training

Training can be categorized into individual efforts such as self-study, night school, correspondence schools, and formal group training. Although independent training is very important to the individual, particularly in keeping current with advancing technology, it will not be discussed further in this publication. Group training sessions are available from vendors, schools, specialty contractors, technical societies, and on-the-job in-house training by many user companies.

6.2.3.1 Vendor Training

Most vendors of analyzers offer training sessions for their own equipment. The cost of these sessions varies from no charge to a modest fee and the sessions are held in the vendor's plants or in locations more convenient to the students. Classes may be held in the vendor's regional offices or in hotel or motel facilities in geographic areas where a particular vendor's in-service analyzers are concentrated. Vendor training may also be conducted in the user's plant in conjunction with new analyzer commissioning and startup.

Vendor training is generally of high quality. Most companies use a format that combines classroom sessions, demonstrations, and hands-on familiarization. The classroom portion covers the principles and theory involved in the design of the analyzers and the proper application of the analyzers to processes. The hands-on training is designed to teach proper functioning, maintenance, calibration, testing, diagnostic procedures, adjustments, tuning, assembly and disassembly.

6.2.3.2 Classroom Training

Training provided by schools can be quite varied. It may be in the form of an evening class held in a local college or high school. The instructor for such a class is often recruited from local industry, and is usually someone involved in the application or maintenance of analyzers. In many respects, this type of training session can be quite similar to vendor training classes except that the scope is broader, covering analyzers from many vendor companies.

Some colleges and universities offer a series of short courses or seminars pertaining to analyzers. These are designed for persons interested in analyzers who can the time away from their normal work to attend the sessions.

Most of these short courses are of one week or duration. The teaching staff may be a combination of university and industry personnel. Course content is usually more theoretical and application oriented than maintenance oriented, and therefore, more directed toward professionals rather than specialists. Because of the wide variety of courses, the course content, the qualifications and experience of instructors, and recommended prerequisites must be reviewed carefully in order to select the most suitable training.

6.2.3.3 Technical Societies

Technical societies also offer a wide variety of training opportunities. Written standards and practices pertaining to analyzers, technical talks at society meetings, seminars, symposia, and short courses may be available. Exhibits of analyzer equipment are frequently included at technical society functions. This enhances the overall training aspect. In many instances, the authors of technical papers, standards and practices, the speakers at society meetings, and classroom instructors at seminars and symposia are recruited from the membership roles of technical societies. Once again the reader is cautioned to be selective in choosing the specific training events.

Analyzer training opportunities offered by technical societies include the following.

a) American Institute of Chemical Engineers (AIChE) conferences and exhibits and continuing education courses.

b) American Petroleum Institute (API) standards, recommended practices, and technical sessions at professional meetings.

c) International Society of Automation (ISA) cassette packages, films, DVD, on-line training material and videotapes; standards and recommended practices; books and proceedings; symposia short courses; and conferences and exhibits.

6.2.3.4 User Training

6.2.3.4.1 Startup Training

Many user organizations have established in-house training for individuals involved with analyzers. In its simplest form this consists of a one-on-one training in which a trainee is paired with a more experienced maintenance person during normal working hours. In this system, the trainee receives individual instruction and hands-on experience. This can be a very effective training technique, particularly where only one or a small number of people are trained or where group classroom work is to be supplemented with field work; however, it is an inefficient method in that it requires one instructor for each student. A potential problem may exist in that the experienced maintenance person may be effective in analyzer work but not in teaching.

6.2.3.4.2 New packaged equipment training

With new packaged systems the maintenance personnel should be trained in the analyzers, equipment and the system in which they are contained (e.g. analyzer house or shelter). It is effective to have the maintenance personnel who will be responsible for routine maintenance attend classes for the analyzers directly before the Factory Acceptance Test (FAT) at the PSS. Upon completion of training these maintenance personnel can attend the FAT to reinforce the class work and learn the system. This often includes Gas and other hazard detection, Heating Ventilation and Air Conditioning (HVAC), sample system design, alarms, communications, and maintenance procedures.

6.2.3.4.3 In-house Training

In-house training is frequently held in conjunction with the commissioning of one or more new analyzers. Ideally this training should be held prior to startup of the equipment but with the analyzers actually operating with calibration samples. The analyzers can be located in the shop, in a training area, or in the plant. The instructor may be a local employee or a vendor representative. This type of training can be very effective for maintenance personnel and for familiarizing operating personnel with new equipment. Operators should be encouraged to ask questions about the application of the equipment and to learn how the information obtained is used. This type of familiarization in advance of startup can help bridge the credibility gap between operations and maintenance on analyzer performance.

6.2.3.4.4 Location Training

Many users have established analyzer training sessions designed to train a group of people to maintain a variety of different analyzers in use in their plants. These sessions consist of two to three hours of training held one or more times each week, usually during working hours. Training can continue for many weeks until all subjects are covered. Instructors often include vendor personnel for specific analyzers and in-house experts for more general subjects. The personnel chosen for training should be those who will be assigned responsibility in that area following the training. The classroom should not be filled with people who will not use the training. Small classes are more effective than large ones.

6.2.3.4.5 Corporate Training

Some users have set up corporate training centers at a central location drawing students from several plants. This is a very formalized technique and can be effective because it is a full-time effort with the students relieved from all other responsibilities during the training. One company holds this type training every year or two with sessions lasting from 6 months to 9 months. The goal is to convert the best available candidates into highly skilled analyzer specialists through intensive training. A full-time instructor plans the training and is supplemented by the vendor's personnel and corporate experts in various subjects. The class visits vendor locations for some of its sessions and usually conducts a major part of its training at an analyzer systems house. This permits hands-on training on various analyzers and sampling systems, which have been purchased by this company. The timing is arranged so that the class performs the necessary checkout, calibration, and inspection of analyzers before they are shipped to the plants. Such a training course may include basic subjects (math, physics, chemistry, and electronics), 25 %; analyzer subjects (laboratory methods, sample systems, and analyzers), 10 %; miscellaneous subjects (purchasing, safety, and documentation), 3 %; vendor instruction, 30 %; hands-on testing, 12 %; and classroom study, 20 %.

6.2.4 Retraining

A great need exists to continuously update and re-train persons already working with analyzers. The technology is advancing so rapidly that continual retraining is required to keep current. Analyzers today are field programmable, contain microprocessors, and employ measurement techniques previously not available. Personnel must be provided with retraining opportunities to improve their skills and retain their effectiveness.

Training discussed thus far can be used for retraining as well; however, it is probably even more important in retraining to choose the right student for each type analyzer to assure he is trainable. As analyzers become more complex, analyzer personnel will become more specialized. All personnel will not be equally proficient with all types of analyzers. A plant will be doing very well indeed through its recruitment, training, and retraining to provide analyzer personnel with sufficient skills to effectively apply and maintain today's analytical instrumentation.

6.3 Installation and Safety

General considerations for the installation and safety of analyzer systems include the following.

a) The system must meet all safety requirements.

b) The system must provide an accurate, reliable analysis.

c) Utilities must be provided for testing, calibration, isolation (blocking in, valves, switches, and so forth), and maintenance.

d) The system should be installed for the lowest cost commensurate with required performance.

e) The system and its components must be accessible for removal and service.

6.3.1 Analyzer System Installation

6.3.1.1 Code Compliance

The analyzer system must be designed and installed in accordance with the latest edition of local, state, and national codes that are applicable.

6.3.1.2 Equipment Protection

The type of analyzer involved and the environment surrounding it determine the protection required for ensuring reliable, accurate, and safe operation. Analyzer systems must be protected from extreme ambient temperatures, weather variations (rain, snow, wind, dust, sand, and humidity), direct sunlight, and a corrosive atmosphere.

When the analyzer instrument case is not sufficient to provide the protection needed to ensure satisfactory performance of the instrument, an analyzer housing of some type is usually required. The specific type will depend on the analyzer and the environment in which it will operate. Economics and ease of maintenance may also call for centralizing analyzers in a specific housing.

The housing selection should be made after considering these factors:

a) electrical area classification;

b) governing codes and standards;

c) environmental factors;

d) protection required;

e) accessibility;

f) sample line length;

g) waste disposal.

Four types of enclosures are available.

1) If the analyzer is insensitive to ambient temperature and requires only minimal maintenance, the case provided with the analyzer may be adequate. Conductivity and pH analyzers are examples of analyzers that can frequently be mounted in the open (enclosed only in their cases).

2) One or more analyzer systems in a cabinet is acceptable if the environment in the cabinet satisfies the electrical area classification, the ambient temperature requirement of the analyzer, and the equipment is easily accessible for maintenance.

3) A shelter is useful for limited protection of equipment and personnel. It is important that the shelter be designed so that the electrical area classification does not become more hazardous.

4) Those analyzers requiring ambient protection and frequent maintenance and calibration may be installed in a house. This type of protection is especially useful where extreme ambient conditions are encountered. Provision for ventilation may be necessary for safety reasons.

6.3.1.3 Equipment Location

In certain situations it may be necessary or desirable to insert the assembled sensor in its mounting probe directly into the process (in-situ location). Measurements of pH and conductivity, for instance, are often taken in situ. In-situ operation requires that the probe of the analyzer be compatible with the process conditions.

The advantages of an in-situ installation are:

a) Sampling system requirements are minimal;

b) Transportation lag is minimized;

c) The sample is representative and original without being altered.

The disadvantages of an in-situ installation are:

a) The probe may be located in a position that is difficult to reach for maintenance.

b) Distance restrictions between probe and analyzer may place the analyzer in a less desirable area.

c) The probe may not be removable for service without shutdown of the process line or exposing maintenance personnel to hazardous conditions.

d) Variations in process pressure and temperature may require compensation of analyzer measurements.

e) Calibration is often difficult without shutdown or removal.

f) Performance of detectors and electronics is generally less when exposed to large ambient conditions and temperature variations.

In contrast to in-situ installations, slip-stream samples may be extracted from a specific location in the process by a sampling probe and transported via a sample line to the analyzer for measurement. This sample is then vented, drained, or returned to the process. In installations where the analyzer is remote from the sample point, smaller samples are usually drawn from a fast circulation sample loop to reduce sample transportation lag.

The advantages of an extractive sample system are:

a) The analyzer can be located in a more desirable area than the sampling point.

b) The sensor can be located in an accessible location.

c) Analyzers can be grouped for convenience of operation and maintenance.

d) Calibration is generally enhanced.

The disadvantages of an extractive sample system are:

a) Maintenance requirements and opportunities for failure may be increased as a result of the added components required in the extractive sampling system.

b) There will be transportation lag.

c) Long sample lines may create measurement problems.

d) Composition may be altered due to adsorption or condensation.

e) The possibility of sample system leaks may increase, requiring additional design precautions.

6.3.1.4 Location of Auxiliaries

It is important that the utilities, including waste disposal facilities, required for analyzer operation or calibration be available at the site.

6.3.1.5 Analyzer House Considerations

An analyzer house not only provides an enclosed environment to ensure satisfactory operation of the instruments and protection for service personnel from the elements, but may also be utilized for centralizing a group of analyzers.

The choice of analyzer house location is determined by the following:

a) the availability of required utilities;

b) the electrical area classification;

c) the source of safe ventilation air, if forced ventilation is required;

d) the location of sample supply and return connections.

The house should be large enough to allow sufficient headroom and free access to three sides of wall-mounted equipment. The best arrangement of equipment should be determined before dimensions are finalized. Space should be considered for facilities such as cabinets and a workbench. Storage cabinets should be fitted with wire mesh doors to prevent accumulation of toxic or flammable vapors.

Shipping the house to the job site is an important factor to consider in determining the size. Shipping regulations may limit the dimensions of the house.

The house should be constructed of materials that are fire resistant and inert to oil and chemicals likely to come in contact, and be properly insulated to minimize the effects of fluctuations of environmental factors (such as humidity, frost, solar radiation, rain, and snow). The need for insulation should be evaluated individually. Fireproof insulation may be required.

When used as a support for equipment, the house should have sufficient rigidity to minimize vibration.

Either a gable or shed-type roof is acceptable. Either type should be sloped for water runoff and to facilitate snow removal. For areas with significant snowfall, the roof must be structurally designed to support a snow load as required by local building codes.

In most cases, the analyzer house is shipped to the job site completely assembled and ready for installation. The analyzer house should be located on a concrete pad, which serves as the base for the enclosure. The house should have an integrated floor with a non slip surface. The floor should be easy to clean and suitably sloped for proper drainage.

A drain and vent system may also be provided for sample disposal. The vent should be fitted with a U trap to prevent gasses being expelled at low level. The vent should not be directly connected to the drain. Excess liquids in the vent can be expelled from the U trap into a funnel connected to the drain. This prevents back pressures in the drain from being transmitted to analyzer detectors. Steam lines should be insulated for personnel protection. Adequate lighting around the analyzers and other equipment is required in the enclosure. Thirty foot-candles (322 lux) should be considered a minimum general lighting level inside the house Lighting for outside (cylinder/sample panel area) should be 15 ft candles (160 lux)

Flammable or toxic materials handled by analyzers mounted in a house can create an unsafe environment for personnel and endanger the safe operation of a plant. Continuous dissipation of heat from instruments, as well as solar heat, may create an unsuitable environment for the analyzer operation. For these reasons ventilation may be required.

The house is usually force ventilated. The air intake should be through a stack with a rain hood. The air should be provided from a non-hazardous area free of corrosive, flammable, or toxic gases. The flow of air within the house should ensure air movement throughout the house and around all instruments. The location and number of air entry and exit ports depends on the properties of the hazardous materials handled, the pressure to be maintained in the house, and the number of air changes needed. A positive pressure of 0.1 in. of water is considered adequate to prevent flammable and toxic gases from entering the house through its exterior walls. This pressure can be maintained using weighted louvers in the exit port.

The effects of leakage from the sampling system components within the house may be dissipated by adequate ventilation. The quantity of air to be circulated can be established using equations from NFPA 496.

The fan should have aluminum non-sparking-type blades and a directly coupled motor driver. This offers the advantage of compact installation and assures constant speed. The motor should be acceptable for the electrical area classification associated with the installation.

An air filter should be installed in the inlet duct either before or after the fan. The location should allow easy cleaning and replacement.

The prevailing weather in the geographic area where the house is to be installed determines the degree of heating or cooling required. The temperature to be maintained in the house should be determined by the analyzer specifications and comfort of personnel.

The analyzer house door or doors should be sized for safety and free passage of the largest equipment to be installed in the house. An alternate escape door (a second door) is required for houses over 8 ft long. The doors should have wire-reinforced, clear glass windows. If the door or doors are to be provided with a lock, it should only lock on the outside. A crash bar should be provided inside and should open the door both in the locked and unlocked condition.

6.3.2 Safety

The design of the analyzer system and the proper location require a thorough understanding of the working environment. Careful planning and engineering of an analyzer system cannot be overemphasized.

Electrical outlets intended for power tool use should be max 120v AC with a grounded neutral.

6.3.2.1 Electrical Area Classification

All electrical equipment in the analyzer system should be suitable for use in the area. Dependent upon location there are safety codes of practice that allow the inside of the analyzer house to be assigned non hazardous while air is flowing through the purged system from a safe area at the rate recommended to give the required house volume air changes per hour. However if air purge is lost the non certified equipment must have power safely removed. The condition must also apply that with the worst case leak in the house the Lower Explosive Level (LEL) must not exceed a given value (typically 25 % LEL) while purge air is flowing. Purging should meet the requirements of ANSI/NFPA 496, or other applicable international standard.

6.3.2.2 Ventilation

For ventilation requirements refer to 6.3.1.5. Additionally, the following safety precaution should be considered when designing the ventilation system. When an enclosure is purged for the purpose of changing the electric classification, a visual and audible alarm should be indicate failure of the purge.

6.3.2.3 Venting

Flammable and toxic materials should be vented to a safe location in accordance with regulatory codes.

6.3.2.4 Explosion Prevention

To determine the method of protecting equipment from explosions, the surrounding area must first be classified. Analyzers differ from most other equipment containing electrical apparatus in that the flammable substance is of necessity brought into the same enclosure and confined together with the electrical components. When the analyzer enclosure contains a source of potential sample release, the method of protection required is determined by the area classification, the probability of the release of flammable substance within the enclosure, and the electrical design of components and circuits within the enclosure. Sources of ignition located within the sampling system, particularly within the measuring cell, must be evaluated if the composition of the sample gas may enter the flammable region. Sources of ignition include surfaces that may be heated to the proper ignition temperature and the energy of electrical circuits exposed to the sample gas under normal and faulty conditions.

The following types of protection are recognized as ensuring safe operation in hazardous areas.

a) Analyzers may be fully enclosed in explosion-proof housings.

b) Analyzers may be fully enclosed in a general-purpose enclosure. Air is introduced into the enclosure at sufficient flow to remove any hazardous vapors present and with sufficient pressure to prevent their entry. Inert gas purging should only be used in well-ventilated areas. Where purged air is used from a site common supply it must be insured that the air supply is not supplemented with nitrogen on reduced pressure, or air is not substituted by nitrogen in any circumstance.

When an analyzer can be a continuous source of atmospheric ignition, the installation must be designed to ensure against loss of purge medium, overheating of the external case, and inadvertent opening of cases.

Some permitting authorities permit or require a continuous dilution flow of purging medium through the analyzer enclosure to minimize the risk that can occur when a flammable sample vapor may leak into the analyzer case.

For guidance and specific requirements, reference should be made to standards describing requirements for purged and pressurized enclosures for electrical equipment in hazardous locations.

6.3.2.5 Intrinsically Safe and Non-incentive Equipment

Systems certified as intrinsically safe by recognized testing laboratories may be installed in hazardous locations without explosion-proof housings or other means of protection. Non-incentive equipment may be installed in Division 2 areas in general purpose enclosures. Requirements for construction, installation, and testing of intrinsically safe and non-incentive equipment are provided in NFPA 70 and API 500.

6.3.2.6 Safety of Personnel

Analyzer systems should be designed, installed, and operated in such a manner that hazards to personnel are minimized. The following are safety guidelines for the design of all analyzer sample systems.

a) Fast loop sample systems of a toxic or hazardous nature must not be transported through any analyzer shelter or enclosure.

b) Flowmeters on all process streams of a hazardous or toxic nature must be armored.

c) The use of glass variable area meters on process streams must be reviewed by appropriate safety and environmental personnel of the end user company.

d) Sample streams of a toxic or hazardous nature must transport only the minimum required quantity of sample to assure a representative and timely analysis of the process stream.

e) Fast loop sample systems containing hazardous or toxic materials must be provided with a means of flushing the system with an inert gas or liquid prior to opening up the system to perform maintenance.

f) The use of glass or plastic sample system components must be approved by safety and operational personnel of the end user company.

g) All surfaces that exceed 150 °F in normal operation must be insulated or shielded from maintenance personnel protection.

h) The design of sample systems must minimize personnel exposure to toxic or hazardous sample during normal maintenance procedures.

i) The design of systems that require the use of personnel protection equipment for normal maintenance activities must be approved by safety and operations personnel of the end user company.

6.3.2.7 Toxic Materials

Regulations and increased public awareness have expanded concern on potentially hazardous materials, including carcinogens, mutagens, or teratogens. The effects of breathing, ingestion, and skin contact with toxic materials should be explained in detail to all employees.

The presence of toxic or inert materials in the atmosphere of the housing may require monitoring. An enclosed shelter or building may be located in a general purpose area, but process samples piped to and through the shelter may contain toxic or hazardous materials, such that a minor leak in the building could result in a hazardous environment for maintenance personnel.

Appropriate safeguards can be implemented to reduce the potential hazard, but not eliminate it entirely. For example, fast loop sample systems containing high volumetric flow rates should be located on the exterior of the shelter and only the minimum sample required for a timely analysis would be transported through the shelter. Inside the shelter, the samples are transported in what is often termed "well-maintained piping systems." That is, small diameter tubing is employed (typically $^1/_8$ in. diameter), the number of fittings in the shelter is minimized, and the sample lines enter and exit the shelter so as to minimize the length of tubing inside the shelter.

Ventilation is often provided to maintain the temperature in a range that will maximize the accuracy and operation of the analyzers contained in the shelter. Where extremes of temperature and/or humidity are encountered, air-conditioning may be required to maintain the temperature in an acceptable level for maximum analyzer accuracy.

If a shelter were located in a classified area where a leak in process equipment could result in a concentration of hazardous material inside the shelter, then a ventilation system that employs pressurization may be required. The intake of the ventilation system would employ a stack design of adequate height to ensure air is brought into the shelter from a safe area. Pressurization of 0.1 in. water is generally considered to be adequate to prevent the entrance of potentially hazardous gases.

Despite all of these efforts, it is necessary to place toxic monitors inside a shelter to alarm on specific hazards. Some examples include the following.

a) An H_2S analyzer may be required for shelters containing analyzers measuring streams with high concentrations of H_2S (e.g. a tail gas analyzer in a sulfur plant).

b) For process streams containing a high level of carbon dioxide, a ppm-level CO monitor will be required.

c) For process streams containing ethylene oxide, a ppm-level EO monitor will be required.

In one less obvious case, an oxygen-deficiency monitor may be required if the practice in the plant is to backup the instrument air system with nitrogen, AND a shelter contains a large number of high-volume users of instrument air (e.g. gas chromatographs) that are vented into the shelter. In this particular case, the need for a monitor may be avoided by ensuring that ALL analyzer vents are piped outside the shelter.

Warning lights activated by toxic monitors should be located above all entry/exit doors for shelters when monitors are required. The color of the warning lights should not confuse operating or maintenance personnel as to the potential hazard inside a shelter. For example red should not be used if red is a plant standard warning for fires. Appropriate warning signs should be located at eye level on the entry/exit doors describing the purpose of the warning lights.

The design of all enclosed shelters or buildings should be reviewed by appropriate safety personnel to ensure that a hazard monitor is not required.

Entry into a housing where toxic materials can be present above the threshold limit values should be prohibited without supervision and appropriate means of detection and protection.

6.3.2.8 Pressurized Cylinders

Pressurized cylinders used for analyzer systems should be securely mounted and located outside the house.

An appropriately sized orifice should be installed in the lines coming into a shelter on the exterior walls for all pressurized cylinders to prevent an explosive atmosphere inside of the shelter.

6.3.3 Installation Checklist

The purpose of this checklist is to outline the methods used in checking field-installed analyzers and sample conditioning systems.

a) Visually inspect all analyzers and sample conditioning systems for damage after installation. If damage is observed, take corrective action. There should be a sheet with calibration and check-out data for every analyzer and analyzer loop that is inspected.

b) Compare all analyzer installations against flow and installation drawings for proper location as well as for compliance with any special provisions that may be called out in these drawings.

c) Temporary protective devices must be removed before startup.

d) Verify that all analyzers, sample systems, and tubing are correctly tagged, labeled, and installed at the correct locations.

e) All sample systems and sample probes must be tagged and checked for proper installation with respect to direction of flow, elevation, orientation, insertion, and depth. A warning must be posted so that the process valve is not closed on the probe and the probe is not removed unless proper safety procedures are followed.

f) Analyzer and sample system wiring should be checked for circuit continuity, proper terminal connection, and labels.

g) Piping and tubing which is process-connected should be checked for agreement with P & IDs and for appropriate materials, connection sizes, and ratings. Verify that adequate brackets and supports have been used to maintain rigid construction.

h) If steam tracing is used, verify the correct installation of all utilities including proper steam addition and trapping of prefabricated, steam-traced bundles. Check the manufacturer’s engineering data for these requirements.

i) All analyzers should be isolated from the process lines by block valves. Sample tubing lines should be thoroughly cleaned before process is allowed into the lines.

6.4 Inspection and Testing

6.4.1 General

Because analyzers are complex, their inspection requirements are complicated, detailed, and difficult compared to those of other instruments. Therefore, inspection requirements and the techniques and procedures to be followed must be thorough, detailed, and clearly described in procurement specifications. That personnel must be particularly knowledgeable and experienced in the field is no less important.

Since analyzers may be categorized into many types and by such a variety of applications, and even by a spectrum of design complexity, this chapter becomes a set of guidelines and checklists rather than a standard. Nevertheless, customized inspection and test procedures and techniques can be developed for analyzers or analyzer systems from these guidelines.

Inspection is defined as the nonfunctional verification of the physical characteristics of an analyzer or analyzer system against the associated documentation. Nonfunctional verification can include visual inspection or analysis, including reduction or translation of data, analysis of factory test data, review of analytical data, or performance of detailed analysis.

Testing is defined as the functional verification of an analyzer and includes actual operation of the analyzer and analyzer system.

6.4.2 Personnel Qualifications and Organization

Analyzers are considered to be among the most complex and difficult instruments to inspect; therefore, assignments should go to skilled, experienced personnel. The personnel who are assigned to the inspection of analyzers must have both training and experience in the inspection of conventional instrumentation. They must have a comprehensive knowledge of electronics, chemistry, chemical processes, and laboratory methods as well. Refer to 6.2.3 for more detailed training requirements:

The most effective inspection groups frequently are those in which professionally trained personnel are involved, at least part time. Their efficiency and effectiveness are a result of background knowledge developed from:

a) involvement in prior inspections;

b) direct experience in selecting and specifying analyzers;

c) knowledge of the principles of analyzer operation, use, and application;

d) knowledge of design requirements for those analyzers that incorporate specially designed sample-conditioning systems;

e) knowledge of operational and maintenance requirements and characteristics of sampling systems.

6.4.3 Inspection Procedures for Analyzer Systems

For purposes of inspection and preparation of inspection procedures, analyzer systems can be partitioned into three distinct categories: the shelter, the analyzer, and the sample conditioning system.

6.4.3.1 Analyzer Shelter

The analyzer shelter (where the analyzer is physically mounted) shall be inspected for compliance with design criteria.

6.4.3.2 Process Stream Analyzers

The process stream analyzer is an instrument for measuring or inferring physical or chemical properties or chemical composition of gases, liquids, or solids in process streams. Complete factory test data for the analyzer should be furnished to the inspector. This data should include test sample composition, charts, records, test results, and settings and adjustments that apply to the specific analyzer.

6.4.3.3 Sample Conditioning system

The sample conditioning system is the combination of components or modules installed directly upstream of an analyzer inlet used to prepare process samples for analysis and downstream for return to process. Examples of modules that are used include filters, vaporizers, reducing regulators, scrubbers, separators, and temperature controllers. The system should be checked for compliance with drawings and specifications.

6.4.4 Inspection and Test at Vendor’s Location

6.4.4.1 General

Inspection at the vendor’s location could mean inspections conducted at the manufacturer’s factory or at the facility of an analyzer systems supplier who has a contract or subcontract to furnish a package with several analyzers, complete with sample systems, racks, and shelters. It is usually desirable to perform all work in the shop rather than in the field for those analyzers for which prepackaging is feasible. Craft work performed in the shop should be inspected and tested for acceptance at the source prior to shipment to the location for installation. The craft work to be specified includes fabrication, painting, mounting of equipment, piping, and wiring.

Although inspection at the user's site is possible, inspection at the vendor' location is preferable because the inspection and test equipment required may not be available at the user's site. Correction of any deficiencies is easier before shipment.

Customer checkout is to be divided into two parts: inspection and functional testing. Inspection should include a visual check of the instruments and equipment against specifications. The arrangement of equipment for accessibility and craft workmanship should also be reviewed. Inspection should include a leak test of piping and tubing. Functional testing should emphasize the total system operation as well as demonstrate the ability of the analyzer to make the required determination with a known sample as a stability test.

Paragraph 6.4.4.2, Paragraph 6.4.4.3, and Paragraph 6.4.4.4 provide a typical procedure for final inspection and checkout of analyzers and systems at the vendor's site to ensure complete compliance with specifications for performance, design, completeness, and workmanship.

6.4.4.2 Pre-checkout Preparations

The final factory inspection must be completed, and the system calibration must be performed by the analyzer vendor, before the user's engineering personnel arrive to conduct checkout of the analyzers. As part of the pre-checkout preparation, arrangements must be made in advance to set up the system and/or systems complete with sample, sample conditioning cabinet, the analyzer to be checked out, and any control unit.

6.4.4.3 Checkout Reference Documentation

The following documents should be used as working references during checkout procedures on analyzers:

a) purchase order file, complete with copies of purchase order, supplements, specifications, and correspondence;

b) vendor's data file, including electrical and piping drawings;

c) vendor's service parts and instruction manual.

6.4.4.4 Final Inspection and Checkout Procedure

Visual inspection should consist of visually verifying that all features of the quotation or purchase order are included. With the factory check sheet as a guide, all hardware should be visually checked for defects and misalignment and their proper locations.

The following specific visual checks should be made.

a) The sample conditioning apparatus should be checked for completeness and for workmanship of the tubing.

b) The wiring to the terminal boards should be visually inspected for neatness, labeling, and compliance with codes.

c) The case dimensions should be verified against any certified dimensional outlines to preclude discrepancies when panels are mounted.

d) The model number of the components should be checked against the specification and the purchase order.

e) The materials should be checked for appropriateness of use with the particular stream being analyzed.

Operation testing should include the following.

a) The factory test should be an operating test to demonstrate that the analyzer's performance complies with the purchase specification.

b) Testing shall be performed only after the system has been warmed up and stabilized for 24 hours.

c) Results of final factory calibration and testing should be reviewed.

d) Leak testing shall be done on the entire system.

e) The performance of the analyzer during a run on calibration gas (or liquid or mixture) should be witnessed.

f) Reproducibility should be demonstrated continuously for a minimum period of 8 hours using one or more standard samples.

g) Calibration should be demonstrated with a test sample giving approximately one-half scale reading for the component of interest. The concentration of the component of interest in the test sample should be at least 25 % of span different from the concentration of the same component in the standard sample used for the reproducibility test.

h) On multi-stream analyzers, operation of the auto-select and/or manual-select switches and valves should be verified. Standard gas should be connected to enable verification that the analysis is repeatable. This procedure verifies the stream selector valve and switching program. It should be confirmed that the instrument is capable of analyzing the number of streams as specified.

i) The range of the recorder used to track the analysis should be verified against the range given in the specification. If a transducer is used to condition output signals, the signal levels for compatibility with furnished panel-mounted components, such as recorders and controllers, should be verified. This is important for all analyzers, including chromatographs and thermal conductivity and infrared analyzers.

j) The tag number, date of test, identification of each peak or trace, attenuator settings, and signatures of test personnel should be recorded.

k) The functionality of all analyzer specific software must be demonstrated and a complete source code listing must be provided on all analyzers capable of being programmed by the user.

l) All ancillary equipment must be functionally test including software and computer peripherals.

m) The operation of digital outputs and the range of analog outputs must be verified to meet the bid specification requirements.

n) A punch list of all items requiring correction should be prepared.

o) An inspection report listing the tests performed, and the results obtained, should be signed by inspectors for both the vendor and user.

6.4.5 Inspection and Test at User's Site

On-site inspection at the user's site prior to installation consists of inspections to verify that the analyzer and the documentation concur. The purchase order, as well as the engineering specifications and drawings, must be used since both sets of documents provide most of the information used in the purchase. This type of inspection should be performed on all analyzers and systems.

Of primary importance in the inspection program at the user's site is the performance of any inspections that were not performed at the vendor location. Redundant testing should be minimized.

A careful inspection should be made to determine any damage that may have occurred during shipping.

Final loop checking and functional testing of the analyzer system should be performed after the installation has been completed.

6.4.6 Checklists of Test Procedures and Inspections

The specific components listed in Table 6-2 should be checked, at a minimum, for the items listed. The tests or inspections listed should be performed on the components during acceptance testing, either at the vendor location or at the user site. For each specific analyzer system, additional checklist items may be required.

Table 6-3 is a checklist for a typical inspection procedure for an analyzer system. Such a checklist would be tailored to a particular inspection. but the general categories of information would either be filled in with the test results or checked off as being satisfactory. The comment column should be used for any comments regarding the tests performed and the results obtained. This checklist, when properly signed, becomes an integral part of the inspection report.

6.5 Commissioning

6.5.1 General

Commissioning is similar to a process plant startup.

Complete manufacturer's equipment manuals are necessary and must be thoroughly understood before commissioning is begun. During and after the installation of an analyzer inspection should be made of the system to ensure proper installation and adherence to the manufacturer's specifications. The pre-startup steps and safeguards detailed in 6.5.1.1, 6.5.1.2, and 6.5.1.3 are recommended to ensure a successful analyzer commissioning.

6.5.1.1 Documentation

Complete analyzer system manuals are required for commissioning. These manuals will be used for initial operation and maintenance of the system. The manuals shall include as a minimum a complete set of as-built drawings to include:

a) sample system schematic diagrams showing sample tap identification, field mounted components, sample system components, line sizes, and operation ranges;

b) analyzer piping interconnection diagram;

c) analyzer wiring interconnection diagram;

d) analyzer outline and mounting dimensions;

e) complete parts list for all components and equipment used;

f) recommended spare parts list.

6.5.1.2 Personnel

Specialists are usually involved in the commissioning of process analyzer systems because these systems are generally more complex than other types of instrumentation. Plant personnel, preferably trained by the analyzer manufacturer, can be of valuable assistance. Sometimes commissioning and startup are part of the training program for analyzer operations and maintenance personnel. Expertise can also be provided by instrument contractors, who have experience in many analyzer fields, or by the manufacturer's representatives, who can provide the service either as a part of the purchase price or under a separate contract. The warranted operation of the device is often subject to certification by factory startup personnel.

Commissioning the analytical device usually requires some knowledge of the chemistry and physics involved, as well as a general background in piping, wiring, and safety guidelines. Much of the modern equipment demands some skill in electronics and an understanding of microprocessors. Refer to 6.2 for additional information.

6.5.1.3 Tools, Equipment, and Permits

During commissioning, tools and test equipment will be necessary for inspection of utilities as well as servicing of the analyzer, control module, and receiver instruments associated with the system. The following test instruments may be needed for field commissioning: an oscilloscope, a pressure test bench, multimeters (digital), a resistor box, a power supply, an ambient temperature indicator, and an anemometer.

A startup spare parts list must be developed to ensure that the most critical parts will be on hand for startup. These spare parts are in addition to the recommended spare parts required for normal operation and maintenance.

Some form of test fluid is usually requited in commissioning an analyzer. This can be a calibration standard (see Chapter 3), a clean sample of a pure gas or liquid, or a clean plant sample. Proper containers, regulators, valves, and connecting tubing are also required to introduce the standard.

Safety department clearances, hot-work permits, and operations personnel approval must be a part of the analyzer startup.

6.5.2 Pre-commissioning

Pre-commissioning shall be defined as all work required to calibrate, test, and make the analyzer fully operational up to the point when the block valves on the process line are opened to admit process samples to the analyzer.

Part of the pre-commissioning includes a final inspection to determine whether the process analyzer is properly installed. The installation should be visually inspected, including the analyzer and control units, the sample system, and the associated wiring and piping. Careful attention should be paid to critical areas, such as electrical grounding, interconnecting wiring, tubing fittings, and any other items that could endanger personnel, the process, or the analyzer.

The electrical power should be verified as correct for the analyzer (for example, not 220 volts on 110 volt service). Make sure power and signal wiring are connected to the proper terminals. The signal wiring should also be verified for proper termination. This can prevent an error such as applying power to an amplifier output line. Refer to Table 6-2 for inspection requirements.

Utilities should not be supplied to the analyzer and the associated sample conditioning system until the quality of each utility has been verified to be in accordance with the specifications. Once verified, the utilities must be supplied in the proper sequence.

All field-installed utility lines must be disconnected and flushed where they enter the analyzer system. Allow a reasonable amount of water, air, or steam flow through the open-ended connectors to flush out trapped dirt and construction trash.

6.5.3 Warm-up

Verify that the analyzer vent is directed to a safe place for sample disposal before opening the span or zero block valves.

Table 6-2—Checklist of Test Procedures for Analyzer Sample Conditioning Systems

Component	Item for Test and Inspection
Filters/strainers	Rotating filters turnable by hand Mesh size of fixed filters pressure drop, when possible Proper materials, retention rating, proper drainage
Pressure reducers	Response of output pressure to adjustment
Vaporizers	Refer to manufacturer's instructions
Pressure gages	Visual check of zero point Materials of welded parts
Coolers	Materials of construction
Coalescers	Materials of construction Installation of element
Pumps	Row rate versus discharge pressure
Flowmeters	Response to flow change Materials of construction Cleanliness
Relief Valves	Setpoint Materials of construction
Non-return valves	No visible reverse flow
Local indicators	Comparison of reading against receiver
Valves (including solenoid)	Tight shutoff, where necessary Materials of construction
Drain line/vent lines	Adequate size, proper materials, slope

Verify that any timers, automatic switches, and flow controls are in a safe mode, such as power off, switches on manual or off, block valves closed, and carrier gas and utilities properly connected, before turning on electrical power. Adjust pressures and flow rates as required. If a minimum flow or pressure of purge gas is necessary to meet safety requirements, interlocks may prevent startup without this gas. Carrier or reference gas should be flowing to purge air or moisture that could affect the detector mechanism. An analyzer may take several hours or more to warm up to a steady operating temperature. The temperature can be observed on a thermometer or other readout device, normally provided with the equipment. The sample system must also be allowed to stabilize at the control temperature.

6.5.4 Initial Operation

6.5.4.1 Initial Control Settings

If an inert fluid is required for "zero" or background condition, set the flow to match the application specifications. Adjust the output signal by potentiometer setting or auto-zero activation, whichever applies. These settings should be identical to those used to test the analyzer at the factory. A "lined out" condition can usually be determined by visual monitoring for several minutes.

Table 6-3—Typical Checklist at Analyzer System Inspections

Item	Vendor's Location	User's Location	Comment
1. Ventilation System			
(based on six air changes)			
a. Maximum air flow inlet _____ scfh			
b. First fan running _____ scm			
c. Second fan running _____ scfh			
d. Flow switch operation			
e. Calculation of changes per hour			
f. Demonstration of adequate air circulation			
g. Back pressure on cabinet			
2. Explosivity Alarm			
a. Calibration check lower explosimeter at 20 percent of lower explosive limit on n-butane			
b. Calibration check under explosimeter at 20 percent of lower explosive limit on hydrogen			
c. Test of alarm set point lower explosimeter			
d. Test of alarm set point upper explosimeter			
e. Purge failure alarm			
3. Utilities			
a. Steam			
hydrostatic test ______ psig			
tracing			
function			
b. Air			
hydrostatic test ______ psig			
function			
c. Water			
hydrostatic test ______ psig			
tracing			
function			
d. Steam trap operation			
e. Power circuit			
voltage			
continuity			
megger 500 V function			
f. Lighting			
continuity			
megger 500 V function			
luminosity _____lux			

Table 6-3—Typical Checklist at Analyzer System Inspections (Continued)

Item	Vendor's Location	User's Location	Comment
4. Temperature Control			
a. Check operation of heating/cooling systems			
5. Mechanical and Finishing Inspection			
a. Doors			
b. Panic bolts			
c. Adjustable louvers			
d. Paint			
e. Others			
6. Fast Loop and Sampling System			
a. Check as-built drawings			
b. Easy accessibility			
c. Filter			
d. Pressure			
e. Pressure regulators			
f. Pressure-relief valves			
g. Flowmeters			
h. Temperature indicators			
i. Pump			
j. Cooler			
k. Stream indicator (function)			
l. Stream selection solenoid valves (function)			
m. Level gages			
n. Three-way ball valve (operational)			
o. Valves (operational)			
p. Checkvalves			
q. Local indicator			
r. Purge system			
s. Pressure switch			
7.Functional Test			
a. Fast loop			
b. Sample conditioning system			

6.5.4.2 Calibration Check

The ideal initial sample to enter into the analyzer system is the synthetic mixture used for analyzer checkout at the factory. This sample should be shipped with the equipment, along with a recorder chart and printed record of all voltages, flows, settings, and other pertinent readings. The first sample introduced to the analyzer in the field should be the factory synthetic sample, with all analyzer settings the same as shown on the printed factory checkout record. Any significant difference between the factory results and these initial field results could indicate possible damage to the analyzer during shipment or installation. If a difference is found, preliminary troubleshooting would be in order. Subsequent samples introduced into the analyzer should be clean and at known, controlled pressures and flows. A synthetic blend, containing the component or property to be measured in roughly a mid-range concentration can confirm that detectors and sample valves are working properly. All operations should be conducted while observing the system for leaks or other system weaknesses.

6.5.4.3 Checking Receivers

When the analyzer has run enough test samples to stabilize, checks can be made on remote receivers (indicators, recorders, and digital signal outputs) to verify proper operation of the output circuitry.

6.5.5 Startup and Decommissioning

6.5.5.1 Process Sample to Analyzer

Lines carrying the process stream sample to the analyzer sample conditioning system must be flushed before connecting to the system. With the analyzer flow blocked, adjust all other flow or flows through the sample system to specifications. Only then should a process stream be admitted to the sample injection valve or to any other sample flow port in the analyzer.

NOTE Variable area meters can provide indications of the presence of dirt, water, or air in a sample stream.

After all line flushing and cleaning of sample systems is complete, filters should be checked or replaced. When purging air from systems, care must be taken not to allow air to return to the process.

6.5.5.2 Steady-state Operation

In addition to the warm-up noted in 6.5.3, allow time for all the components of the sample system, controlled temperature zones, and the electronics sections to reach an equilibrium condition. During this time (which can be minutes or hours, depending upon the equipment), readout devices may show drift. Final calibration of the analyzer for on-line operation should not be attempted until this “lined-out” condition has been achieved.

6.5.5.3 Calibration

After the analyzer has been completely and successfully commissioned, the next step is calibration. Refer to Chapter 3.

6.5.5.4 Decommissioning

In the event of a process shutdown, certain decommissioning steps should be followed to ensure the future availability of the analyzer. If the shutdown occurs for a short time (from hours to a few days), a standby procedure should be followed. This includes shutting off process sample lines, and switching off any timer functions, while keeping utilities, such as chromatograph carrier gas or purge flows, and electrical power turned on to the analyzer. In this way, the analyzer system is ready to go back on line with a minimum of re-commissioning.

A longer-term, or mothballing, procedure will also include draining the process sample and water lines. In addition, all utilities, electrical power, and carrier supplies to the analyzer should be shut off. Consideration should be given to injecting an inert gas into the sample and reference systems to prevent corrosion, which can occur within these critical systems if they are allowed to soak in the ambient atmosphere. The inert gas may be sealed in or a positive pressure maintained on these systems from a cylinder. At a minimum, open lines such as vents should be capped during an extended shutdown.

7 Safety Requirements

7.1 General

The safety of operating and maintenance personnel shall be taken into consideration when designing an analyzer installation.

7.2 Samples Lines and Sample System Components

Sample lines and sample systems must be leak checked before being placed in service.

Where pumps are required in the sampling system, a means of collecting and disposing of possible leakage should be provided. To minimize the amount of hydrocarbons inside a confined area, sample pumps, speed loops, and sample flow restrictors should be installed outside the analyzer shelter. All sample system components inside the analyzer enclosure should be close-coupled. Sample lines inside a shelter should be designed to minimize the number of tubing connections.

7.3 Electrical Safety

Sample systems and analyzers include electronics and electrical components, such as motors, electrical heat tracing, solenoid valves, pressure switches, and the like, which must meet the electrical area classification. API RP 500, API RP 505, and other local and international codes should be consulted for determining the electrical area classification and for design requirements for systems installed in these locations.

System designs used to comply with electrical code requirements for equipment installed in hazardous locations include the following:

a) containing a hazardous device in an approved enclosure certified for the electrical area classification;

b) changing the nature of the atmosphere surrounding the source of ignition through providing a forced ventilation system or continuous dilution system, in other words, purging in accordance with NFPA 496 or other local equivalent;

c) providing installation of the hazardous device in an isolated non-hazardous area;

d) using non-incentive or intrinsically safe circuit designs.

7.4 Personal Safety

Where there is potential for abnormal release of hazardous or combustible gases, appropriate gas detectors should be used (see 6.3.2.7). Where inert gases are used for purging, oxygen depletion detectors should be permanently installed, alarmed locally and alarmed to a permanently occupied location.

7.5 Maintenance Requirements

Proper maintenance of the analyzer and sample system is an essential factor for the on-stream availability of the analyzer data and should be considered in the design and installation of the system.

The following considerations should be addressed based on the equipment and components used in the system.

a) Simplicity, consistency between designs, and accessibility for maintenance. A means for identifying a malfunction should be provided, and any malfunctioning part or piece should be easily and quickly replaceable.

b) When operating at elevated temperatures, components should be mounted in an enclosure, not insulated and packed individually.

c) Proper valving should be provided for venting the system's operating pressure safely before maintenance.

d) Flow meters and pressure gauges should be provided at points throughout the sample systems to aid in locating plugged components, flashing samples, condensable materials, and proper flow rates.

e) Systems that handle corrosive or extremely hazardous streams should have purge capabilities for safely cleaning and flushing the system before maintenance is performed.

f) Sample volumes should be kept as small as possible.

Annex A—References

A.1 Publications

The following publications are cited in this document. See the Annex for additional references.

API Recommended Practice 500, *Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities*

ANSI Publication ZI 17.1 [1], *Safety Requirements for Working in Tanks and Other Confined Spaces*

ASTM D86 [2], *Test Method for Distillation of Petroleum Products*

ASTM D2887, *Fast Method for Boiling Range Distillation of Petroleum Fractions of Gas Chromatography*

EPA 40 *Code of Federal Regulations* Part 51 [3], "Existing Sources"

EPA 40 *Code of Federal Regulations* Part 60, Appendix A, "Test Methods"

EPA 40 *Code of Federal Regulations* Part 60, Appendix B, "Performance Specifications"

EPA 40 *Code of Federal Regulations* Part 60, Appendix F, "Quality Assurance Procedures"

EPA 40 *Code of Federal Regulations* Part 60, Subpart Db, "Standards of Performance for Industrial-Commercial-Institutional Steam Generating Units"

EPA 40 *Code of Federal Regulations* Part 60, Subpart J, "Standards of Performance for Petroleum Refineries," Continuous Air Pollution Source Monitoring Handbook, USEPA "Technology Transfer"

NFPA 70 [4], *National Electrical Code*

NFPA 496, *Purged and Pressurized Enclosures for Electrical Equipment*

Public Law 101-549 [5], *Clean Air Act Amendments* of November 15,1990,104 STAT. 2399-2712

USBM Bulletin 503 [6], *Limits of Flammability*

USBM Bulletin 627, *Flammability Characteristics of Combustible Gases and Vapors*

Swagelok Tube Fitting and Installation Manual [7]

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[1] American National Standards Institute, II West 42nd Street, New York, NY 10036-8002.

[2] American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

[3] Environmental Protection Agency. The Code of Federal Regulations is available from the U.S. Government Printing Office, Washington, DC 20402.

[4] National Fire Protection Association, P.O. Box 9101, 1 Batterymarch Park, Quincy, MA 02269-9109.

[5] Available from the U.S. Government Printing Office, Washington, D.C. 20402.

[6] U.S. Bureau of Mines, 810 7th St. NW, Washington, D.C. 20241.

[7] Swagelok, 29500 Solon Road, Solon, OH 44139.

A.2 References

Houser, E. A., *Principles of Sample Handling System Design*, Instrument Society of America, Research Triangle Park, North Carolina, 1977.

Clevett, Kenneth J., *Process Analyzer Technology*, Wiley Interscience, New York, 1986.

Cornish, D. C., Jepson, G., and Smarthwaite, M. J., *Sampling Systems for Process Analyzers*, Butterworth, London, 1981.

Profeta, B. P., “Process Analyzer Sampling and Conditioning for Process Control,” *Analytical Instrumentation*, 22, 53, 1986.

Huskins, D. J., *General Handbook of On-line Process Analyzers*, Ellis Harwood Ltd., Chichester, 1981.

Flow of Fluids Through Valves, Fittings, and Pipe, Technical Paper No. 410, Crane Co., 4100 S. Kedzie Ave., Chicago, Illinois 60632, 1978.

Section B—Safety and Environmental Considerations

B.1 Scope

The areas of safety and environmental compliance monitoring are extremely important in today's refinery. Significant expenditures are being made in these areas by refineries and especially on those requirements mandated by government regulations. These areas of application require analyzers meeting the requirements of the specific component measurements and of methods, standards, or values established by governmental regulations. Process analyzers modified to meet such requirements as well as specifically designed analyzers and related sample systems are available for such applications. This section covers area safety monitors, continuous emission monitors, and waste treatment analyzers.

The term *area safety monitors* refers to the use of specific toxic and combustible gas detectors to monitor an area within a refinery. When safety limits are exceeded, these detectors provide alarms alerting personnel to take the necessary steps to correct the alarm condition, or shut down systems to protect personnel and equipment.

Chapter 8 covers the application, selection, and installation of area safety monitors commonly used in petroleum refineries for (a) toxic gas detection and (b) combustible gas detection, and is limited to non-extractive systems. Extractive hazardous vapor monitoring systems (employing gas chromatographs for example), portable analyzers, and instruments whose primary function is laboratory analysis are not treated here.

Only the common types of gas detection devices generally employed in the refinery environment are covered. Emerging technologies such as FTIR (Fourier Transform Infrared) spectroscopy and LIDAR (Light Detection and Ranging) for perimeter and wide area monitoring are beyond the scope of this section. Systems for environmental compliance are covered in Chapter 9.

Continuous Emission Monitoring Systems (CEMs) refers to the analyzer systems required for monitoring source emissions compliance with governmental regulations. These systems are specifically engineered to meet mandated emissions monitoring requirements, reporting methods, and calibration and certification requirements.

Chapter 9 covers the application and installation of the more commonly used continuous emissions monitoring systems (CEMS) designed for refineries. This section is intended to provide guidelines for the application and selection of monitors. Also, the advantages and limitations of several types of monitoring system designs are reviewed.

Many types of analyzers are utilized in refinery wastewater applications. The more commonly used are described.

Chapter 10 covers total carbon (TC), total organic carbon (TOC), and total oxygen demand (TOD) analyzers. These systems employ the oxidation of organic compounds in wastewater as a measure of the oxygen demand of the sample. Both total organic carbon and total oxygen demand correlate with the long and tedious laboratory methods of determining biochemical oxygen demand (BOD) and chemical oxygen demand (COD) as indicators of organic pollution in many waters and wastewater streams. Generally, the manpower intensive and lengthy BOD and COD analyses are not generally suited to process applications.

Chapter 10 also covers Turbidity, Residual Chlorine, Hydrocarbons-in-water, pH, Dissolved Oxygen analyzers, and Waste Treatment analyzers. Turbidity analyzers employ a light scattering technique to measure particulate matter and other matter that affect the clarity of waste streams. Residual chlorine analyzers are used to monitor the excess chlorine remaining after a waste stream is chlorinated to eliminate substances that are potentially toxic or hazardous to aquatic life in natural waterways. Hydrocarbon-in-water analyzers are usually implemented as "spill detectors" to provide an early warning to operating personnel of a hydrocarbon release before it can enter a natural waterway. pH limits are often specified on permitted wastewater streams to avoid disruption of the aquatic ecosystem of natural waterways.

8 Area Safety Monitors

8.1 General

The analyses of toxic gases described in this section include those for hydrogen sulfide and chlorine. The analysis described for hydrogen sulfide will be limited to two techniques: electrochemical (see Chapter 10) and photometric (see Chapters 11 and 19). Other procedures are available, including colorimetry (Chapter 29), chromatography (see Chapter 17), and infrared spectroscopy (see Chapter 11). The analysis described for chlorine is limited to the ultraviolet/photometric analyzer (see Chapter 10).

The types of combustible gas analyzers discussed are (1) electrolytic cell, (2) catalytic combustion, (3) infrared spectroscopy, and (4) thermal incineration. The first two noted are the most common for hydrocarbon processing operations.

The types of fire and smoke detectors described are ionization, photoelectric, infrared, and thermal.

Other analysis methods not covered in this section but used to monitor common air pollutants emitted from refineries are:

a) Chromatography (Chapter 17) or nondispersive infrared (Chapter 11) techniques to analyze for carbon monoxide (CO), a product of incomplete combustion.

b) Chemiluminescent optical detection technology (Chapter 9) to analyze for either (a) oxides of nitrogen (NO, NO_2, NOx) products of combustion from process heaters, or (b) ozone (O_3) and oxidants formed in the atmosphere by the reaction of nitrogen oxides and hydrocarbon vapors under the stimulation of ultraviolet light.

c) Flame ionization (see Chromatography detectors in Chapter 17) to analyze ambient air for total hydrocarbons (vapor) emitted primarily from storage tanks. This technique uses a sensitive electrometer to detect the increase in ion intensity resulting from the combustion of hydrocarbon compounds in a hydrogen/air flame.

d) Photometry to measure particulate emissions and opacity.

Other, less common techniques, such as colorimetry or coulometry, can be used to analyze for air pollutants but are beyond the scope of this publication.

8.2 Area Monitoring For Toxic Gases

8.2.1 General

A toxic hazard can be defined as a condition where the concentration of lethal chemicals poses a danger to life and health. The Occupational Safety and Health Administration (OSHA) has set standards [1] limiting the concentrations of various toxic materials to which an employee may be subjected.

8.2.2 Monitoring Hydrogen Sulfide

The two most common toxic gas analyzers for hydrogen sulfide (H_2S) are:

1) photometric sensors (paper-tape monitors); and

2) semiconductor toxic gas sensors.

The principles of operation of each type are described in 8.2.2.1 and 8.2.2.2.

8.2.2.1 Photometric Analyzers

The photometric type of analyzer operates on the principle that chemically sensitive material changes color in the presence of H_2S. When an ambient air sample flows through the reaction window or sample chamber and passes over an exposed surface of lead acetate-impregnated paper (the sensing tape), it causes the surface to darken from lead sulfide formation. The rate of darkening of the exposed tape is proportional to the H_2S concentration. A photoelectric cell and a light source measure this change, and the signals from the measuring and reference photocells are compared to provide a meter deflection (in the electronics module) proportional to the gas concentration (see Figure 8-1 and Figure 8-2). This toxic monitoring system only alerts the user to the presence of the toxic gas.

Wide area monitoring of H_2S in ambient air can be accomplished by drawing ambient air samples from remote locations through sample lines. These lines are connected to a collection manifold by a sample pump that introduces the sample to the analyzer (see 8.5).

Photometric analyzers provide the following advantages.

a) Photometric analyzers using chemical sensitive material (lead acetate) responds to H_2S.

b) These analyzers are highly responsive to low parts-per-billion levels of H_2S in ambient air.

The disadvantages of photometric analyzers include the following.

a) Extractive sampling can introduce substantial dead time if a large area is monitored.

b) The tape must be replaced periodically and must be handled carefully.

c) Photometric analyzers are heavy and bulky.

d) Photometric analyzers must be calibrated frequently.

e) Occasionally, ambient H_2S permeates the unexposed tape and darkens it beyond use.

8.2.2.2 Semiconductor Toxic Gas Sensors

The metal oxide semiconductor gas sensors use a technique whereby a mixture comprised largely of carefully selected metal oxides is impregnated in a solid-state matrix material supported by conductive elements (semiconductor). The semiconductor is sensitive to a particular gas and insensitive to others depending on its design.

The semiconductor is contained within a flame arrestor, which allows diffusion and convection of the ambient air and toxic gas inside the detector volume. The sensor is housed in an explosion-proof unit and connected to a remote measurement module. Power to heat the semiconductor and measure its resistance is supplied from the module. Heating the semiconductor to approximately 390 °F (200 °C) controls the absorption and desorption and the reaction of the gas on the device. In the presence of small concentrations of H_2S, the reduction reaction causes the sensor conductance to increase, creating a current flow that is measured. The current produced is proportional to the H_2S reaction rate on the semiconductor surface, and the output signal is logarithmic with respect to the concentration.

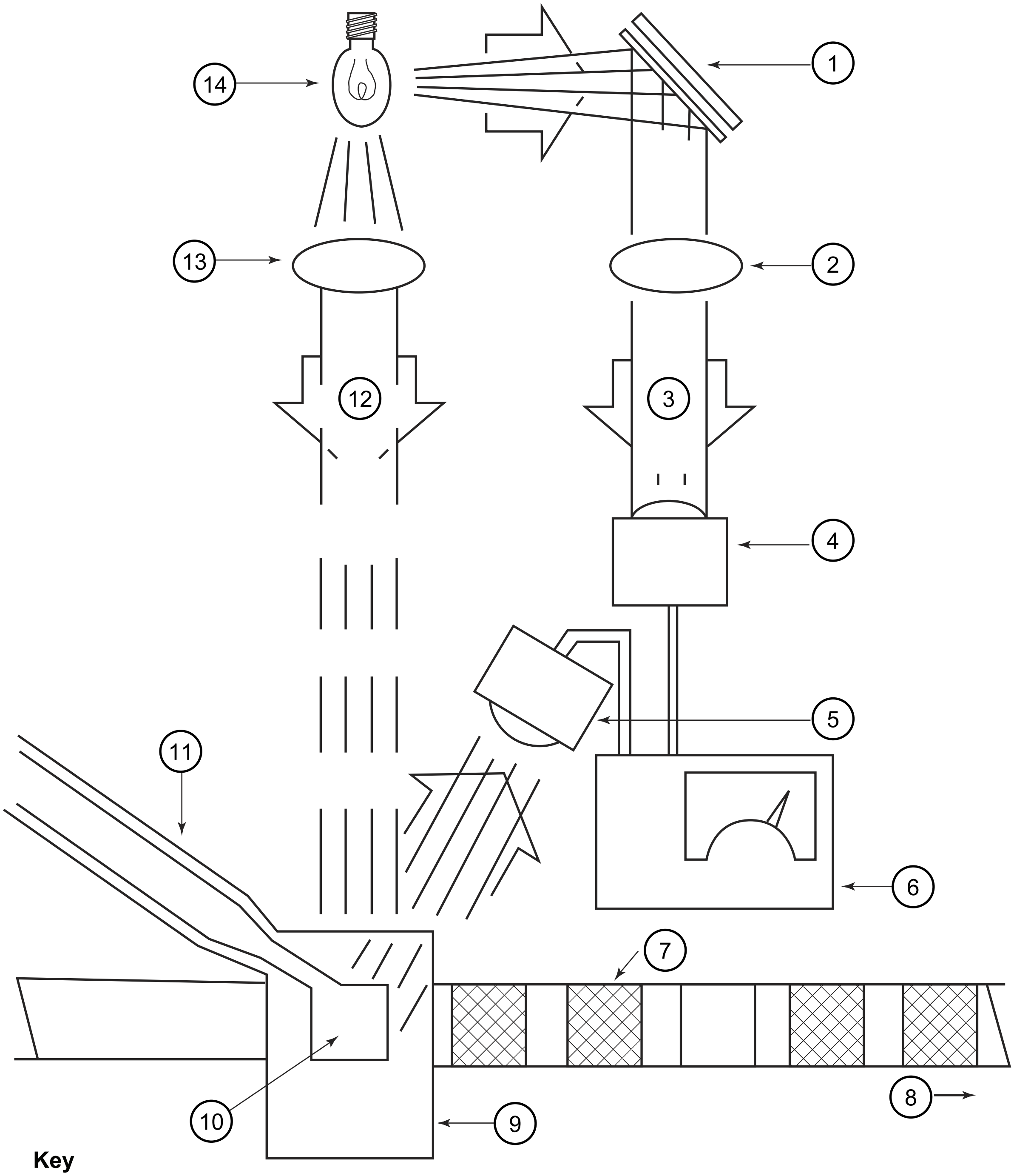
An electronic measurement module mounted in a separate enclosure is connected to the diffusion sensor. The power supply for the heater and measuring circuits is contained within the module.

The advantages of the semiconductor sensor include the following.

a) Because this is a diffusion sampling instrument there are no moving parts or chemicals.

b) It is low in cost and requires minimum maintenance.

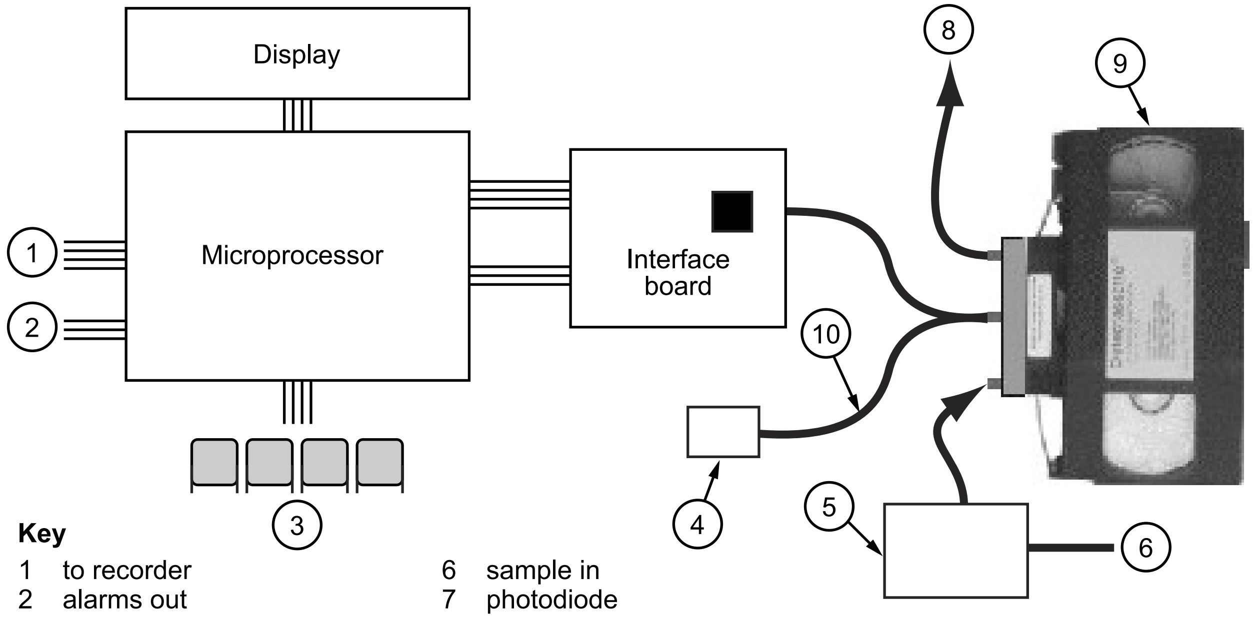
c) The remote location of the sensor offers added flexibility.



Key

1	mirror
2	photocell fine focus balancing lens
3	reference beam
4	reference photocell
5	measuring photocell
6	rate-of-change indicator
7	exposed sensing tape
8	tape movement
9	sample chamber
10	reaction window
11	H_2S sample
12	focused beam
13	primary focusing lens
14	tungsten lamp

Figure 8-1—Photometric Analyzer Principle of Operation



Key

1 to recorder
2 alarms out
3 pushbuttons
4 optical feedback controlled LED light source
5 bubbler to moisten sample
6 sample in
7 photodiode
8 to vent
9 detectassette*
10 Bifurcated fiber optics

Figure 8-2—Photometric Analyzer

The disadvantages include the following.

a) The instrument requires periodic calibration.

b) Light hydrocarbons and other combustibles can cause interference.

8.2.3 Monitoring Chlorine

Ultraviolet/visible photometric analysis is the most commonly used method to determine chlorine in ambient air. The ultraviolet absorption spectrum for chlorine is shown in Figure 8-3. The band extends from 270 nanometers to 370 nanometers, with absorbance peaking at 330 nanometers. An ultraviolet/visible photometric analyzer using a differential measurement technique is the most acceptable method of measurement in the spectral range shown. The two most common designs of photometers use either the dual frequency or dual path systems.

In the dual frequency design, light energy of the desired bandwidth, including both the measured and reference wavelength (Lambda) frequencies, is passed through a sample cell containing the gas to be analyzed. The energy is divided so that it falls on two detectors that are sensitized to the reference and the measure frequencies (see Figure 8-4). A circuit provides a signal that is proportional to the logarithm of the ratio of the two detector signals, that is, proportional to changes of component concentration in the cell. The dual frequency design is not sensitive to dirty cell windows. Changes caused by power fluctuations, lamp aging, and temperature variations can cause discrepancies in the measurement.

In the dual path design, the light energy is split at the source into two beams, only one of which passes through the sample cell (Figure 8-5). Measure and reference detectors that are both sensitive to the same frequency each measure the intensity of the energy that has not been transmitted by the sample cell. As above, the signals of the measure and reference detectors are processed electronically to give an output signal linearly related to sample concentration. This type of photometer reading is not affected by fluctuations in source intensity because both detectors measure the same and corresponding spectral frequency deviations emitted from the source; however, it is affected by a dirty sample cell window.

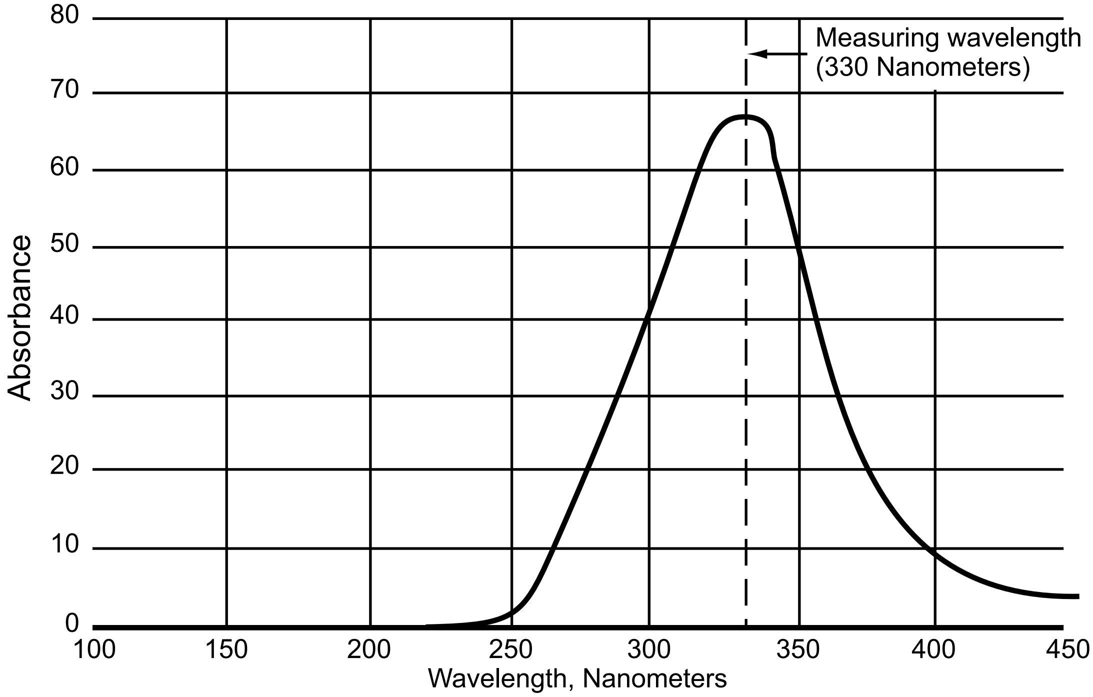


Figure 8-3—Chlorine Gas Spectrum

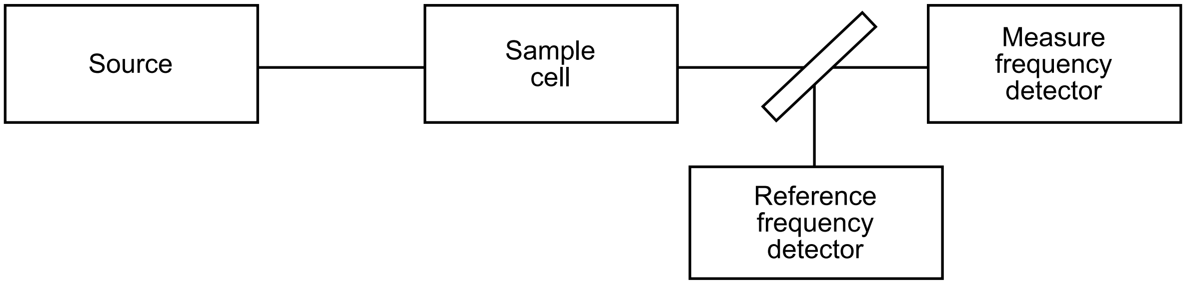


Figure 8-4—Dual Frequency Design

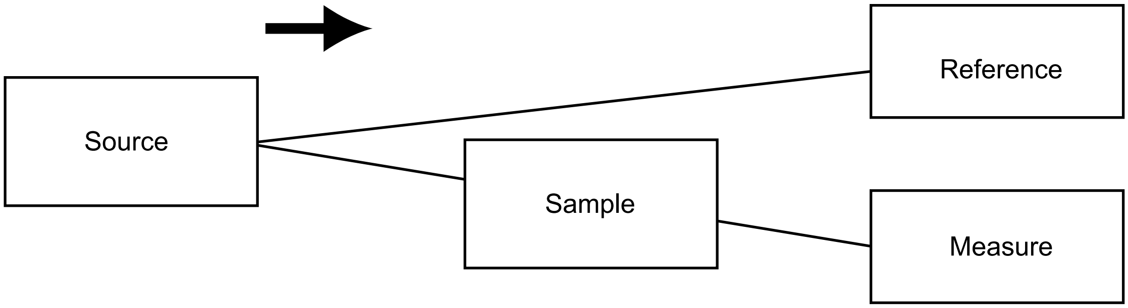


Figure 8-5—Dual Path Design

8.2.4 Electrochemical Toxic Gas Sensors

Electrochemical toxic gas sensors function on the principle of the electrochemical cell producing an electrical output proportional to the toxic gas concentration. As the gas diffuses into the cell, it is oxidized or reduced (oxidized in the case of H_2S), and an electric current proportional to the gas concentration flows through the electrolyte. Sensors specific to H_2S, CO, SO_2, H_2, Cl_2, and other gases are available.

The advantages of the electrochemical sensor are as follows:

a) good specificity.

b) unlike the solid state sensor, there is no requirement for regular exposure to the gas of interest to retain sensitivity.

c) low drift and long-term stability.

d) not very sensitive to humidity.

Some disadvantages of the electrochemical sensor are the following.

a) Some designs require replenishment of the cell electrolyte; however, replaceable throwaway elements are available from many suppliers, which can be changed out at the end of their useful life—typically two years.

b) Extreme levels of humidity or heat can affect response.

c) The electrolyte may freeze in some cases.

8.2.5 Ion-mobility Spectroscopy

Point detectors employing ion-mobility spectroscopy (IMS) may be used for area monitoring of toxic gases. Compact, rugged, and reliable instruments based on this technique have been proven and are available for the detection of hydrogen fluoride, ammonia, chlorine, sulfur dioxide, hydrogen chloride, and many other toxic gases.

Detailed information on the use of IMS in process applications may be found in Chapter 15.

The advantages of the IMS detector are as follows:

a) high level of specificity;

b) very low drift;

c) low maintenance;

d) easily calibrated utilizing an on-board microprocessor, and the required calibration frequency is low.

However, compared to other types of toxic gas point sensors, the cost is high.

8.3 Area Monitoring for Combustible Gas

8.3.1 The Catalytic Cell Detector

In order to generate a hazardous condition, it is necessary to have flammable materials, a source for ignition, and air to support combustion. For each combustible gas or vapor, there is a particular mixture with air that has the minimum oxygen to support combustion. Some combustible gas mixtures ignite more readily than others. Mixtures of the same constituents (gases in different proportions) will require different ignition temperatures to cause combustion.

The following terms are used in this discussion.

- — *Lower flammable limit (LFL)* is the minimum concentration of vapor or gas in air below which propagation of flame does not occur on contact with a source of ignition.
- — *Upper flammable limit (UFL)* is the maximum concentration of vapor or gas in air above which propagation of flame does not occur.
- — *Flash point* of a liquid is the minimum temperature at which the liquid gives off sufficient vapor to form an ignitable mixture with air near the surface of the liquid.
- — *Ignition temperature* of a gas or vapor is the minimum temperature required to initiate, or cause, self-sustained combustion independent of heat (or heated element).

To calculate the flammability limits for a mixture of gases, refer to the U.S. Department of the Interior, Bureau of Mines, Bulletin 503, *Limits of Flammability of Gases and Vapors,* and the U.S. Department of the Interior. Bureau of Mines, Bulletin 627, *Flammability Characteristics of Combustible Gases and Vapors* [4].

Generally, four characteristics are required of instruments used for detecting flammable (explosive) hazards. They should be:

1) rapid in response time;

2) sensitive over the range zero to the lower flammability limit;

3) selective to the gas to be detected; and

4) incapable of providing an ignition source should the concentration reach the flammable range.

The most commonly used combustible gas analyzer currently manufactured is the catalytic cell detector. The catalytic cell detector operates on the principle of catalytic combustion of the gases/vapors being analyzed on the surface of a heated catalytic surface. The combustion process increases the temperature of the element, which is detected by the change in resistance of the element. A typical catalytic cell detector uses two elements. One is exposed to the detected gas (detector element), and the other (reference element) is protected either by providing it with a non-reactive surface or by protecting it from gas exposure. The detector and reference elements are two legs of a Wheatstone bridge that provides an output signal as a function of combustible gas concentration. Flame arrestors are provided in the detector.

The active detector element can be either mounted in a measuring chamber through which the gas being analyzed flows, or mounted in a diffusion head, which is permeable to the sample movement by diffusion, density difference and convection.

The disadvantages of the catalytic cell include:

a) it requires frequent calibration;

b) it suffers “burn out” in high gas concentrations;

c) the sensor may be poisoned by silicones, halogens, or sulfur dioxide.

8.3.2 Infrared (NDIR) Detectors

In infrared detectors, an infrared (IR) beam is passed through the gas, and the transmitted light is analyzed via two narrow band interference filters (one at a hydrocarbon absorption wavelength and one at a reference wavelength). A ratio of the reference signal to the hydrocarbon signal is computed to provide an output signal proportional to the total hydrocarbon content in the beam path.

In the compact open-cell-short-path-design, the IR beam traverses a very short path, and the instrument functions as a point detector.

In the long-path-system, the IR beam traverses a relatively long path using a transmitter and receiver system (the typical upper limit is approximately 300 ft), and the system may be used for perimeter monitoring of an area. The measurement is a path-integrated concentration, which in the absence of other data becomes less and less useful as the path length increases. In other words, it is difficult to derive quantitative information; for example, an 0.5-ppm gas background over a 100-ft segment of the path length will give the same sensor response as a 50 parts-per-million (ppm) release over a 1-ft segment.

The advantages of the IR combustibles detectors are as follows:

a) very stable sensor, sensitivity not degraded with time or gas exposure;

b) not susceptible to being poisoned by chemical agents or the environment;

c) immunity to interference from other gases and water vapor;

d) is an "active" device, with a self-checking operation and malfunction alarms are typically provided;

e) fast response time;

f) line-of-sight coverage instead of point detection.

The disadvantages are as follows.

a) Heavy precipitation or fog conditions could render the long-path instrument ineffective.

b) This type will not detect a non-hydrocarbon combustible gas such as hydrogen.

c) In the case of the long-path instrument, it is difficult to quantitatively interpret the meter reading unless the gas concentration is uniform over the entire path length.

d) There is a potential for the beam to be blocked (the instrument should have a built-in beam blockage alarm).

8.4 Area Monitoring for Fire and Smoke

Fires associated with liquids, gases, or vapors are almost instantaneous, whereas fires associated with solid combustibles develop in four stages (see Figure 8-6):

1) Incipient stage I—Invisible products of combustion are given off. No heat or visible smoke or flame are present.

2) Smoldering stage II—Combustion products are visible as smoke. Neither flames nor appreciable heat are present.

3) Flame stage III—Fire now exists: appreciable heat is not yet present, but follows almost instantaneously.

4) Heat stage IV—Uncontrolled heat and rapidly expanding combustible products and air complete the dangerous conditions.

Fire detectors are of three types: smoke detectors, flame detectors, and thermal detectors.

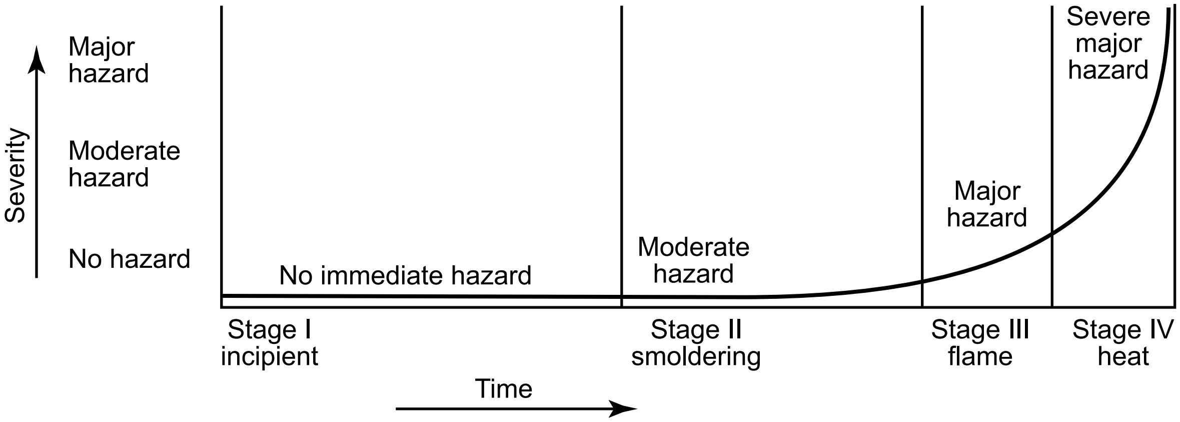


Figure 8-6—Stages of Fire Associated with Solid Combustibles

8.4.1 Smoke Detectors

8.4.1.1 Ionization Type

The heart of the ionization detector is the ionization chamber (see Figure 8-7), which contains a minute quantity (microcuries) of radioactive material. Alpha emissions from this material ionize the air between the plates (P1 and P2) in the chamber, making them electrically conductive. Invisible combustion products enter the sensing chamber and impede the ionization current flow. The reduced current flow activates an alarm relay. Most ionization detectors use dual chambers, one for sensing and the other for reference. The reference chamber is vented to outside air through a small orifice that blocks smoke particles. Temperature, pressure, and humidity changes affect both chambers equally to provide uniform operating sensitivity, regardless of ambient air conditions.

The ionization detector is normally specified in areas of high combustibility solids and in areas that contain low-temperature-rise smoldering-type materials.

8.4.1.2 Photoelectric Type

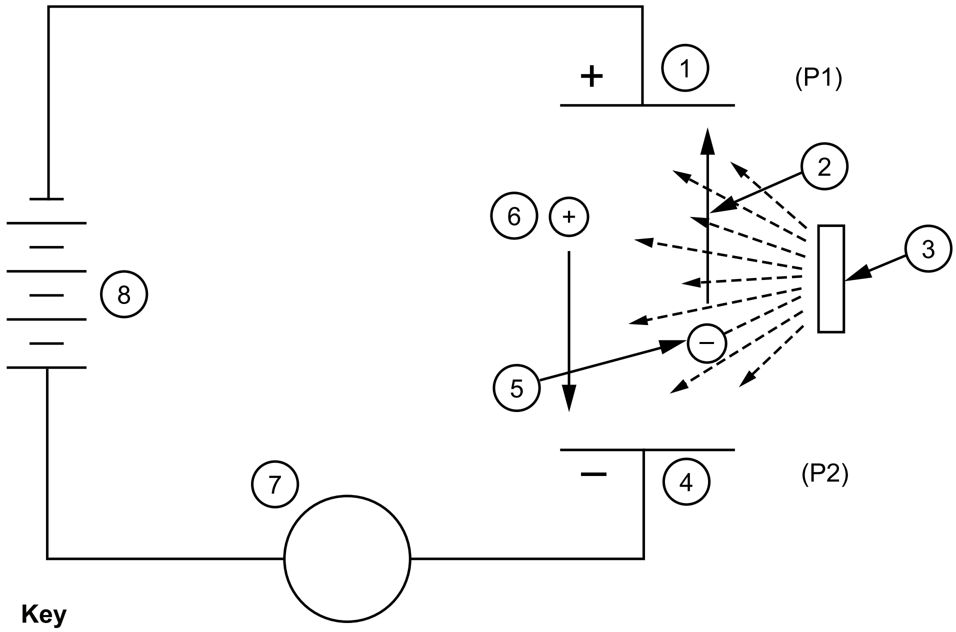
Photoelectric detectors employ a light source and a photocell arranged in a labyrinth-like chamber so that no direct light can reach the photocell. Smoke particles entering the chamber are illuminated, and when the scattered light resulting from such particles reaches the photocell, a signal is generated and amplified, causing the actuation of an alarm.

The light source is a gas-filled flash tube, developed for this purpose, which generates a high-intensity light flash every 2 to 3 seconds. Two light flashes are required to initiate an alarm: smoke concentration must be present in the labyrinth for at least 5 to 10 seconds. False alarm actuation by ambient light (illumination, lightning, welding operations, and the like) or by short, temporary smoke concentrations are therefore minimized.

8.4.2 Flame Detectors

8.4.2.1 Infrared Type

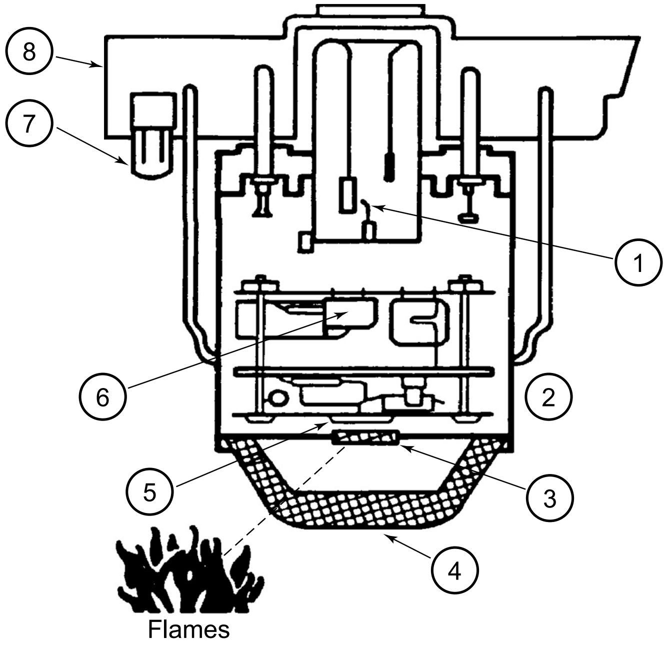
The infrared detector (flame stage III) is designed to sense radiant energy with a wave length slightly below the visible light band. The detector (see Figure 8-8) accomplishes this with a silicon solar cell mounted behind a double infrared lens filter arrangement. The dual infrared lens permits only infrared energy to pass. To separate the infrared energy of flames from the infrared energy from other sources, an electronic filter circuit limits the detector response to energy modulated at a frequency of 5 hertz to 30 hertz, which corresponds to the flickering of flames. Time delays are built into the detector circuitry to prevent false activations. Response to constant infrared radiation or to short flickering phenomena is excluded.



Key

1 positive electrode
2 alpha particles
3 radioactive material
4 negative electrode
5 negative ion
6 positive ion
7 alarm relay
8 battery (direct current power source)

Figure 8-7—Ionization Chamber Principle



Key

1 cold cathode tube
2 time delay
3 secondary infared lens
4 primary infrared lens
5 photo-sensitive cell
6 amplifying and filtering circuits
7 alarm lamp
8 detector base

Figure 8-8—Infrared Flame Detector with Lenses and Cathode Tube

8.4.2.2 Ultraviolet Type

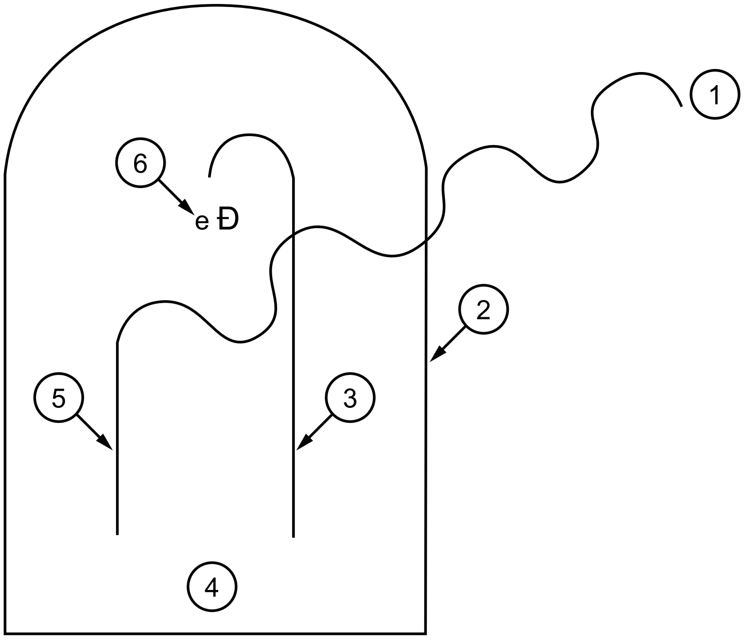
Ultraviolet flame detectors respond to radiant energy of the specific wavelength produced by a flame. The typical ultraviolet detector is a hydrogen-filled electronic photomultiplier with an anode and cathode sealed in an ultraviolet-transmitting glass envelope (see Figure 8-9). In operation, a high voltage is applied to the electrodes. When the Ultraviolet radiation (with wavelengths above 1900 and below 2600 angstrom units) strikes the cathode, photoelectrons are released and travel toward the anode, owing to the potential difference across the electrodes. In transit from the cathode to the anode, the emitted electrons collide with the hydrogen molecules, causing a dissociation of those molecules. The ionized molecules cause further ionization, and as a result, the tube is rendered conductive. The hydrogen gas acts to amplify the initially very small photoelectric current.

A control unit sensor circuit converts the current created in the ultraviolet tube to standardized voltage pulses by continuously applying and draining the high potential across the electrodes. The voltage pulses are created at a level proportional to the intensity of the incident ultraviolet energy. An integrator circuit evaluates the total effect of all the voltage pulses and converts these pulses to a direct current voltage, which is applied to a buffer/threshold circuit. The addition of all the pulses creates a voltage that activates a relay.

The ultraviolet detectors are spot-type detectors and have a 90-degree cone of vision.

8.4.3 Thermal Heat Detectors

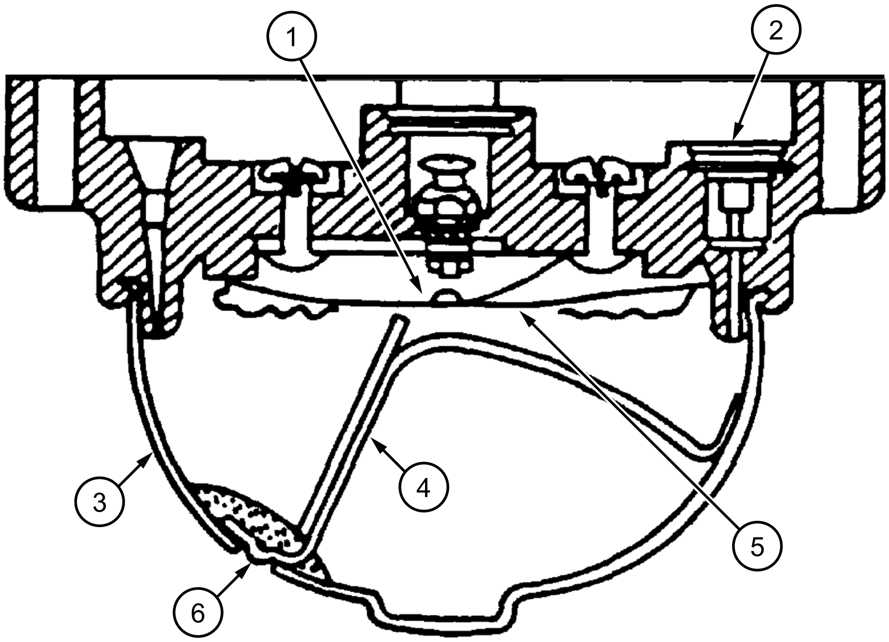
Thermal heat detectors are either fixed-temperature thermal detectors or rate-of-rise temperature detectors in combination with fixed-temperature detectors (see Figure 8-10). Thermal detectors are normally supplied at 136 °F (58 °C) and 190°F (88 °C) ratings for fixed-temperature devices and 136 °F (58 °C) and 190°F (88 °C) plus a rise-per-minute rating of 15 °F (8.3 °C) on the combination units.



Key

1 incident ultraviolet radiation (photons)
2 quartz tube
3 anode (nickel)
4 gaseous medium (hydrogen filled) slightly pressurized
5 cathode (nickel)
6 photo electron

Figure 8-9—Ultraviolet Detector Principle



Key

1	diaphragm contacts	4	fixed-temperature spring
2	calibrated vent hole	5	diaphragm
3	sealed chamber shell	6	fixed-temperature fusible element and tell-tale spot

Figure 8-10—Operating Elements of Combination Fixed-temperature and Rate-of-rise Thermal Detector

Thermal detector designs available include the following.

a) Bimetallic type (fixed) which uses a bimetallic strip; when heated it bends, allowing contacts to activate.

b) Fusible metal link (fixed), which uses a fusible metal link to hold spring-loaded electrical contacts open. When heated to its rated temperature, the metal melts, allowing the contacts to activate.

c) Flexible diaphragm (rate-of-rise plus fixed), which uses a specially constructed chamber, a flexible diaphragm, and a vent arrangement to sense the pressure of the expanded air created by the heat from the fire. The expanded air (encapsulated) cannot be vented fast enough, and the diaphragm contacts close to actuate an alarm. This is a rate-of-rise type and responds when the air is heated at a rate greater than 15 °F (8.3 °C) per minute.

8.5 Area Monitoring Sampling Systems

The sampling systems (see Chapter 4) for area monitors should be designed to incorporate the unique features of the area to be protected. The hazardous gas or vapor in the contaminated area will vary in concentration, depending upon such factors as:

a) distance from the source;

b) density of the hazardous material;

c) equipment configuration;

d) plan and elevation details;

e) ventilation;

f) wind velocity and direction.

The sample admitted to the analyzer should be representative of that present in the monitored area and free of particulate matter and water droplets.

8.5.1 Location of Sample Points

To determine the source point potential and predict a concentration profile, a study is required of the process area equipment location drawings, or a model of the process area is necessary. A drawing similar to an area classification (electrical) drawing should be prepared indicating the potentially hazardous areas. Spacing of sensors should be based on the manufacturer's recommendation.

Once the most representative sample points are located, the requirements to convey and condition the sample for analysis are determined. If the sample is a gas and must be conveyed a distance, the sampling system must be designed not to alter or dilute the sample's properties. A motive device must be used to cause flow when the sample is at atmospheric or lower pressure. A sample pump or fluid eductor is normally used for this purpose. (A potential disposal problem can occur if the motivating fluid of a fluid eductor is contaminated with the sample.)

The desired speed of response will determine the flow rate necessary to convey the sample to the test point. The usual procedure is to convey a sample volume in excess of that actually required for analysis. If heating, cooling, filtering, liquid preparation, or chemical reaction equipment are required for sample pretreatment, consult the analyzer vendor for requirements.

Basically, there are two approaches for determining the location of the analyzer.

1) Locating the sensor in close proximity to the potential location of a leak.

2) Locating the sensor where the leaking gas or vapor is likely to accumulate.

With either approach the following guidelines should be followed.

a) Locate the sensor or sample point near grade for heavier-than-air gases or vapors, and elevate the sensor to detect lighter-than-air gases.

b) Locate the sensor or sample point where the prevailing air currents contain the maximum concentration of the gas being monitored.

c) Locate sensors or sample points close to the potential source of escaping gas or vapors.

d) Sensors have ambient temperature limitations. Install the sensor within the specified range.

e) Avoid vibration when locating the sensor.

f) Sensors require calibration on a periodic basis: therefore, they should be either accessible or have remote test devices.

g) Protect sensors from immersion or direct contact with water.

h) Provide dust covers for sensors in dirty or dusty environments.

i) Sensors in high-velocity air streams, such as ducts, may require stilling tubes.

j) Sensors must not cause ignition of flammable vapor in the area.

8.5.2 Extractive Sampling Systems

8.5.2.1 General

Extractive systems are used where rapid response is required, and the detector must be located away from the sample head. Remote calibration from a centralized point is desirable.

Generally, one of three basic sampling systems should be considered:

1) remote sample head (continuous measurements and continuous readout and alarm);
2) multi-sample head (continuous measurement and sequential readout and alarm); and
3) tube sampling (sequential measurement, readout, and alarm). For further information refer to Chapter 4.

8.5.2.2 Remote Head System [5]

This system (see Figure 8-11) consists of a number of remote-mounted sample heads (suitable for hazardous areas) and an equal number of panel-mounted control and readout devices. The sample heads are located in the areas to be monitored. Samples are continuously drawn to the detector cells by sample pumps. An electrical signal corresponding to the combustible gas concentration is transmitted to the control unit continuously. Expended sample is exhausted to a safe location. The sample head and tubing should be heat-traced sufficiently to prevent condensation.

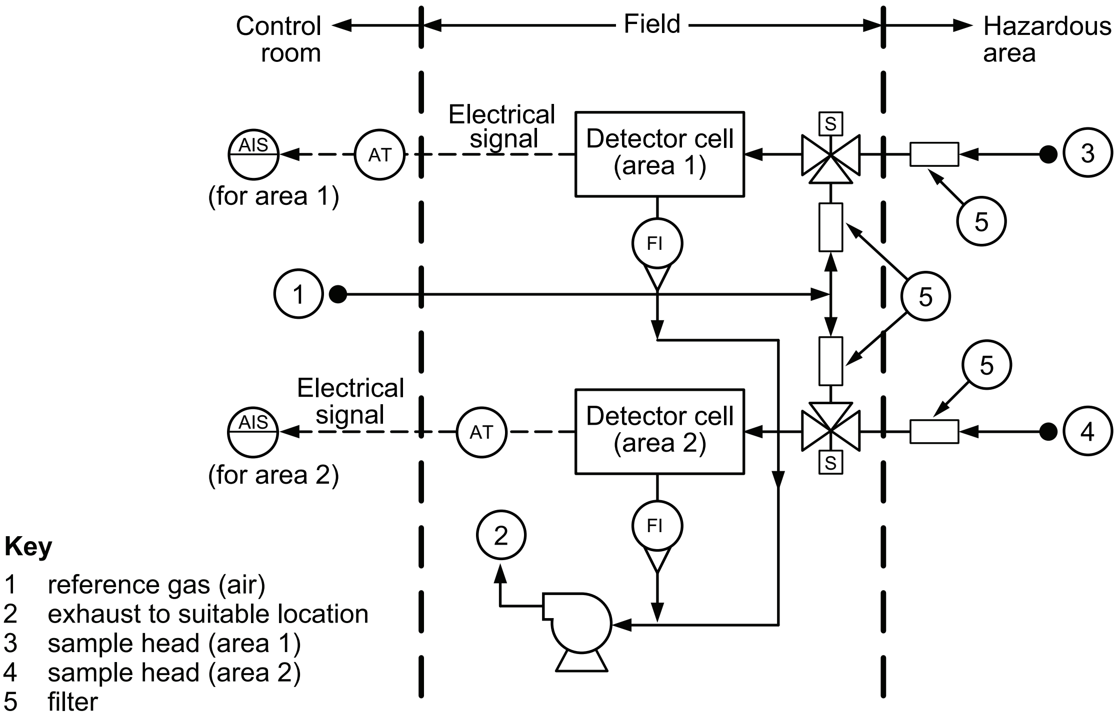
8.5.2.3 Multiple Head System [5]

The multiple head system (see Figure 8-12) is used where multiple areas are monitored and cyclic readout with accompanying time delay can be tolerated. The multiple head system consists of a number of sample heads (one for each area to be monitored), one control unit, one readout, and a sample pump. The electrical circuit incorporates a single readout device common to all detector cells. The sample is drawn continuously to each detector cell. The expended sample is continuously withdrawn by the pump. The electrical output of each unit is transmitted to the panel, where sequential readout is provided.

The dwell time for each area depends on the response time of the analyzer and the purge time of the sample system. A 10-second dwell time per point is typical: that is, 40 seconds would elapse between subsequent readings for a given area. This system is less costly than the remote sample heads arrangement and can be used where only a slow increase in gas concentration can occur.

8.5.2.4 Tube Sampling System

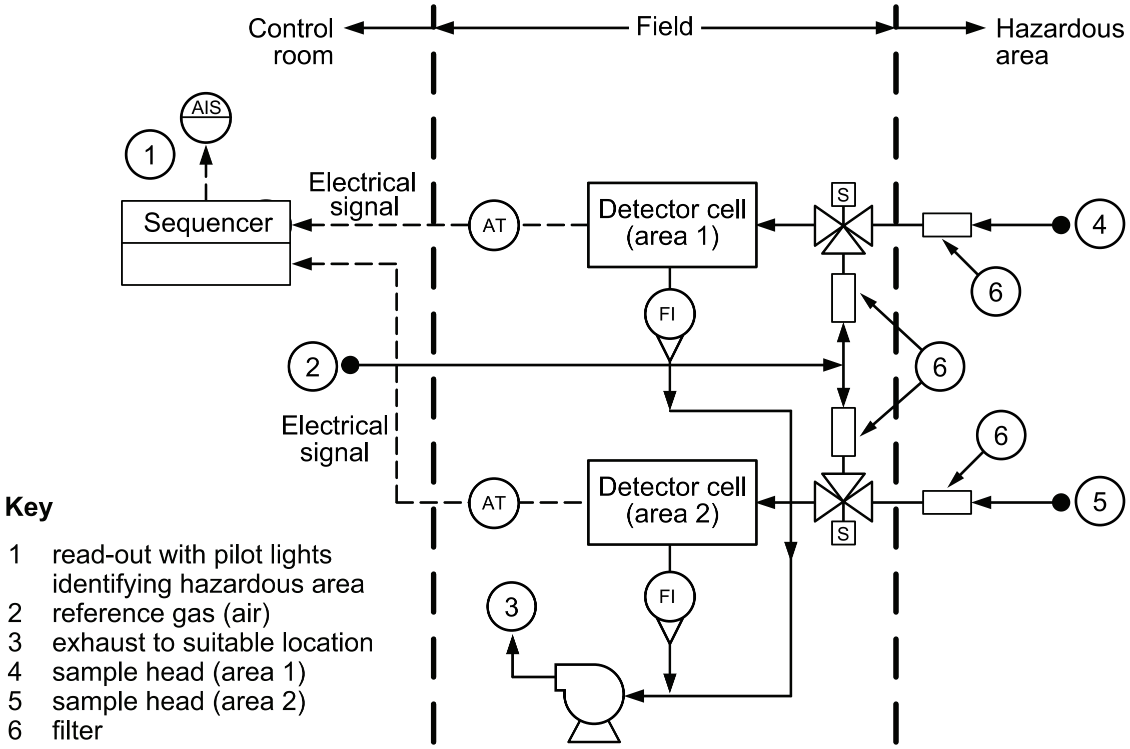
The tube sampling system (see Figure 8-13) consists of multiple sample heads, one sample selector and detector cell head, one readout device, and a sample pump. All tubing used in the sample system shall be compatible with the sample and concentration levels to be detected. The tubing shall not adsorb the component being measured. Samples from a common area are admitted sequentially to the detector cell. The sample is analyzed, and an electrical signal corresponding to the measured gas concentration is transmitted to the readout device. The sample selector unit consists of time-sequenced solenoid valves, arranged to admit one sample at a time to the detector. A sample is drawn continuously through each line, minimizing delays caused by travel time of the sample. Because the sample selector is located at the detector cell, lag time between successive analyses is also minimized. A clean gas purge is provided after each analysis to prevent erroneous readings caused by residual carryover.



Key

1 reference gas (air)
2 exhaust to suitable location
3 sample head (area 1)
4 sample head (area 2)
5 filter

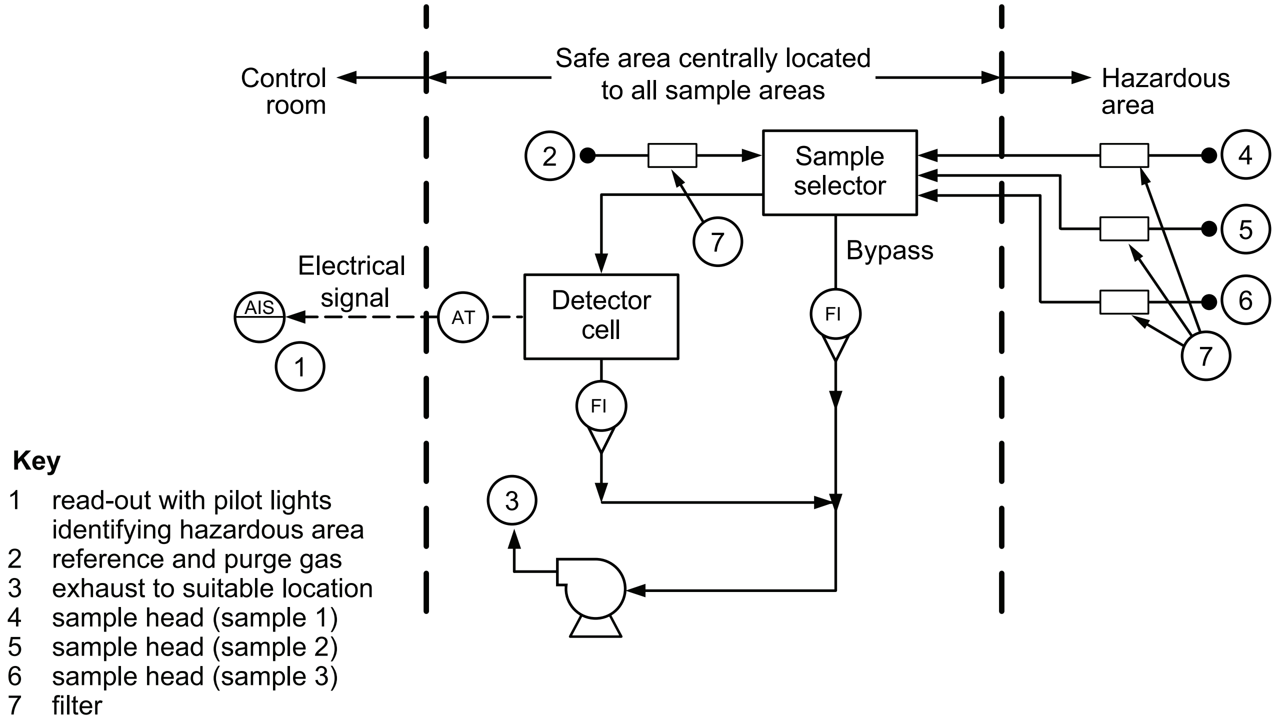
Figure 8-11—Typical Remote Head System



Key

1 read-out with pilot lights identifying hazardous area
2 reference gas (air)
3 exhaust to suitable location
4 sample head (area 1)
5 sample head (area 2)
6 filter

Figure 8-12—Typical Multiple Head System



Key

1 read-out with pilot lights identifying hazardous area
2 reference and purge gas
3 exhaust to suitable location
4 sample head (sample 1)
5 sample head (sample 2)
6 sample head (sample 3)
7 filter

Figure 8-13—Typical Tube Sampling System

Tube sampling systems usually have at least a 30-second dwell time per point. Therefore, they should be considered for use where such a slow response can be tolerated. Additionally, tube sampling arrangements should be used only with gases with boiling points well below ambient temperatures. Heat tracing should be considered to prevent condensation. Outdoor sample heads should be protected from adverse weather conditions.

8.5.3 In-situ Systems

The in-situ analyzer requires no sample system. Figure 8-14 shows various points for locating toxic or combustible analyzers.

8.6 Calibration, Startup, and Maintenance

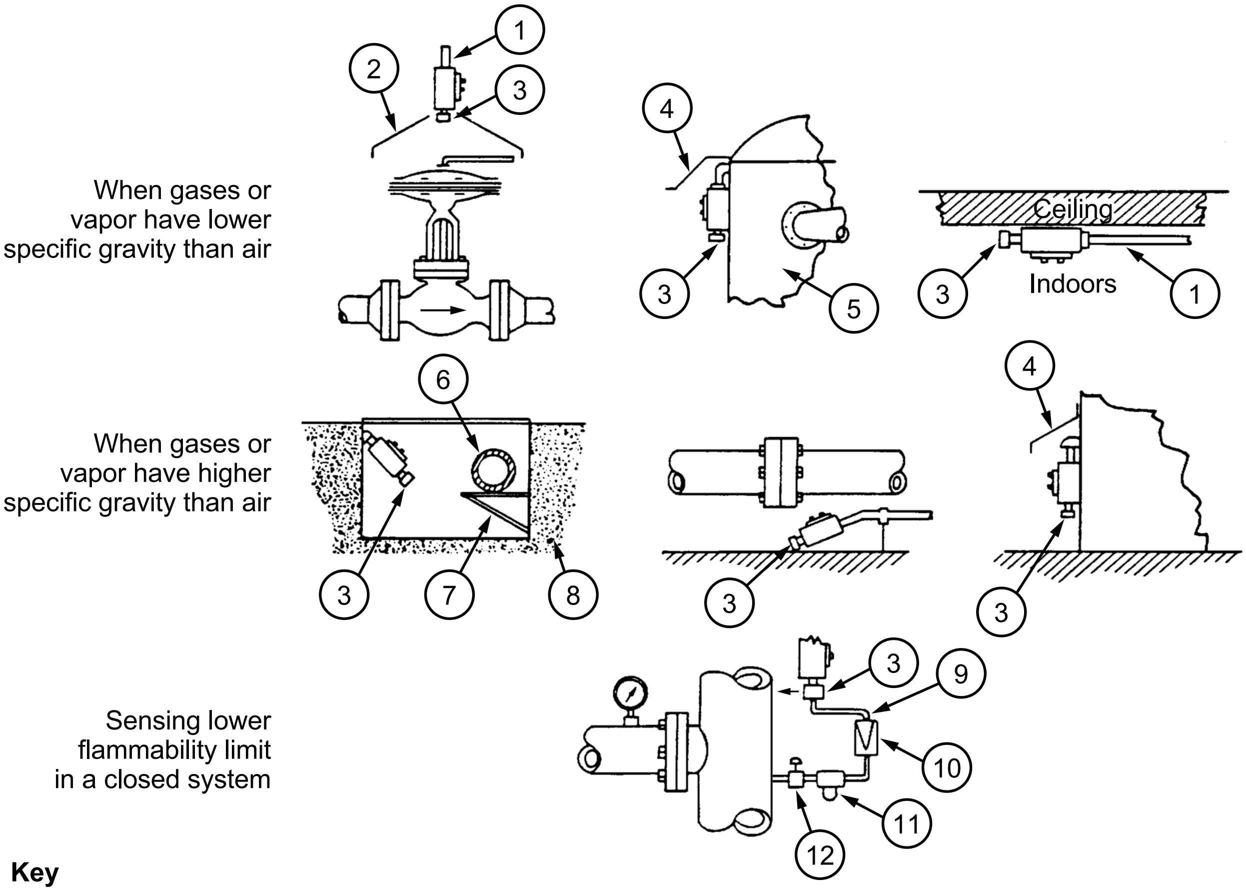
8.6.1 Toxic Gas Analyzers (H_2S)

Calibration, startup, and maintenance of toxic analyzers are unique to each type of sensor. Periodic calibration checks should occur every 30 days or as recommended by the vendor. Two methods of calibrating H_2S systems are commonly used. The following information explains how the two systems are used but does not attempt to describe how to calibrate H_2S systems in detail (refer to vendor instruction manuals). Extra precaution should be taken to ensure that the system is leak-free because of the toxic or hazardous nature of the gas.

The H_2S mixture from either of the two systems noted is applied to the sensor head with an adapter (with an O-ring), as illustrated in Figure 8-15.

8.6.1.1 H_2S Ampule

The simplest method of generating a known sample for calibration uses an H_2S ampule. In this method, a sealed ampul of a known volume containing a known concentration is smashed inside a plastic bottle (of known volume), and the resulting mixture is contained inside the bottle. By varying the concentration of H_2S inside the sealed ampul, the



Key

1	conduit	5	vessel	9	tubing
2	deflector	6	pipe	10	rotameter
3	sensor entrance	7	pipe rack	11	filter
4	drip shield	8	powder	12	needle valve

Figure 8-14—Typical Location for In-situ Systems

volume of the bottle, and the size and number of ampules, different concentrations can be obtained. The advantages of this system are that it is simple, inexpensive, and lightweight.

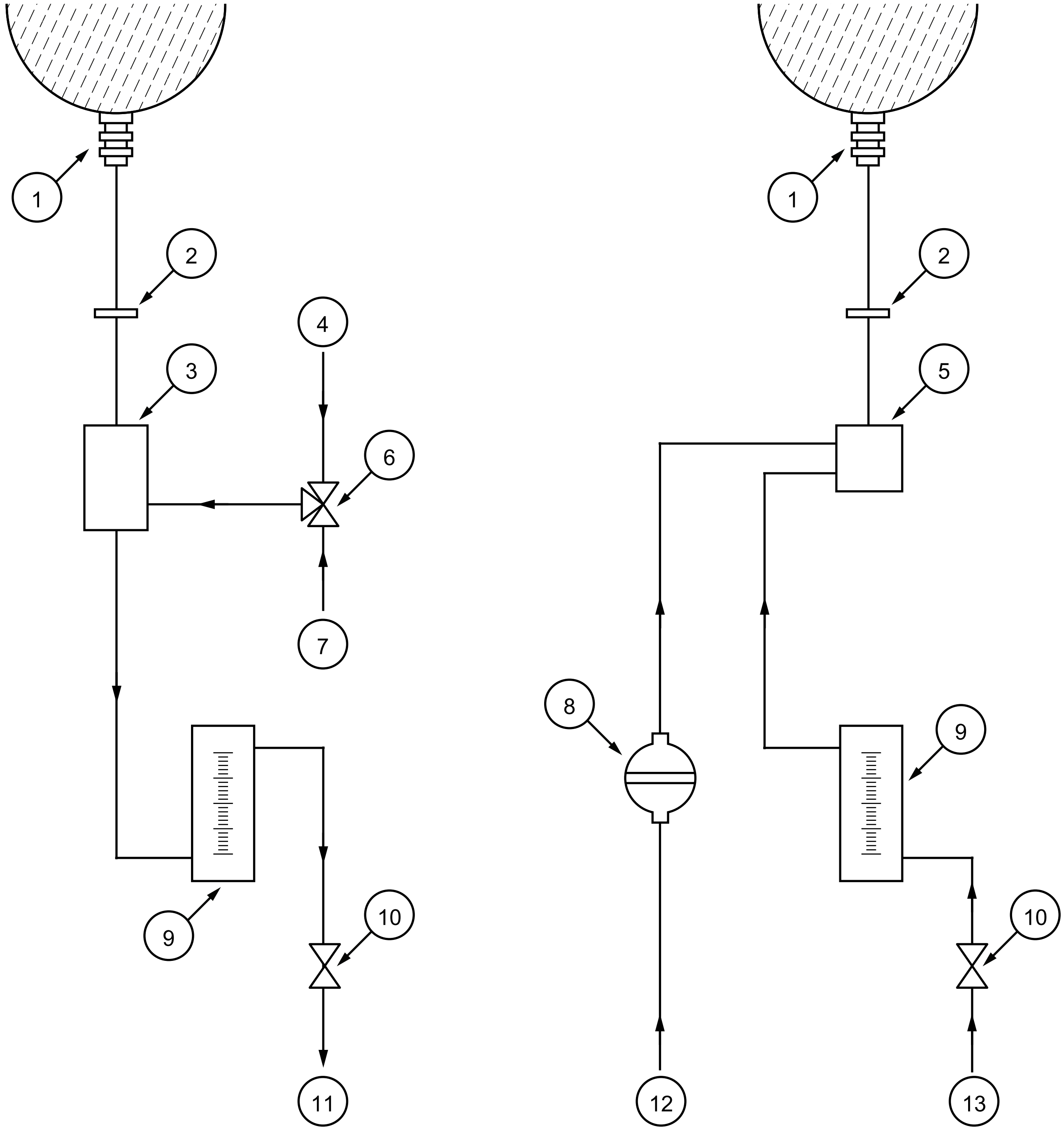
8.6.1.2 Permeation Tubes

Another method of generating a known sample uses permeation tubes containing liquid H_2S under pressure. The H_2S permeates the tube at a fixed rate at constant temperature. The permeation (leak rate) is found by determining the change in weight of the tube over a time period (this is determined by the manufacturer, not the end user). By carefully controlling the flow of air over the tube, various parts-per-million levels of H_2S can be obtained. The H_2S concentration is determined by the air flow rate and the permeation (leak) rate of the tube. Varying the air flow rate results in different H_2S concentrations. A packaged system can be purchased that includes a calibrated permeation tube, temperature controller, air flow controller, and connecting tubes.

For startup procedure and maintenance, refer to vendors' instructions.

8.6.2 Combustible Gas Analyzers

The type of sensor determines the calibration, startup, and maintenance of combustible gas analyzers. The most common procedure is accomplished with the use of a test gas kit that includes a cylinder containing a known



Drawn sampling method

Diffusion sampling method

Key

1 sensor
2 o-ring
3 flow cell
4 sample inlet
5 collar
6 3-way valve
7 air or calibration gas inlet
8 aspirator bulb
9 flow meter
10 flow control valve
11 pump or air aspirator
12 probe to pinpoint suspected leak source
13 calibration gas

Figure 8-15—Test and Calibration Means for Diffusion and Drawn Sampling concentration of a combustible gas (usually 50% of the lower flammable limit). The calibration gas is applied to the sensor in the same manner as for H_2S (see Figure 8-15) or the sample gas is applied to the system inlet. This causes the output meter to give a specific reading, which should be the same as the sample concentration.

Refer to vendor instructions for startup procedures and maintenance.

9 Continuous Emission Monitoring Systems

9.1 Applications

CEMS are required by the U.S. Environmental Protection Agency (EPA), as well as by state and local environmental agencies, to demonstrate compliance with rules and regulations as set forth in the plant or refinery permits to operate.

Data acquired from mandated CEMS can prove valuable for other uses such as determining mass balances to improve process operations and for developing plans for personnel protection.

The application of continuous monitoring techniques for the measurement of pollutants emitted from stationary sources has become an area of growing interest in both industry and government. The promulgation of regulations dealing with source level continuous monitors (on October 6, 1975) has developed a growing need for information on monitoring systems and their ability to meet the performance specifications defined in the regulations. It is also becoming apparent to personnel in industries affected by the regulations that continuous monitors can save money and improve plant performance, in addition to providing continuous source-emissions data.

The performance requirements as defined by EPA in the *Code of Federal Regulations* for installed monitoring systems are addressed and referenced in 9.2. Siting requirements, drift and calibration limitations, the definition of relative accuracy, and the statistical methods established by EPA for instrument evaluation are all elements of the Performance Specification Test that must be met by CEMS.

9.2 Regulations and Monitoring Requirements

9.2.1 Introduction

Specific source categories are required by law to install and maintain continuous emissions monitoring systems. The United States government publishes the *Code of Federal Regulations* (*CFR*) once a year, which is supplemented by *the Federal Register.* In these two publications, the regulations concerned with stationary source emissions and emission monitoring can be found. The Federal regulations establish standards and monitoring requirements for new sources. Individual states, however, were required by the Clean Air Act of 1970 to draft regulations for existing sources. It is important that refineries keep abreast of the *Code of Federal Regulations* and the *Federal Register* to determine how a facility is to comply with the regulations.

9.2.2 New Sources—Part 60

Regulations concerning new stationary sources are found under 40 *CFR* Part 60. Title 40 deals with the protection of the environment, and Part 60 deals with the standards of performance for new stationary sources or *New Source Performance Standards (NSPS* I 1). Petroleum refineries are among those source categories required by Part 60 for continuous monitoring of either opacity or some type of gaseous pollutant. The *Federal Register* published on October 6, 1975, is the document in which the EPA performance specifications for continuous monitoring systems were promulgated. Some revisions have been published, but this document covers continuous monitors for new sources. What is established is the Performance Specification Test *(40 CFR* Part 60, Appendix B). EPA provides latitude in continuous monitoring system design and application to allow sources to handle individual problems. The installed system must prove that it meets specified minimum requirements for instrument location, drift, accuracy, and other parameters. The accuracy of the CEMS is determined by comparison of data generated from the EPA Test Methods as detailed in 40 *CFR* Part 60, Appendix A.

Once it has been determined that a continuous monitoring system is required for measuring either opacity or a criterion pollutant, the type of system that will best satisfy the EPA performance regulations and the needs of the plant must be selected.

The performance specifications are clearly defined procedures for checking the installed analyzer systems. These test methods can be found in 40 *CFR* Part 60, Appendix B.

There are currently performance specification test methods and procedures for opacity, SO_2, NO, CO, CO_2, and O_2, which must be complied with by the refineries.

9.2.3 Existing Sources—Part 51

There are significant differences between regulations for new sources versus existing sources. As part of the Clean Air Act, states are required to develop a State Implementation Plan (SIP) to assure compliance with the Clean Air Act. They are required to use the Federal rules established in *CFR,* Title 40 as a minimum. New sources or those that make significant revisions will have to comply with the NSPS regulations. Older sources may not have to, depending on the extent of “grandfathering” allowed. States must petition the EPA for approval of modifications in the SIP.

The SIP is an ongoing evolving document that establishes the procedures through which the state plans to meet the national Ambient Air Quality Standards set by the EPA. Refineries are presently one of the source categories for which the state must draft continuous monitoring regulations.

Once it has been established that an existing source must install a continuous monitoring system, the analyzer specifications, data reporting requirements, and performance specification test requirements are the same as those for new sources. States have the right to assign additional requirements based on their SEP or other special conditions.

In fact, in 40 *CFR* Part 51, which gives the minimum requirements for the state regulations, states that each state plan must incorporate, as a minimum, the contents of 40 *CFR* Part 60, Appendix B, (which gives the performance specification for monitoring systems on new sources).

The states are allowed some degree of latitude on a case-by-case basis in making exceptions or in permitting alternative monitoring requirements for an existing source. Examples of special cases would be the presence of condensed water in the flue gas stream, infrequent operation of a facility, or difficulties in installing a continuous monitoring system because of physical limitations at the facility.

In summary, the intentions of requirements of 40 *CFR* Part 51 are that the continuous monitoring regulations of the states satisfy the following points.

a) Allow the utilization of existing instrumentation where possible.

b) Reduce installation cost where possible.

c) Reduce maintenance costs where possible.

d) Reduce the number of monitors where possible.

e) Encourage new technology.

9.3 Measurement Techniques Utilized In CEM Systems

Continuous emission monitors (CEM) commonly measure concentrations of pollutants prior to their release to the environment. Certain situations may require those measurements before and after a scrubbing or gas cleaning process. Many analytical techniques have been used in CEMS. Several of the more important techniques are listed in 9.3.1, 9.3.2, 9.3.3, 9.3.4, and 9.3.5.

9.3.1 Non-dispersive Infrared Analyzers (NDIR)

9.3.1.1 There are several types of NDIR analyzers. The most common are the Luft or modified Luft-type photometer, gas filter correlation photometer, and interference filter photometer. Generally, the following gases can be measured by NDIR analyzers on a dry basis: sulfur dioxide (SO_2), oxides of nitrogen (NO and NO_2), carbon monoxide (CO), and carbon dioxide (CO_2).

NDIR analyzers consist of an infrared light source, a sample cell and a detector system. The detection system is the major difference in the three techniques of NDIR analyzers as further noted in 9.3.1.2, 9.3.1.3, and 9.3.1.4.

9.3.1.2 *Luft and modified Luft photometer*: In these types of photometer, the detector is filled with the same gaseous species that the analyzer will measure. These photometers achieve their specificity to a single gas by comparison of spectral absorption of the sample gas with the spectral absorption of an inert gas, usually nitrogen (N_2).

9.3.1.3 *Gas filter correlation photometer*: In the gas filter correlation photometer, gas cells containing the same gas species to be measured (the reference gas filter) and nitrogen (the measuring gas filter) are rotated so that the infrared light passing through the sample cell, also passes alternately through the reference and measuring filters. By comparing the optical energy transmitted through each gas filter, the analyzer can determine the sample gas concentration.

9.3.1.4 *Interference filter correlation photometer*: The interference filter correlation photometer is very similar to the gas filter correlation photometer. Instead of gas filters, the interference filter photometer utilizes special optical filters (commonly called *interference filters)* to select the proper wavelengths that correspond to the species of gas being measured.

9.3.2 Electrochemical Analyzers

Electrochemical analyzers consist of at least two metallic electrodes in physical contact with an appropriate electrolyte. The chemical reactions occurring in the cell produces an output current or voltage that is a function of the number of molecules reacting with the electrolyte.

The analyzers can use liquid or solid electrolytes. In these analyzers, great care must be taken to avoid contaminating or poisoning the electrolyte by interfering compounds that will render the cell useless. In general, these devices require clean stream gases that remain relatively homogenous and are not prone to upset conditions with acid or halogen gases present in sizeable quantities.

9.3.3 Chemiluminescent Analyzers

Chemiluminescent analyzers detect light that is produced by chemical reactions that give off photons. These analyzers use the chemiluminescent reaction between ozone (O_3) and nitric oxide (NO) as its basis of measurement. In general, chemiluminescent analyzers offer good sensitivity. Interferents are usually gases that are present in large quantities that “quench” the light-producing reactions, in other words, the energy is transferred to the interfering gas instead of being emitted as light.

9.3.4 Paramagnetic Analyzers

Paramagnetic analyzers utilize the magnetic properties of oxygen to make quantitative measurement of oxygen. There are three basic types: magnetodynamic, thermomagnetic, and susceptibility pressure (Quinke effect) types. See Chapter 18 for details.

9.3.5 Gas Chromatography

Gas chromatography as described in detail in Chapter 17 is a flexible method for analyzing several components in a gas discharge stream. For example, a gas chromatograph with a Flame Photometric Detector (FPD) can be used to analyze sulfur compounds such as H_2S, SO_2, and mercaptans. Gas chromatographs are used to measure such pollutants as vinyl chloride, hydrogen sulfide, benzene, ammonia, and other sulfur, chlorinated, and hydrocarbon compounds.

9.3.6 Tunable Diode Laser Analyzers

Tunable Diode Laser (TDL) analyzers are an infra-red based analyzer that uses a tunable diode laser to generate an infra-red beam. Since the analyzer transmits a TDL beam through the sample, the non-contacting nature allows the analyzer to measure corrosive compounds not easily accomplished with other techniques such as hydrochloric acid (HCl) and hydrofluoric acid (HF).

9.4 In-Situ Analyzers

9.4.1 In-situ analyzers offer techniques to make measurements without the necessity of a sampling system.

9.4.2 *In-situ oxygen analyzers*: See Chapter 19 for more information on this type of analyzer.

9.4.3 *In-situ optical analyzers*: There are two basic types of in-situ optical analyzers: The across-stack type and the insertion probe type. The across-stack analyzer uses a light source and detector, as in normal NDIR analyzers. Light traverses the stack and strikes a detector or a mirror and is reflected back to the detector assembly. The inside of the stack becomes the sample cell. Due to the ill-behaved character of gases in the stack, this type of analyzer in general must deal with more variables than extractive types. The result is impaired performance as a trade off of no sample handling problems. Achieving extremely low ranges can be a problem with across-stack designs, since the available path length may be limited.

The probe-type in-situ analyzer is similar to the across-stack type, but the mirror is contained within a probe that contains a fixed optical path that the emission gases diffuse through. This type has an advantage (over the across-stack type) in that the output of the analyzer can be verified directly by calibration gases in the same manner that the sample is analyzed.

9.5 Types of CEMS

9.5.1 General

The two categories of CEMS are the wet and dry basis systems. The term c*omposition on a wet basis* is commonly used to denote the component mole fractions of a gas that contains water; *composition on a dry basis* signifies the component mole fractions of the same gas without water. For example, a gas that contains 33.3 mole% CO_2, 33.3% N_2, and 33.3% H_2O on a wet basis contains 50% CO_2 and 50% N_2 on a dry basis.

9.5.2 Dry Basis Systems

The dry basis system is the more predominant form of CEMS that are found in petroleum refineries. In the dry basis system, the water vapor is removed from the sample gases by either drying with condensation methods or by utilizing selective permeation membranes, or by both. The condensation methods require lowering the temperature of the gas sample to about 41 °F (5 °C) and separating the liquid condensate from the gas stream. Refrigerated gas coolers are commonly utilized for this function, as well as thermoelectrically operated gas coolers.

Special attention must be paid to the materials of construction of these devices, since a small amount of the flue gases will be dissolved in the condensate and form a diluted solution of corrosive acids (H_2SO_4 and HNO_3). Teflon or high-grade alloys or both are the most commonly used materials for such sample handling. Once the sample gases have been dried, their corrosive properties are greatly diminished. It is still prudent, however, to assure that the materials of construction of the gas analyzer(s) is compatible with the sample gas stream.

Another point that deserves consideration is the solubility of gas to be measured in the condensate. Carbon monoxide, oxygen, and nitrogen are virtually insoluble in water. Carbon dioxide, nitrogen dioxide, hydrogen sulfide, and sulfur dioxide are moderately soluble. Hydrogen chloride and ammonia are extremely soluble. Gases that are extremely soluble in water cannot be measured on a dry basis with a condensing type of sample system. With hydrogen chloride, for example, the HCl completely dissolves in the condensate (water, primarily) leaving only a trace of HCl in the sample stream that is delivered to the analyzer.

Moderately soluble gases can be dried in a condensing type of sample system. The design of the separator in the sample cooler is of importance in this technique. The separator should remove the liquid quickly and effectively so that prolonged exposure to the sample gas will not allow the gases to dissolve in the condensate. Experience has demonstrated that less than 0.5 % of the measured component gas is lost to the condensate in SO_2 and NOx systems.

Extractive systems can operate effectively on sample temperatures of up to about 1832 °F (1000 °C) when using metal alloy sample probes, and ceramics can be used at higher temperatures.

Pressure fluctuations make no difference in an extractive, dry basis system so long as the fluctuations do not interfere with the sample extraction process. That is, samples are not extracted from high-vacuum processes.

High-particulate samples are handled effectively on dry basis extractive systems by the utilization of self-cleaning particulate filters.

9.5.3 Wet Basis Systems

Wet basis systems are usually some type of in-situ device, whether optical or using some other method. Wet basis extractive systems are available that employ a dilution sample probe or hot sampling system. Before installing an in-situ analyzer, one should consider the conditions of the gas and process.

The conditions within a stack are usually very hostile and aggressive. One must consider the maximum and minimum temperatures and the magnitude of the temperature deviations. Sensitive instruments usually cannot tolerate temperatures greater than 392 °F (200 °C). The sample pressure must also be considered. If the pressure is not relatively constant, compensation may be required. Particulate matter can cause failure of optical components inserted into the stack. Particulates can also clog flow control devices inserted into the stack. Great care is advised in the application of wet basis systems.

The extractive wet basis systems dilute the sample at the sample probe. In the wet basis extractive system, there is no removal of condensate. The dilution sample system effectively “dries” the stream using instrument air or another dry, inert gas by altering the dew point of the sample. Great care should be exercised in the construction materials of the analyzers and sample systems if the temperature falls below the dew point and causes the condensation of dilute acids (H_2SO_4 and HNO_3) that could destroy the analyzer and/or sample system if not properly constructed. Higher sensitivity analyzers are required as a typical dilution ratio may be between 20:1 to 100:1.

9.6 Special Considerations

Before installing a CEM, one should consult the permit to operate the facility to see if the regulatory agency has added or modified any of the standard rules governing CEMS. With this knowledge, the engineer can address all situations by supplying redundant systems or purchasing a special type of service/maintenance contract in order to comply with the regulations.

The permit to operate usually details the data and the type of format the regulatory agency requires, as well as defined violation levels. For example, if the emission of carbon monoxide from a boiler stack was permitted at a maximum of 100 ppm volume dry basis corrected to 7 % O_2 reported as hourly averages, this will alert plant personnel immediately:

a) to monitor both CO and O_2;

b) that the range of the CO analyzer must be greater than 100 ppm volume. Usually the span of the analyzer is two times the pollutant violation level, or greater than the highest anticipated level of the pollutant (0 to 200 ppm in this example);

c) the measurement must be on a dry basis; and

d) hourly averages must be recorded for submittal to the agency.

If the operating permit says that one is in a compliance mode or must implement Appendix F QA/QC procedures, a quarterly calibration audit using EPA protocol gases is required. A relative accuracy test will be required on a yearly basis. These audits should become part of a written quality assurance plan that should include the following as a minimum:

a) daily calibration checks;

b) quarterly calibration audits;

c) data collection;

d) data reduction and validation;

e) yearly independent laboratory audit;

f) report submittals.

Since penalties have been levied in certain cases for missing compliance data, the data acquisition system becomes an integral and important part of any CEMS. While some refineries have chosen to collect data via their in-house DCS computer systems, others have kept the compliance reporting requirements as a separate function. Special consideration for compliance reporting should be given because of its extreme importance.

9.7 Safety of CEM Systems

9.7.1 Electrical

Petroleum refineries have many classified electrical areas due to the nature of the refineries' products and raw materials. With any analyzer system, it is important to consider the electrical classification of the area where the system is to be installed. Vendors of analyzers and CEMS can build their instruments and systems to the required standards and area classifications.

The nature of the gas sample must also be carefully evaluated. If the sample gas is flammable or could contain mixtures of oxygen and combustibles above the lower flammable limits (LFL), this must be indicated to the analyzer and/or system supplier so that proper precautions can be taken with regard to the electrical components.

9.7.2 Hazardous Gases

Many of the gases that are measured in the CEMS are toxic. Great caution must be exercised when using such gases for calibration. A well-ventilated area is strongly recommended. The use of any gases in high-pressure cylinders should follow the recommendations of the Compressed Gas Manufacturers Association.

9.8 Calibration of CEM Systems

The recent trend of EPA regulations has been to improve on the quality of the data generated by CEMS. The main thrust in this area has been through the use of EPA-approved calibration standards and special calibration procedures.

The EPA has published a protocol for the certification of cylinder gases used for calibrations. These gases are required when Appendix F QA/QC procedures are mandated. Otherwise, good quality gases that have been analyzed are adequate.

Most CEMS are required to have a calibration check “at the probe” or as near as practical. The system shall have the ability to introduce calibration gases at the analyzers for troubleshooting purposes. This is a hardware requirement of having the necessary equipment on the sample probe. Note that in-situ “across-stack” equipment cannot be calibration checked in this fashion. The process gas would need to be replaced with the calibration gas.

9.9 Maintenance of CEM Systems

In order to perform satisfactorily, CEMS must be properly maintained. It is important for a CEMS user to obtain information from the analyzer and/or system vendor about maintenance requirements. A spare parts inventory per the manufacturer’s recommendation is necessary to maintain CEMS reliably on line.

10 Wastewater and Water Treatment Analyzers

10.1 Total Carbon (TC) and Total Organic Carbon (TOC)

10.1.1 General

Although total carbon (TC) and total organic carbon (TOC) analyzers may be found in refinery applications that are not wastewater related, the overwhelming majority are specified as continuous monitors on aqueous effluent streams discharged in public waterways. These analyzers provide an early warning of a potential discharge of hydrocarbons and allow operating personnel to divert the stream to a temporary holding tank or pond where the hydrocarbon may be treated or diluted for subsequent release at an acceptable level. Fines and levies for a single incident (hydrocarbon discharge with a subsequent fish kill) may far exceed the cost of installation of a TC or TOC analyzer.

10.1.2 Typical TC and TOC Application Specifications

Sample system complexity:	complex
Typical analysis spans:	ppm up to % level
Typical analyzer outputs:	alarms, local meter, 4 mA to 20 mA
Manufacturer’s listed accuracy:	± 2 % of scale
Typical analysis precision:	± 2 % of scale
Typical analysis time:	3 minutes
Typical on-stream time:	> 95 % if routine maintenance is performed
Relative installed cost:	> $30 K
Relative maintenance frequency:	1+ man-hour/day, visual inspections
Average startup:	< 3 man-days
Typical refinery applications:	wastewater, biotreaters, process streams

10.1.3 High-temperature Combustion TC and TOC Analyzers

High-temperature combustion analyzers for total carbon and total organic carbon receive a precise amount of sample, either continuously or by discrete injection, into a high temperature reaction chamber at 1400 °F to 1700 °F (750 °C to 950 °C). The furnace of the analyzer may be constructed of metal alloy, ceramic, or quartz. Carbon compounds in the sample are oxidized with air or oxygen to carbon dioxide (CO_2). Some versions of the analyzer employ a catalyst to aid the reaction. The reaction products pass through a cooler and a gas/liquid separator in which water vapor is condensed and removed. The remaining non-condensable gases are swept through an infrared spectrophotometer tuned to CO_2. non-dispersive infrared is the most common detection method (see Chapter 11 for additional details on infrared analyzers.)

In another version of the high-temperature combustion analyzer, CO_2 is reduced to methane, which is then measured by a flame ionization detector. And, in yet another version, the reaction product is treated with barium hydroxide to form a precipitate, barium carbonate. The quantity of precipitate formed is measured by a light scattering technique with a nephelometer. The total carbon concentration of the original sample is determined by comparison with a calibration curve generated from standard solutions.

Analyzers for total organic carbon (TOC) generally use the same techniques as analyzers for total carbon (TC) except that the sample is pretreated before oxidation to remove inorganic carbon, such as carbonates and bicarbonates, which would be converted to CO_2 at high combustion temperatures. The original sample is mixed with mineral acid to a pH of about 2 to convert inorganic carbon to CO_2, which is then removed from the solution by sparging. Following inorganic carbon removal, analysis for total carbon is performed on the carbonate-free sample. See Chapter 30 for detailed information on pH measurements.

Figure 10-1 provides a diagram of the high-temperature apparatus version. The advantages of the high-temperature combustion analyzers the following.

a) The analyses are fast enough to be useful in process control.

b) The method is more reproducible than biological or chemical oxygen demand. Oxidation efficiency is 98% to 100 % for most organic compounds.

c) Analyses are not affected by nitrifying bacteria and oxidizable material, such as sulfides, sulfites, or ferrous compounds.

The disadvantages of the high-temperature combustion analyzers include the following.

a) Measures of total organic carbon include all organic carbon without regard to its biodegradability and may not reflect the true oxygen demand.

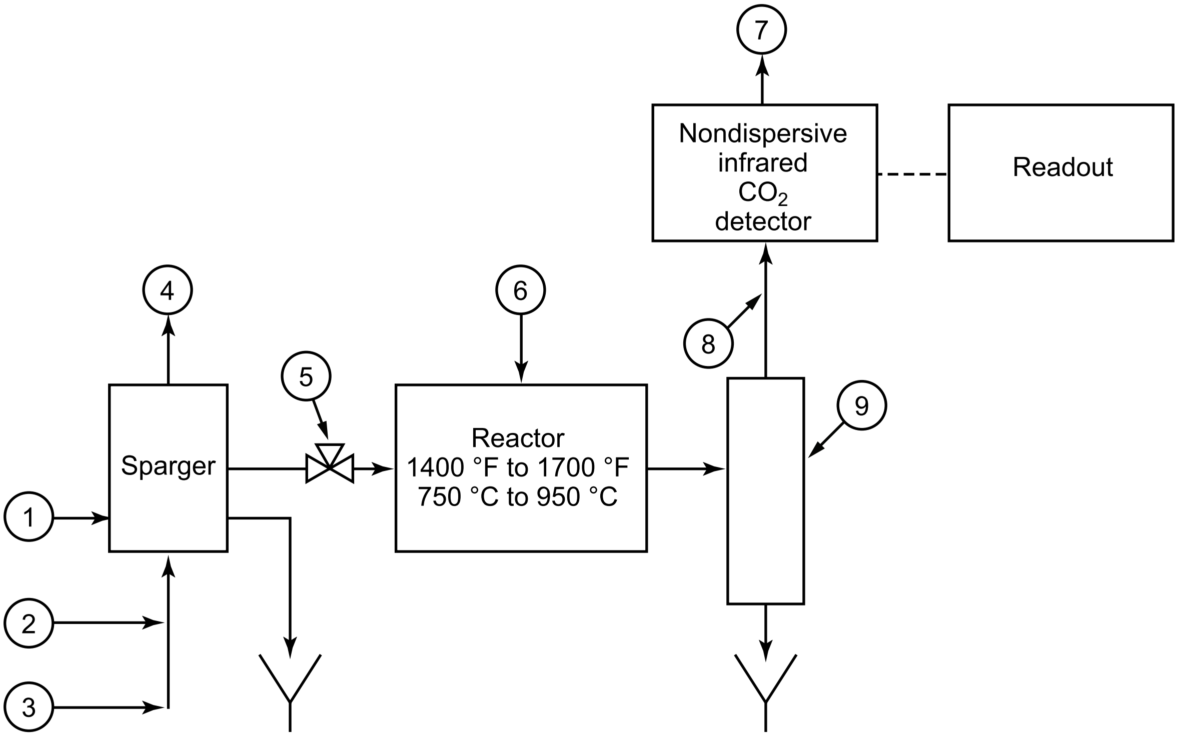
b) Streams with high salt content eventually cause corrosion and plugging of the analyzer. Analysis of these streams may result in a potential fire hazard if proper maintenance procedures are not followed due to the volatile nature of these salts.

c) The particle size that can be accommodated in instruments using discrete injection is usually limited by the size of the valve ports to about 200 micrometers. Organic matter on filtered particulate matter is not measured.

d) Volatile hydrocarbons may be lost during inorganic carbon removal.

10.1.4 Ultraviolet-promoted Chemical Oxidation Analyzers

Inorganic carbon is removed by acidifying and sparging the sample before chemical oxidation. An ultraviolet-promoted chemical oxidation reaction, as shown in Figure 10-2 can be used to convert total carbon and total organic carbon to CO_2 at a low temperature (~140 °F = 60 °C). The sample is mixed with an oxidizing agent, potassium



Key

1	sparge gas	5	calibration standard
2	acid	6	air
3	sample	7	vent
4	vent containing CO_2 from inorganic carbon	8	air containing CO_2 from reactor
		9	condenser for water removal

Figure 10-1—High-temperature Oxidation Analyzer for Total Organic Carbon

persulfate, and passed through a quartz tube reaction zone, where it is irradiated by a low-pressure mercury vapor ultraviolet source. Carbon compounds are converted to CO_2 which, with other non-condensable matter, is separated from the water in a gas/liquid separator and measured by a nondispersive infrared analyzer sensitized to CO_2.

The advantages of the ultraviolet type analyzers include the following.

a) Corrosion, plugging problems, and potential of fire hazards during maintenance which are associated with high salt content are minimized by eliminating the high-temperature combustion furnace.

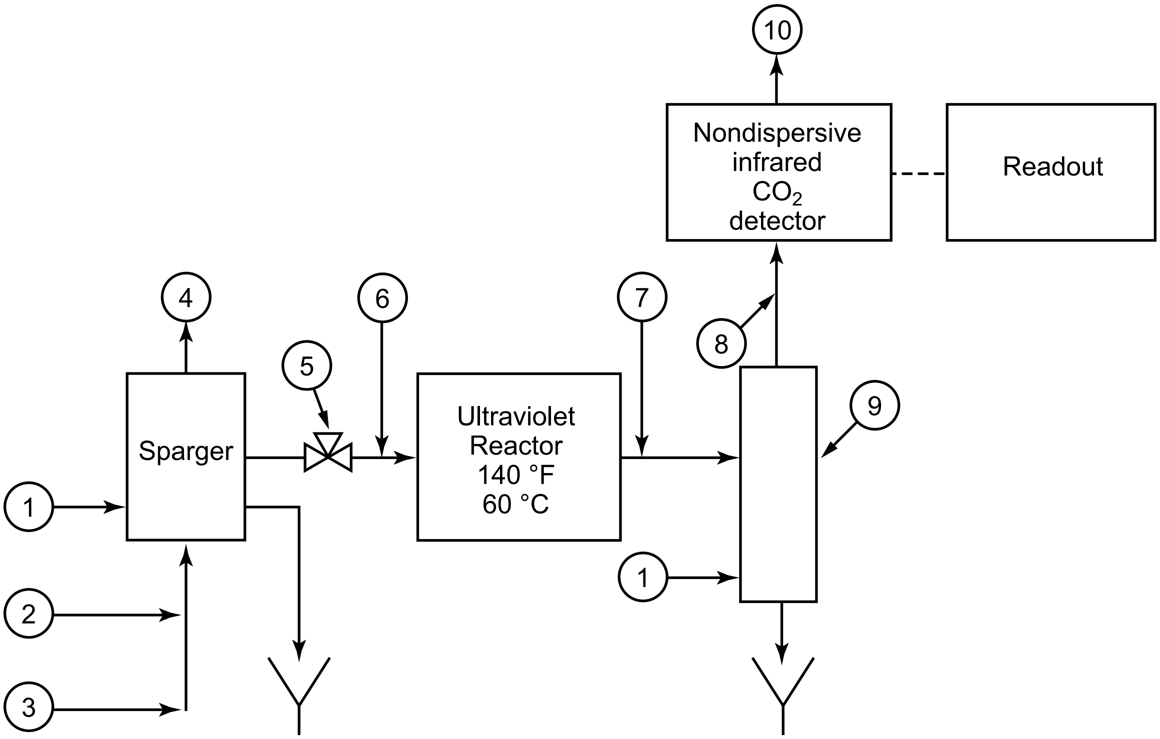
b) Sampling by continuous flow through $^1/_8$-in. tubing can accommodate particles up to 2500 micrometers without plugging (greater overall recovery of organic materials in streams with significant solids content).

c) The analysis is rapid enough for process control applications.

d) The method is more reproducible than biological or chemical oxygen demand. Oxidation efficiency is greater than 95 % for most organic compounds.

The disadvantages of the ultraviolet-type analyzers include the following.

a) Measurements of total organic carbon includes all organic carbon without regard to biodegradability and, therefore, may not reflect true oxygen demand.



Key

1 sparge gas
2 acid
3 sample
4 vent containing CO_2 from inorganic carbon
5 calibration standard
6 potassium persulfate
7 sodium sulfite
8 gas containing CO_2 from stripper
9 gas/liquid separator (CO_2 stripper)
10 vent

Figure 10-2—Ultraviolet Promoted Oxidation Analyzer for Total Organic Carbon

b) Volatile hydrocarbons may be lost during inorganic carbon removal.

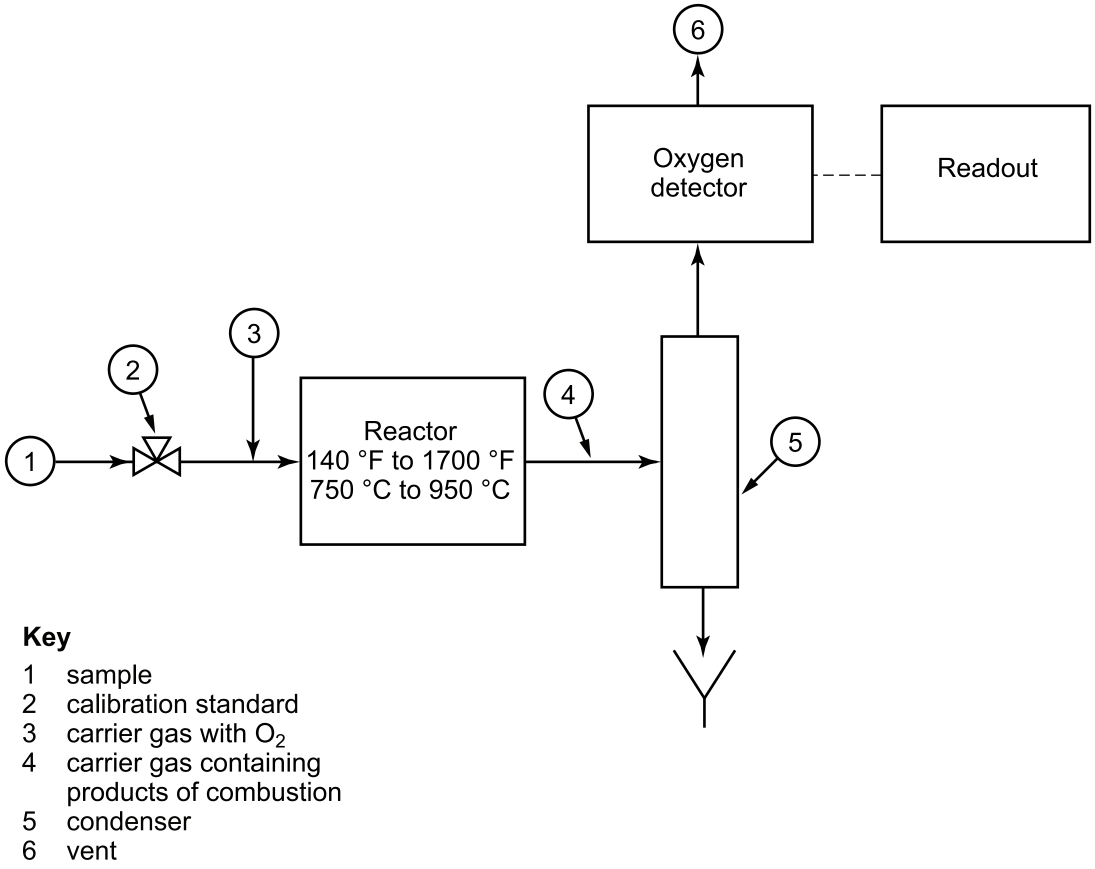
c) Some hydrocarbons are not oxidizable by this technique and are not measured.

d) The method normally uses three peristaltic pump channels for introducing reagents. Peristaltic pumps require frequent maintenance.

10.2 Total Oxygen Demand Wastewater Analyzers

10.2.1 General

Total oxygen demand (TOD) analyzers are similar to high temperature combustion total organic carbon analyzers except the removal of inorganic carbon is not required. The sample is introduced into the reaction zone, either continuously or by discrete injection, together with a carrier gas containing a constant level of oxygen. All oxidizable components in the sample are converted to their stable oxides. In some versions of the analyzer the reaction takes place in the presence of a catalyst. An oxygen sensor monitors the level of oxygen in the carrier gas and ensures the depletion of oxygen following combustion. The oxygen depletion is the total oxygen demand value to the sample. Figure 10-3 is a diagram of a typical total oxygen demand analyzer.



Key

1 sample
2 calibration standard
3 carrier gas with O_2
4 carrier gas containing products of combustion
5 condenser
6 vent

Figure 10-3—Analyzer for Total Oxygen Demand

The advantages of total oxygen demand analyzers are:

a) No liquid chemical reagents are used.

b) Inorganic carbon does not interfere with the analyses.

c) Volatile hydrocarbons are not lost.

The disadvantages are:

a) Streams with high salt content eventually cause corrosion, plugging, and potential fire hazard during routine maintenance of the analyzer.

b) Nitrates, if present, decompose to form nitric oxide and O_2. This reduces the apparent oxygen demand of the sample.

10.3 Turbidity Analyzers

10.3.1 General

Turbidity is a measure of clarity of water which is Important in products to be used for human consumption and in many manufacturing processes. Turbidity is a measure of effectiveness of the water treatment or manufacturing process.

Suspended matter such as clay, silt, organic, inorganic particulates, and other organisms cause turbidity. Turbidity is measured in Nephelometric Turbidity Units (NTU) which is based on measurement of the light scattered in one direction, predominantly at a right angle to the incident of light. Formazin polymer is used as a reference turbidity standard suspension.

All turbidity-measuring instruments utilize a light beam reflected from, projected into, or transmitted through the sample liquid. The light beam is scattered and/or absorbed by particles on or in the liquid to a degree that can be related to the number and size of particles in the sample liquid (turbidity).

The direction and intensity of scattered light is a function of the ratio of particle diameter to light wavelength. The wavelength of visible light ranges from 0.38 micrometers to 0.76 micrometers, but for this discussion is considered to be 0.50 micrometers, the wavelength of blue-green light.

Particle diameters less than 0.10 micrometer will produce forward and backward scattered light intensities that are equal and side scatter intensities one-half the forward/backward intensity as shown in Figure 10-4.

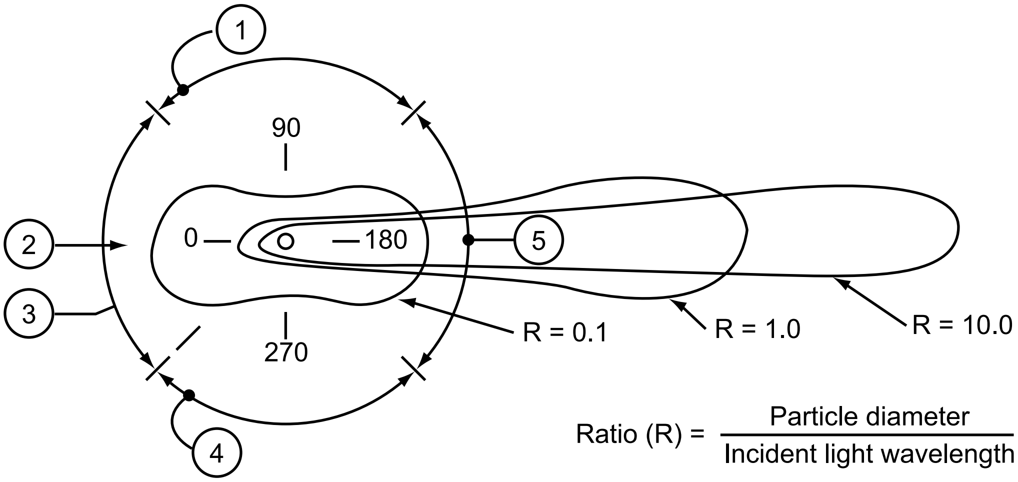
Particle diameters between 0.10 micrometer and 1.00 micrometer produce a complex intensity pattern that peaks when the particle diameter and wavelength are about equal. Since most applications will consist of particles having varying diameters, this resonance effect will probably not be observed. The larger particles will significantly increase the forward scatter component as shown in Figure 10-4.

Particle diameters greater than one micrometer scatter light strongly into the forward scatter area and weakly into the side and backward scatter areas. For particle diameters equal to or greater than the wavelength, the forward scattering intensity is at least a hundred times greater than the side or backward scattering intensity. In this range the total scattering efficiency of a particle increases with the cross-sectional area of the particle. Since 99% of the scattering is in the forward area it is possible to select optics that detect intensities that vary proportionately with the particle volume, and therefore particle mass. However, as particle size increases, it becomes more difficult to differentiate between the incident light and the scattered light because of the decreasing scattering angle.

The basic types of turbidity meters are the light-scatter (Nephelometric) type and the ratio type. The characteristics of the various light scatter turbidimeters are shown in Table 10-1.

10.3.2 Typical Turbidity Application Specifications

Sample system complexity:	simple
Typical analysis ranges:	0 through 1 NTU up to 0 through 1000 NTU
Typical analyzer outputs:	alarms, local meter, recorder, 4 mA to 20 mA
Manufacturer’s listed accuracy:	± 1 % of scale
Typical analysis precision:	± 0.5 % of scale
Typical analysis time:	continuous
Typical on-stream time:	85 % to 95 %
Relative installed price:	$15 K to $30 K+
Relative maintenance frequency:	as much as 1 man-hour/day
Average startup:	< 2 man-days
Typical refinery applications:	wastewater, clarifiers, process streams



Key

1 side scatter area
2 incident light
3 back scatter area
4 side scatter area
5 forward scatter area

Figure 10-4—Scattered Light Intensity Patterns

Table 10-1—Characteristics of Turbidity Meter Types

Characteristics	Surface Scatter	Side and Back Scatter	Forward Scatter	Ratio Scatter
Sensitivity	Medium	Low	Medium	High
Rangeability	High[1]	High → Med.	High → Low	High → Low
Response	Slow	Fast	Fast	Fast
Maintenance	Low	High	Medium	Low
Accuracy Affected by				
Coated Optics	No[2]	Yes	Yes	No[3]
Light Source Aging	Yes	Yes	Yes	No[5]
Stray Light	Yes	Yes	Yes	Yes
Secondary Scatter	Yes	Yes	Yes	No[5]
Changing Liquid Color	Yes	Yes	Yes	No[5]
Bubble or Ice	Yes	Yes	Yes	No[5]
Vibration	Yes[4]	No	No	No
Sample System				
Open[5]	Yes	No	No	No
Closed[6]	No	Yes	Yes	Yes
Inline	No	Yes	Yes	Yes

Notes:

1) Up to 5000 NTU.
2) Optics are not in direct contact with sample liquid.
3) Ratio remains unchanged because forward scattered and attenuated beams are equally affected.
4) Surface waves reduce flicker in detector.
5) Open sample systems are usually at atmospheric pressure and temperature.
6) Closed sample systems usually contain high pressure, high temperature, or toxic streams.

10.3.3 Light Scatter (Nephelometric) Turbidimeters

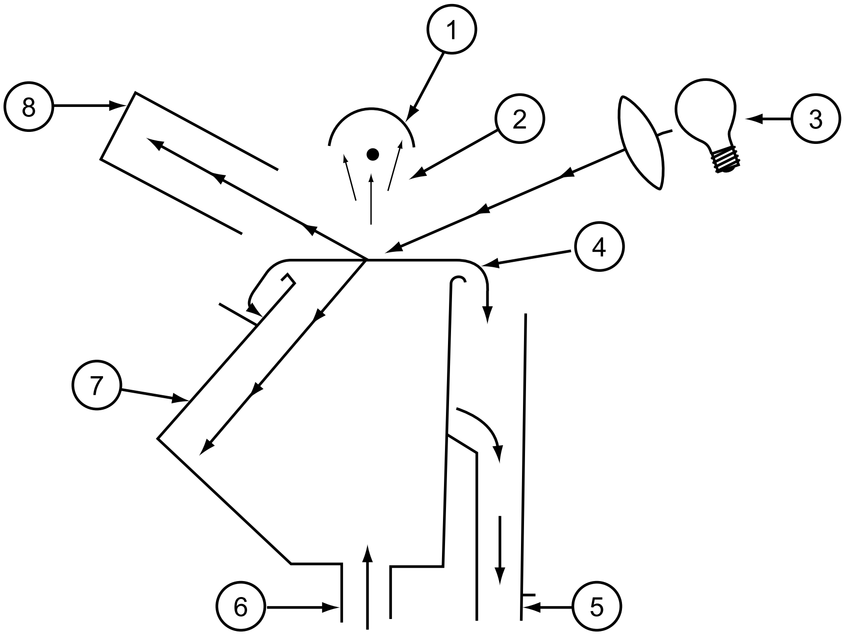
Surface scatter instruments direct a light beam onto the surface of an upwelling sample liquid. The angle of incidence of the light beam is such that a clean liquid surface reflects the beam into a light trap while the scattered light detector output is zero. As particles come up to the surface, some of the light is scattered into the detector whose output increases as shown in Figure 10-5.

Back and side scatter instruments project a light beam into a sample liquid contained in or flowing through an optical chamber. Scattered light detectors located inside or outside the chamber, either perpendicularly or axially to the incident light beam, produce a signal proportional to the scattered light received.

Forward scatter instruments project a light beam into a sample liquid contained in or flowing through an optical chamber. The forward scattered light projects through the sample to a detector located approximately 180 degrees from the incident light source while the non-scattered incident light passing through the sample is masked by a suitable light trap.

10.3.4 Ratio Turbidimeter

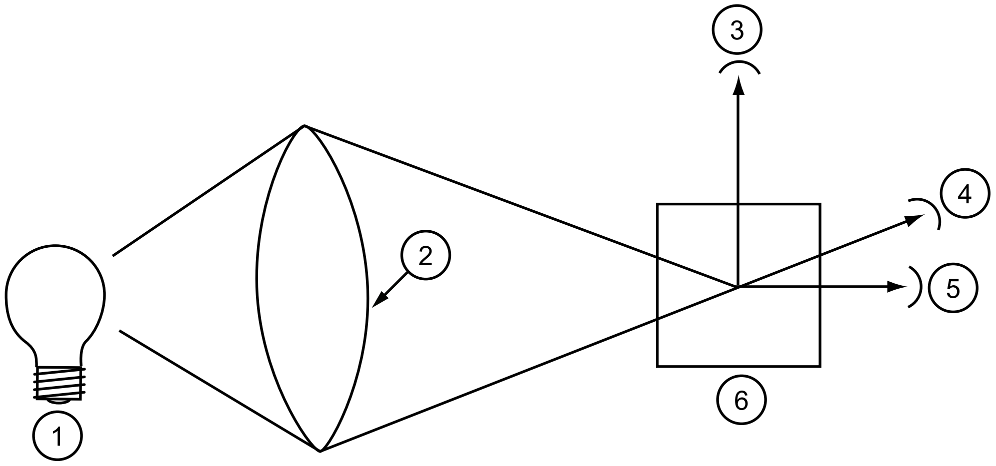
The ratio instrument directs a light beam through a sample liquid contained in or flowing through an optical chamber. In addition to measuring the light scattered at 90 degrees to the incident light (i.e. the standard Nephelometric method), the ratio turbidimeter measures transmitted light and forward scattered light (a total of 3 detectors). Electronic circuitry calculates the ratio between scattered and non-scattered light and produces an output that is not affected by color, changes of color, secondary scattering, coated optics, or an aged light source. Both the scattered and non-scattered light are equally affected as shown in Figure 10-6.



Key

1 detector
2 scattered light
3 light source
4 liquid surface
5 drain
6 upwelling turbid liquid sample
7 refracted light trap
8 reflected light trap

Figure 10-5—Surface Scatter Turbidimeter



Key

1	light source
2	lens
3	90 degree detector
4	forward scatter detector
5	transmitted light detector
6	sample cell

Figure 10-6—Radio Turbidimeter

10.4 Residual Chlorine Analyzers

10.4.1 General

Wastewater streams are often chlorinated to remove potentially hazardous components (for example hydrogen cyanide, or some heavy metals) prior to discharge into a public waterway. Chlorine treatment processes must be monitored to ensure that discharge streams do not contain unacceptably high levels of residual chlorine (which may be as toxic to aquatic life as the components being removed). The common techniques employed to measure residual chlorine are described in this chapter.

10.4.2 Amperometric Residual Chlorine Analyzers

10.4.2.1 General

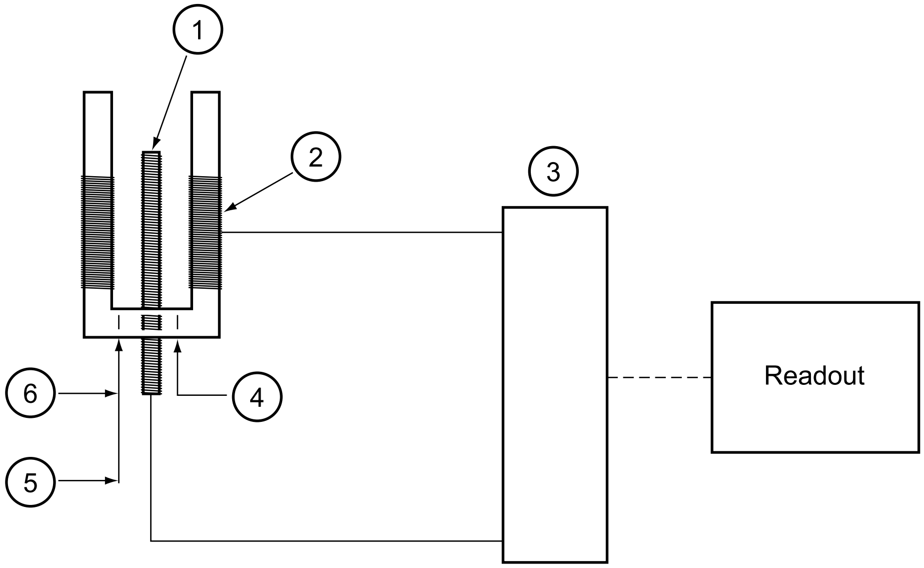
The sample cell in amperometric type analyzers consists of concentrically mounted electrodes, and an outer copper counter electrode and an inner gold measuring electrode, over which the sample flows.

The continuously flowing water sample is adjusted to a pH of 4.0 to 4.5 with buffered acetic acid solution and then reacts with a potassium iodide (KI) solution introduced at a constant rate of flow (pH analyzers are discussed in detail in Chapter 30). Potassium iodide reacts with both free and combined chlorine to liberate iodine in direct proportion to the amount of chlorine present. As the treated sample passes between the electrodes in the sensing cell a small direct current is generated. This signal is amplified and sent to a readout device that is calibrated in milligrams per liter of residual chlorine, as shown in Figure 10-7.

The advantages of the amperometric method are:

a) fast response time (4 seconds) which makes it suitable for use in a control loop;

b) high sensitivity (0. 01 milligram per liter).



Key

1 measuring electrode
2 counter electrode
3 signal conditioner electronics
4 potassium iodide solution
5 sample
6 acetic acid buffer

Figure 10-7—Amperometric Residual Chlorine Analyzer

The disadvantages of the amperometric method are:

a) high concentrations of metal ions interfere with the determination;

b) inorganic salts in high concentrations interfere with the measurement;

c) high maintenance;

d) high cost because several chemical reagents are required.

10.4.2.2 Typical Amperometric Application Specifications

Sample system complexity:	average to complex (depends on application)
Typical analysis spans:	0 ppm to 0.5 ppm up to 0 ppm to 20 ppm
Typical analyzer outputs:	4 mA to 20 mA
Manufacturer’s listed accuracy:	± 1 % of scale
Typical analysis precision:	± 1 % of scale
Typical analysis time:	continuous
Typical on-stream time:	< 95 % stream factor, usually 85% to 95%
Relative installed cost:	$15 K to $30 K

Relative maintenance	average to high, depends on frequency:application
Average startup:	< 2 man-days
Typical refinery applications:	potable water, water treatment, wastewater

10.4.3 Colorimetric Residual Chlorine Analyzers

10.4.3.1 General

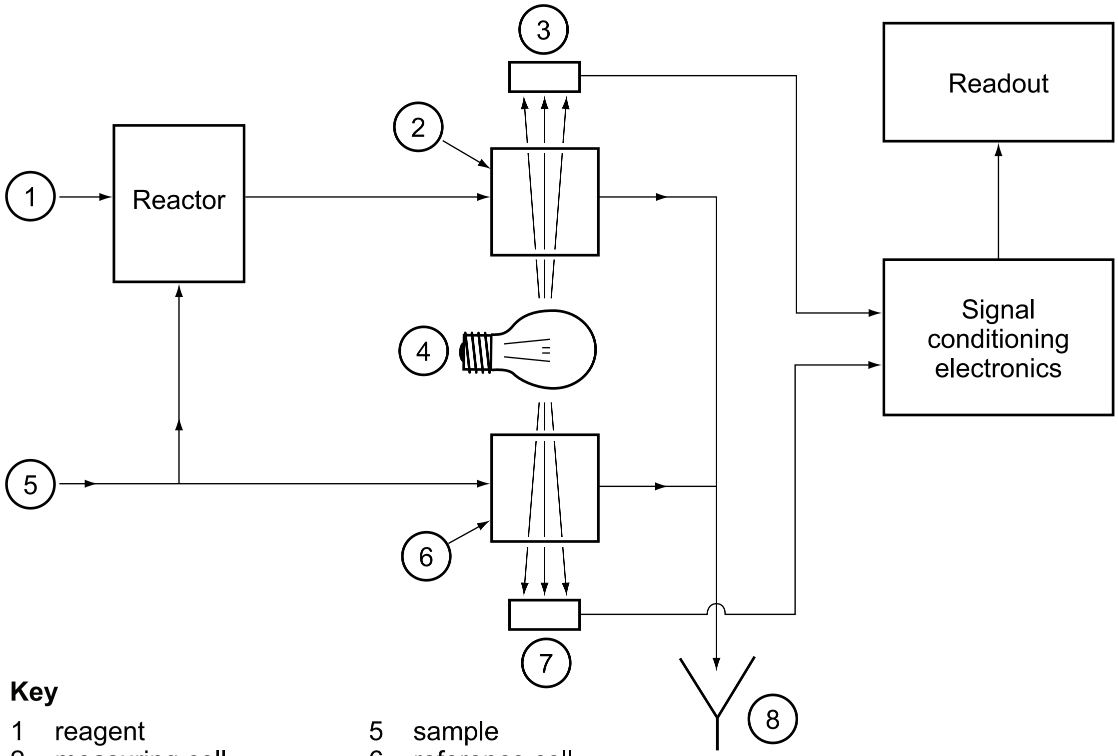
In colorimetric residual chlorine analyzers a continuously flowing water sample is reacted with either o-toluidine or diethyl-paraphenylenediamine (DPD) introduced at a constant rate of flow. Residual chlorine is monitored continuously by detecting the color change with a dual beam spectrophotometer as shown in Figure 10-8 (see Chapter 29 for further information on colorimetric analyzers). The readout is calibrated in milligrams per liter of residual chlorine.

The primary advantage of the colorimetric method is that no interference from hexavalent chromium ions or salts occur.

The disadvantages of the colorimetric method are:

a) slow response time up to 20 minutes for stabilization;

b) wetted optic components may get fouled.



Key

1	reagent	5	sample
2	measuring cell	6	reference cell
3	measuring detector	7	reference detector
4	source	8	drain

Figure 10-8—Spectrophotometric Wet Chemistry Analyzer

10.4.3.2 Typical Colorimetric Residual Chlorine Specifications

Sample system complexity: average (depends on application)

Typical analysis spans: + 25 to 16 color units, or
0 to 6 ASTM

Typical analyzer outputs: alarms, 4 mA to 20mA, RS–232

Manufacturer’s listed accuracy: ± 2 % of scale

Typical analysis precision: ± 2 % of scale

Typical analysis time: continuous

Typical on-stream time: < 95 % stream factor, usually 85% to 95%

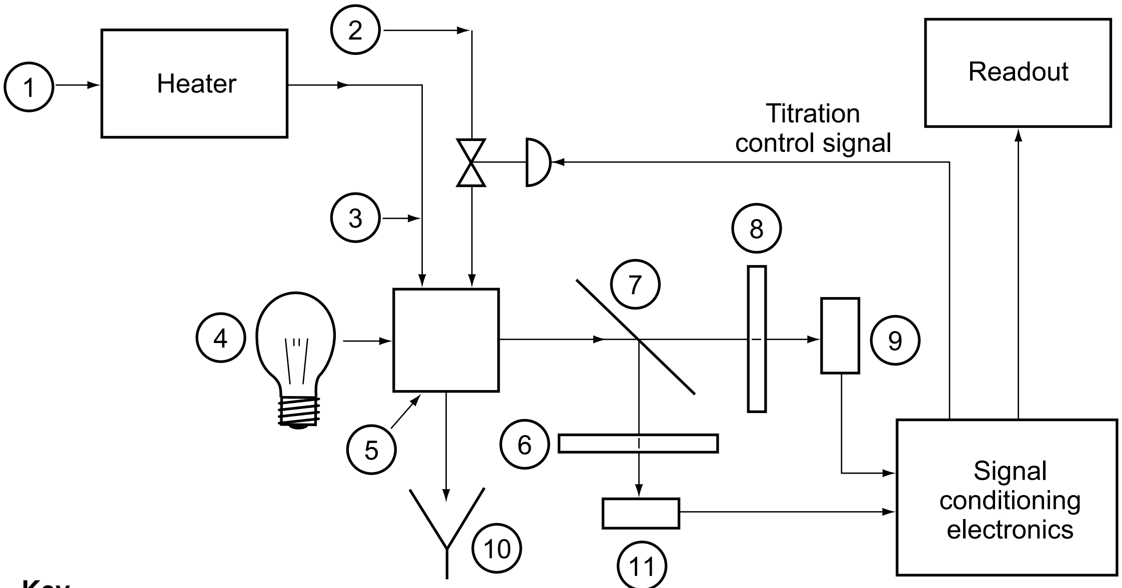
Relative installed cost: $15 K to $30 K

Relative maintenance frequency: < 1 man-hour/day

Average startup: < 2 man-days

Typical refinery applications: kerosenes, lube oils, gasolines

On-line colorimetric titration methods are also employed to measure chlorine (see Figure 10-9).



Key

1 sample
2 titrating solution
3 indicator solution
4 radiation source
5 colorimeter cell
6 reference filter
7 partially transmitting mirror
8 measurement filter
9 measurement photocell
10 drain
11 reference photocell

Figure 10-9—Colorimetric Titrimeter

10.5 Hydrocarbons-In-Water Analyzers

10.5.1 General

When selecting an analyzer to monitor hydrocarbons in water, it is necessary to determine whether the hydrocarbons are volatiles or non-volatiles, occur undissolved, emulsified, or dissolved in varying concentrations. The determination is usually affected by the type of contaminants, temperature, contact or mixing time, pH, and the quantity of salts or other chemical compounds present in the wastewater stream.

More precise quantitative/qualitative analysis of wastewater may be obtained by complex (and expensive) techniques, such as mass spectrometry and chromatography; however, the usual wastewater application for hydrocarbon-in-water analyzers is the detection of a broad spectrum of contaminates and providing an alarm quickly enough for corrective action to be taken. The types of analyzers described in 10.5.2, 10.5.3, and 10.5.4 are broad spectrum analyzers that will detect small quantities of contaminates in a stream but will not necessarily indicate composition.

10.5.2 Ultraviolet and Infrared Absorption Detectors

Hydrocarbons can frequently be detected by absorption spectrophotometry where energy in the ultraviolet or infrared portion of the spectrum is passed through a sample and the amount of energy absorbed is measured. The specific radiation range is selected to match a specific absorption wavelength for the molecule or compound of interest. Ultraviolet and infrared absorption versus wavelength curves for almost all hydrocarbons have been developed and are available from manufacturers of analyzers.

In one method, first the oils (which mainly are hydrocarbons), are extracted from a water sample by using a solvent fluorocarbon such as S-316. The extracted oils are then analyzed using infrared technology. Hydrocarbons have a major infrared (NDIR) absorption band in the region of 3.4 microns to 3.5 microns, a region in which the fluorocarbon S-316 does not absorb (see Figure 10-10). Thus, the infrared absorption that occurs is the result of the oil concentration in the sample water. This kind of oil-in-water monitor is highly sensitive to all oils, but is unaffected by suspended solids, or color of the sample.

For additional information on ultraviolet and infrared spectrographic analyzers refer to Chapter 11 and Chapter 12.

The advantages of the ultraviolet and infrared methods for wastewater applications are:

a) undissolved, emulsified, and dissolved oils are detected;

b) ultraviolet analyzers are suitable for a wide range of hydrocarbons;

c) ultraviolet analyzers are suitable for trace detection;

d) Infrared analyzers are suitable for compound identification.

The disadvantages are:

a) analysis may require intermediate steps such as distillation solvent extraction, or homogenizing;

b) measurements are susceptible to changes in pH;

c) samples must be filtered, due to the fact that turbid samples will scatter ultraviolet and infrared light;

d) wetted optics require frequent cleaning;

e) volatiles are lost.

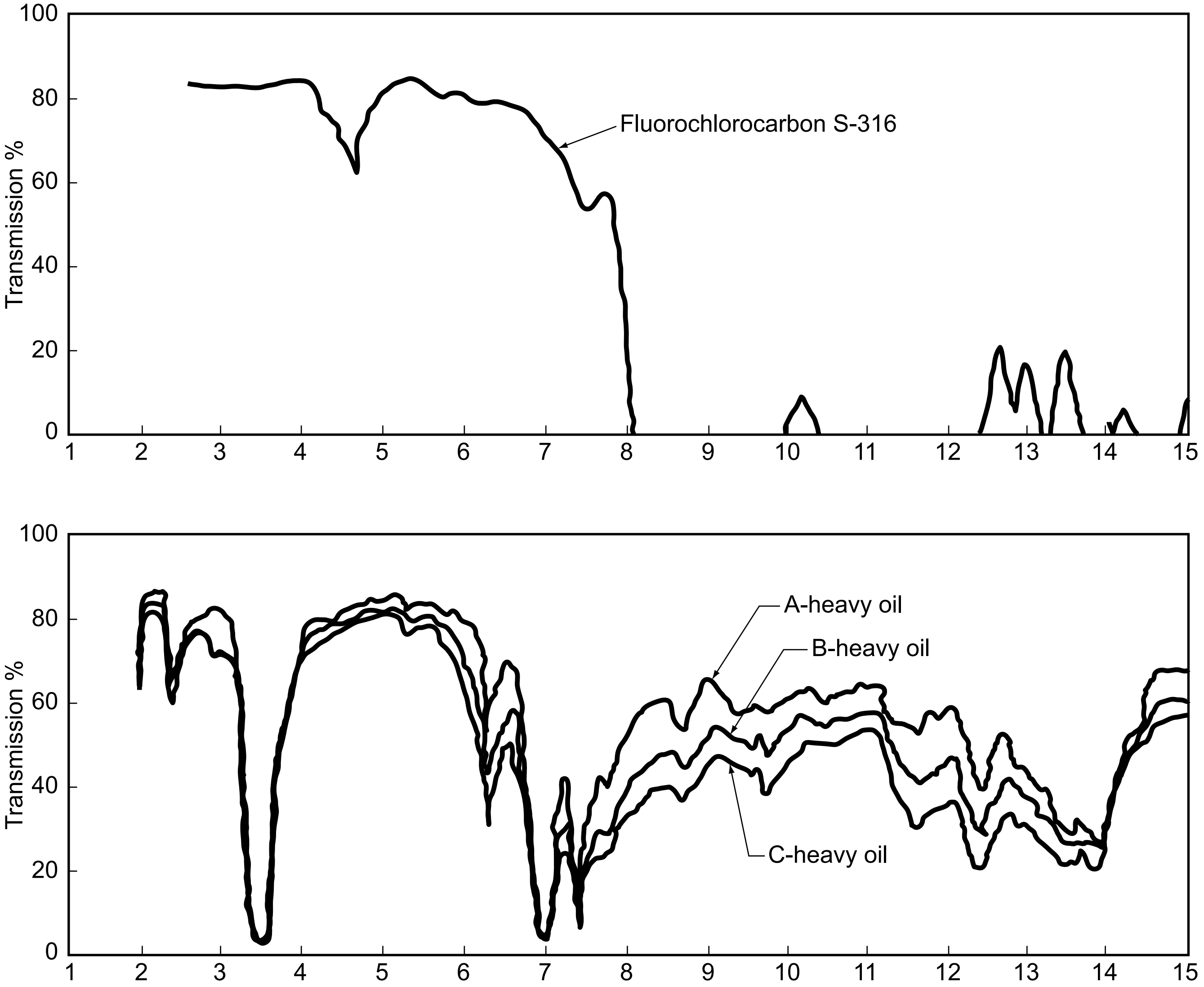


Figure 10-10—Absorption Spectrum for Hydrocarbons (Oils)

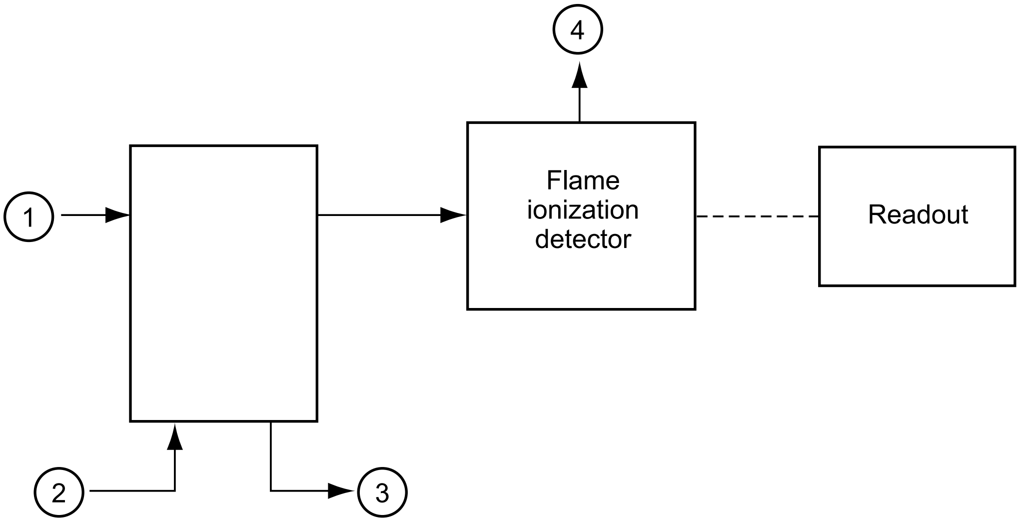
10.5.3 Flame Ionization Detectors

In this method, the hydrocarbons and the volatile organics are first stripped from the process sample by a stripping gas such as nitrogen. The stripping gas, containing the volatile compounds, is then analyzed utilizing the flame ionization detection (FID) principle. Figure 10-11 depicts this method of hydrocarbons-in-water monitoring. This technique is useful for detection of volatile hydrocarbon spills.

This method of monitoring is especially suitable for detection of compounds with a low solubility in water. The output is continuous and suitable for real-time monitoring, and no sample preparation is required (handling of chemicals is not necessary); however, it is not a suitable detection method for heavy or non-volatile oils and greases.

10.5.4 Turbidity Detectors

Hydrocarbons that are undissolved or emulsified in wastewater streams may be detected by turbidity instruments but dissolved hydrocarbons usually cannot.



Key

1 sample
2 stripping gas (nitrogen)
3 drain
4 vent

Figure 10-11—Flame Ionization Hydrocarbons-in-water Monitor

The advantage of the turbidity method is that very low levels of emulsified oil, less than 0.005 milligrams per liter, can be detected.

The disadvantages of the turbidity method are:

a) determination of measurable oil quantities may be masked by other particles that scatter light;

b) dissolved oils are not detected;

c) pumping of sample streams tends to further dissolve oils in water reducing detection sensitivity;

d) homogeneous samples are difficult to obtain.

10.5.5 Typical Hydrocarbon-in-water Application Specifications

Sample system complexity:	simple
Typical analysis spans:	0 ppm to 10 ppm
Typical analyzer outputs:	alarms, local meter, 4 mA to 20mA
Manufacturer's listed accuracy:	± 1 % full scale
Typical analysis precision:	± 1 % full scale
Typical analysis time:	continuous
Typical on-stream time:	95 % + stream factor

Relative installed cost:	\$15 K to \$30 K
Relative maintenance frequency:	< 1 man-hour/day
Average startup:	< 2 man-days
Typical refinery applications:	wastewater, condensate

10.6 pH Measurements for Wastewater Analysis

10.6.1 General

The use of pH measurement for refinery wastewater stream analysis is well established and is described in detail in Chapter 30.

The actual pH of a solution usually changes with the solution temperature. Temperature compensated pH systems change the gain or slope of the pH instrument thus producing the actual pH at the temperature of measurement. In-line and laboratory pH values may be different.

Since the pH electrode measures only the layer of solution in direct contact with the electrode surface this layer must be representative of the solution. Obtaining a representative sample of a wastewater stream can be a problem since flow rate is usually not controlled. Oils may coat the electrodes and render them inoperative or solids in the stream may destroy the electrodes.

Although pH electrodes are usually installed in a sump, pit, or trough, they should be designed for easy removal, cleaning and replacement. Electrode assemblies are available with built in ultrasonic or mechanical cleaners, which reduce but do not eliminate the need for manual cleaning.

Other specific-ion type electrodes may be used for aqueous effluent monitoring.

10.7 Dissolved Oxygen In Wastewater Analysis

10.7.1 General

The quantity of dissolved oxygen in a wastewater stream, usually measured in parts-per-million, is a measure of the stream's ability to support aquatic life. Almost all organic wastes consume oxygen from the surrounding fluid. The remaining dissolved oxygen in a wastewater stream is an indication of the quality of the effluent.

The solubility of oxygen in water decreases with increases in temperature and reductions in pressure; therefore, dissolved oxygen analyzers should be temperature and pressure compensated.

10.7.2 Typical Dissolved Oxygen Application Specifications

Sample system complexity:	simple
Typical analysis spans:	0 ppb through 20 ppb up to 0 ppm through 20 ppm
Typical analyzer outputs:	0 VDC to 1VDC, local meter, 4 mA to 20 mA
Manufacturer's listed accuracy:	± 0.01 % full scale
Typical analysis precision:	± 6 % full scale
Typical analysis time:	continuous

Typical on-stream time:	85 % to 95 %
Relative installed cost:	$15 K to $30 K
Relative maintenance frequency:	< 1 man-hour/day
Average startup:	< 2 man-days
Typical refinery applications:	wastewater, biotreaters, process streams

10.8 Water Treatment Analyzers

10.8.1 Conductivity Measurement

The electrical conductivity of a wastewater stream, usually measured in microsiemens per centimeter (μS/cm), is a measure of the dissolved ionized salts in the stream. Conductivity is a nonspecific measurement that includes most ions present in the stream compared to pH measurements that are specific to hydrogen ion activity. The conductivity of distilled water may be as low as 1 μS/cm**,** and that of sea water as high as 50 μS/cm. An increase in wastewater conductivity indicates an increase in ionized substances in the stream, which could be caused by strong acids or bases and indicates that specific analysis is required. Conductivity of water changes with solution temperature, therefore temperature compensation should be utilized for this measurement. Usually this will correct the reading to a reference temperature.

Electrolytic conductivity is covered in detail in Chapter 32.

10.8.2 Specific-ion Measurement

A specific-ion electrode will measure the chemical activity of free ions in a wastewater stream but not necessarily its concentration. Typical ions of interest in wastewater streams are calcium, chloride, cyanide, fluoride, hydrogen (pH), lead, nitrate, and sulfide. Effluent streams issuing from storage areas containing known hazardous or polluting materials should be monitored with ion electrodes specific to the stored material.

Comparison to laboratory methods often differ in that reagent additions free completed ions and mask interfering species, thus the methods determine different measurements of ions.

Advantages of the specific ion measurement are:

a) it is a simple and direct method of measurement;

b) measurement is continuous and this can be applied to closed loop controls;

c) response is fast;

d) the measurement is non-destructive of the sample.

Disadvantages of the specific ion measurement are:

a) chemical activity of an ion is measured, but not necessarily its concentration;

b) subject to interference by other ions present in the stream;

c) accuracy may be in the range of 4 % to 8 %.

10.8.3 Typical Specific Ion Application Specifications

Sample system complexity:	simple
Typical analysis ranges:	ppb to ppm
Typical analyzer outputs:	0v to 5v, local meter, 4 mA to 20mA
Manufacturer's listed accuracy:	± 1 % to 2 % full scale
Typical analysis precision:	± 0.02 % full scale
Typical analysis time:	continuous
Typical on-stream time:	low (85 % to 95 %)
Relative installed price:	high ($50 K to $75 K)
Relative maintenance frequency:	average (1 man-hour/day)
Average startup:	2 to 3 man-days
Typical applications:	wastewater, process streams

10.8.4 Titration and Wet Chemistry Analyzers

In wet chemistry analyzers a known volume of sample is reacted with a metered flow of one or more reagents. There are two general types of detectors: those in which the concentration of a component is determined by means of a titration end point and the types that measure the desired parameter in terms of color change of the sample solution.

The residual chlorine analyzers mentioned in 10.4 are special types of wet chemistry analyzers.

10.8.5 Titrimeters

Titration analyzers are available for determining the following parameters: alkalinity, hardness, and the phosphate, calcium, or sulfide content.

End points may be determined colorimetrically or potentiometrically.

In colorimetric titrations (see Figure 10-9), a continuous flow of sample is heated (to maintain a constant temperature) and fed to the analyzer together with a small amount of indicator solution.

A titrating solution is added at a rate proportional to the concentration of the component being measured. The mixture enters the stirred colorimeter cell. The rate of flow of the titrating solution is controlled by a signal from the colorimeter. As the colorimeter senses a deviation from the color end point, a signal is applied to reposition the valve to restore the color balance of the solution in the sample cell.

The advantages of the colorimetric titrimeter are:

a) high sensitivity;

b) no electrodes or probes contact the sample.

The disadvantages of the colorimetric titrimeter are:

a) the optics require frequent cleaning;

b) metering pumps require frequent maintenance;

c) requires handling of chemicals such as titrants and reagents.

A potentiometric titrimeter is also available. In this analyzer, discrete samples of water are reacted with one or more reagents in a stirred titration cell. Sample and reagent burettes and the sample cell are housed in a temperature-controlled oven. The end point of the titration curve is determined by monitoring the first derivative of the potentiometric titration curve, that is, the change in the electrode signal per increment of reagent addition. The analyzer measures the volume of reagent required for the specified end point on a measured volume of sample, automatically subtracts a titration blank, calculates the answer in specified engineering units, and displays the results on a readout device.

This is one of the few water pollution analyzers available in an explosion-proof configuration.

The advantages of the potentiometric titrimeter are:

a) high accuracy;

b) most single or double end points may be determined.

A disadvantage is that the instrument is complex mechanically and electronically.

10.8.6 Typical On-line Titration (Silica) Application Specifications

Sample system complexity:	complex
Typical analysis ranges:	0 through 0.5 to 0 through 5 mg/l
Typical analyzer outputs:	alarms, local meter, 4 mA to 20 mA
Manufacturer's listed accuracy:	± 3 % full scale
Typical analysis precision:	± 1 % full scale
Typical analysis time:	3 minutes
Typical on-stream time:	average (90 % to 95 %)
Relative installed price:	average ($15 K to $30 K)
Relative maintenance frequency:	high (1.5 man-hour/day)
Average startup:	3 man-days
Typical applications:	boiler water, wastewater, process streams

10.8.7 Wet Chemistry Analyzers

All other wet chemical methods use straightforward chemical reactions monitored by colorimeters. Instruments are available for monitoring the following compounds: ammonia, chloride, copper, cyanide, hexavalent chromium, molybdenum, hydrazine, iron, nitrate and nitrite, phosphate and silica. Hardness may also be monitored.

In practice a continuous flow of sample is mixed with one or more reagents in a reaction zone before it enters the sample cell. The sample cell and the reference cell, containing a continuous flow of unrelated sample, are monitored simultaneously by a dual beam colorimeter similar to that shown in Figure 10-9. Response times may vary from 5 to 15 minutes, depending on the component being measured.

The advantages of these wet chemistry analyzers are:

a) they can be applied to most pollutants for which colorimetric reactions are known;

b) most are mechanically simple;

c) most are relatively inexpensive.

The disadvantages of those wet chemistry analyzers are:

a) the optics require frequent cleaning;

b) requires handling of chemicals;

c) metering pumps require frequent maintenance.

Annex B—References

Chapter 8—Area Safety Monitors

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Liptak, Bela G., *The Instrument Engineers' Handbook,* Volume 1, "Process Measurement," Chilton Book Co., Radnor, Pennsylvania, 1985.

Chapter 9—Continuous Emission Monitors

40 *CFR* Part 60, Appendix A, "Test Methods."

40 *CFR* Part 60, Appendix B, "Performance Specifications."

40 *CFR* Part 60, Appendix F, "Quality Assurance Procedures."

40 *CFR* Part 51, "Existing Sources."

40 *CFR* Part 60, Subpart Db, "Standards of Performance for Industrial-Commercial-Institutional Steam Generating Units."

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Section C—Spectroscopic Chemical Composition Analyzers

C.1 Scope

This section covers the description, application, and installation of spectroscopic analyzers utilized for refinery gas, flue gas, and liquid process streams. Enhancements to spectroscopic analyzer designs have enabled vendors of applications of these analyzers to shift analyses from the laboratory to the process.

Spectroscopic analysis entails the measurement of the radiant energy absorbed or emitted by a substance in any of the common regions of the electromagnetic spectrum, in response to excitation by an external source. The types of absorption and emission spectroscopy are usually identified by the wavelength involved, namely gamma ray, X-ray, ultraviolet, visible, infrared, microwave, and radio frequency.

It is the intent of this document to draw upon proven spectroscopic technologies and, for each, describe the method of analysis, common refinery applications, the equipment for interfacing to the process, the computational capabilities, and the specific installation and maintenance considerations.

Chapter 11 describes the application of Infrared Spectroscopy to process monitoring, Chapter 12 describes the application of Ultraviolet Spectroscopy, Chapter 13 Mass Spectroscopy, Chapter 14 X-ray Absorption Spectroscopy, Chapter 15 describes Ion Mobility Spectroscopy, and Chapter 16 describes Nuclear Magnetic Resonance.

11 Infrared Spectroscopy

11.1 General

Spectroscopic and radiation analyzers have numerous applications in process control and in pollution monitoring in refineries and petrochemical plants. When absorbance of energy is in the visible range, the term *colorimetry* is used (see Chapter 29).

Radiant energy passing through samples of liquids or gases is absorbed by the sample molecules. The amount of energy absorbed over a band of wavelengths is a function of both the structure of the molecules (absorption coefficient) path length and their concentration. The band of wavelengths is known as a *sample spectrum* and can be determined for practically any gas or liquid. Materials absorb radiant energy and have their own characteristic spectra. A detailed understanding of the basis for molecular spectra is not necessary for the selection and application of continuous process analyzers of this type.

Many spectroscopic analyzers are referred to as *optical-type analyzers* because they utilize optics to direct and isolate selected bands of radiant energy. Typical optical elements used in process-type analyzers include lenses, mirrors, slits and optical filters.

Figure 11-1 shows the electromagnetic radiation spectrum with its frequency ranges and corresponding wavelengths. The common unit of measurement of wavelengths in the ultraviolet and visible regions is the nanometer and in the infrared region the unit is the micron (micrometers). The unit Angstrom (A) is also used. Optical methods utilized in spectroscopic analyzers include both invisible and visible radiation from 200 nanometers in the ultraviolet to 15 microns (micrometers) in the infrared.

Figure 11-2 illustrates a typical spectrum for carbon monoxide. This spectrum indicates significant absorption (reduced transmittance) in the infrared range of about 4.5 microns to 4.8 microns. Similar spectra for gases, vapors, and liquid have been determined and are catalogued for use in spectroscopic work.

The process infrared analyzer does not generally scan the entire frequency band. Analyzers are designed with optical filters or selective detectors that span the wavelengths of the component of interest.

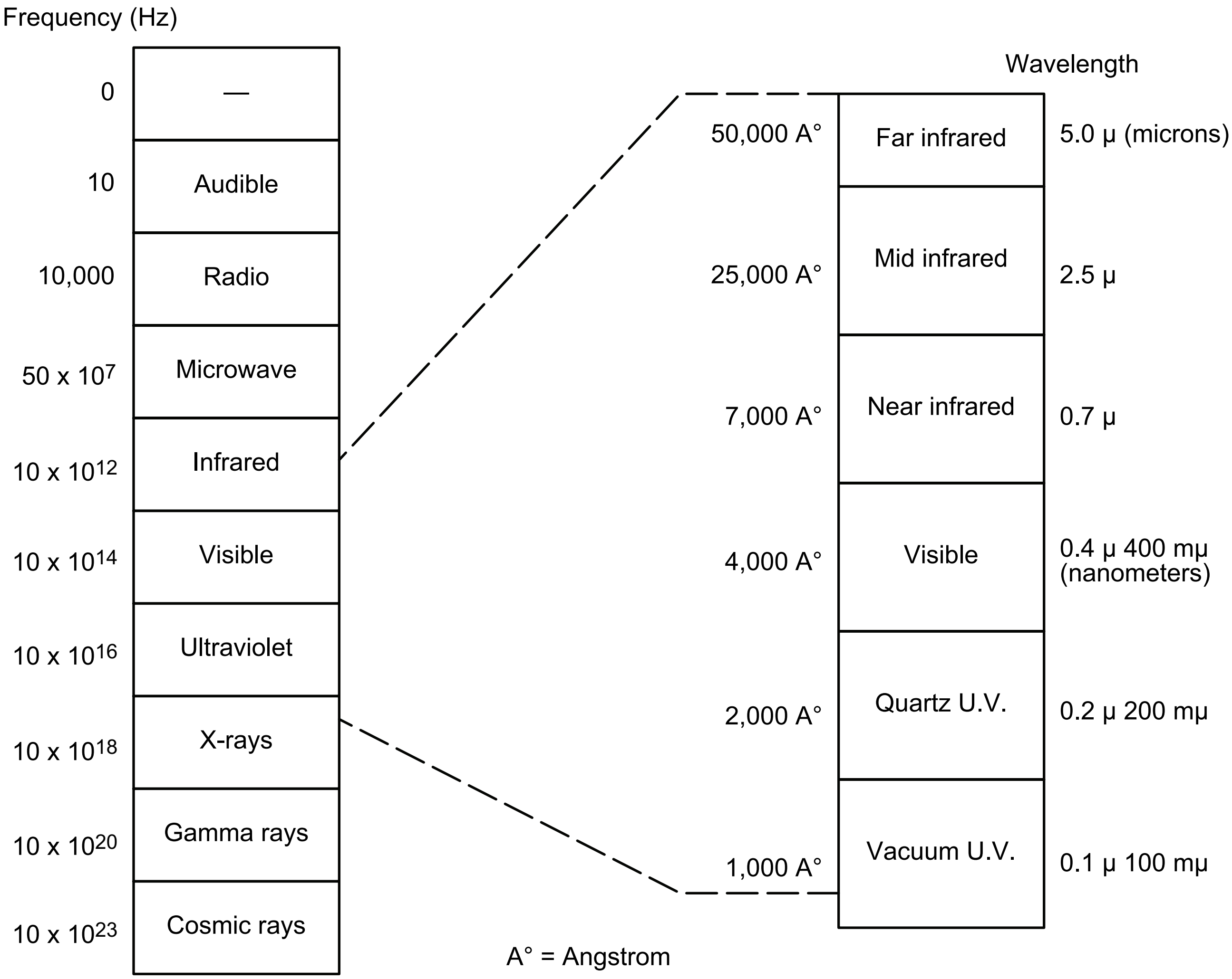


Figure 11-1—Electromagnetic Radiation Spectrum

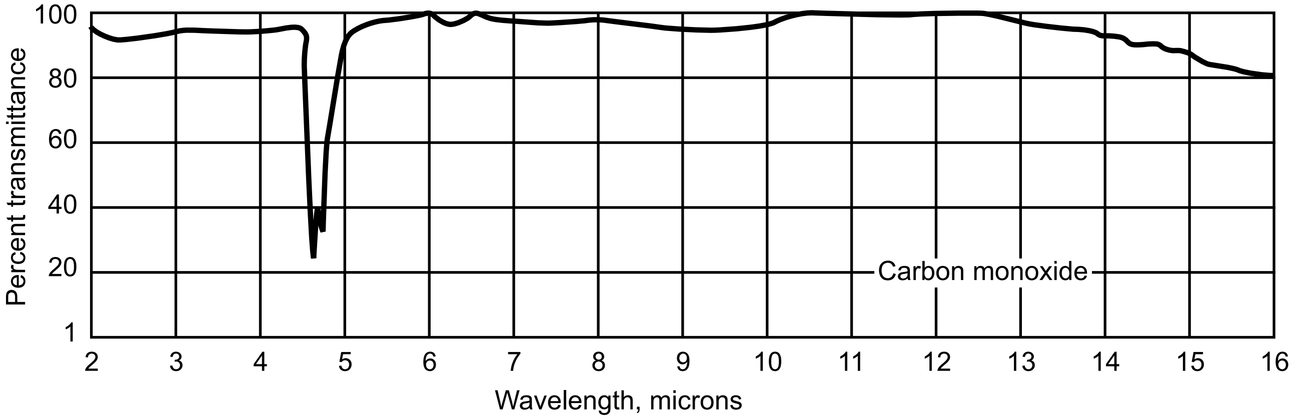


Figure 11-2—Carbon Monoxide Spectrum

A spectroscopic process analyzer determines the concentrations in a sample by measuring the amount of radiant energy transmitted through a given optical path of fixed length. The relationships between these parameters is expressed by Beer's law of absorbance which states:

(a) $A = -\log T$

where

A is the absorbance (at given spectral frequency);

T is the percent of energy transmitted.

(b) and $A = abc$

where

a is the absorption coefficient for the sample;

b is the length of the sample cell;

c is the concentration of the sample.

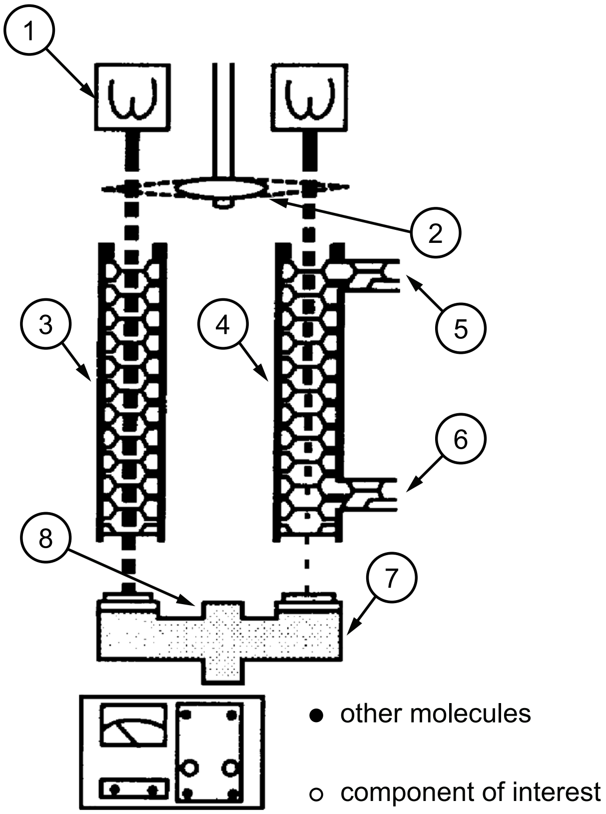
11.2 Infrared Detectors

11.2.1 The Infrared region of the electromagnetic spectrum extends from about 0.70 microns to about 15 microns. An Infrared analyzer consists of four main components: (a) the light source, (b) the optical section including light filtering, (c) the chopper and sample cell, and (d) the detector for conversion of the transmitted light to an electrical signal. Electronic amplification is included to provide an output signal for chart recording, digital display, or a computer printout. There are two types of Infrared analyzers: dual-beam nondispersive and single-beam dual wavelength.

11.2.2 *Dual-beam, nondispersive infrared analyzers* (NDIR) are used on applications wherein the desired wavelengths from the source are isolated by selective detectors and appropriate filters.

These analyzers typically operate in the spectrum range of 2 microns to 15 microns and are built to provide varying degrees of sensitivity and selectivity for a broad range of applications involving gas or liquid samples. Figure 11-3 shows the schematic representation of a dual-beam analyzer. Two beams of Infrared radiation are projected through a rotating chopper that alternately blocks radiation to a reference cell containing a non-absorbing gas and a sample cell with a flowing sample. These beams are then directed to the detector cell. When the percentage of transmission of the two beams are equal, an equal amount of radiation enters the detector cell from each beam. This results in a zero output from the detector. If the gas sample absorbs a portion of the Infrared radiation, the amount reaching the sample side of the detector cell is reduced. The detector cell, which is filled with the component of interest, absorbs radiation of the wavelength specific to that component of interest, absorbs radiation of the wavelength specific to that component. When the beams become unequal, the energy entering the detector will vary as the beams are alternated by the chopper, and the gas in the detector will expand or contract in response. The expansion or contraction of the detector gas will cause the membrane between the sample and reference sides of the detector to move. The membrane movement produces an electrical output proportional to the concentration of the component of interest. This movement is amplified and converted into a signal suitable for display or control.

The use of filters can eliminate interference caused by sample components with a partially overlapping absorption wavelength of the component of interest.



Key

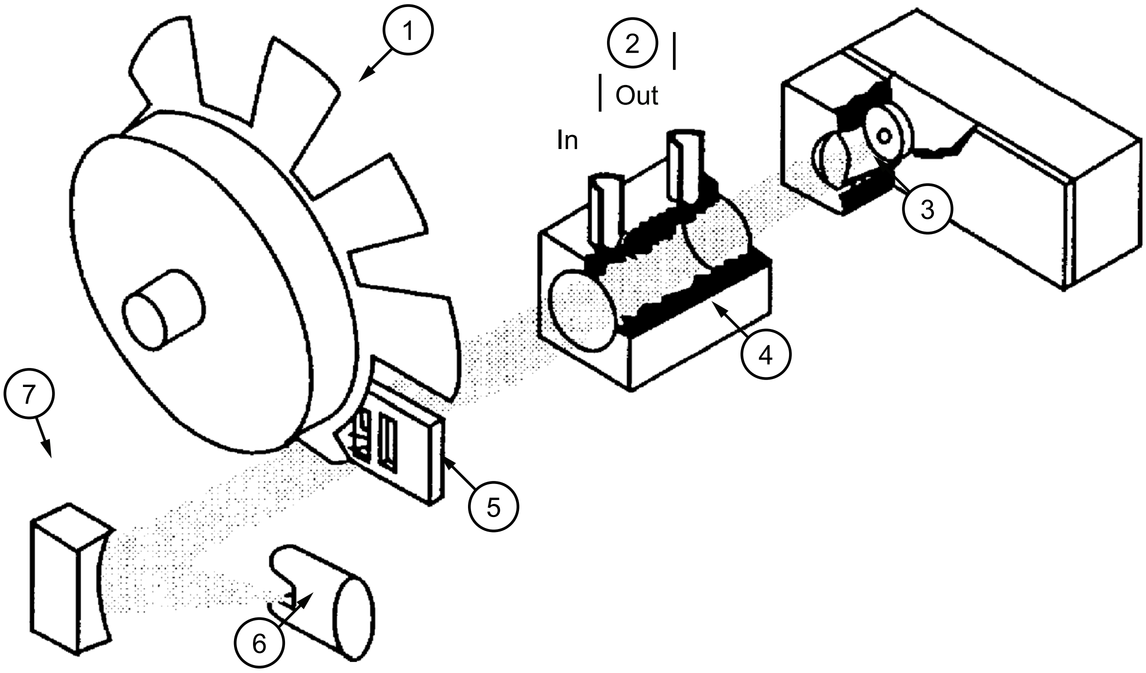
1 infared source
2 chopper
3 reference cell
4 sample cell
5 sample in
6 sample out
7 detector cell
8 diaphragm distended

Figure 11-3—Dual-beam Nondispersive Infrared Analyzer

11.2.3 Figure 11-4 is a schematic representation of a *single-beam, dual wavelength, nondispersive infrared unit.* The analyzer's optical path involves a source lamp, sample cell, and detector. Depending on the manufacturer, there is a synchronous motor rotating a filter wheel with two small filter windows 180 degrees apart, or a chopper wheel with a filter flag that is located between the Infrared source lamp and the sample cell. In either system, the filters alternate in and out of the optical path. One filter window permits the energy of the wavelength specific to the desired measurement to pass through. The other window allows the energy of a reference wavelength to pass through to detect interference and other transmittance changes not relevant to the component of interest. The analyzer's detector and electronic circuitry sense the two different pulses and provide a ratio calculation with linearization to give a linear output specific to the concentration of the component of interest present in the sample flowing through the sample cell. The single-beam, dual wavelength analyzer technique is used in the analysis of liquid samples more often than other infrared techniques.

11.3 Infrared Applications

Infrared analyzers are typically used for single component analysis. Considerable investigation has provided a large library of application knowledge regarding the absorption spectra of gases and liquids. Moreover, the compensations are available for various interferences with similar absorbency to the component of interest. Sample cells for these



Key

1	chopper	5	filter flag
2	sample	6	source
3	detector	7	focusing mirror
4	sample cell		

NOTE The filter in this case limits the infrared energy to a single, very narrow and specific band, often making it possible to make measurement in the presence of related species.

Figure 11-4—Schematic of a Single-beam Filter-based Instrument

analyzers usually vary in length from a few millimeters to over one meter, depending on the gas or liquid, the measuring range required, and the sample concentration. Selection of cell lengths, filters, and detectors are determined by the manufacturer for a given application.

11.4 Typical Infrared Application Specifications

Sample system complexity:	simple to complex (depends on application)
Typical analysis spans:	0 ppm to 50 ppm up to 0 % to 100 %
Typical analyzer outputs:	0 mV to 100 mV, local meter, 4 mA to 20 mA
Manufacturer’s listed accuracy:	±1 % of full scale
Typical analysis precision:	±1 % of full scale
Typical analysis time:	continuous
Typical on-stream time:	95 %+

Relative installed cost: $15 K to $50 K
Relative maintenance frequency: < 1 to 1 man-hour/day
Average startup: < 2 man-days
Typical applications: single components in liquid streams

11.5 Sampling Systems

Particular consideration must be given to sample point location to avoid excessive lag time. Fast sample loops may be used to minimize lag time with the excess sample being reused to minimize lag time with the excess sample being returned back to the process. Particulate contaminants in the sample should be removed by filtration upstream of the analyzer. All materials in the system should be selected so that the absorption and subsequent desorption of the sample components is minimized. For gaseous or vapor sample with high dew points, the entire sample system should be heated to prevent condensation. Some applications will require sample vaporization. For in-situ analyses, such as the determination of CO in flue gas by NDIR, the location of the sample point is contingent upon the possibilities of air leakage into the system. A typical extractive sample system for spectroscopic analyzers is illustrated in Figure 13-2.

11.6 Tunable Diode Laser (TDL) Spectroscopy

11.6.1 Principle of Operation

Tunable Diode Laser (TDL) analyzers are similar to Non-Dispersive Infrared (NDIR) analyzers in that they measure the infrared absorption of the component of interest by shining an infrared beam through the process sample. The concentration of the component of interest is then calculated using a proprietary algorithm which employs the Beer-Lambert law as well as other methods. There are two significant differences between a TDL based infrared analyzer and a typical NDIR. One is how the infrared beam is created. Rather than using an IR-lamp and filtering out the non-useful wavelengths, a TDL based analyzer uses a diode laser that has been manufactured to generate a very specific wavelength of infrared light. Furthermore the infrared beam the laser generates is a very narrow bandwidth (usually < 0.00004 nm wide). This allows the analyzer to focus on the fine line spectral details of the absorption line to be measured. The information garnered from the detailed absorption line measurement can be used to compensate for different broadening issues and provide an accurate analysis. The other significant difference is the advanced signal processing techniques employed.

While the wavelength generated by the diode laser is very precise, it can be tuned to over a spectral region (typically 2 nanometers to 3 nanometers) by ramping the power (current) that flows through the diode thereby ramping the temperature (the laser's refractive properties are a function of its temperature). During each measurement scan the power output of the laser looks like Figure 11-5. If the component that is being measured is present, it will absorb some of the infrared light that is directly related to that components concentration (see Figure 11-6). This would then result in a spectral peak that can then be processed by the TDL analyzer. Among TDL analyzer suppliers, there are two general approaches for processing the absorption peak into a measurement result: Direct Absorption Spectroscopy (DAS) and Wavelength Modulation Spectroscopy (WMS).

11.6.1.1 Direct Absorption Technique

Direct Absorption is the technique that measures the size of the peak (peak area) to determine the component concentration (see Figure 11-7). This approach has the advantage of giving a true representation of the actual absorption without any distortion due to changes in background gas compositions as well as minimizing the errors from changes in background pressure where changes as small as 5 psi to 10 psi can cause noticeable measurement error. The Direct Absorption technique is limited in sensitivity due to the inherent signal noise that is found in the laser beam; thereby, limiting the signal to noise ratio needed for extremely low level measurements. This often restricts analyzers based on the Direct Absorption technique to applications where minimum sensitivities are in the parts-per-million range.

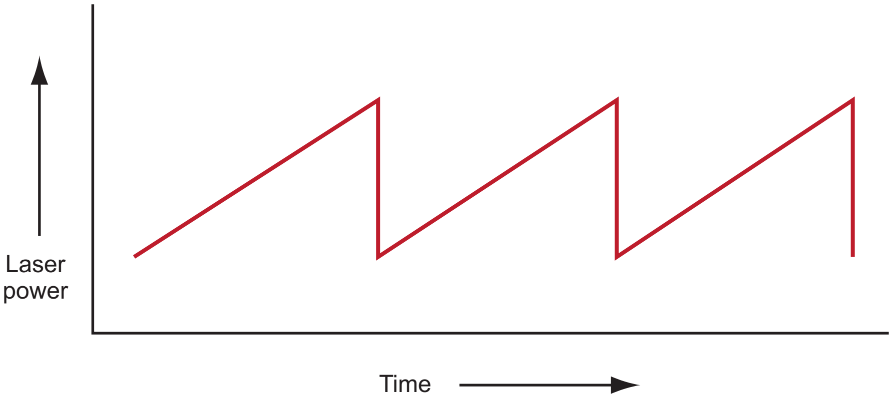


Figure 11-5—Current Input to the TDL is Ramped Several Times A Second

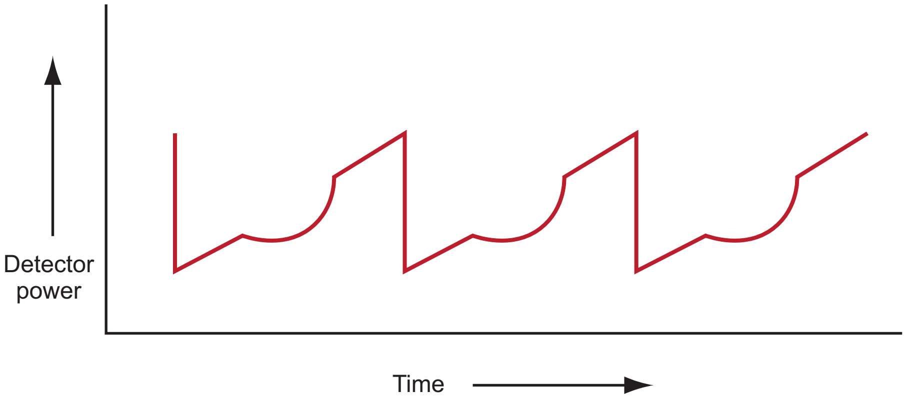


Figure 11-6—The TDL Power Adsorption Varies In Accordance With The Current Input

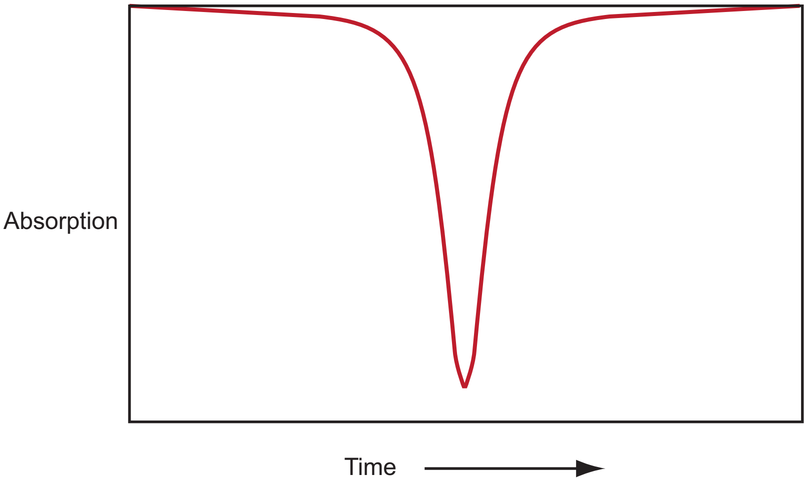


Figure 11-7—Infrared Absorption Peak of the Component Being Measured

11.6.1.2 Wave Modulation Technique

The other technique for processing the infrared signal is called Wave Modulation. It overlays a very high frequency signal onto the current ramping circuit of the laser. By processing the signal from the analyzer detector at twice the high frequency (2f), much of the background noise of the laser is eliminated (see Figure 11-8). The concentration is determined by measuring peak height rather than peak area using in the Direct Absorption technique. The net result is that a TDL analyzer based on 2f signal processing has extremely high sensitivity; often in the very low parts-per-billion range. This makes it ideal for applications where product purity measurements are needed. During the 2f signal processing, much of the original spectral details are lost introducing errors due to changing background gas compositions.

11.6.2 Tunable Diode Laser (TDL) Applications

The TDL analyzer is usually limited to the measurement of a single component due to its narrow tuning range. Diode lasers are also limited to the near infrared spectral region (roughly 600 nm to 2900 nm region).

— Moisture: Traditional moisture analyzers suffer with errors due to contamination that occurs from the sensing probe being directly in contact with the process gas. Since the TDL shines an infrared beam through the sample, errors due to contamination are eliminated. Also, due to the highly focused spectral region of the laser beam, and the capability for compensation, cross interferences that are normally seen for moisture measurement with NDIRs are mitigated or eliminated.

— Trace measurements: One advantage is the non-contacting nature of TDL analyzers. Traditional analyzers for trace measurement of Ammonia, Hydrochloric Acid, Acetylene, and Hydrogen Sulfide suffer from reliability due to the direct contact of the process sample with the cell and/or the detection element.

— Oxygen in process applications: TDL analyzers have an interference free spectral absorption which can be an advantage over paramagnetic analyzers (which can have significant interferences at low concentrations).

— Combustion control for CO, CO_2, Methane, etc.: In-situ TDL designs are available that can make these measurements within the firebox of the process heater or furnace by shining the laser beam across the combustion zone, and flue gas stack.

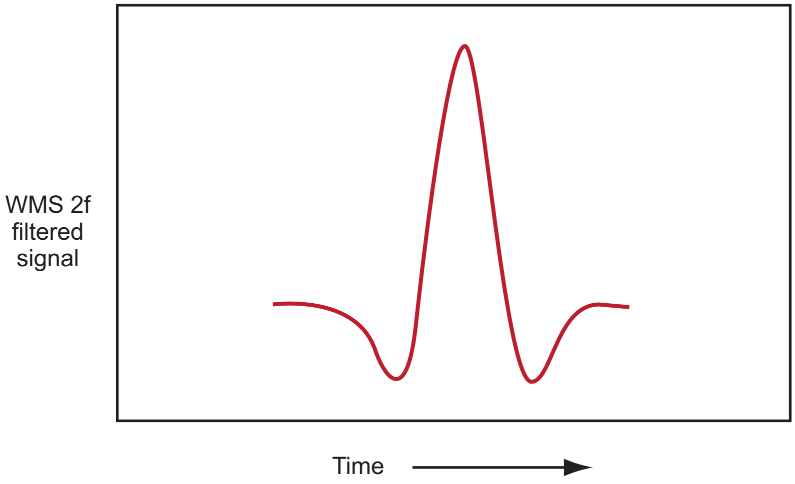


Figure 11-8—Measurement Signal Using Wave Modulation Spectra (2f), which is IR Absorption After 2f Filtering

11.6.3 Sampling Systems

Particular consideration must be given to sample point location to avoid excessive lag time. Fast sample loops may be used to minimize lag time with the excess sample being returned back to the process. Particulate contaminants in the sample should be removed by filtration upstream of the analyzer. All materials in the system should be selected so that the absorption and subsequent desorption of the sample components is minimized. For gaseous or vapor sample with high dew points, the entire sample system should be heated to prevent condensation. Some applications will require sample vaporization. For in-situ analyses, such as the determination of CO in flue gas, the location of the sample point is contingent upon the possibilities of air leakage into the system. A typical extractive sample system for spectroscopic analyzers is illustrated in Figure 13-2.

12 Ultraviolet (UV) Spectroscopy

12.1 General

Many gas and liquid components absorb radiation in the UV or visible region. These include organic components containing aromatic structures, carbonyl groups, dienes, and many inorganic salts. Concentrations of specific components or contaminants can be determined with analyzers of this type.

Figure 12-1 illustrates a typical UV absorption spectrum for the aromatic hydrocarbon, benzene. For some components, UV analyzers are capable of more sensitivity than the IR units, and trace analyzers are common.

A UV analyzer consists of a light source, a sample cell, a detector, and conditioning electronics to provide a measurement output. Various arrangements are discussed in the following sections.

12.2 Measurement Principles

12.2.1 Single-beam

Nondispersive ultraviolet analyzers (NDUV) are available in a variety of industrial designs. Figure 12-2 shows a typical analyzer arrangement. A synchronous motor rotating a filter wheel with two filter windows mounted 180 degrees apart is located in from of the sample cell. The windows are rotated in and out of the optical path. One filter window permits energy of the wavelength specific to the desired measurement to pass through. The other window passes the reference wavelength used to compensate for changes other than those causing changes in concentration of the desired component.

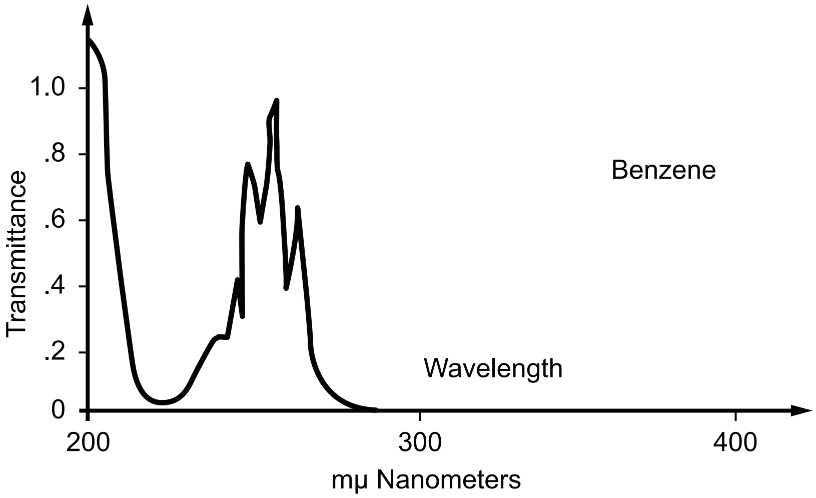
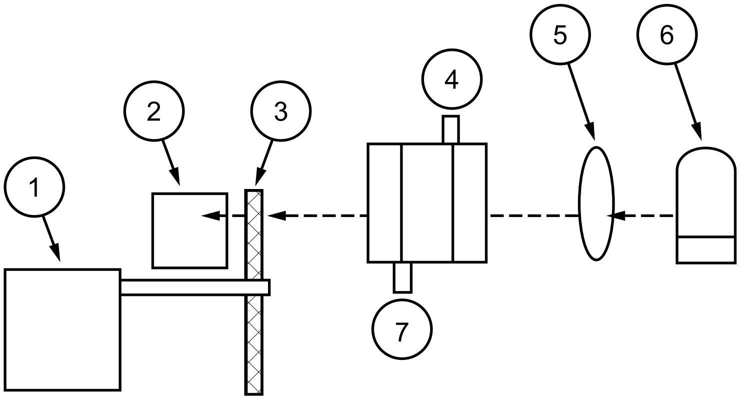


Figure 12-1—Ultraviolet Spectrum for Benzene



Key

1	chopper motor	5	lens
2	detector	6	source
3	filter wheel (chopper)	7	sample in
4	sample out		

Figure 12-2—Single-beam Ultraviolet Analyzer

12.2.2 Split-beam

Figure 12-3 illustrates the split-beam type Ultraviolet analyzer. This analyzer utilizes a single beam relative to the sample cell but has a beam splitter after the cell to create two paths of energy-one for the measuring wavelength and one for the reference wavelength.

Radiation from the selected light source passes through the sample cell to a semi-transparent mirror that splits the light into the two beams. One beam is directed to the measuring wavelength detector through an optical filter that excludes all wavelengths except the wavelength that is absorbed strongly by the sample of interest. The other beam falls on the reference detector after passing through its own filter, which transmits only the reference wavelength.

The ratio of the absorbed energies of the measured and referenced wavelengths is proportional to the concentration of the component of interest compensated for changes in other components.

12.3 Applications

Typical refinery applications for the UV analyzer include the following:

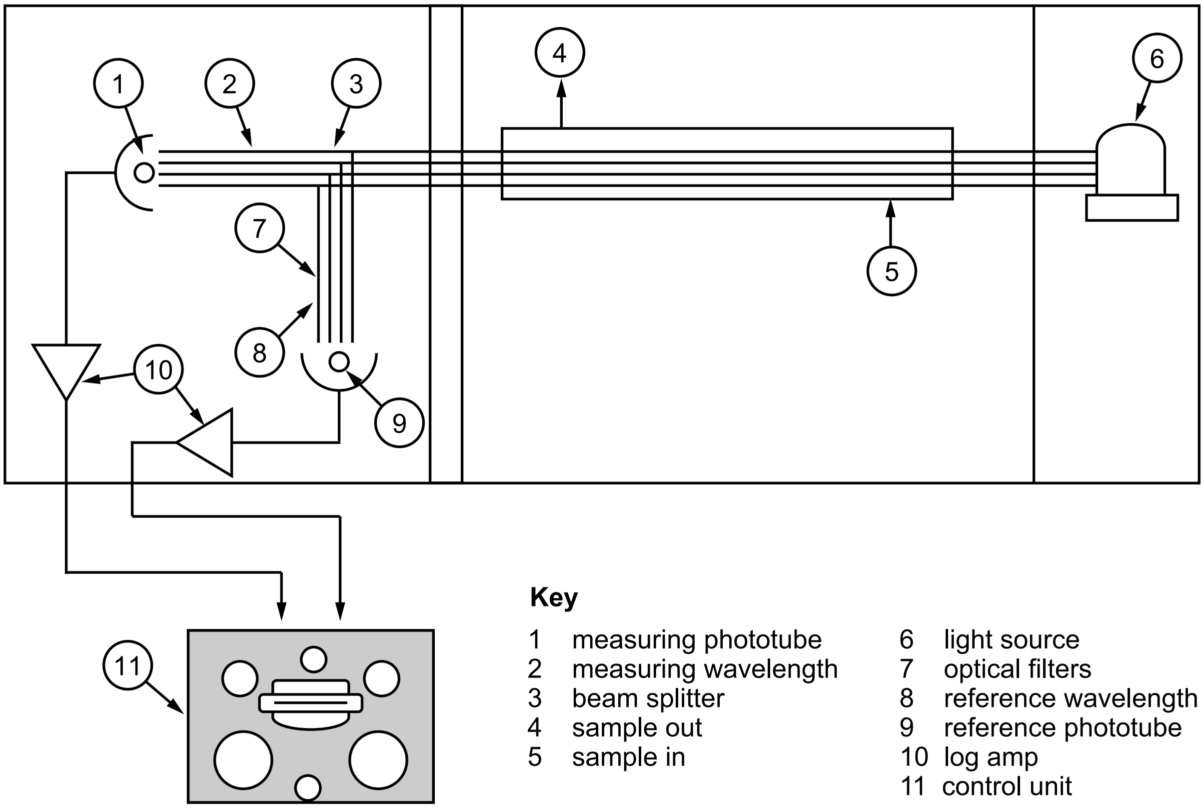
a) H_2S, SO_2, H_2S/SO_2 ratio for sulfur recovery;

b) benzene in N2 for absorption filter beds;

c) hydrocarbons in H_20 in water treatment;

d) aldehydes, acids, and salts;

e) ammonia in natural gas.



Key

1	measuring phototube	6	light source
2	measuring wavelength	7	optical filters
3	beam splitter	8	reference wavelength
4	sample out	9	reference phototube
5	sample in	10	log amp
		11	control unit

Figure 12-3—Split-beam Ultraviolet Analyzer

12.3.1 Typical Ultraviolet Application Specifications

Sample system complexity: simple to complex (depends on application)

Typical analysis spans: 0 to 0.05 Abs. units up to 0 to 4 Abs. units

Typical analyzer outputs: alarms, local meter, recorder, 4 mA to 20mA

Manufacturer’s listed accuracy: ± 2 % of full scale

Typical analysis precision: ± 1 % of full scale

Typical analysis time: continuous

Typical on-stream time: 95%+

Relative installed price: $15 K to $50 K

Relative maintenance frequency: 1 to 1.5 man-hour/day

Average startup: < 2 man-days

Typical applications: wastewater, product quality, environmental

12.4 Sampling Systems

Particular consideration must be given to sample point location to avoid excessive lag time. Fast sample loops may be used to minimize lag time with the excess sample being returned back to the process. Particulate contaminants in the sample should be removed by filtration upstream of the analyzer. All materials in the system should be selected so that the absorption and subsequent desorption of the sample components is minimized. For gaseous or vapor sample with high dew points, the entire sample system should be heated to prevent condensation. Some applications will require sample vaporization. For in-situ analyses, such as the determination of SO_2 in flue gas, the location of the sample point is contingent upon the possibilities of air leakage into the system. A typical extractive sample system for spectroscopic analyzers is illustrated in Figure 13-2.

12.5 Installation, Safety, Startup

These topics are discussed in detail in Chapter 6.

13 Mass Spectrometry

13.1 General

Mass spectrometers are used for the analysis of gases in process streams. Originally these instruments were used in laboratory applications, but now are available for use in process monitoring and control.

Functionally, a process mass spectrometer can be seen as a sophisticated electron tube mass spectrograph. It consists of a vacuum envelope, a filament for the production of an electron beam, and various focusing and current collecting devices. Mass spectrometers all operate on the same basic principle, fragmenting molecules into charged ion fragments with the subsequent application of an electrostatic or magnetic field to separate the fragments of the sample according to their mass. This separation process makes it possible to identify and quantify the elements and compounds present in the sample.

Mass spectrometers take process samples and introduce them into a high-vacuum chamber, where the molecules are subjected to an electron beam. The utility of the mass spectrometer would be very limited if it were not for the fact that during the ionization process, the sample molecules crack into fragments of different mass-to-charge ratio. Because of this fragmentation, the mass spectrometer can detect, for example, the different isomers of propanol. When isopropanol cracks, the largest fragments have a mass of 43 or 45. When n-propanol cracks, the largest fragments have a mass of 29 or 31. Thus, the two isomers can be easily distinguished. The identification of paraffins, olefins, naphthenes, aromatics, oxygenated hydrocarbons, diatomic gases, and other gaseous and easily vaporized liquid compounds can be accomplished similarly.

Compounds that have some fragments at the same mass as others can be measured quantitatively as long as there is one mass unique to each of the components present. The use of microprocessor or computer-based data systems has made the quantification of multi-component mixtures by mass spectrometry practical.

13.2 Operation

Figure 13-1 shows a block diagram of a typical complete mass spectrometer system.

The analysis of a sample begins with the introduction of a gas into the ionization region through a sample inlet system. A portion of the sample is ionized, and the electrostatic and magnetic field inside the analyzer section act upon the resulting ions.

These ions are focused into a beam by an electrostatic lens system, and this beam is directed into the analyzer section, where the ions are separated according to their masses and are successively scanned across a series of

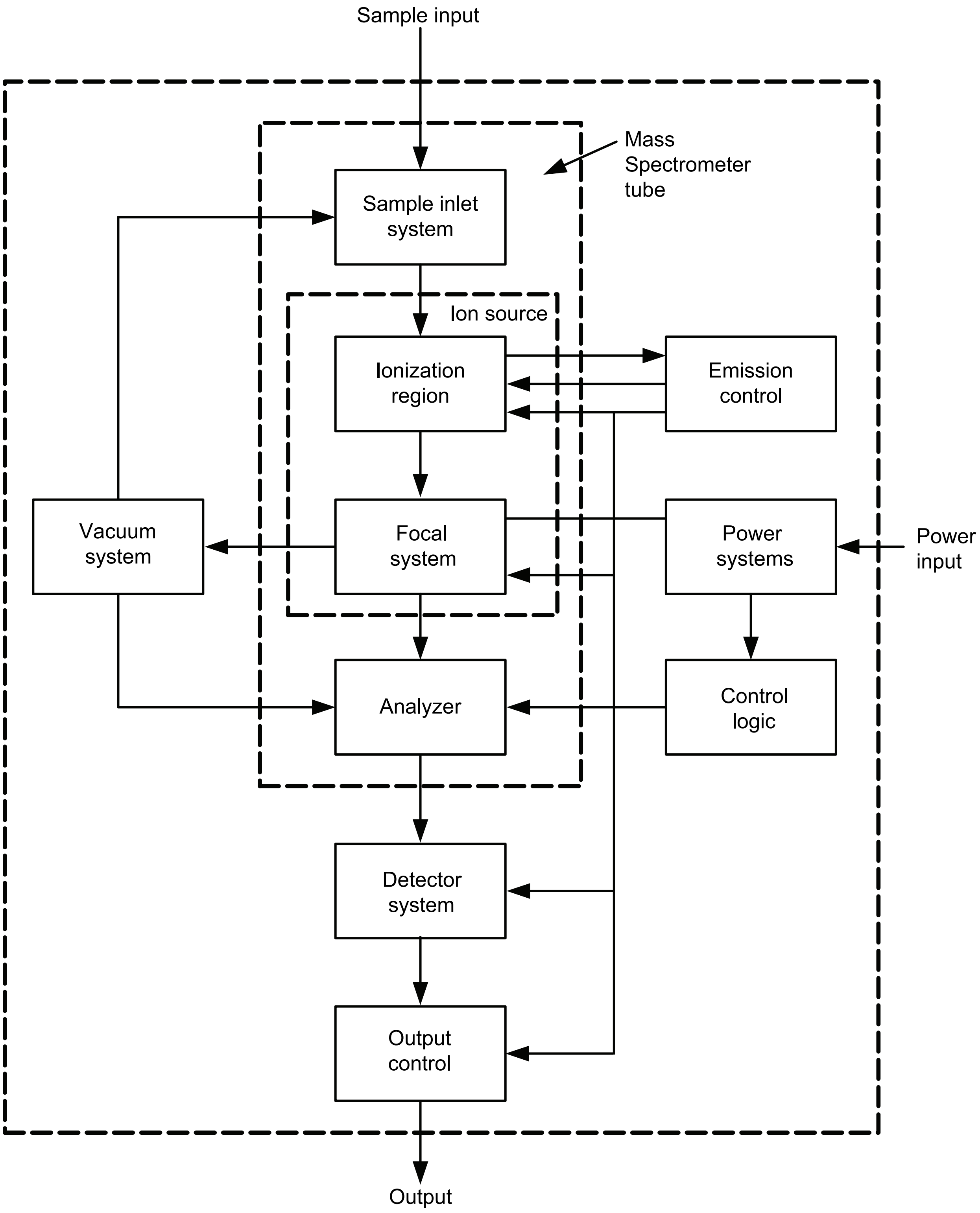


Figure 13-1—Mass Spectrometer System

collectors where the ions pick up electrons. The resulting currents are amplified with electrometers and then recorded.

On-line process mass spectrometers are used in many of the same applications as gas chromatographs. Their prime advantages over gas chromatographs are faster response and (with certain types of mass spectrometer) the ability to perform a complete scan of the components present in the process stream up to an atomic mass number (AMU) of approximately 200.

Many mass spectrometer systems have the ability to be pre-set to monitor selected components (masses) of interest. This feature is inherent to the magnetic-sector type of mass spectrometer, using multiple detectors, each one corresponding to the component (mass) of interest. While this system offers advantages in simplicity and stability, it has limited flexibility. Resolution is limited by the spacing of the collectors. This type is useful in well-defined processes where the ratios of components are more important than their absolute concentrations; however, it does not allow for the measurement of undesirable side products that may be produced during process upsets or of any diluents that may be present.

Double-focusing mass spectrometers have the capability to operate in two modes, scanning and monitoring. This offers a great deal of flexibility, which is an excellent aid to process trouble-shooting. These spectrometers can be run in the monitoring mode during normal operations, but can be run in the scan mode during process upsets. These scans can then be compared with those obtained during normal operation to assist in the determination of the cause of the upset.

13.3 Applications

Mass Spectrometers are used to monitor stack emissions, specific compounds in process streams, feed stocks and refinery products. The fast response and near continuous output of mass spectrometers allows them to be configured to monitor multiple streams, as this somewhat helps offset the relatively high cost of the installed hardware relative to comparable analyses methods such as Gas Chromatography.

13.4 Analyzer Location

At a minimum, mass spectrometers should be sheltered from extreme changes in climate such as sun, wind and rain. Mass spectrometers contain complex electronics that performs optimally in controlled climates (analyzer houses). Routine maintenance includes calibrations and precise adjustments best performed by experienced mechanics under climate controlled conditions. New, more robust systems are becoming available which should provide more reliable operation under less than ideal conditions.

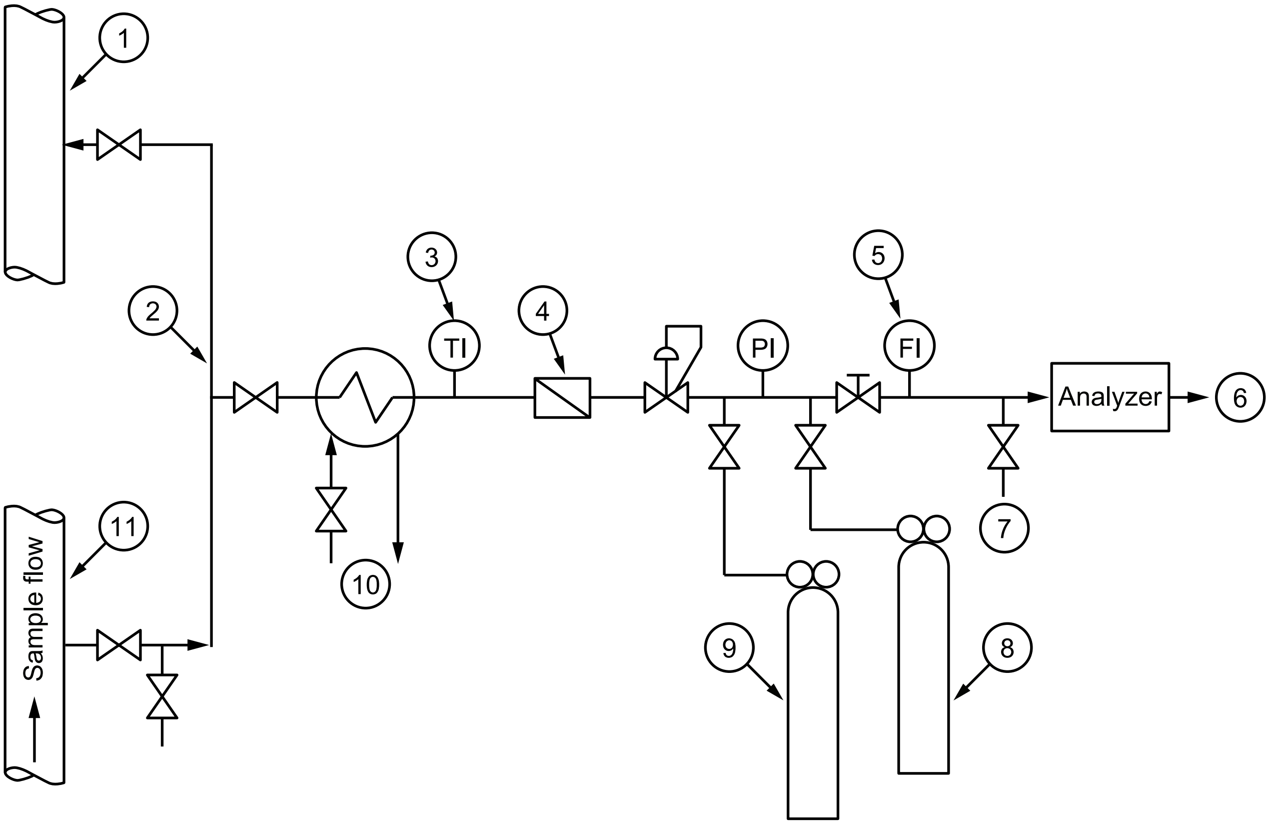
13.5 Sampling Systems

Because mass spectrometers operate at high vacuum, special consideration must be given to atmospheric leakage into the sample system. The vacuum part of the system should be designed to minimize joints, filters, valve stem packing, diaphragms, and other components that can contribute to leakage. Liquid samples must be vaporized prior to introduction into mass spectrometers. Proper filtration of the sample is critical, since microscopic particles can clog the sample inlet system.

A typical sample system for spectroscopic type analyzers is illustrated in Figure 13-2.

13.6 Safety Considerations

There are no special precautions to be taken in the operation of mass spectrometers other than the normal safety concerns in the design and operation of the sample preparation system and the handling of calibration standards. See Chapter 4 and Chapter 6 for detailed information on these issues.



Key

1	sample return	5	rotameter	8	span fluid
2	fast sample loop	6	vent to process or flare	9	zero fluid
3	sample cooler			10	cooling water in/out
4	filter	7	lab sample	11	sample point

NOTE 1 Heat trace sample lines if required.
NOTE 2 Provide sample cooler if required.
NOTE 3 Provide pressure regulator if required.

Figure 13-2—Typical System for Spectroscopic-type Analyzers

13.7 Calibration

Calibration of process mass spectrometers is performed with standard gas samples. As an alternative, an approximate method based upon ionization factors (a measure of how easily a species is ionized) may be used. For accurate analysis, it is best to calibrate on pure samples of the components of interest, or accurate reference gas mixtures. Microprocessor-based systems can use these reference gases for auto-calibration.

Since it is physically impossible to achieve a perfect vacuum, some interference will remain. This interference may be significant for accurate and/or low-level analysis. The ability to determine this interference is important, and calibration is usually required once a day. If the sample composition remains relatively constant, the background also remains constant.

13.8 Startup

Prior to calibration or startup of a mass spectrometer, all utilities, such as air, water, steam, electrical power, calibration fluids, and the like, should be checked to confirm that they conform to specifications.

All safety checks should be performed, including inspection of electrical, mechanical, piping and pneumatic systems to ensure that they conform to the engineering and analyzer manufacturer’s specifications and drawings.

Start the sample system in accordance with manufacturer’s specifications and drawings.

14 X-ray Absorption

14.1 General

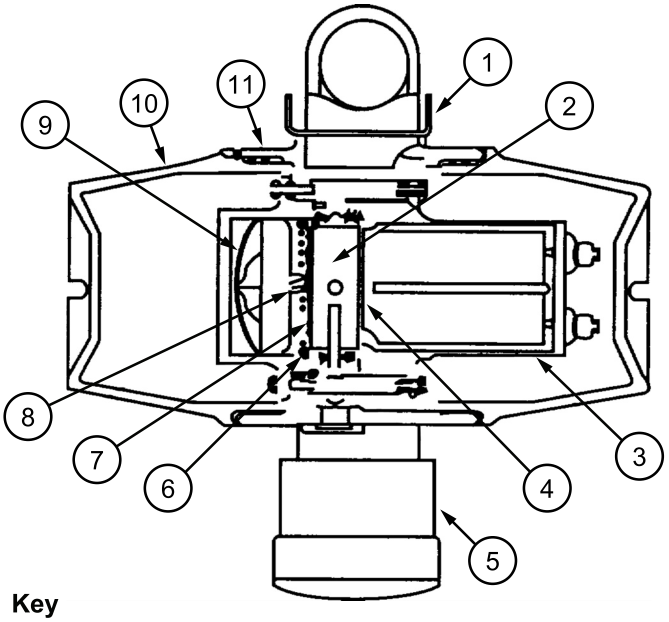
The electrons of the atoms in the sample absorb X-ray energy passing through samples of liquids and gases. As each element has it s own characteristic X-ray absorption spectrum, which is dependent upon its atomic number, this technique is used to identify and quantify specific elements in the sample. X-ray absorption is applicable to any sample that contains one element that is considerably heavier than the others present for a given composition. The measurement is affected by changes in specific gravity and, therefore, must be compensated.

Process X-ray absorption analyzers consist of four main components: (a) A nuclear source, which includes a means of producing and focusing the X-ray beam, (b) the sample cell, (c) the ionization chamber detector, and (d) the electronics required to provide an output (see Figure 14-1).

14.2 Safety Concerns

X-ray analyzers may require special safety considerations if they include the presence of radioactive materials. The analyzers contain radioactive isotopes and require licenses from regulatory agencies.

Special considerations for X-ray absorption analyzers are that seals or locks are to be removed only by qualified personnel. The area around such a device must be marked with appropriate signs.



Key

1 mounting hardware
2 sample cell
3 ionization chamber
4 teflon diaphragm
5 terminal box
6 transistor temperature sensor
7 rear plate
8 radiation source
9 target
10 cover
11 case

Figure 14-1—X-ray Source, Sample Cell and Detector

14.3 X-ray Absorption Applications

The primary uses for process X-ray absorption analyzers are to determine the concentrations of either elemental contaminants or additives in blended product and intermediate process streams.

The most common elements detected by these analyzers are sulfur, lead, and the halogens (for example, chlorine bromine and so on). Total sulfur analyzers are used to monitor crude oil streams prior to introduction into a distillation tower, to monitor blended product streams, and to determine the efficiency of desulfurization units (see Chapter 20).

X-ray absorption analyzers are subject to interference by heavy elements present in the hydrocarbon sample. For example, sulfur analyzers are sensitive to the presence of iron, nickel and vanadium, which will make the analyzer indicate a higher sulfur content than that actually present.

14.4 Analyzer Location

Most commercially available models are suitable for operation in classified areas. This design allows the analyzer to be located in a minimal sun and rain shelter. The analyzer should be located as near the sample point as possible to minimize sample lag time and the quantity of sample typically found in fast loop extractive systems.

14.5 Sampling Systems

These analyzers are usually used with liquid samples. The primary sample system considerations are lag time, sample conditions (temperature and pressure), and ambient conditions. Sample systems for streams containing large quantities of water or vapor should be provided with separators to remove those contaminants to minimize interferences with the measurement. For high-pour-point fluids, the entire sample system should be heated to minimize plugging in the sample system or the analyzer itself. A typical sampling system for a radiation-type analyzer is illustrated in Figure 14-2.

14.6 Calibration and Startup

Prior to calibration or startup, all utilities, such as air, water, steam, electrical power, calibration fluids, and the like, should be checked to confirm that they conform to specifications.

All safety checks should be performed, including inspection of electrical, mechanical, piping and pneumatic systems to ensure that they conform to the engineering and analyzer manufacturer’s specifications and drawings.

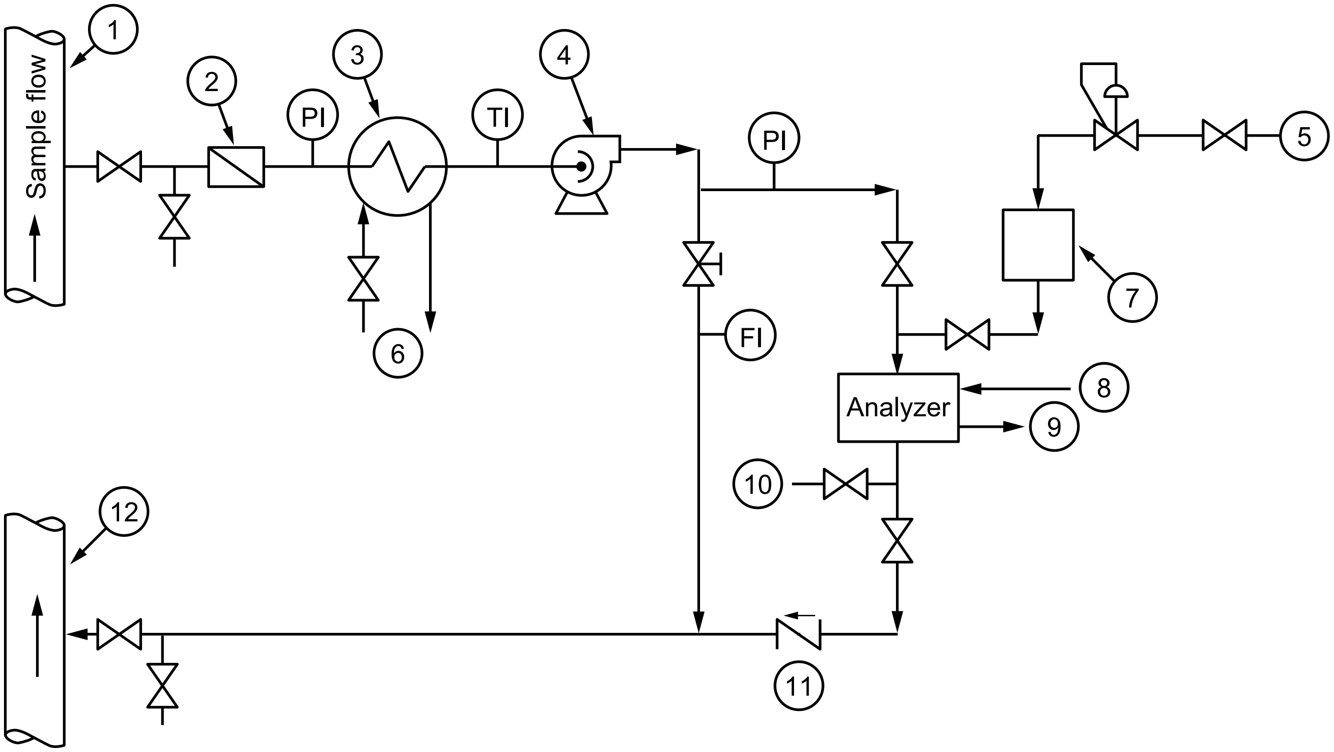
Start the sample system in accordance with manufacturer’s specifications and instructions.

A general listing of the main features of spectroscopic and other types of analyzers is given in Table 14-1.

15 Ion Mobility Spectroscopy

15.1 General

IMS is basically an atmospheric pressure time-of-flight technique. A sample is drawn into the instrument by means of a venturi across a membrane that provides a preliminary degree of selectivity, blocks out particulate matter, and limits the effects of humidity. The gas of interest permeates through the membrane and is transported by a carrier gas to the reaction region of the cell where the gas is ionized in a series of ion-molecule reactions initiated by beta particles emanating from a radioactive source. Under the influence of an electric field, the ions are gated into a drift tube where they are separated out according to the size and shape of the specific ion. The ions arrive at the collector at a unique drift time based on these factors as well as the strength of the electric field, drift tube length, temperature, and pressure.



Key

1	sample point	5	air	9	condensate out
2	filter	6	cooling water in/out	10	lab sample
3	sample cooler	7	calibration fluid tank	11	check valve
4	sample pump	8	steam in	12	sample return

NOTE 1 Provide heat tracing sample lines, if required.
NOTE 2 Provide sample pump, if required.
NOTE 3 Provide sample cooler, if required.

Figure 14-2—Typical Sample System for X-ray Absorption-type Analyzers

Specificity is obtained by: the proper selection of the sample inlet membrane; by biasing the polarity of the electric field; by using various dopant materials that alter the ionization process of the target component; and by optimizing the drift time of the selected components by varying the detector temperature and carrier flow. While multiple components can be measured, the greatest advantage of IMS is the low detection limit of single gases (in the presence of other gases that typically interfere when other techniques are utilized).

Total analysis time is less than 1 second. Positive or negative ions may be detected by biasing the tube. Numerous troubleshooting sensors and panel display lights are provided (temperature of heated zones, low carrier rate, etc.) Output is typically a 4 mA to 20 mA trend signal. Alarms are provided for high/low concentration and analyzer trouble. Accuracy and repeatability are component specific. A typical schematic of an IMS cell is shown in Figure 15-1.

15.2 Safety Concerns

Ion Mobility Spectroscopy analyzers may require special safety considerations if they include the presence of radioactive materials. The analyzers contain radioactive isotopes and require licenses from regulatory agencies.

Special considerations for IMS analyzers are that seals or locks are to be removed only by qualified personnel. The area around such a device must be marked with appropriate signs.

Table 14-1—Typical Applications and Specifications of Spectroscopic and Other Types of Analyzers

	Spectroscopic Types				Other Types	
	Near Infrared	**NDIR**	**Ultraviolet**	**UV-Visible**	**Mass Spectrometry**	**X-ray Absorption**
Typical Applications	Trace H_2O in hydrocarbons	Trace CO or CO_2 in H_2 recycle gas	H_2S in acid gases	Color per ASTM method D-1500	Component analysis in ethylene oxide plants	Sulfur in fuel oils
Range	50 ppm – 1%	10 ppm – 100%	0 % to 5 %	0 ASTM to 6 ASTM	1 AMU to 300 AMU	0 % to 5 % wt.
Sensitivity	10 ppm	10 ppm	10 ppm	Ca. 0.1 ASTM	0.01 ppm	0.01 %
Repeatability	± 1 % full scale	± 1 % full scale	± 2 % full scale	± 1 % full scale	± 1 % resolution, ± 0.001 % std. dev.	± 0.5 % full scale
Sample Pressure	0 to 50 PSIG Std.	0 to 250 PSIG Std.	0 to 50 PSIG Std.	0 to 50 PSIG Std.	Atmospheric	0 to 250 psig Std.
Sample Temperature	amb—122 °F Std.	amb—122 °F Std.	amb—122 °F Std.	amb—122 °F Std	amb—122 °F Std.	amb—212 °F Std.
Construction	NEMA—4, 7, or 12	NEMA—4, 7, or 12	NEMA—4, 7, or 12	NEMA—4, 7, or 12	NEMA—4, 7, or 12	NEMA 7
Relative Cost	Low	Low	Medium	Medium	Very high	High
Maintenance Level	Medium	Medium	Medium-high	Medium	Medium-high	Medium
Interferences	Low-moderate	Low-moderate	Low-moderate	Low-moderate	low	Low-moderate
Features	Continuous analysis, fast response	Continuous analysis, fast response	Continuous analysis, fast analysis	Continuous analysis, fast response	Rapid multi-component analysis 0.3 sec cycle speed	Continuous analysis, high stability
Special Requirements	Sample-conditioning required	Sample-conditioning required	Sample-conditioning required	Sample-conditioning required	Sample-conditioning required	Sample-conditioning required, requires special license

15.3 IMS Applications

In addition to the use of IMS for area safety monitors (see Chapter 7) IMS applications include Continuous Emission Monitoring Systems (CEMS), process stream monitoring and control, and ambient air monitoring for toxic or specific components. Typical stack components that may be monitored include NH_3, Cl_2, HF, and HCl. Detection limits vary from PPB to percent level according to the component measured.

15.4 Analyzer Location

Most commercially available models are suitable for operation in classified areas. This design allows the analyzer to be located in a minimal sun and rain shelter. The analyzer should be located as near the sample point as possible to minimize sample lag time and the quantity of sample typically found in fast loop extractive systems.

15.5 Sampling Systems

IMS analyzers are limited to gas samples (or liquid streams that can be completely vaporized at a reasonable temperature). The ability to measure extremely low concentration of reactive components allows sample systems to employ dilution probes. Dilution-type systems are ideally adapted to IMS analyzers as this eliminates most problems with samples containing significant concentrations of water (such as stack gas analyses). Reactive molecules may be adsorbed by water vapor and lost to coalescers or other means of removing water from the sample. This is especially true for PPM or PPB concentrations of target components. Alternately, heat tracing sample lines to avoid condensation or sample loss has shown some promise. An overall system for an IMS analyzer employed in a CEMS application is illustrated in Figure 15-2.

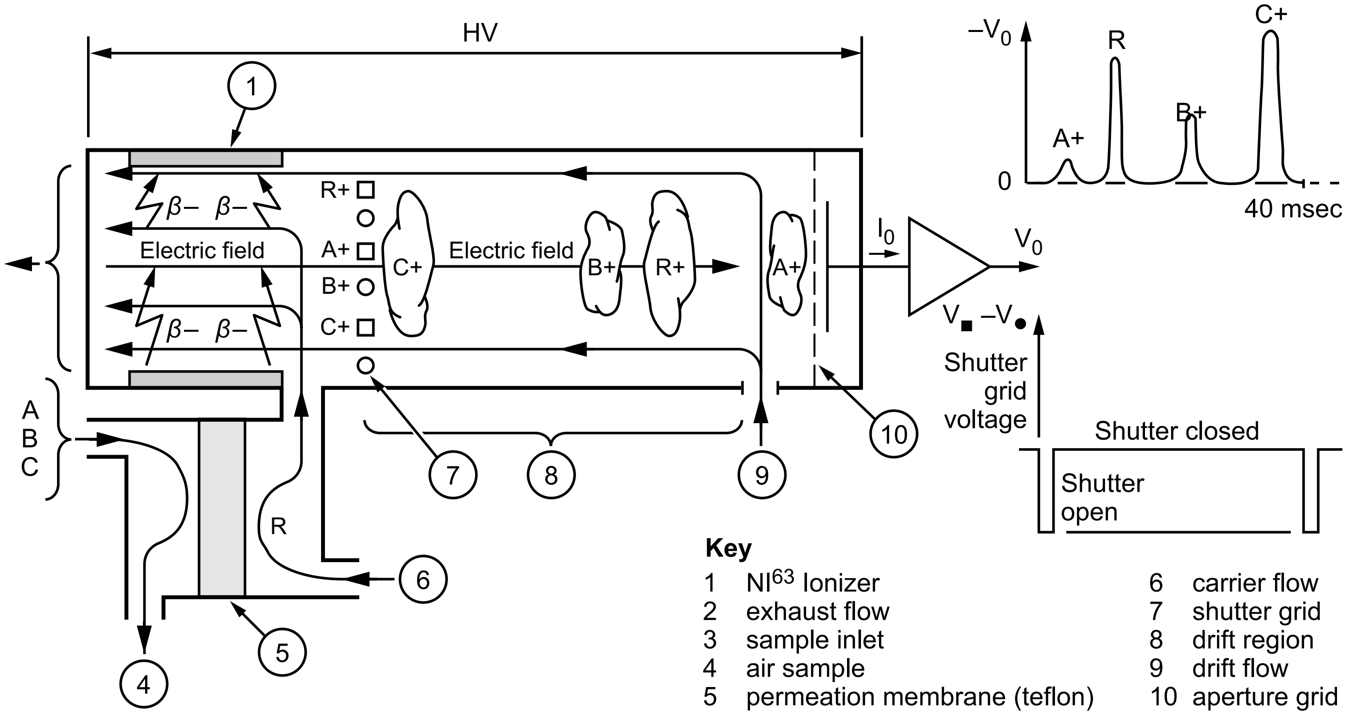


Figure 15-1—IMS Sample Cell Schematic Diagram

15.6 Calibration and Startup

IMS sample system provided by the manufacturer typically include a provision for automatically or semi-automatically introducing a calibration sample on a programmed basis.

Prior to calibration or startup, all utilities, such as air, water, steam, electrical power, calibration fluids, and the like, should be checked to confirm that they conform to specifications.

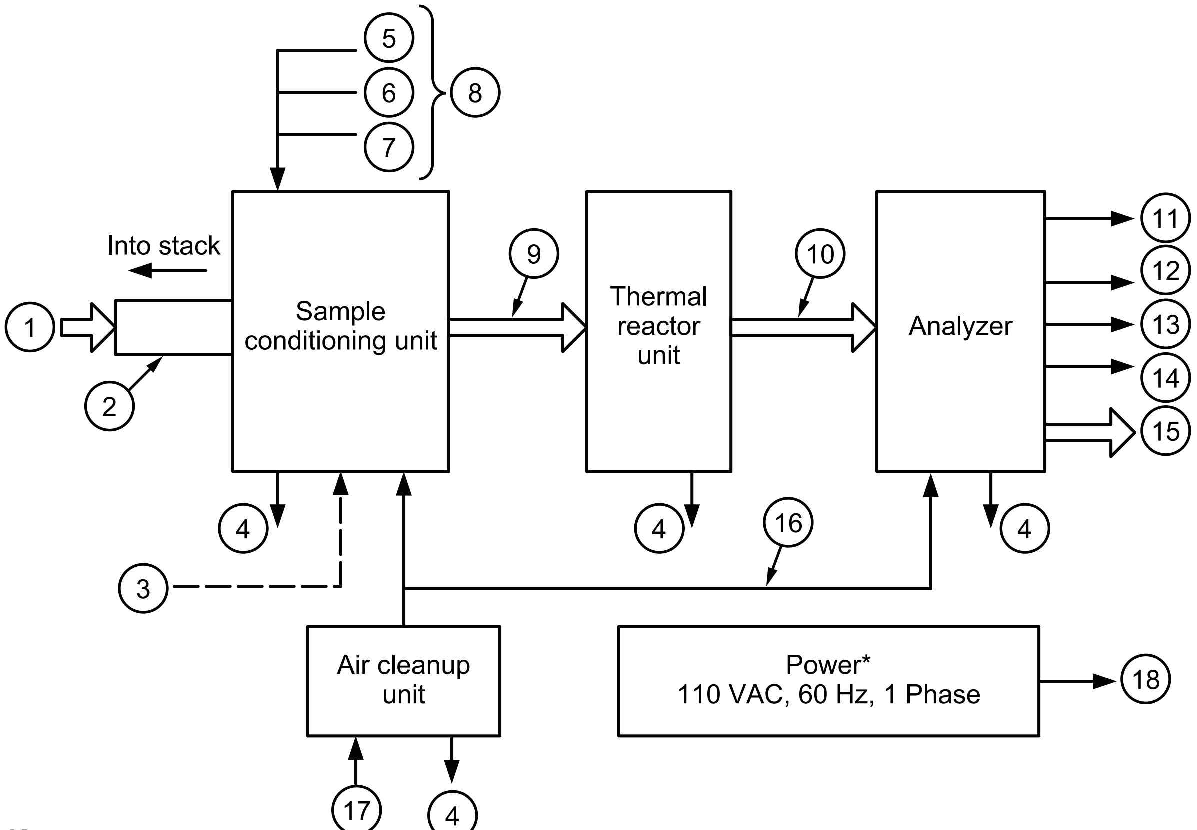
All safety checks should be performed, including inspection of electrical, mechanical, piping and pneumatic systems to ensure that they conform to the engineering and analyzer manufacturer's specifications and drawings.

Start the sample system in accordance with manufacturer's specifications and instructions.

16 Nuclear Magnetic Resonance

16.1 General

In simple terms, Nuclear Magnetic Resonance (NMR), also known as Magnetic Resonance Analysis, spectroscopy is comprised of a precisely controlled magnetic field through which a stream to be analyzed passes. The protons of the sample "line up" within the homogeneous magnetic field. Once aligned, they are pulsed with radio frequency energy to deflect them off their aligned axis. The amount of the deflection and the time to return to alignment is determined by the molecule's structure. Since all protons are spinning, the resulting re-alignment of the protons is received back as a radio frequency (rf) signal. This signal is transformed into a spectrum showing chemical species and their concentrations. Multiple pulses are averaged and the analysis is available within minutes. In addition to chemical composition information, physical properties can be correlated to the spectrum. Multiple parameters can be determined from a single spectrum. Since this is not an optical technology, NMR analysis is essentially independent of the physical state of the sample (i.e., solid, gas, liquid) and sample physical conditions (pressure and temperature).



Key

1 sample in
2 probe
3 cal gas supply*
4 vent
5 remote zero
6 remote span
7 remote control blowback
8 from remote valve control (115 VAC)
9 diluted sample
10 conditioned gas sample
11 analyzer signal 4 to 20 mA
12 low alarm
13 high alarm
14 fault alarm
15 sample out
16 dry air
17 instrument air supply*
18 to all units

* Utility requirement to be provided by user.

Figure 15-2—IMS-based CEM System Block Diagram

16.1.1 Applications

A refinery's alkylation unit may be a prime location for a NMR analyzer. Only one analyzer is necessary, and it can sample all streams in minutes. It is used to determine acid strength for acid use optimization, the emulsion character (acid-to-HC ratio), the isoparaffin-to-olefin ratio, and the acid-soluble oil content. Other unit or offsite applications for stream characterization and control may include crude distillation, coking, fluid catalytic cracking, heavy oil upgrading, lube oil, catalytic reforming, gasoline blending, diesel blending, and tank farm management.

16.1.2 Measurement Principles

The property of nuclear spin is the fundamental property for observing nuclear magnetic resonance. By analogy, a spinning nucleus is similar to an electric current flowing in a wire loop. In a wire loop, as charge flows around the loop, it generates an effective bar magnet whose poles are perpendicular to the current flow. Similarly, a nucleus spinning about its axis generates a small magnetic dipole, similar to a bar magnet. Since a dipole is present, a magnetic moment exists for that nucleus. Magnetic moments are defined as the torque felt by the nuclear charge divided by the strength of the applied magnetic field, when the nuclear spins are placed in a magnetic field. This torque exists until the net magnetic moment is either aligned with the magnetic field (lower energy state), against the magnetic field (higher energy state) or perturbed from alignment with or against the magnetic field. As there are always slightly more spins aligned with the external magnetic field (lower energy) than aligned against the external magnetic field (higher energy), there is an effective net magnetic moment aligned with the external field under equilibrium (no torque) conditions. The NMR assay involves the movement of that net nuclear magnetic moment off the axis of alignment with the external magnetic field.

The application of a short (5 μsec to 15 μsec), low energy (approximately 1 watt) radio frequency pulse perpendicular to the net magnetic moment provides enough torque to move that net magnetic moment off the axis of alignment. Once the pulse is stopped, the bulk magnetic moment relaxes back toward the alignment axis. Chemical information is obtained by observing the different component relaxation rates of individual magnetic moments. These individual relaxing magnetic moments induce electric currents, which are picked up in the receiver coil as free induction decay. Fourier transformation converts the free induction decay from the time domain to the frequency domain. NMR then uses differences in the frequencies of differing nuclear spins to analyze molecular structures, mixtures of molecules, and/or kinetics of spin exchange. Utilization of NMR information can then be used to correlate NMR spectral information to the chemical and physical properties of the samples that are being analyzed by NMR (Figure 16-1).

Quantitative analysis is inherent in the NMR assay. During the RF pulse, nuclei absorb the RF energy exciting the nuclear spins to higher energy states. Unlike any other spectroscopy, this absorption of energy by the nuclei is linearly quantitative across the entire NMR spectral range; absorption of RF energy is only dependent on the number of nuclei present and is not enhanced or dampened by specific molecular environments or chemical functionality. All NMR energy level transitions induced by the RF pulse are equal, in specific contrast to infrared transitions that are dependent on both energy absorption as well as chemical/molecular environment. After the RF pulse, the relaxing nuclei emit RF energy at specific frequencies based on their specific molecular/chemical environment. That energy is detected as an emission signal for which the intensity is proportional to the total energy emitted and, therefore, is directly proportional to the number of nuclei exited. The NMR signal intensity contains the quantitative information for the total number of nuclei, while the frequency information contains the chemical/molecular structural information.

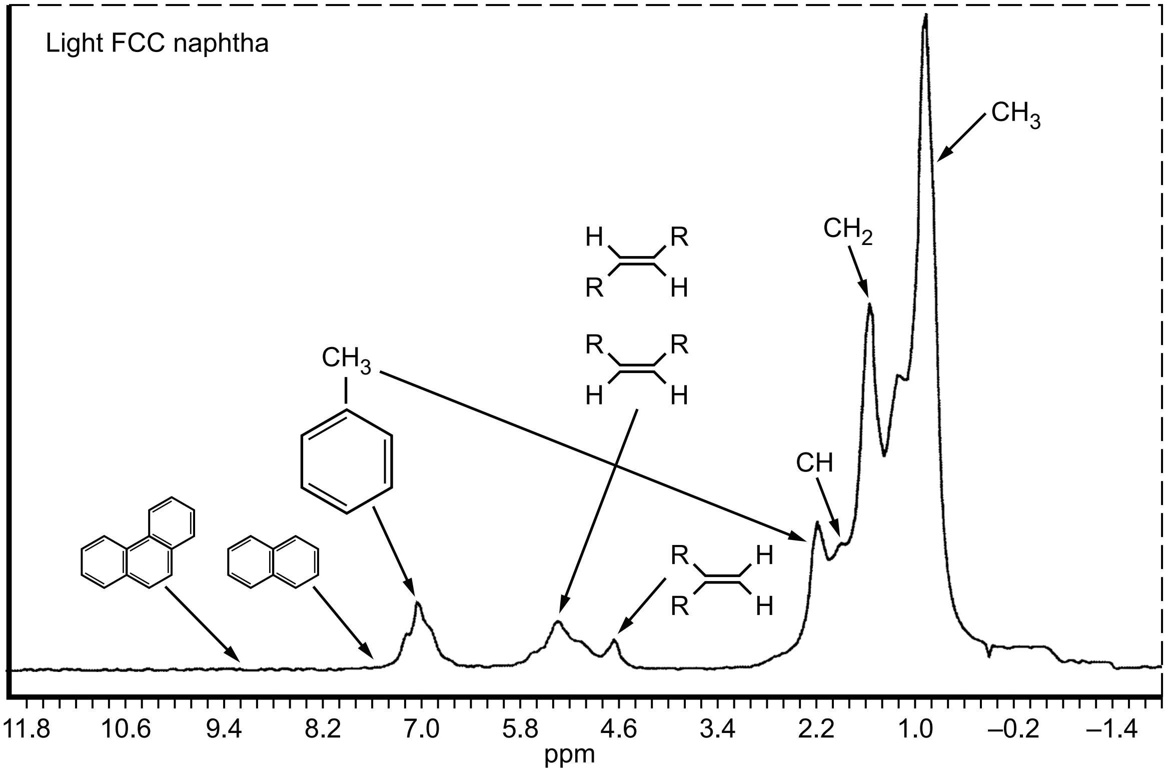


Figure 16-1—Example of the Chemical Information Available by Type for a Naptha Steam

Accurate, quantitative measurement of NMR signals is achieved by:

a) Generation of precise, square rf transmitter pulses;

b) Rapid detection coils with minimal dead times between transmitter pulses and detection; and

c) High digitization rates combined with wide dynamic range (A/D converter technology).

Recent enhancements of rf technology, computing capability, metallurgy, etc. have enabled NMR technology to enter the process control domain.

16.2 Typical NMR Specifications

Sample system complexity:	simple
Typical analyzer outputs:	4 mA to 20 mA, Modbus
Typical analyzer precision:	equal or better than lab method correlated against (dependent on application)
Typical analyzer accuracy:	same as above
Typical on-stream time:	95 %+
Relative installed cost:	$350 K to 450 K
Relative maintenance frequency:	very low (< 1 man-hour/day)
Average start-up:	1 week
Typical applications:	stream parameters and characterization

16.3 Sampling Systems

Sampling requirements are quite simple. Since the technique doesn't require actual contact with the sample, the sample is sent through the magnetic field in a tube. The sample isn't changed in any way as a result of the analysis; so, it can be returned downstream of the originating point, if desired. Small particulate matter, bubbles, or changes in temperature have little or no effect in the analysis. Thus, the need for sample conditioning is minimized or in some cases eliminated.

Realizing the benefit of non-invasive sampling, the use of NMR spectroscopy in acid stream applications makes it especially attractive and, perhaps, the safest technique. Corrosion, response deterioration, wear, and/or contamination problems are not symptomatic of an NMR system installation.

Annex C—References

Scope

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Chapter 11 Infrared Analyzers

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Silverstein, R. M. and G. C. Bassler, *Spectrometric Identification of Organic Compounds,* John Wiley and Sons, New York, 1963.

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Section D—Non-Spectroscopic Chemical Composition Analyzers

D.1 Scope

The application of Gas Chromatography to process analyses is described in Chapter 17. Detailed gas chromatography column technology is beyond the scope of this section, and the reader is referred the literature references in the appendix for further information. The application of Gas Chromatography to determined distillation properties, also known as Simulated Distillation, is covered in detail.

Moisture, oxygen and sulfur analyzers are non-spectroscopic analyzers that are often used in refineries to determine specific chemical composition of process streams. Chapter 18 provides detailed information on the application of moisture analyzers, Chapter 19 provides information on the various types of oxygen analyzers in use, and Chapter 20 describes several methods for determining total sulfur and selected sulfur compounds in process streams.

17 Gas Chromatographs

17.1 General

The process gas chromatograph is used to obtain on-line composition information of selected process streams for process operation and effluent monitoring. A gas chromatograph is a multi-component analyzer that is able to measure virtually any component. The analysis requires a period of time ranging from ~60 seconds to ~20 minutes depending on how many components are being measured and the complexity of the application.

The gas chromatograph may be designed to determine the concentration of one or more components in a multi-component stream. The gas chromatograph can determine component concentrations from parts-per-billion (PPB) ranges to 100 %.

Before the decision is made to use a gas chromatograph, a determination should be made of alternatives that can be used to satisfy the functional requirements of the application. For example, infrared or ultraviolet analyzers may be applicable. In some applications, composition may be inferred from other variables, such as temperature, pressure, density, viscosity, or thermal conductivity, which may be easier to measure.

A gas chromatograph separates a sample of the stream to be analyzed into component parts and then detects how much of each component is present. In order to do this, temperatures, pressures, flows, and timed valve sequences must be controlled within tolerances. In other words, chromatographs are complex and, therefore, more difficult to operate and maintain than most other instruments.

The physical and chemical stream characteristics of importance to the gas chromatograph are:

a) total stream composition, including intermittent trace impurities;

b) dew point and/or vaporization temperature;

c) particulate content;

d) abnormal concentrations of stream components during process upset.

The following items should be specified to best accommodate the functional purpose of the application:

a) number of components that must be measured;

b) number of different streams to be analyzed with a single chromatograph analyzer;

c) time required for each analysis;

d) location of the analyzer system hardware components;

e) accuracy and repeatability requirements;

f) mechanical reliability and maintenance requirements;

g) ease of operation;

h) information display.

Gas chromatographs mounted in the field require protection from the environment. Most gas chromatographs require a separate shelter, but there are gas chromatographs supplied in weather protected enclosures that meet the hazardous area classifications.

17.2 Utilization In Refineries

Gas chromatographs are used to measure process stream component concentrations of C1 through C30 hydrocarbons and other chemicals in refineries and petrochemical plants. Gas chromatographs may be considered as concentration transmitters (Figure 17-1). The process is analyzed by the analytical method and a process-compatible output signal is presented to a trend recorder, controller, DCS (Digital Control System or process computer), or other device, proportional to component concentration. Gas chromatographs are complex transmitters, but provides very important information for process monitoring and control.

Boiling point determinations can also be accomplished with a gas chromatograph. The ASTM method D2887 describes a “simulated distillation” that produces true boiling-point data. Boiling-point determinations may be accomplished for samples with an initial boiling point as low as 30 °F to a final boiling point up to 1000 °F. While many distillation applications are now done by gas chromatographs, many product specifications still require the single plate distillation method, D86, for which some empirical correlations exist to method D2887. The correlations are not exact due to the fact that single plate distillations provide volume percent versus temperature boiling point data, whereas gas chromatograph generated “simulated distillations” provide weight percent versus temperature data.

17.3 Typical Applications

Process chromatographs are typically used for the following.

a) Process control. For example the analysis of isobutane in the butane splitter column bottoms.

b) Product quality monitors. For example, the analysis of Methane, Ethane, and Ethylene in product ethylene.

c) Process study. For example components in the catalytic cracker unit fractionator.

d) Process development.

e) Material balance determination.

f) Waste effluent monitors. For example, monitoring of H_2S and SO_2 in Sulfur plant tail gas.

g) Area safety monitors. For example, monitoring Carbon Monoxide in the air near a heater.

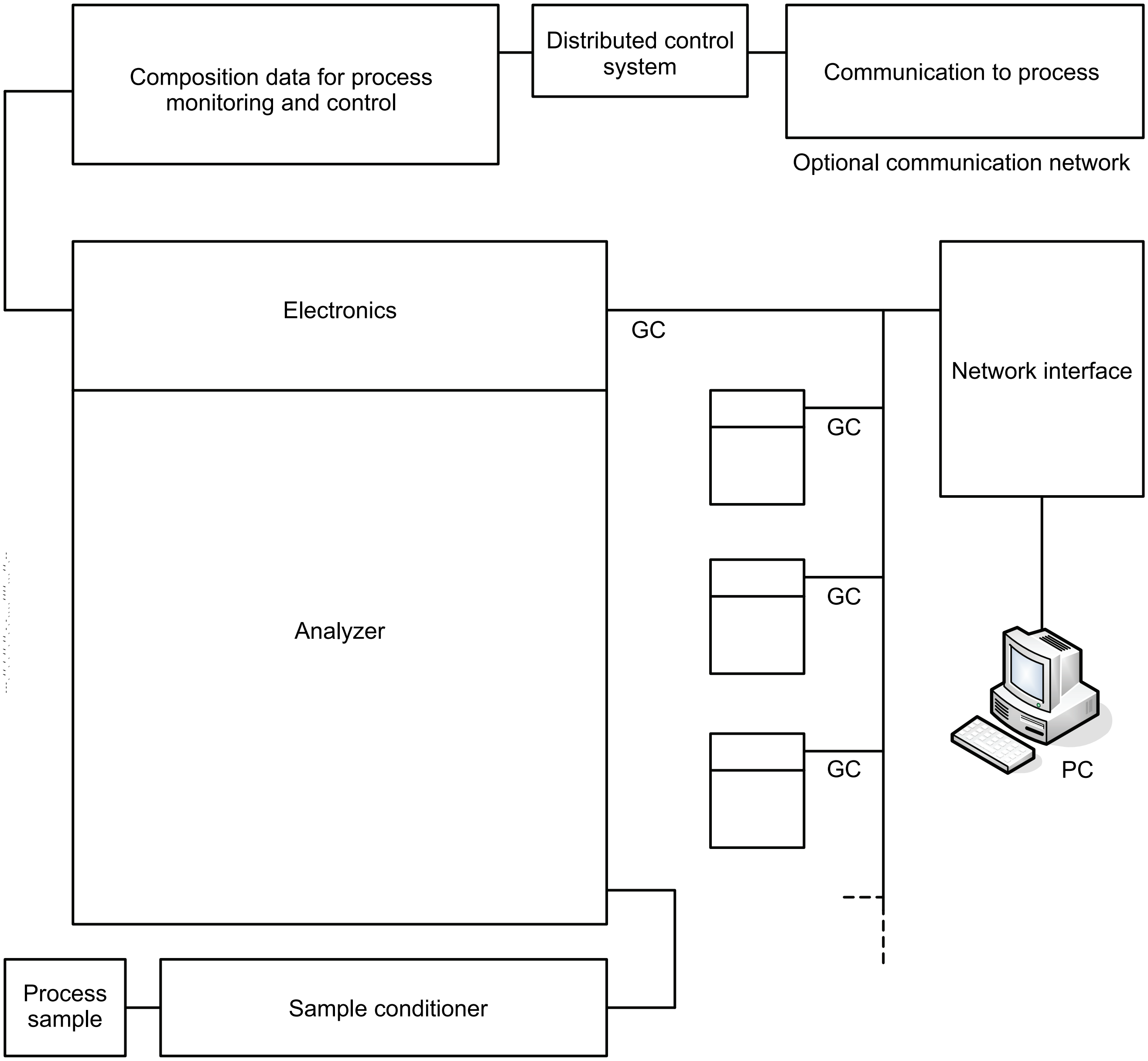


Figure 17-1—Typical Stand-alone Gas Chromatograph (GC) with Optional Network

17.3.1 Process Control

Process control is the most rigorous service for the process chromatograph. Both open loop control (the process operator uses composition data to manipulate the process) and closed loop control (the composition data is used to automatically adjust the process) are in common use.

Process control chromatograph requirements are as follows.

a) Maximum mechanical reliability (a minimum number of failures and a design to facilitate fast repair).

b) Maximum degree of repeatability (accuracy is desirable but secondary).

c) Short analysis time.

d) Data display must be convenient for use by process operators.

e) Easy, uncomplicated chromatograph operation.

Design criteria necessary to implement these requirements are as follow.

a) Analyze only for the critical control components. One key component is preferable. Do not analyze for components not needed.

b) Dedicate one analyzer to one stream.

c) Install a fast loop in the sample line from process to analyzer to limit transport dead time to a maximum of 30 seconds. As a minimum, the fast loop flow rate should be sufficient to cause three volume changes of the sample line during an analysis cycle. Locate the analyzer as close to the sample point as feasible.

d) The time required to perform the analysis must be fast enough to be compatible with the control system.

e) Provide alarms on composition and equipment components to indicate out-of-limit operations and/or equipment malfunctions.

f) Incorporate means for a remote calibration check (validation). Locate the calibration selector convenient to the process operators.

g) Present composition information in the same format as other process variables.

17.3.2 Product Quality Monitoring

A chromatograph used to monitor product quality requires many of the same attributes as a control analyzer; however, depending upon the end use of the composition data, some of the operating requirements may be less stringent.

Product quality monitoring requirements are as follows.

a) Mechanical reliability compatible with the application. It is sometimes feasible to back up these chromatographs with laboratory analyzers; however, some applications may require a maximum reliability including a back-up on-stream analyzer.

b) Maximum accuracy and repeatability.

c) Liberal analysis time (normally not critical).

d) Data display should facilitate the required end use.

e) Easy, uncomplicated chromatograph operation.

Design criteria necessary to implement these requirements are as follows.

a) Analyze only for the components required. Do not determine the major component if determining purity. Determine the impurities.

b) Use one analyzer per stream where possible. More than one stream may be sampled if the end use permits this practice (for example, sales contracts). Remember, however, that the simpler the system the better the reliability.

c) Install a fast loop in the sample line from process to analyzer to limit transport dead time to not more than 2 minutes to 5 minutes. As a minimum, the fast loop flow rate should be sufficient to cause three volume changes of the sample line during an analysis cycle.

d) Provide alarms on composition to alert operators to off-specification operation.

e) Incorporate a means for a remote calibration check. Locate the calibration selector convenient to the process operator.

f) Present composition data in a form most convenient for its intended use (for example, log, bar graph, or trend record). In most cases the information needs to be a permanent recording.

17.3.3 Process Study, Process Development, and Material Balance

Chromatographs used for process study and development have a set of operating priorities different from control or quality monitoring chromatographs. Data are normally interpreted by technical personnel familiar with the analytical techniques. Prompt decisions affecting process operations do not normally hinge upon the composition data obtained. Required composition data may be extensive.

Process study and development chromatograph requirements are as follows.

a) Fair mechanical reliability. When necessary, a laboratory analyzer can be used as a backup.

b) Maximum accuracy and repeatability.

c) Long analysis times are acceptable.

d) Data presentation may be chosen to facilitate analyzer operation, or the end use (for example, computer input) may dictate the type of presentation.

e) Complex analyzer operation is acceptable.

Design criteria necessary to implement these requirements are as follows.

a) Analyze for all required components. A complete stream analysis of 12 or more components is not uncommon.

b) Use of one analyzer for several different streams is acceptable.

c) Installation of a high velocity circulating loop in sample line from process to analyzer to limit sample dead time to a known value of no more than 5 minutes to 8 minutes. As a minimum, the fast loop flow rate should be sufficient to cause three volume changes of the sample line during an analysis cycle.

d) Alarms are not necessary.

e) Remote calibration is not usually required.

f) Present composition data in a form convenient to analyzer operation, such as bar graph, log printout, or chromatograms, or as necessary for the intended methods of data interpretation.

17.3.4 Waste Effluent Monitoring

Chromatographs used to monitor waste effluents are in limited use; and depending upon the nature of the application, the operating requirements vary considerably.

Waste effluent monitoring chromatograph requirements are as follows.

a) Mechanical reliability compatible with the application. It is sometimes feasible to back up these chromatographs with laboratory analyzers.

b) Provide a degree of repeatability and accuracy to meet application requirements.

c) Analysis lime selected to meet application requirements.

d) Process operator oriented display. These records may have to be permanent.

e) Easy, uncomplicated chromatograph operation.

Design criteria necessary to implement these requirements are as follows.

a) Analyze only for the components required.

b) Use only one analyzer per stream whenever possible.

c) Install a fast loop in the sample line from process to analyzer to limit transport dead time to the requirements of the application. As a minimum, the fast loop flow rate should be sufficient to cause three volume changes of the sample line during an analysis cycle.

d) Provide alarms on composition to alert operators to out-of-tolerance operation.

e) Incorporate a means for remote calibration check. Locate the automatic calibration switches convenient to the process operator.

f) Present composition information in a form convenient for its intended use. In many cases the information must be a permanent recording.

17.3.5 Area Safety Monitoring

Chromatographs are used for personnel safety area monitoring where the composition information required is beyond the capability of other instruments. Area safety monitors are covered in detail in Chapter 8.

Area monitoring chromatograph requirements are as follows.

a) Maximum mechanical reliability (a minimum number of failures and a design to facilitate fast repair).

b) Provide a degree of repeatability and accuracy to meet application requirements.

c) Short analysis time.

d) Process operator oriented display.

e) Easy, uncomplicated chromatograph operation.

Design criteria necessary to implement these requirements are as follows.

a) Where possible, analyze for only one component. The number of components selected must not compromise reliability, accuracy, or repeatability.

b) Use of one analyzer for several streams is acceptable.

c) Install a fast loop in the sample line from the sample point to the analyzer to limit transport dead time to a minimum. As a minimum, the fast loop flow rate should be sufficient to cause three volume changes of the sample line during an analysis cycle. Locate the analyzer as close to the sample point as feasible.

d) Provide alarms on composition to alert personnel of danger and its location. Also provide alarms to indicate analyzer malfunction.

e) Incorporate means for simple test and calibration procedures to be performed at the sample inlet.

f) Present composition data in a form convenient for its intended use. In some cases, a permanent record is required.

17.3.6 Sulfur Analysis

Both TCDs and flame photometric detectors (FPD) respond to sulfur-containing compounds, and are used in gas chromatographs to sense low parts-per-million sulfur compounds in a hydrocarbon sample. This is a common application performed by gas chromatographs in refineries. Detailed measurement of sulfur species are described in Chapter 19.

17.3.7 Simulated Distillation (SimDis)

17.3.7.1 General

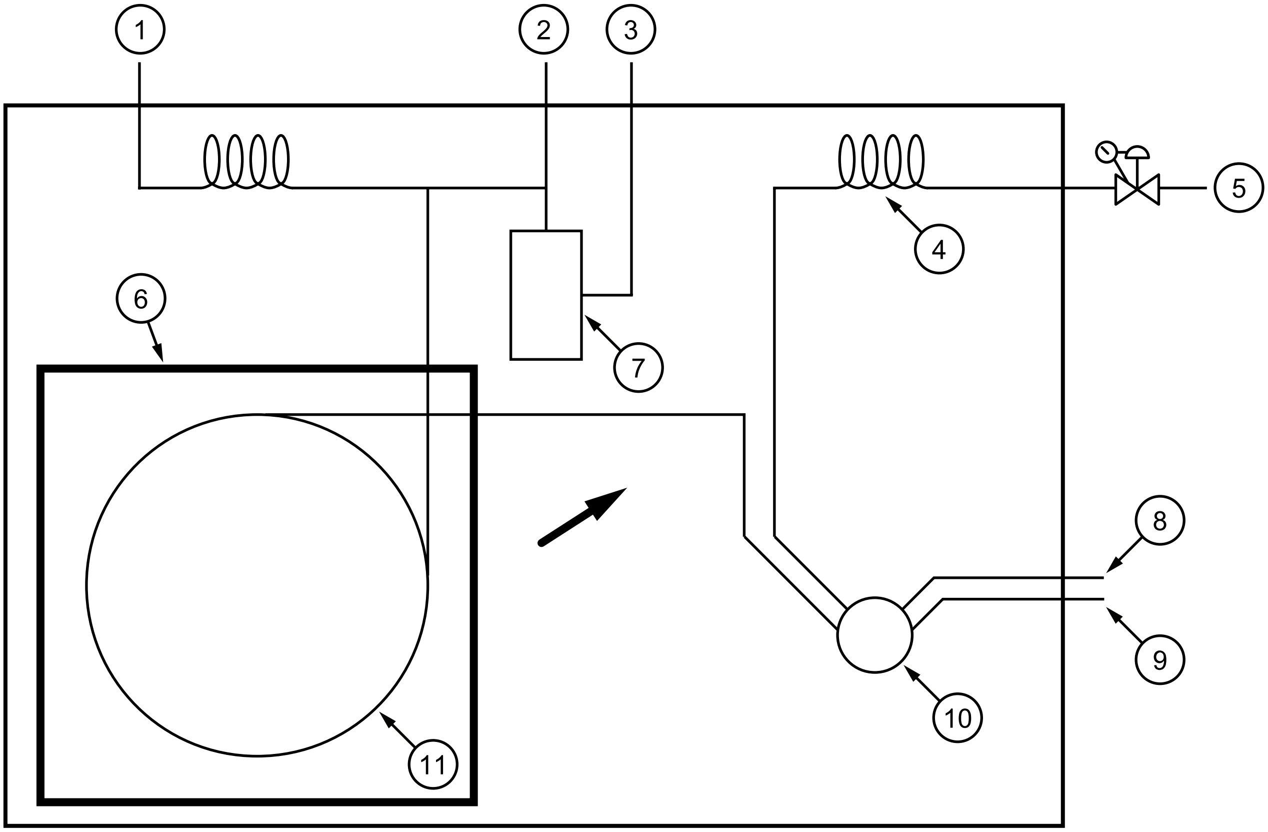
Distillation analyzers determine the boiling range of volatile organic mixtures. The output of a boiling range instrument is the temperature at which a certain percentage of the mixture boils such as 5 % or 50 %. This is referred to as the boiling point at percent off (e.g. 50 % point is 475 °F). The alternative is to express the results as a percent off at a particular temperature such as the percent boiling (or evaporated) at 300 °F. This point is referred to as the percent off at temperature (e.g. E200 equals 52.6 %). Most distillation instruments determine the boiling point or points by actually distilling the sample at atmospheric pressure.

Gas Chromatographs can simulate this boiling range determination. It is generally easier for a Gas Chromatograph (GC) to determine the complete boiling range of a mixture than it is for a traditional boiling point analyzer. The boiling range application for Gas Chromatographs is generally called Simulated Distillation (or SimDis) as it is not, strictly speaking, distilling the sample. There are three ASTM methods for Simulated Distillation ASTM D2887, ASTM D3710, and ASTM D5399.

The scope of ASTM D2887 includes compounds boiling up to 1013 °F (545 °C). The limitations of some Process GCs limit the range to materials boiling below 840 °F (449 °C). Cycle times for SimDis analyzers are typically 2 minutes to 20 minutes.

17.3.7.2 Types of Simulated Distillation Analyzers

Process SimDis analyzers are always Gas Chromatographs. They are much simpler from a chromatographic point of view than most Process GCs. The Programmed Temperature version has only one valve, one column and one detector, either a Flame Ionization Detector (FID) or a Thermal Conductivity Detector (TCD). Figure 17-2 is a schematic of a typical SimDis Analyzer.



Key

1	splitter vent (mogas only)	5	carrier	9	sample out
2	hydrogen	6	column compartment	10	valco sample valve 0.06 uL
3	air	7	FID	11	metal capillary column
4	restrictor 5 ft, 0.005 in. tubing	8	sample in		

Figure 17-2—Simulated Distillation Schematic

17.3.7.2.1 Isothermal Columns

Simulated distillation can be performed with a isothermal column in a Gas Chromatograph (GC) if the mixture to be analyzed has a very narrow boiling range or if only a few distillation points are required and they are at one end or the other, such as the Initial Boiling Point (IBP) and the 5 % point, or the 90 % and 95 % points. Often, column switching, such as a back-flush to detector method, is used in an isothermal SimDis analyzer.

17.3.7.2.2 Programmed Temperature Columns

The use of Programmed Temperature Gas Chromatography is much more common as it allows the complete determination of the boiling range of the sample over a relatively wide boiling range. The column is held at an isothermal temperature for a short time and then the column temperature is raised at a constant controlled rate (or a "programmed" rate).

17.3.7.3 Theory of Operation

More complete information about Simulated Distillation is available in the literature references (see Appendix).

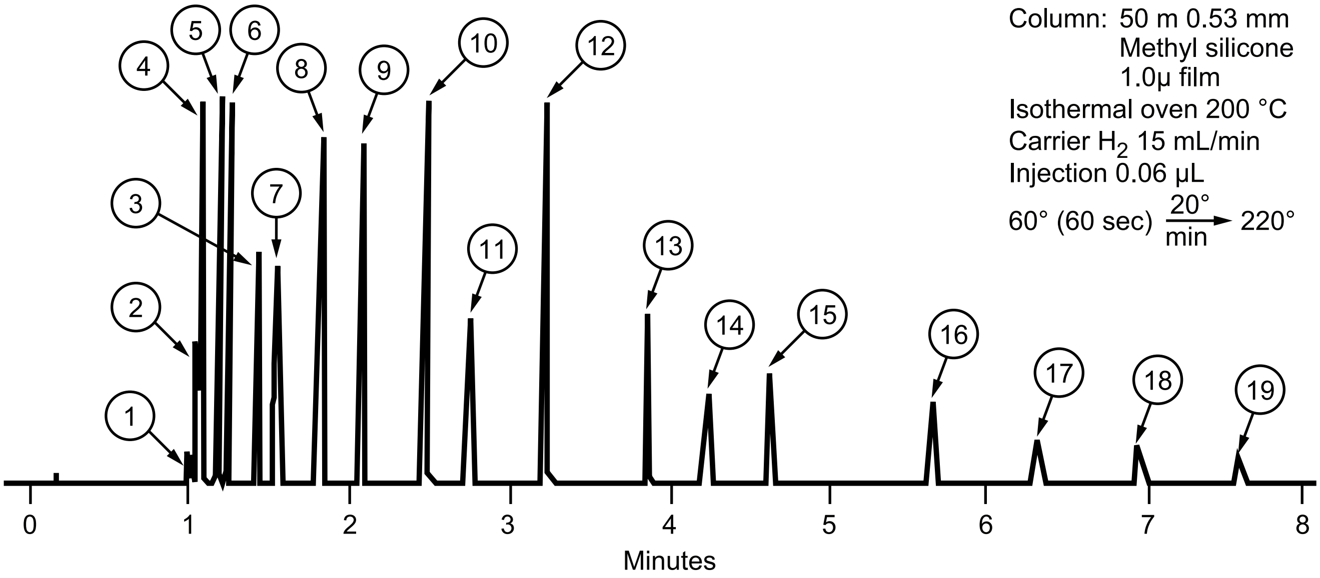
17.3.7.3.1 Calibration

The fundamental assumption of Simulated Distillation is that any chemical compound that elutes from a non-polar column at the same time as another compound run under identical chromatographic conditions will have the same boiling point. Compounds elute from most GC columns at a temperature much below their atmospheric pressure boiling points. Thus the temperature of the GC column at the time of elution is not a measure of the eluent's boiling point. The time a compound takes to elute from a GC column, which is called the Retention Time (RT), can be compared with the retention time of another known compound's RT. We assume that the compound of interest has a similar boiling point if it has a similar RT. Notable exceptions are alcohols such as Methanol or Ethanol. Therefore SimDis is not applicable to gasoline blended with various alcohols, or "Gasohol."

17.3.7.3.1.1 Pure Component Calibration

A mixture of pure components of known boiling points is normally used to calibrate a SimDis chromatograph application. For most applications, the mixture consists of normal straight chain hydrocarbons such as n-Hexane, n-Heptane, n-Octane etc. The retention times (RTs) of the individual compounds are then stored and used to calculate the equivalent boiling point of a compound eluting at any retention time. The D3710 method, which is used for motor gasoline, uses some additional components for the calibration blend. Figure 17-3 shows a calibration chromatogram for a D3710 calibration and Figure 17-4 shows a calibration curve for the D3710 application. The key point is that boiling point temperature is determined by comparison of retention times, not by a thermometer.

Another assumption made is that detector response is proportional to liquid volume. The D3710 method uses response factors to apply to different portions of the chromatogram and therefore requires a quantitative calibration blend. The D2887 and D5399 methods are normally used for higher boiling species that have similar detector response and, therefore, only the retention time of the individual components are used in the calculations. The detector response is assumed to be constant and therefore a qualitative calibration blend can be used.



Key

1	$_nC_3$	4	$_nC_4$	7	2.4 DMP	10	Tol	13	n Pr Bz	16	$_nC_{12}$	19	$_nC_{15}$
2	$_iC_4$	5	$_iC_5$	8	Bz	11	$_nC_8$	14	$_nC_{10}$	17	$_nC_{13}$		
3	$_nC_6$	6	$_nC_5$	9	$_nC_7$	12	p Xyl	15	BuBz	18	$_nC_{14}$		

Figure 17-3—Gasoline Calibration Blend

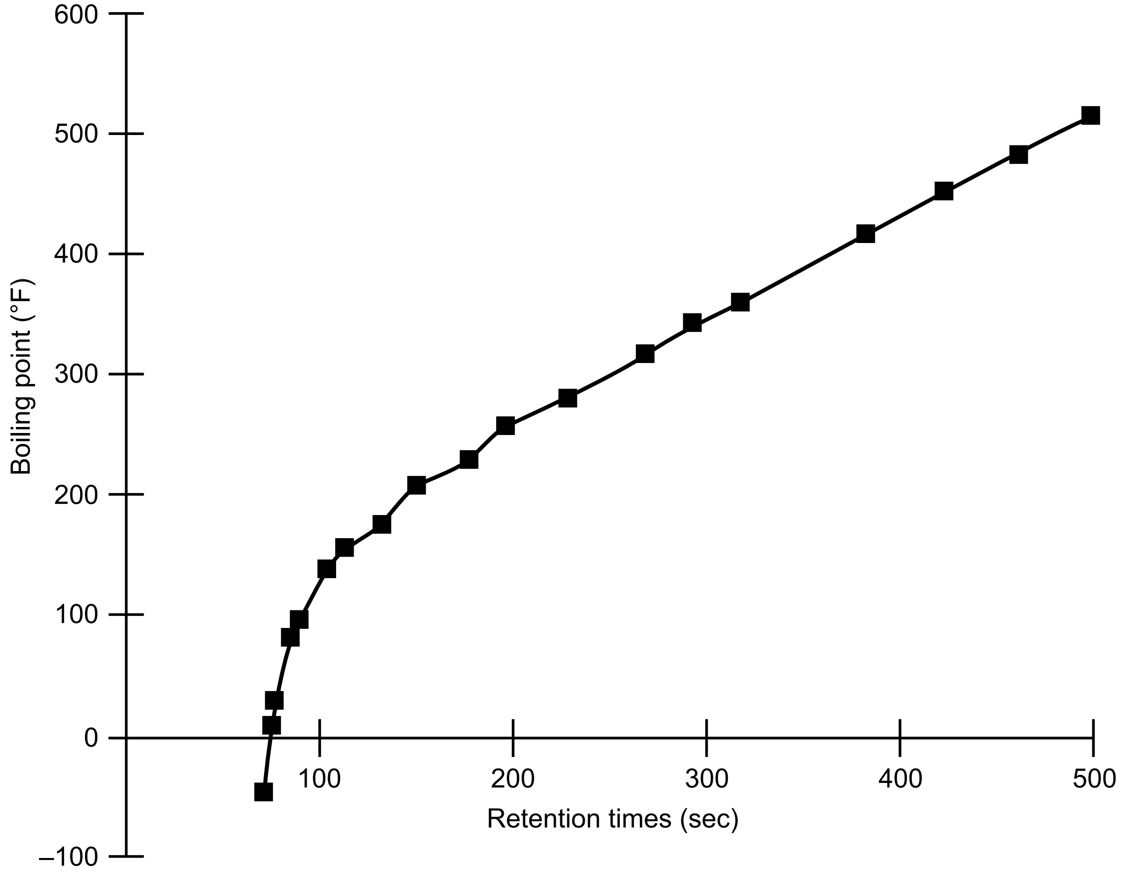


Figure 17-4—D3710 Calibration

17.3.7.3.1.2 Process Sample Calibration

A sample of the process mixture taken during normal plant operation can be used to calibrate a SimDis analyzer. The sample is usually captured in a large sample container (typically 5 gallons or more). The sample is analyzed by the plant laboratory several times to ensure accuracy of the calibration data. The laboratory distillation report is then used to calibrate the analyzer.

The calibration sample is run on the analyzer and a time required for each percent off value to occur is calculated by the software program. For instance, if the lab reports the 5 % off point as 150 °F, then the software program will assign 150 °F to the retention time when 5 % of the sample has eluted. A complete distillation report is normally required from the laboratory for this calibration method in order to construct a complete temperature versus retention time curve. This method of calibration is not covered by any ASTM method.

It should also be noted that this technique is only accurate if the analyzer is calibrated using a sample that is near the boiling range of the unknown sample. This method is best suited to maintaining a normally consistent process near a particular setpoint such as a distillation tower output. It is much less useful for samples that are quite variable such as a feed stream or multiple streams from different sources.

17.3.7.3.2 Calculations

17.3.7.3.2.1 Simulated Distillation

The sample of interest is run on the GC using identical conditions as were used to run the calibration sample. The chromatographic software integrates the signal differently for Simulated Distillation than traditional GC applications.

The detector signal is stored in small increments, normally referred to as data slices (1000 slices per chromatogram is typical). Simulated Distillation calculations are done "post run" rather than "on the fly" as is commonly done on Process GCs. The program sums the total area of the chromatogram (detector response factors are applied if ASTM D3710 is used) and then starts a process of summing the area a second time but looking for specific percentages of the total. The 0.5 % point is analogous to the initial boiling point (IBP) of a normal distillation. The 99.5% point is likewise analogous to the final boiling point (FBP) of a physical distillation method. Any point in between can be calculated, but the most common points utilized are the 10 %, 20 %, 30 %, 50 %, 70 %, 80 %, 90 %, and 95 % points. The retention time of the data slice that pushes the total into each desired % off (percent of total area) is noted and compared with the calibration data. The temperature of that slice is calculated by doing a linear extrapolation between the two bracketing calibration retention times.

17.3.7.3.2.2 Correlations

17.3.7.3.2.2.1 ASTM D86 and ASTM D2892

ASTM D86 is the most commonly used laboratory distillation method. It is essentially a single plate distillation, which means it does a very poor job separating chemical compounds. The method does not use a cold condenser and receiver, which means light components can be lost and not measured. GCs on the other hand do not lose light ends and do a far better job of separating the components. Thus a SimDis output is much closer to a true boiling point such as would be obtained by ASTM D2892. Figure 17-5 shows the relationship between data from a SimDis (D3710) and laboratory data using D86.

Since many product specifications are written using ASTM D86, correlation equations have been developed to convert ASTM D3710 or ASTM D2887 results to ASTM D86 results. Ford *et. al.* at Arco, and Bird and Kimball at Exxon (see appendix) have published such correlations.

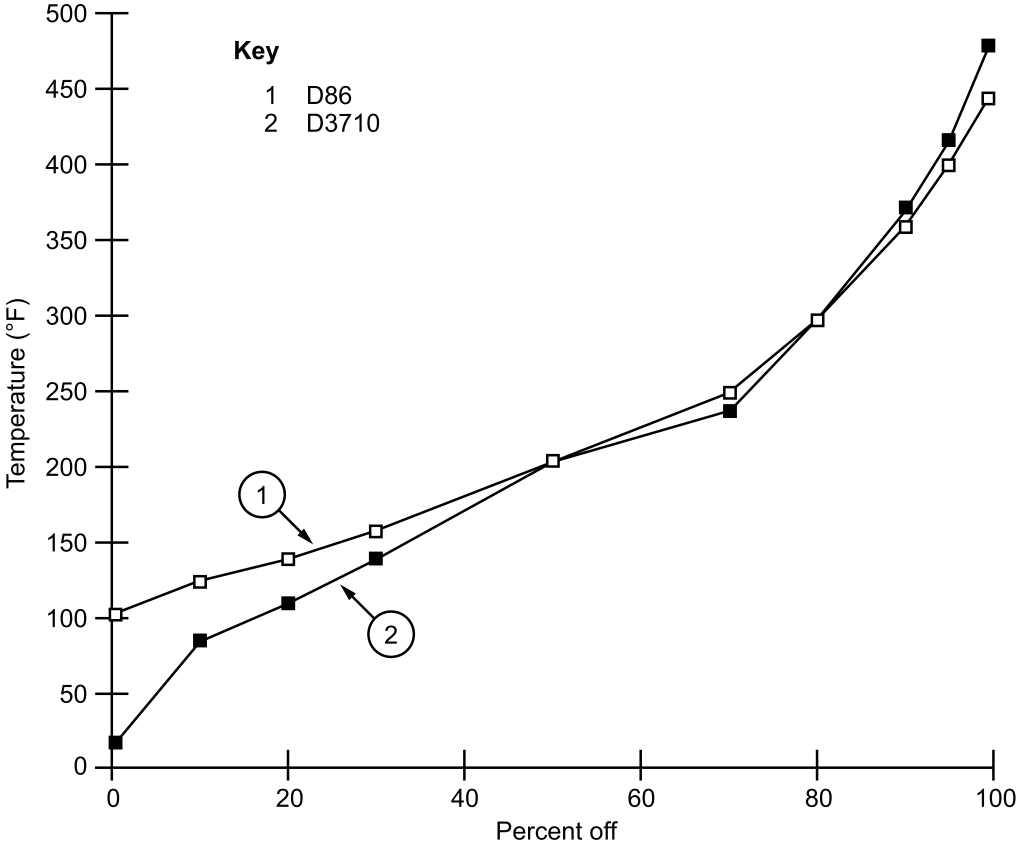


Figure 17-5—Comparison of D86 and D3710 Distillation Data

17.3.7.3.2.2.2 Reid Vapor Pressure (RVP)

Other properties such as RVP can be calculated as well (see Bird and Kimball).

17.3.7.3.3 Applications

Simulated Distillation is most frequently used in distillation tower control and blending control. Typical streams include motor gasoline, naphtha, kerosene, diesel and gas oil. Method ASTM D5399 is used for various solvents.

17.3.7.3.4 Sampling Systems

The sampling system for a SimDis Analyzer is typically the same as for any other liquid sample Process GC. Filtration is mandatory. Temperature control is not usually necessary although cooling may be required for some Distillation Tower applications. It is important that sufficient sample pressure be available to prevent bubbling of the sample in the sample valve. Sampling system components are normally made of Stainless Steel. Viton cannot be used for many gasoline samples due to the presence of Ethers such as Methyl-t-Butyl Ether (MTBE).

Plumbing for calibration sample introduction needs to be of a lower volume than is normally used for Process GCs because of the high cost of calibration samples. Low volume sample introduction can greatly reduce the consumption of calibration samples.

17.3.7.3.5 Maintenance and Troubleshooting

It is good practice to periodically check the calibration of the SimDis Analyzer with either the Calibration Sample or a Validation Sample which can be simply a container of process material stored in such a way as to prevent sample degradation (at the proper pressure and temperature).

The proper operation of a SimDis Analyzer requires the retention time of any component to be consistent from run to run. This requires that the temperature and flow be extremely consistent from run to run. The most common problems with SimDis Analyzers are caused by changes in flow or temperature. Leaks in the column and valving application are the number one cause of problems.

17.4 Application Variables

Gas chromatography is a highly versatile, field-proven analysis method. The separation column and flow configuration is application-engineered for each analysis to perform a large percentage of the analyses required in the petroleum business. Detailed applications information must be supplied to the vendor to assure that the system is properly engineered both as to sampling and GC analysis. Typical information required is noted below and detailed in Chapter 4.

17.4.1 Sample Conditions

Stream data required for the proper design of a sample system includes the following:

a) pressure:

  1) at sample point and sample return;

  2) extremes during plant upset.

b) Temperature;

c) sample phase (liquid or gas);

d) sample dew point/bubble point;

e) particulates;

f) chemical hazard information (Material Safety Data Sheets);

g) material compatibility with wetted parts.

17.4.2 Sample Composition

Data for sample composition should include normal, maximum, and minimum values.

a) Detailed sample composition-all possible compounds, including plant upset conditions, must be listed to check for interference.

b) Sample components to be determined (the analysis). Include only those required for process operation.

c) All streams to be analyzed must be listed individually.

17.4.3 Calibration System Requirements

Calibration system requirements are as follows:

a) determine if calibration is to be automatic or manual;

b) calibration frequency;

c) determine process sample or blend standards;

d) establish calibration check (validation) procedure.

17.4.4 Data Management

Data management considerations are as follows:

a) analog outputs;

b) digital communications requirements/format;

c) maximum time allowable for each data update (for control loops);

d) special data display requirements (locally and in control center).

17.4.5 Alarm Requirements

Alarm requirements are as follows:

a) concentration alarms;

b) GC alarms-carrier gas, detector, temperature, and so on;

c) system alarms-data transmission, reset, system diagnostics, and others.

17.4.6 Inputs to GC

Digital or contact closures include (a) start/stop running, (b) calibrate, (c) hardware status alarms, and (d) in maintenance.

17.4.7 Installation and External Details

Installation and external details are important to the overall performance of the system. Refer to Chapter 6 for applicable considerations.

17.5 Simplified Chromatograph Theory

The chromatograph is an analyzer designed to determine the concentration of component parts of a multi-component stream. The chromatograph separates a sample of the stream to be analyzed into selected parts and then detects the concentration of each part. The parts selected may be composed of individual components or groups of components.

In gas chromatography the separation of the sample into parts is achieved by passing a discrete measured volume of sample, diluted with an inert “carrier” gas, through a packed or coated column. The flow of each selected part of the sample is retarded to a different extent by sorption in or on the packing or coating. Thus, as the sample passes through the column, the selected parts are separated from each other and they emerge from the column sequentially.

A sensitive detector in the stream emerging from the column detects the amount of each component part present in the sample. The greater the amount of a component part present the greater the signal generated by the detector. The detector signal plotted against time on a strip chart recorder results in a pattern of signal peaks distributed along the base line. The time at which a peak is generated identifies the component part being detected and the size of the peak generated defines the amount of the component part present. This recording of detector signal versus time is called a chromatogram (see Figure 17-6).

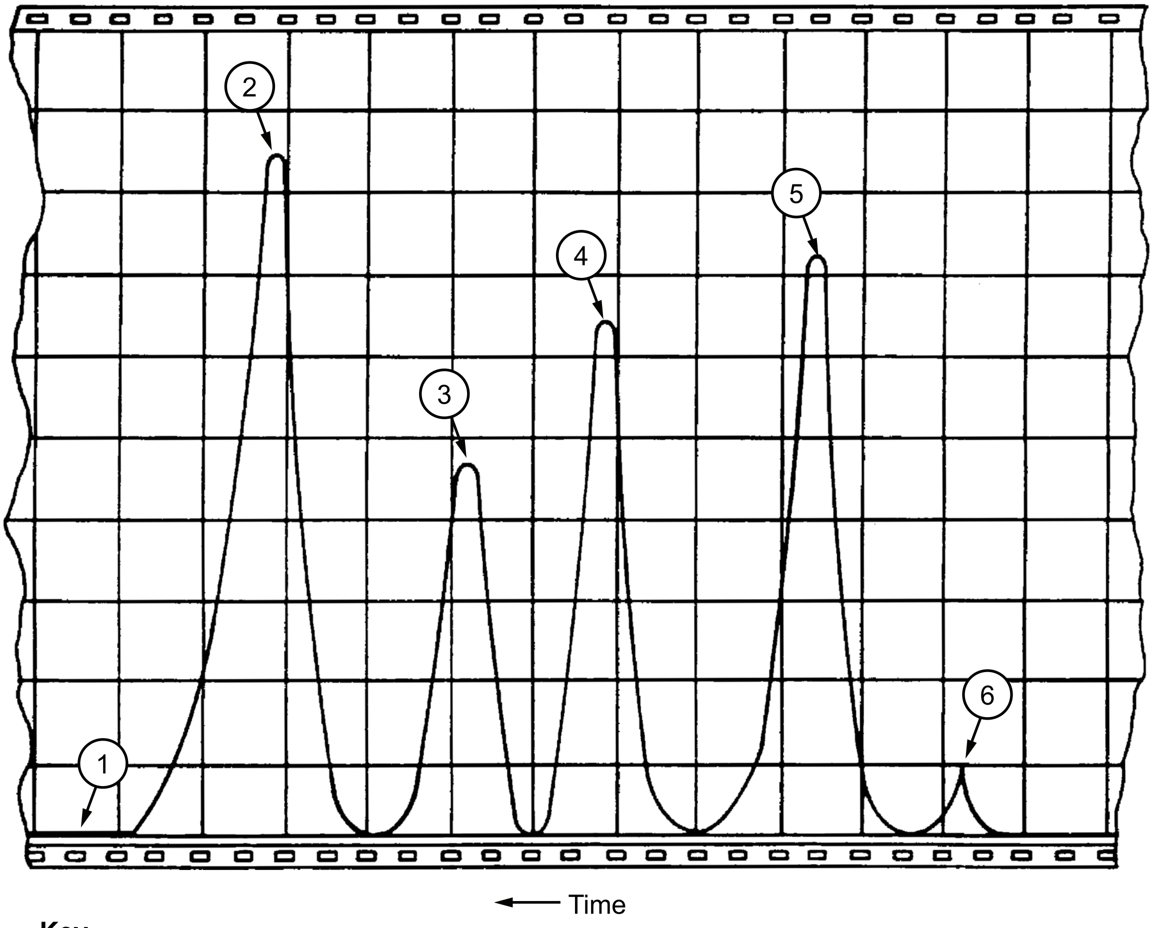
There are many factors that can affect the performance of chromatograph columns and cause the chromatogram of a particular mixture sample to change. For example changes in the packing or coating material or changes in the column temperature change the separation characteristics of a column. Ideally the chromatograph is designed to hold all of these factors constant so that repetitive analysis of a mixture of constant composition will yield identical chromatograms. Thus, changes in the chromatograms should reflect only changes in the composition of the sample mixture.

17.6 Components Of The Process Chromatograph

A process chromatograph system includes an analyzer, a sample system, and a readout to facilitate use of the analytical data obtained (see Figure 17-7). Proper design of each of these parts is essential to continuous automatic operation. Each of these parts is discussed below to enable an appreciation of the necessary design criteria.

17.6.1 Analyzer Section

The analyzer includes a chromatographic column(s), sample injection and switching valves, a detector, a temperature controller, flow controls for the carrier and detector medium(s), and the necessary electronics. The controller function may be separate or may be in the field with the analyzer, which thereby becomes a stand-alone gas chromatograph. Both systems provide analog outputs for concentration data and digital outputs for alarms, external stream select, and other external functions. If communication is required to a Digital Control System (DCS) or a Personal Computer (PC) or other data-gathering unit, a communication network may be specified to implement this. Refer to Figure 17-1 for a more detailed description of the system.



Key

1 base line
2 components E and F
3 component D
4 component C
5 component B
6 component A

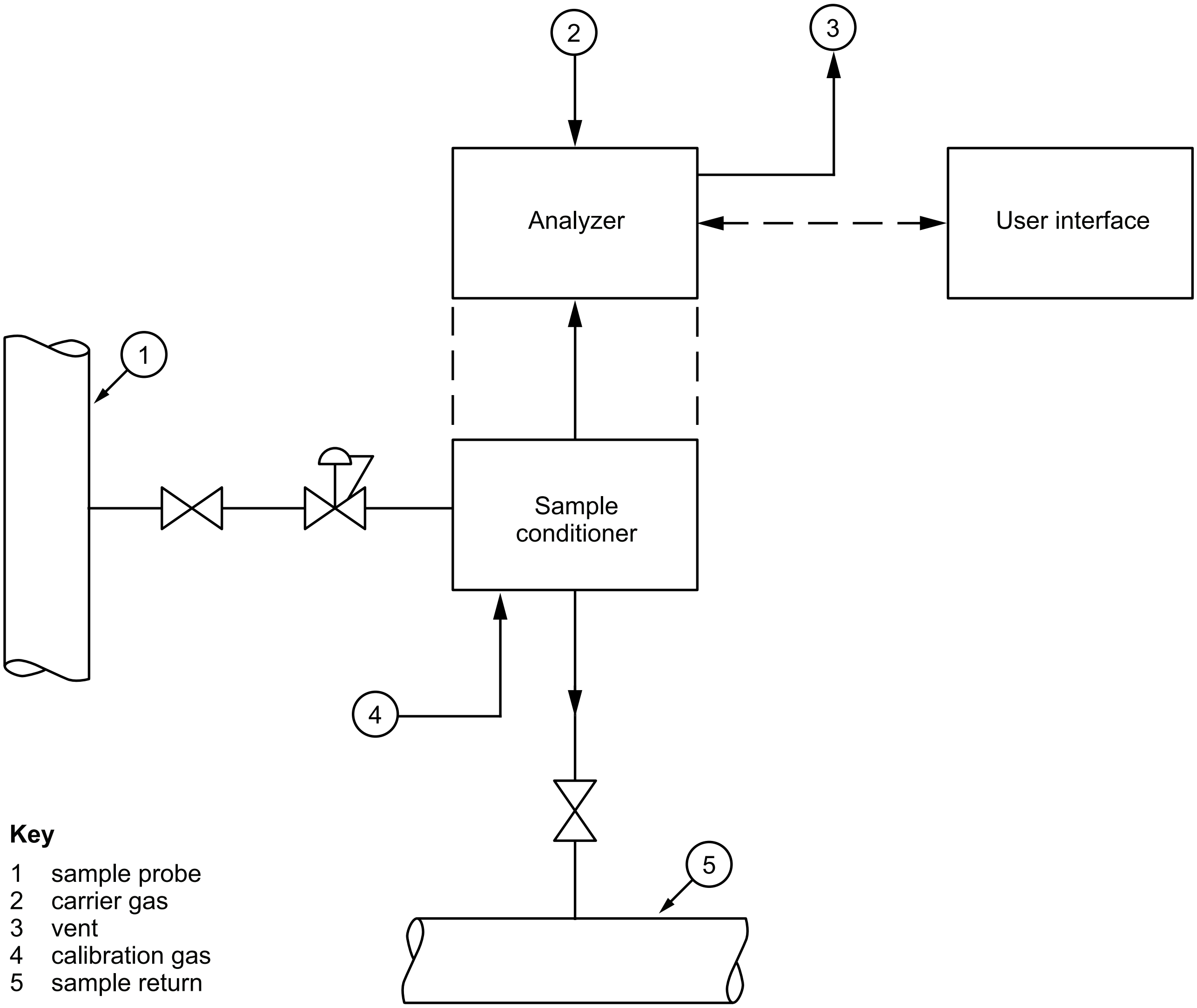
Figure 17-6—Sample Chromatogram

17.6.1.1 Housing

The analyzer components are grouped in three sections consisting of the oven compartment, the electronic section, and the flow control section. Although not strictly a part of the analyzer, a stream selection and sample conditioning section is often housed with the analyzer (see Figure 17-8).

The oven compartment contains the chromatographic column(s), the sample injection and switching valves, and the detector (Liquid Chromatograph valves are sometimes located outside of the oven to avoid leakage within the oven compartment.). The components housed in this insulated and heated compartment must be maintained at a precise temperature during operation to obtain accurate and repeatable results.

The most common heating method is referred to as an air bath in which air is forced to flow across electrical heating elements within the oven compartment. The air temperature is sensed near the column with a platinum resistance temperature detector or thermistor and controlled to within ~0.05 °C. Operating temperature ranges for this type oven are usually between 122 °F (50 °C) and 437 °F (225 °C). Most analysis can be made below 320 °F (160 °C). The National Electrical Code (ANSI/NFPA 70) Article 501, requires that oven temperature not exceed 80 % of the ignition temperature of any gas sampled unless otherwise approved by Underwriters Laboratories.



Key

1 sample probe
2 carrier gas
3 vent
4 calibration gas
5 sample return

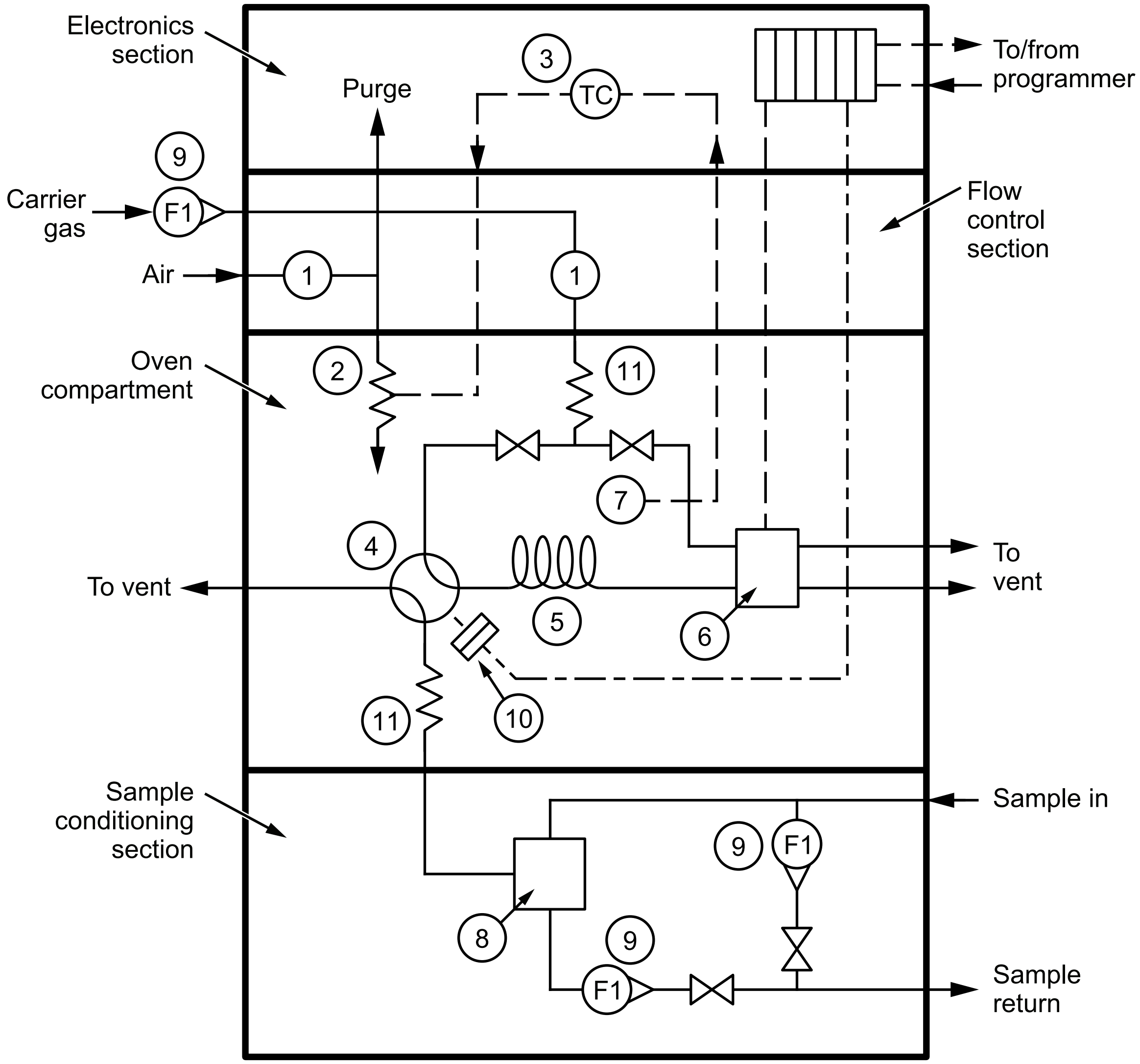
Figure 17-7—Typical Process Chromatograph System

Another heating method uses a metal mandrel heat sink with the column(s) wound tightly on the periphery. The mandrel is heated with embedded heating elements and the control sensor is placed in a well within the mandrel. The normal operating temperature range is 122 °F (50 °C) to 248 °F (120 °C) with control to ~0.2 °C.

The electronic compartment contains the temperature controller, detector amplifiers, and solenoid valves to convert electronic signals from the programmer to pneumatic signals to drive the analyzer valves. From the safety standpoint, the user must be sure that all electrical apparatus is suitable for the area electrical classification (see Chapter 7).

The flow controls for the carrier medium, hydrogen, and air (when a hydrogen flame ionization detector or flame photometric detector are used) and for the sample circulating loop may be mounted in a compartment, on a flat plate, or on a structural member so long as they are secure and protected from mechanical damage and the environment.

The separation column that resolves the sample components for individual measurement must be maintained under reproducible conditions of flow and temperature. A pressure regulator or flow controller maintains flow. The analysis dictates the method of temperature control. Isothermal or constant temperature is normally used maintaining the same temperature throughout the analysis. If the analysis is lengthy or the late emerging peaks are too broad, the temperature may be increased with time via temperature-programmed gas chromatographs (TPGC). The column



Key

1 flow regulator
2 heater
3 temperature controller
4 sample and injection valve
5 chromatograph column
6 detector
7 temperature sensor
8 bypass filter
9 flow indicator
10 valve actuator
11 heat exchanger

Figure 17-8—Typical Chromatograph Analyzer Section

temperature may be ramped, typically at a constant rate (degrees per minute) to accomplish this. When appropriate, TPGC reduces the analysis time and sharpens the late emerging peaks. More complex temperature programs may be required to solve special analytical problems.

17.6.1.2 Chromatographic column

The chromatographic column separates and elutes the sample components at different, yet repeatable times, as measured by the detector. As the components are propelled through the column by the carrier gas, they are decelerated in proportion to their affinity for the column. There are two basic types of columns—adsorption columns and partition columns.

17.6.1.2.1 Adsorption Columns

Adsorption columns are used in gas-solid chromatography for the separation of gases, such as nitrogen, oxygen, carbon dioxide, hydrogen sulfide, and rare gases, such as helium, argon, and neon. These columns can also be used to separate hydrocarbons in the C_1 to C_3 range. Components are separated by their differences in adsorption, which can be defined as their tendency to adhere to the adsorbent. Packing materials are surface-active solids, such as activated alumina, charcoal, molecular sieves, silica gel, and synthetic zeolites. These materials are operated dry, that is, they are not coated with a liquid. For petroleum service, adsorption columns have a limited range of application except when used in combination with other columns.

Adsorption columns are used in liquid-solid chromatography for the separation of organic isomers, organic compounds containing different functional groups, and hydrocarbon classes according to their polarity. Polarity, in this sense, is a semi-theoretical scale used in chromatography to aid in determining the relative retention of compounds on the stationary column material. Several physical effects cause interactions between molecules in the sample and those in the stationary phase, included are London forces, included dipole moments, permanent dipole moments, charge transfer, and hydrogen bonding.

17.6.1.2.2 Partition Columns

Partition columns are used in gas-liquid chromatography for separating complex hydrocarbon samples. The separating medium (the column packing) is a granular solid impregnated with a liquid substrate that is essentially nonvolatile under the conditions of use. The packing appears to be dry, but in reality exposes a large liquid surface to the vaporized sample components as they are borne through the column by the carrier gas. The sample components are partitioned between the gas and liquid phases. Those components least soluble in the liquid pass rapidly through the columns and emerge early; those components most soluble in the liquid are retarded and emerge later. The more volatile components generally emerge earliest. The versatility of gas-liquid chromatography results from the large variety of liquids that can be used to obtain different separations.

The granular solid (solid support) used to support the liquid may be crushed firebrick, celite, or other solids of moderate surface area (1 to 4 square meters per gram). It may be treated to reduce residual adsorptive effects. The stationary liquid must have a very low vapor pressure at the operating temperature in order for the column to have a long service life.

Partition columns are also used in liquid-liquid chromatography. In general, these columns are used when individual component analyses are required. Since the stationary liquid phase often tends to be washed off the packing by the liquid carrier, the stationary liquid phase is often chemically bonded to the packing.

The tubing material, packing solids, and liquid coatings must be inert to all sample components and the carrier gas. Packing materials must have a high surface area, be packed uniformly, resist attrition, and offer low resistance to flow.

17.6.1.2.3 Capillary and Other Columns

Capillary columns have the separation media on the interior surface of a small-inside-diameter tube, normally quartz. The molecular multi-path characteristic of a packed column is contrasted to a straight-through path for the capillary column. Therefore, the capillary column produces peaks with less broadening, resulting in better resolution and sensitivity. Sensitivity of a capillary column is somewhat offset by the smaller sample size required. The column must perform the desired separation and be stable in elution time. Stability is important because the analysis is time based. Both types of columns may be coiled for installation in a reasonably sized oven.

Columns are also built in which an active, rather than an inert, solid is used for support, and only part of it is coated with the substrate. Despite the fact that it is contained in a single tube, this is actually a column combination.

Ion exchange columns are used in liquid-solid chromatography for separation of ionic compounds, such as organic acids and bases and inorganic metal compounds. The packing in these columns is an ionic resin, and the liquid carrier is normally a buffered system necessary to control the degree of ionization of the sample components.

Gel permeation columns are used in liquid-solid chromatography for the separation of components according to their molecular sizes. Polymer analysis would be a typical application. The packing in these columns is a highly porous solid of controlled pore size. Small molecules can enter the pores but large molecules cannot and are therefore eluted first.

17.6.1.3 Valves

The sample injection in an on-stream, automated gas chromatograph is accomplished with a special valve that introduces a reproducible volume of sample into the upstream end of the chromatographic column. The sample valve transfers a measured volume of sample from the flowing sample system to the flowing carrier gas system. The sample valve is configured so that in the off position carrier gas flows through the valve and directly to the column. Also, sample flows through the sample volume side, purging it with fresh sample. When the valve is actuated, the carrier gas sweeps the sample out of the sample volume into the column, where the separation process starts.

The sample valve is the interface between the sample system and the gas chromatograph. This valve is contacted by pure sample and as such must be chemically inert to the sample. Sample valves for gas service normally have an external sample loop or volume. Sample size varies, but is normally between 0.1 and 2 milliliters. Normally, a constant volume of sample is measured at constant pressure and constant temperature; thus, the mass of successive samples of material does not change if the density of the composition does not change; however, vent pressure, and valve and sample temperature must be constant. From the safety standpoint, the possibility of hydrocarbon leaks into the enclosure is a major consideration. Consequently, threaded connections should be used only when necessary for assembly and repair on the valve and other parts of the system.

The sample pressure must be the same each time a gas sample is injected (to ensure the injection of a constant mass). The standard procedure is to reference the sample to atmospheric pressure before and during sample inject. This technique is called block-and-bleed as shown in Figure 17-9.

Liquid samples are not noticeably compressible, so sample pressure is normally not as critical. Samples with volatiles or a high vapor pressure, however, must be sampled under a pressure adequate to assure the sample is completely liquid in the sample volume.

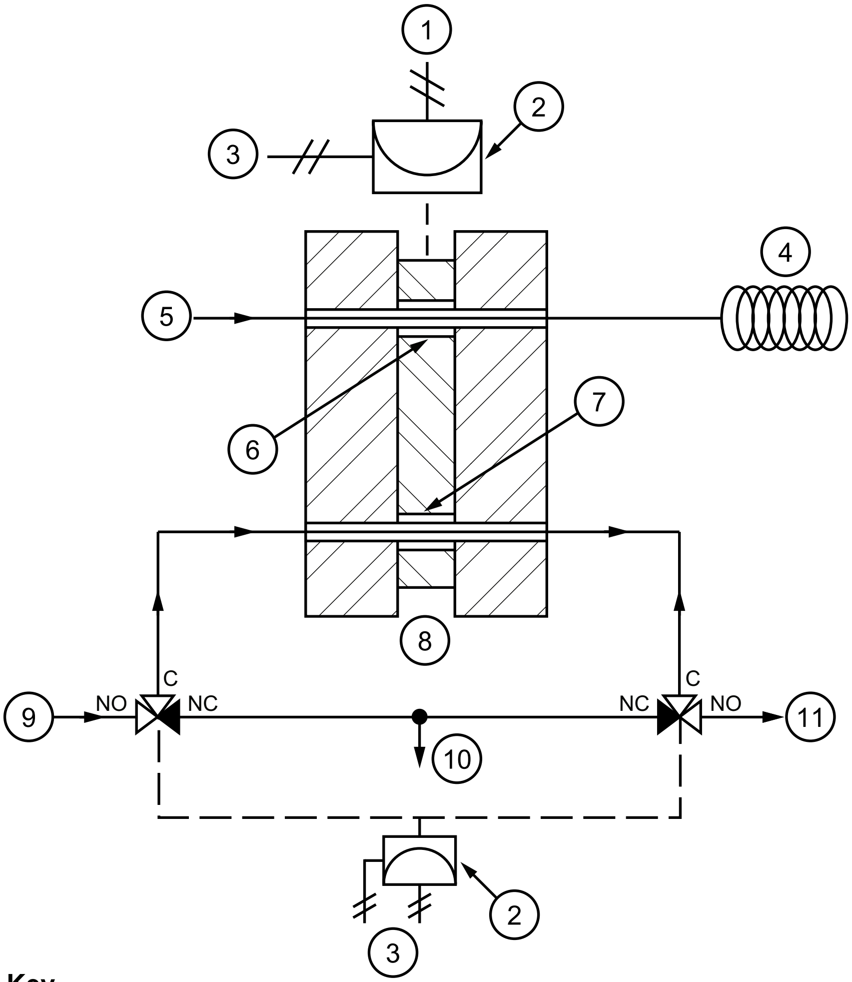
A liquid sample must be presented to the column as a gas. A liquid sample valve and a vaporizer or flasher (as shown in Figure 17-10) is used to ensure that a liquid sample is completely in the gaseous phase prior to injection into the column.

The flasher must vaporize the sample instantaneously so that each component will exist as a gas as it travels through the separating column. Gradual vaporization results in distorted peaks. The liquid sample vaporization method, and the sample inject and column switching valves are integral parts of the analyzer, and the vendor is responsible for their design and operation.

17.6.1.4 Chromatographic column configurations

Component separations are sometimes accomplished using more than one column. One column may separate one group of components while another column may be required to separate another group. Also, the analysis may not require some of the components, for example the heavier later components. These may be vented to the atmosphere to the reduce analysis time.

Column flow systems established by the manufacturer to accomplish the analysis may involve multi-port switching valves. Several terms are used to describe commonly used column configurations and valving. One system is called *back-flush,* in which two columns are in series. The first one is relatively short and is used to hold up the heavies in



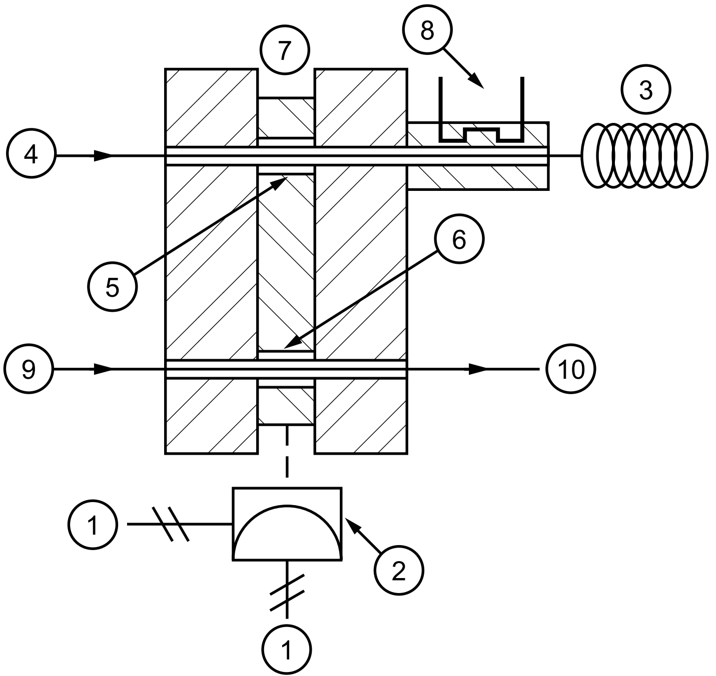
Key

1	air
2	actuator
3	operator air
4	column
5	carrier in
6	sample volume, inject position
7	sample volume, flow-through position
8	sample valve
9	sample from process
10	atmospheric vent
11	sample process return

Figure 17-9—Gas Sample Valve with Double Block-and-bleed Arrangement

the sample. The second is used to separate the lights. When the heavies are in the first (back-flush) column and the lights in the second (analytical) column, a column switching valve diverts the lights to go to the analytical column, then to the detector, after they are separated. The heavies may be vented (back-flushed to the vent) or later sent to the detector (also known as back-flush to measure). The back-flush column carrier flow is then reversed to allow the heavies to be quickly removed. Thus by proper application engineering, the compounds trapped in the back-flush column are timed to elute at about the same time all together. The analytical column is application engineered to separate the lighter components that are presented to the detector.

Application engineering for gas chromatographic separations can embody many column switching combinations. Some common configurations are: heart-cut, column switch, and trap. The heart-cut method separates a small peak from a large peak by removing the portion of the large peak co-eluting with the small peak. This fraction is then introduced into a column that separates the two components. The trap method blocks some of the components in a short column with no carrier flow until the proper time to put them back into the flowing analytical system. The "trap" column may be a different analytical column, or a longer version of the same column material to provide additional separation capability.



Key

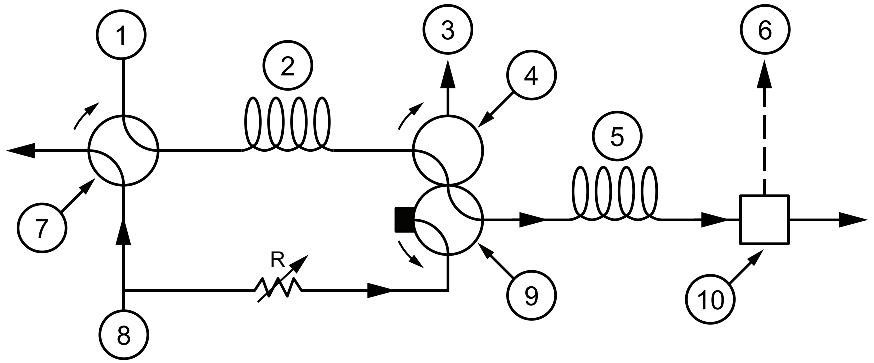
1	operator air	5	sample volume, inject position	7	sample valve
2	actuator			8	heated vaporizer
3	column	6	sample volume, flow-through position	9	sample in
4	carrier in			10	sample out

Figure 17-10—LIquid Sample Valve

Schematic diagrams of dual-column arrangements for three possible services are shown in Figure 17-11, Figure 17-12, and Figure 17-13.

Figure 17-11 depicts a system sometimes used to reduce analysis time for the light components in a complex sample, for example, separation of the components through the C_4s in a gasoline stream. The system operates in the following manner. After sample injection, the sample valve returns to the position shown in Figure 17-11. The carrier gas and the sample then flow until the light ends have passed through Valves 1 and 2 and into Column B. On a time basis, the programmer then rotates switching Valves 1 and 2 in the direction shown. Carrier gas continues to flow into Column A and flushes the heavier components remaining therein out through the vent in Valve 1. Simultaneously, an auxiliary carrier stream enters Column B through Valve 2 and elutes the lighter components in Column B out through the detector. The resistance R in the auxiliary carrier line approximates the pressure drop of Column A to avoid upsetting the detector with different column flow rates.

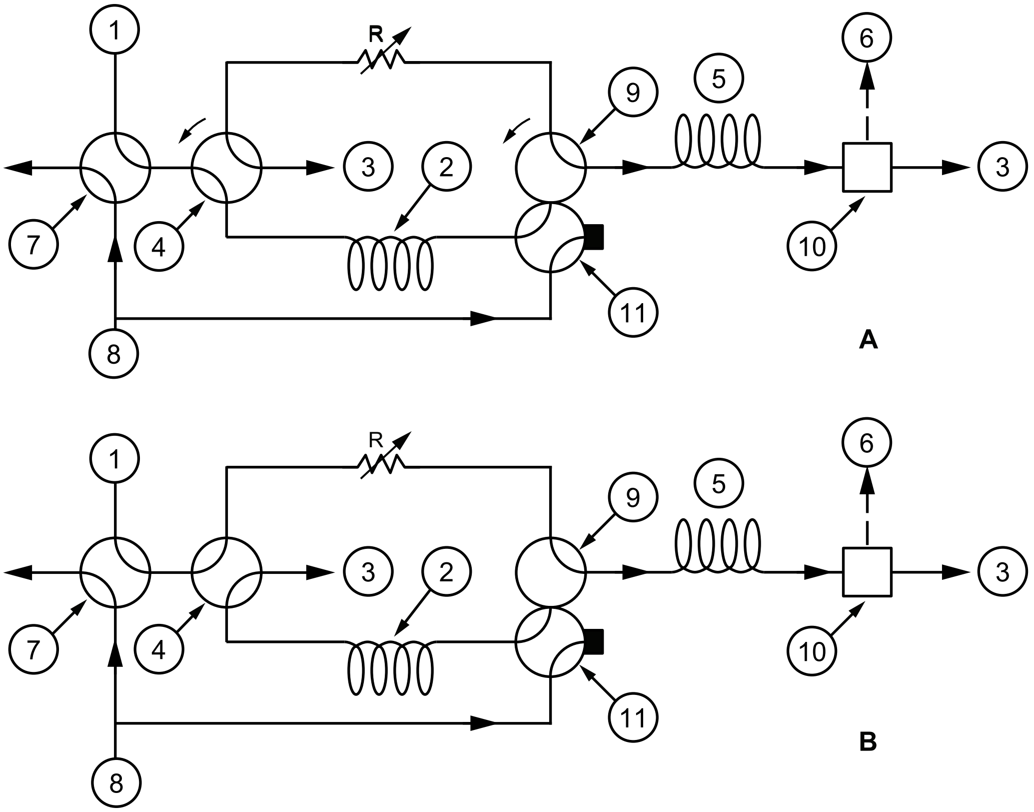
The system shown in Figure 17-12 reduces analysis time as described in the preceding example and also prevents heavy contaminants from damaging the analysis column. The system operates in the following manner. After sample injection, the sample valve returns to the position shown in Figure 17-12A. Carrier gas and sample flow through the sample valve, through Valve 1, through Column A, through Valves 3 and 2, and into Column B. After the lighter components of interest have emerged from Column A and are in Column B, the programmer rotates Valves 1, 2, and 3 in the direction shown, and the carrier gas and sample flow path is as shown in Figure 17-12B. The carrier gas continues to flow through the sample valve, through Valve 1, through resistance R, through Valve 2, and elutes the components in Column B through the detector. Simultaneously, an auxiliary carrier stream enters Valve 3 and flows backward through Column A to back-flush the heavy components out through Valve 1 and the vent. The rate of flow of the back-flush carrier stream is established so that Column A is completely back-flushed of all heavy components by the time the material in Column B is analyzed.



Key

1	sample	6	signal
2	column A	7	sample and injection valve
3	vent	8	carrier gas
4	valve 1	9	valve 2
5	column B	10	detector

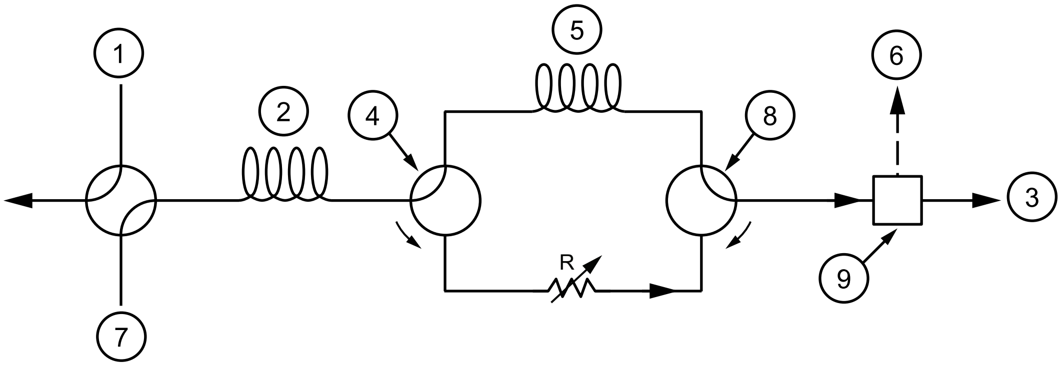
Figure 17-11—Partial Analysis with Forward Flush



Key

1	sample	5	column B	9	valve 2
2	column A	6	signal	10	detector
3	vent	7	sample and injection valve	11	valve 3
4	valve 1	8	carrier gas		

Figure 17-12—Partial Analysis with Back Flush



Key

1	sample	6	signal
2	partition column	7	carrier gas
3	vent	8	valve 2
4	valve 1	9	detector
5	adsorption column		

Figure 17-13—Total Analysis for Hydrocarbons and Fixed Gases

In Figure 17-13, carrier gas and sample flow through the sample valve, through the partition column, through Valve 1, and into the adsorption column until the fixed gases, which are not separated by the partition column, are all in the adsorption column. The programmer then rotates Valves 1 and 2 in the directions shown and traps the fixed gases in this column. Carrier gas continues to flow and elutes the hydrocarbons in the partition column through Valve 1, through resistance R, through Valve 2, and to the detector. When hydrocarbon analysis is complete, the programmer rotates Valves 1 and 2 back to their original positions, and carrier gas again flows through the adsorption column to elute the fixed gases previously trapped and completes the analysis.

Temperature Programmed Gas Chromatographs (TPGCs) normally do not require column switching. They use the principle that the component affinity to the column is inversely proportional to the column temperature. The temperature ramp can usually be designed to produce well resolved, sharp peaks for the lighter components at a low temperature and sharp peaks with a relatively short retention time for the heavies at higher temperatures. The lights are resolved at the initial, low temperature. As the heavier components are traveling at a lower rate and would broaden with time, due to diffusion, the temperature is ramping to higher values. This allows the heavier components to speed up and be presented to the detector before broadening occurs and at much shorter retention times.

17.6.1.5 Carrier gas system

The carrier gas and its control system are crucial to proper operation of the gas chromatograph because they affect resolution and detection and establish the elution times (component, column transport time). In the event of carrier gas failure, the analyzer will not function.

Theoretically, any gas can be used as a carrier if it is pure and inert to the column and sample. Special care must be taken to ensure that the carrier gas is dry. In fact, however, a carrier is selected for its effect on resolution and detection sensitivity. Detector sensitivity is the prime consideration because resolution can be obtained by other means. Selection of the carrier gas is the vendor’s responsibility.

To achieve sensitivity, the carrier gas and detector must be chosen so that eluted components generate large signals. For this reason, gases with high thermal conductivities, such as helium and hydrogen, are used with the thermal-conductivity detector; argon is used with the beta-ray detector; and air is used with the catalytic combustion detector. Any one of several carrier gases may be used with the hydrogen flame ionization detector. In addition to the technical factors affecting carrier gas selection, the gas availability should be considered; helium, for example, is not available at some locations.

No carrier-detector combination is completely satisfactory for all analyses. For example, the popular helium-thermal conductivity combination presents problems if the sample contains varying amounts of hydrogen and hydrogen is a component requiring analysis. A carrier gas can also interfere with the analysis. For example, if helium is used as the carrier in the analysis of combustion flue gases, argon will appear with oxygen as a single peak and cause errors in the oxygen analysis. However, if argon is used as the carrier along with a more sensitive detector, the argon interference with the oxygen peak can be balanced out.

The carrier flow may be controlled by directly regulating pressure or flow. Each has its application and should be a part of the system design by the manufacturer. In either case, retention time must be reproducible. Sometimes pressure control is used to minimize baseline upsets immediately following sample inject to achieve better analysis of the lighter components. Flow control may be used for TPGC applications to speed heavies' elution as it overcomes the changing restriction offered by the column at differing temperatures.

17.6.1.6 Detectors

The detector is the element located at the output of the chromatograph column to detect the presence and concentration of the separated components in the carrier gas. The two most common detectors in use are thermal conductivity and flame ionization. A good detector will respond rapidly and repeatedly to component composition. The response should be linear or linearized electronically. The detector should be protected from environmental changes that would cause noise or drift. Some examples are ambient temperature changes, radio frequency interference, power surges, and vibration that may effect each detector type differently. The user should be aware of these requirements for the equipment used to provide proper installation.

The detector used with a TPGC must remain at a constant temperature. The thermal conductivity detector especially must be isolated from any temperature changes.

Thermal conductivity detector: The thermal conductivity detector (TCD) is the most widely used because of its universal response to all components and its simplicity. The detector measures the thermal conductivity of the gas passing through it. The carrier gas is selected to have a thermal conductivity different from the components being measured. Helium or hydrogen is normally used for this reason.

The TCD is sensitive to vibration and ambient pressure fluctuations. For example, wind blowing across the detector vents may cause base line noise. Opening an outside door may also cause a baseline spike. When operating at maximum sensitivity, the detector output is at the microvolt level. Special shielding and wiring techniques must be used in the GC if the application requires this level of sensitivity.

A special situation exists when analyzing for hydrogen and other compounds in one analysis. A special filament bridge configuration is required in which nitrogen carrier flows over one pair of filaments, and helium or hydrogen carrier flows over the other filament pair. This results in sensitivity to hydrogen in the nitrogen carrier and sensitivity to organics in the helium or hydrogen carrier. All peaks produced are of the same polarity. The vendor will supply this configuration when application engineering dictates.

Two types of elements are used in TC detectors-filaments and thermistors. Filaments are wire coils similar to incandescent bulb filaments. They are typically operated from 80 milliamperes to 300 milliamperes. The sensitivity increases as the cube of the current. The thermistor element detector is highly temperature sensitive. By comparison, a thermistor element has a greater sensitivity than a filament detector up to about 60 °C and is less sensitive (analytically useful) at higher temperatures.

Flame ionization detector: The flame ionization detector (FID) is used when greater detector sensitivity is required or when the application can use the selective response of the FID. The FID is sensitive to hydrocarbons and other organics. Yet the FID is insensitive to compounds that will not ionize in the flame, such as oxygen, nitrogen, moisture, carbon monoxide, and carbon dioxide; however, co-elution of these compounds with a measured component may affect FID response. The FID response is not affected by temperature; nevertheless, the detector must be operated at a temperature where condensation will not take place (above 80 °C). The FID atmospheric vent must also be heated or configured to prevent water (a combustion product) from condensing. Bubbles in the line or a momentary restriction of the flame arrestor will cause baseline upsets. Safety precautions normally provided by the GC manufacturer include a hydrogen shut-off if the FID air supply is lost or if the oven purge where the FID is located is lost. A flame arrestor is normally located on the FID vent. The user must take the necessary safety precautions when installing the hydrogen system.

Other detectors: Other detectors may be used because of their selective response or sensitivity to specific compounds. For example a GC separation may be simplified by use of a detector that responds only to the component being determined. Some detectors are very sensitive to a class of compounds. The flame photometric detector (FPD) is widely used with GCs in refineries to sense low concentrations of sulfur-containing compounds. The thermionic detector (TID) is very sensitive to chlorine and other halogens. The extreme sensitivity of these ionization detectors necessitates additional care in that the supply gases must be cleaner and the electronics must be more noise free than for the less sensitive detectors. Even so, these detectors are field proven and practical for process applications.

17.6.1.7 Critical Parameters

The gas chromatograph relies upon reproducible parameters for accurate analyses. To relate component concentration to peak area the same conditions must exist when analyzing the sample as existed when calibration was established to relate component concentration to peak area by way of calibration factors.

The individual component retention time, or the time from sample inject to the maximum detector response, must be the same for every run. This is controlled by the carrier flow rate and column temperature. For a column in a TPGC, the temperature ramp must be very reproducible. If flow or temperature conditions change, component identification and area measurement can be incorrect.

The instrumental sensitivity and accuracy is a function of retention time, sample size, and detector conditions (stability and response). Peak area measurements are significantly affected by variances and these parameters are thoroughly controlled in a well designed gas chromatograph.

17.6.2 Sample System

The function of the sample system is to deliver a representative sample of process fluid to the gas chromatograph in a timely manner. This is covered extensively in Chapter 4.

17.6.3 Chromatograph Controller

The controller provides the means for automatic chromatograph operations and data presentation. The controller switches the analytical column and stream select valves, transforms the detector signal into a usable form, executes component gating, and performs housekeeping and troubleshooting functions. The controller houses the necessary power supplies, timers, software, memory, calibration routines, and provision for manual operation. The gas chromatograph controller may be a part of the standalone GC, located in the process area, or may be located separate from the analytical function.

The operator interface should be evaluated according to its simplicity. The two common approaches are to incorporate a commonly used or known interface such as a personal computer (PC), or use a proprietary programmer with functional keyboard labeling. In either case, a minimum number of key strokes or discrete movements should be required for data entry and control.

17.6.3.1 Chromatograph Controller Timing

Timing is a basic requirement of gas chromatography in that each operation must be initiated at exactly the same time for each analysis. Sample injection must be at the same time every cycle. Actual component peak retention time must correspond to values specified in the controller’s time table, which are used to identify chemical compounds eluting from the column. Column switching must be reproducible when it occurs in order to isolate groups of peaks. Other operations must occur in each cycle. According to the program timing entered into the controller, interfacing circuitry and electronic signals activate valves and initiate software procedures to accomplish the GC method.

17.6.3.2 Chromatograph Signal Processing and Gating

The GC must have the capability of presenting a complete chromatogram for use in programming and maintenance. Output to plant operations should be limited to only concentration data for the peaks used in process monitoring and control. Chromatograph presentation is the graphic display of the measured peaks that is used for separation analysis to evaluate column performance. The attenuation is set to keep the peaks on scale for the recorder, plotter, or screen display.

The gate or window is a time interval during which a given component will elute. The gate or window is used to identify the peak to the controller, so the proper calibration data may be used to calculate concentration, and so the proper output will transmit the data. In practice the gate or window has an open time and a close time entered in the controller time table. These times bracket the peak.

17.6.3.3 Stream Selectors

Controllers that handle multiple sample streams are equipped with logic which opens the proper stream inlet valve to the analyzer sample inject valve. Timing is established to advance the stream select valves to the next stream to be sampled immediately following the sample inject. This stream advance allows the analyzer portion of the sample system to be purged with the next sample for nearly the length of the analysis before it is injected near the beginning of the next analysis. Variations of this principle by different manufacturers protect against an insufficient purge time if the stream sequence is manually changed after the next stream is automatically selected. Provisions are usually made to run the streams in any sequence, temporarily delete a stream, and manually run a stream out of sequence.

17.6.3.4 Auto Zero

The auto zero performs two functions. It establishes a reproducible level as the base line for chromatogram presentation, and maintains auto zero for the microprocessor’s CPU.

Long-term detector drift could place the base line out of the high-resolution level of the analog to digital converter for the CPU. The auto zero action is more than adequate to maintain the proper zero range.

17.6.4 Data Presentation

Composition data should be presented in its most usable form. Data presentation capabilities are numerous and must interface with plant communication systems, the operator, and the analyzer technician. Process communication systems generally have a Digital Control System (DCS) as the heart of the system. A DCS may accept digital or analog signals. Digital communication may require some software development for interfacing; however, once established, digital communication is simple and reliable. Analog signal transmission (4 milliampere to 20 milliampere) is also available for going directly to a DCS or other controllers or trend recorders.

17.7 Calibration

17.7.1 Preparation and Handling of Standards

Calibration of the process chromatograph is usually accomplished by injecting a sample of known composition. Calibration can also be accomplished by making a “grab” sample laboratory analysis comparison. Grab sample comparisons are not recommended since manual sample handling techniques and sample timing normally result in errors in the laboratory analysis used for the comparison.

Calibration blends should be stored in stainless steel cylinders, which may be permanently connected to the calibration sample inlet of the analyzer sample conditioner. The cylinders should be large enough to hold sufficient calibration sample fluid for at least 4 months normal use. A minimum of 8 gallons of liquid sample or a size 1A gas cylinder is realistic.

The calibration blend should closely approximate the design process stream composition. As nearly as possible, the concentration of each component in the blend should be at least 50 %, preferably 80 % to 90 %, of its calibrated range. Components that are not measured should not be left out unless, both user and vendor are satisfied that column performance is unaffected by these omissions. Omission of, or substitution for, unmeasured components may be desirable in some particular instances, but care must be exercised in selecting such pseudo-blends to ensure column resolution performance remains the same for the components of interest.

Calibration sample blends must be injected into the analyzer in the same state as the process sample (that is, liquid samples as a liquid, and gas samples as a gas). Storage conditions (pressure and temperature) of the cylinders must be such that the composition does not change due to condensation, vaporization, or adsorption. Vapor samples may require storage in the liquid state and vaporization prior to injection.

Maintaining a calibration sample so that the blend remains constant requires careful consideration of the characteristics of the blend and the ambient conditions of the cylinder mounting area. Do not subject sample cylinders to wide extremes in temperature. Do not combine components in the calibration sample that are reactive (for example, H_2S and SO_2). Do not combine components that tend to separate into phases. In some applications, two separate cylinders with separate calibration inlets to the analyzer are required. In a few cases, the sample must be prepared just prior to analysis in saturation vaporizers or permeation equilibrium devices. For example, calibration samples for part-per-million water analysis are extremely difficult to maintain in static storage and may require a device to blend the sample just prior to injection. In a few extreme cases, some device may be required to shake or roll the sample cylinders to maintain uniform sample composition.

Calibration samples should be run routinely to assure proper analyzer performance. A procedure should be developed to introduce the least disturbance to operation of the process unit. Computer-controlled chromatographs can be programmed to perform internal normalization calibration procedures during each analysis performed between calibration samples and be programmed to alert operators to impending faults and abnormal performance. In addition to routine maintenance calibration checks, a simple calibration check procedure should be available to the process operator for those applications where the composition input from the analyzer impinges directly on unit operations.

Due to the nature of the chromatograph, units of calibration for liquid samples are in liquid volume percent or parts-per-million and for vapor and gas samples in mole percent or parts-per-million. If the molecular weight and specific gravity of the sample does not vary, then these values can be directly related to other units such as weight percent. In the case of computer applications, if total stream composition is measured, the output can be programmed in any desirable set of units.

17.7.2 Calculations

The process GC performs all calculations to relate peak data to component concentration. The process sample is analyzed and a process-compatible signal that is proportional to component concentration is produced for plant operation. In order to establish the relationship of component concentration to GC output signal, the GC must be calibrated. Several techniques may be used. The external standard method assigns a response factor based upon detector response to a known concentration of the component. The normalization method divides the component area by the total area of all the peaks to determine concentration. Comparison with lab data may also be used, but the calibration method must be compatible.

The detector response to a given component in the sample is evaluated by measuring the component's peak height or area. Peak area is in arbitrary counts accumulated as the peak elutes from the column. The detector's signal (amplitude) is changed from analog to digital (A/D), and the digital counts are stored for each sampling of the signal. Detector signal sampling is done at some uniform rate (for example, 32 per second) which is multiplied by the amplitude to produce an area value, in counts, for each reading so the sum of these readings is proportional to the peak area.

Whether measuring peak height or area, a response factor must be assigned to each peak from standardization or from the literature to transpose the counts to meaningful data.

The external standard method uses a chemical mixture of known concentration to establish the GC response for each component of interest. Detector response factors are based on the calibration run. The standard sample is manually introduced, or programmed to be automatically introduced into the GC while the GC is in the calibration mode. The outputs to the communication network are maintained at the last analysis value. At the end of the run, the controller's microprocessor calculates a response factor based upon the peak area and the component concentration for the peak entered in the method tables.

$$K = C \div A$$

where

K is the response factor;

C is the component standard concentration;

A is the corrected area counts.

The response factor is used to calculate component concentration for a normal process run.

$$C = X \times A$$

A is the number of counts corrected for the baseline. The baseline is established by peak sensing values entered in the method tables.

This method does not require all peaks to be detected.

Normalization requires all peaks to be measured. Response factors are determined by calibration as under the external standard method for all components by the GC. The area of each component is multiplied by the response factor before concentration is calculated.

Individual component concentration on the process analysis is calculated by dividing the corrected area of the component of interest by the total corrected area.

Rather than using an external standard to establish component response, relative response factors from the literature may be entered manually. Component concentration is calculated by the GC as above, and calibration is not required.

The GC response may be compared to a laboratory analysis of the same sample to establish response factors. Several comparisons should be averaged to reduce spread. The response factor is, then, manually calculated and entered into the GC tables. Special attention should be given to timing and lab sampling conditions. The lab sample should be taken at the time the GC injects its sample, and the lab sample point should be the same as the GC sample point.

The GC provides an output for use in process monitoring and/or control. The electronics must be independently calibrated to produce the desired process signal for a given component concentration. The analog outputs must be electronically adjusted to produce a true value (for example, 4 milliampere to 20 milliampere). This procedure should be in the vendor instruction manual. Digital values are true, and need no correction. Output ranges for a given channel are established by the data entered in the GC method. These ranges may start at zero, or zero suppression may be used to provide better resolution in a visual readout or better accuracy for electronic outputs (for example, 15 % to 20 %).

17.8 Installation and Inspection of New Analyzer Installations

Inspection of new analyzer installations usually begins in the analyzer vendor's shop prior to shipment of the analyzer to the field or to other installation vendors. During this inspection, the user should witness the operation of the chromatograph and all associated components to be included in the system. The analyzer, the programmer, auxiliary switches, and when possible, the recorders to be used in the field system should be used for the inspection tests.

Demonstration chromatograms and, as applicable, trend records, or other outputs, as intended in the final application, should be run on the same calibration samples as those to be used in the field. These demonstration chromatograms should be retained for subsequent comparison to field run chromatograms during pre-startup testing and troubleshooting. At this point, all of the hardware to be used is proven to be operable.

The second inspection may come at the facility of a system vendor who houses the analyzer prior to shipment to the field. This inspection should encompass the sample tubing (including insulation and tracing) to and from the analyzer, the electrical wiring, housing heating and cooling, mechanical mounting, maintenance accessibility, and all necessary appurtenances. The same operational test conducted in the analyzer vendor's shop should be rerun using the installed sample tubing runs. In addition to the mechanical and performance inspection, analyzer system documentation should be inspected to determine that all required documentation is furnished.

After the analyzer, or system including the analyzer, is delivered to the field a complete mechanical inspection should be made to assure proper tie-ins to field run sample tubing, electrical power, and signal wiring. Operational testing can then be started as outlined under initial startup procedures.

17.9 Initial Startup Procedures

Startup and initial operation are a part of the installation procedure because a need for modification may be revealed during this period. Revision may be required, even when all known requirements have been observed in design and inspection, because of some condition not anticipated. If a change is required at this point, it should be made. No chromatograph that operates properly only part of the time should ever be turned over to, or accepted by, an operating department. It is desirable to have a vendor representative at the user site to participate in checking out the analyzer installation, to perform the initial startup, and to train user personnel on maintenance procedures.

If the chromatograph is sent directly to the field, some users conduct a series of preliminary tests on the chromatograph at the site before permanent installation is made. This permits the user to make a complete test of an instrument under laboratory conditions and with clean samples of known composition. Also, personnel may be instructed on the construction, limitations, and use of the instrument, and the importance of reference chromatograms. Startup procedures in the vendor's instruction book must be followed carefully. These will vary, not merely with different vendors, but also with different instruments from the same vendor.

After the analyzer is installed on the unit and all system components (programmer, recorders, switches, and so forth) are mounted and final wiring and piping hook-ups are made, the user should make a thorough visual inspection. All tubing connections should be checked for proper torque. Spot checking tube connections by disconnecting and checking for proper reaming and deburring should be performed. Utility gas lines should be disconnected at the analyzer connection point and blown out to check for debris. This inspection should verify the proper installation of sample and vent tubing runs, steam tracing, insulation, power wiring, and signal wiring. Wiring continuity should then be checked and proper voltage sources confirmed. When a shelter has a heating and cooling system, then test the heating and air conditioning equipment for proper operation.

Once the user is satisfied that the chromatograph system is properly installed, testing can begin. The calibration sample cylinder is now mounted and connected. With the analyzer inlet valved off downstream of the sample conditioning system, fill the calibration sample line and inspect the fluid for cleanliness. The system is now ready for startup. Startup procedures in the vendor's instruction book must be followed carefully. Avoid short cuts indicated by previous experience; startup procedures vary from application to application even when the analyzers are from the same vendor.

Complete chromatograms should be made of the first analysis and successive chromatograms compared. After operation has stabilized, the chromatograms should be compared with those generated in the vendor shop. Laboratory analysis should also be run on the calibration mixture to confirm the analysis. After satisfactory chromatograms are run, the other process readouts should be activated, and readings and recordings obtained from these readouts compared to the chromatogram. On a new unit all of the above tests and checks can be run prior to unit startup.

After proper chromatograph system operation has been established using the calibration sample, the process sample loops can be commissioned. Again, the analyzer inlet from the sample loop, downstream of the sample conditioners, is valved off so that sample flow cannot enter the analyzer. Establish flow in the sample circulating loop and through the sample conditioner. Take grab samples of the sample flow at the analyzer and have them analyzed for cleanliness. Open and inspect filters, coalescers, and other sample system devices as necessary or, as a minimum, just prior to analyzer operation. Check to be sure proper sample loop flows and pressures can be maintained and that sample lines are leak free. A sample loop should not be run to the analyzer until repeated tests assure that the sample is clean and that the composition of the sample is representative of the analyzer design specification. On a multi-stream chromatograph, each sample loop should be commissioned in the same manner.

Sample analysis may now be run on the analyzer. Repeated complete chromatograms should now be made of a single stream and the chromatograms compared until stable operation is observed. In multi-stream operation, each stream analysis should be checked in a similar manner. After the chromatograms are run and stable operation verified, the other readouts can be activated and their records compared to the chromatograms. If all readout components are operating properly, the system is on stream, and in multi-stream applications the sample selector can be put in operation.

Automatic control service calls for particular care. The peak integration, holding circuits, and other elements in the control system should be carefully checked until reliability is established. Initially it is advisable to keep the instrument out of the control circuit and observe the records. When it is placed on control, its action should be limited by stops in the control system so that failure will not create a severe upset. Prior to placing the chromatograph on control, attenuator values, proportional band settings, and other control function adjustments should be checked.

All chromatograph systems should be closely observed for malfunction during the first few days of operation, before they are turned over to unit operating personnel. During this period of observation, process operators should be instructed in the use of the instrument.

18 Moisture Analyzers

18.1 General

In many gas stream applications, the dew point temperature is the variable to be measured. Dew point temperature is defined as the temperature at which water vapor begins to condense out of a gas. Dew point temperature can also be defined as the saturation temperature corresponding to the partial pressure of water vapor. In moisture measurements, the dew point is that temperature at which the water in the sample begins to condense under equilibrium conditions. Figure 18-1 illustrates the relationship between dew point and water vapor content at any sample pressure. In some gas mixtures other components besides water can condense out, so the analyzer could be sensing a dew point other than that of water.

18.2 Types of Moisture Analyzers

The moisture content of a process stream can be determined by using several types of moisture analyzers. This discussion covers only the more commonly used analyzers in both liquid and gas phases analysis. Because installation practices are similar, all variations of each analyzer will not be described.

Table 18-1 provides a comparison of the various types of moisture analyzers, showing relative features, approximate limitations, and advantages and disadvantages of each type of moisture analyzer. A more detailed description of each type is provided in 18.2.1, 18.2.2, 18.2.3, 18.2.4, and 18.2.5.

18.2.1 Electrolytic Instruments

The electrolysis-type analyzer, continuously and quantitatively absorbs and electrolyzes all water present in a gaseous sample stream entering a cell (see schematic in Figure 18-2). The electrolysis current, which is related

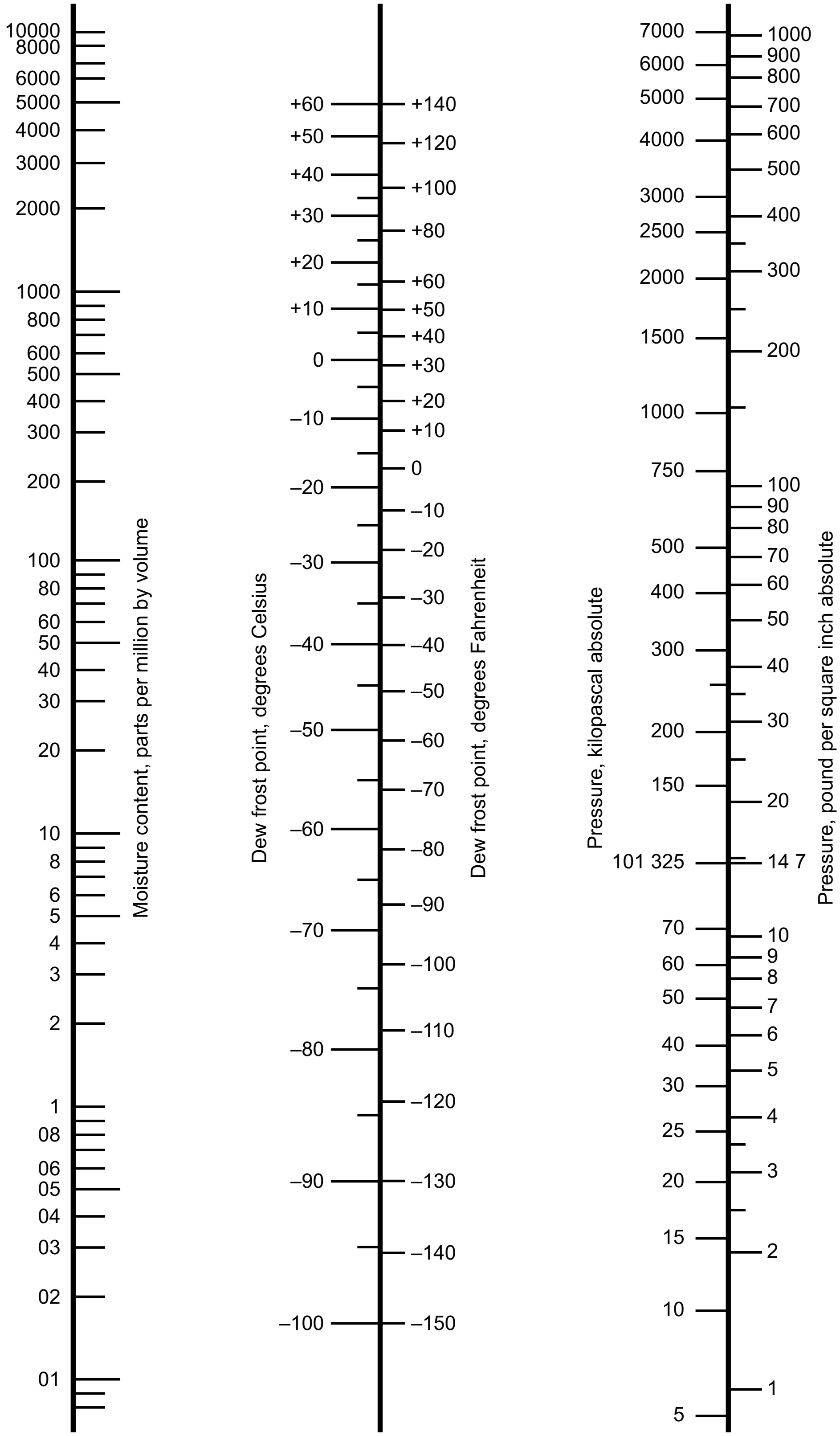


Figure 18-1—Nomograph for Dew Points as a Function of Temperature and Pressure

Table 18-1—Comparison of Moisture Analyzers by Type

	Type of Analyzer				
Feature	**Electrolytic**	**Infrared and Near Infrared**	**Aluminum Oxide**	**Vibrating Crystal**	**Tunable Diode Laser**
Approximate accuracy	+5 % of scale	+2 % of scale	+1 % of reading	+5 % of reading	1 to 5 % of reading
Hysteresis	High	Low	Minimum	Low	Low
Stream phase	Gas	Liquid and gas	Liquid and gas	Gas	Gas
Dew point or moisture range	0 to 1000 ppm^2	2 ppm to 30%	–170 to 140 °F (–110 to 60 °C)	0 to 1 ppm to 0 to 25,000 ppm	0 through 1 ppm to 0 % through 100 %
Maximum pressure	100 psig (700 kPa)	1000 psig (7000 kPa)	5000 psig (35,000 kPa)	100 psig (700 kPa)	30 psig (2100 kPa)
Interference	Hydrogen	Strong infrared absorbers	Compounds absorbed by the dielectric	Compounds absorbed by surface coating of crystal	Application based
Noncompatible compounds	Olefins bases such as ammonia Liquid droplets, excessive water	Dirty fluids Liquid droplets, excessive water	Certain acids and bases with high moisture content, hygroscopic materials Liquid droplets, excessive water	Liquid droplets, excessive water	Liquid droplets, excessive water
Common application areas	Low ppm in gas	Primarily in liquids	All areas in gas	Very low ppm	Applications for ppm and lower

NOTE International System of Units (SI) are in parenthesis. Part per million = ppm; pounds per square in. gage = psig; kilopascals = kPa.

directly by Faraday's law of chemical equivalents to the mass rate of flow of water into the cell, is used as the indication of water content.

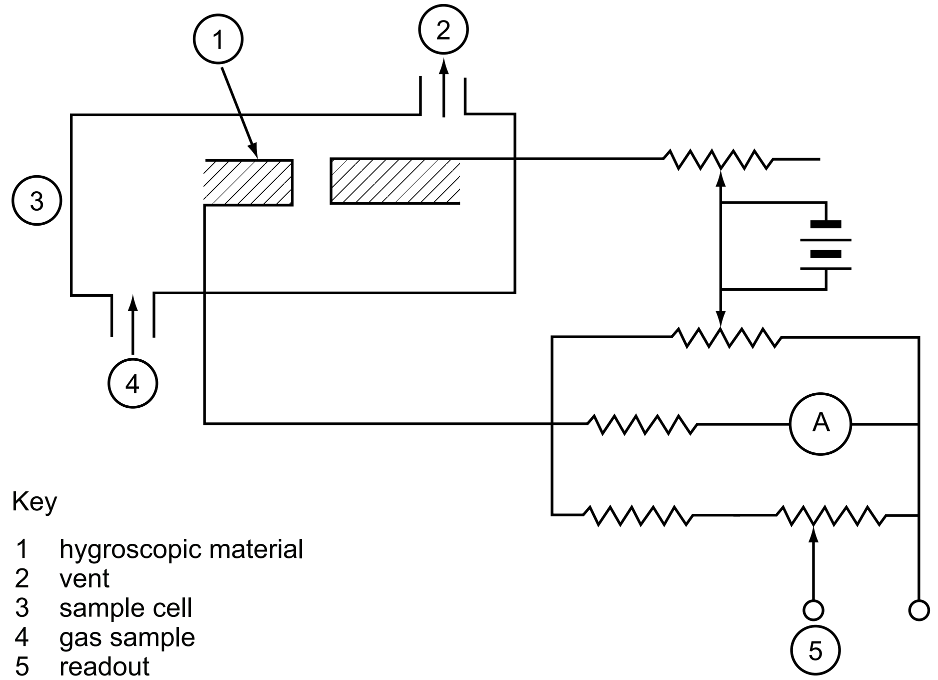
The heart of the instrument is the electrolysis cell in which both absorption and electrolysis take place simultaneously. The cell consists of a tube having a pair of closely spaced wires, usually platinum, wound in a double helix on its inner surface. The space between these wires is filled with phosphorous pentoxide. A direct current voltage is applied to the elements of the cell, and the electrolysis current is measured. With a constant gas flow, the amount of current required for electrolysis is a precise measure of the amount of water present in the parts-per-million (ppm) range.

Electrolysis instruments can be used to determine low concentrations of moisture in liquids. The first step is to strip water from the sample with a dry gas and the second is to pass water vapor and stripping gas through the electrolytic cell. Figure 18-3 illustrates the equipment, showing the dryer for stripping gas, the stripping column, and the gas outlet which is connected to an electrolysis cell similar to that shown in Figure 18-2. The liquid flow rate to the column and the column temperature must be precisely controlled to obtain a quantitative measurement of moisture.

The advantages of the electrolysis-type instrument include the following.

a) Trace amounts of moisture (less than 1 ppm) in gas streams can be detected.

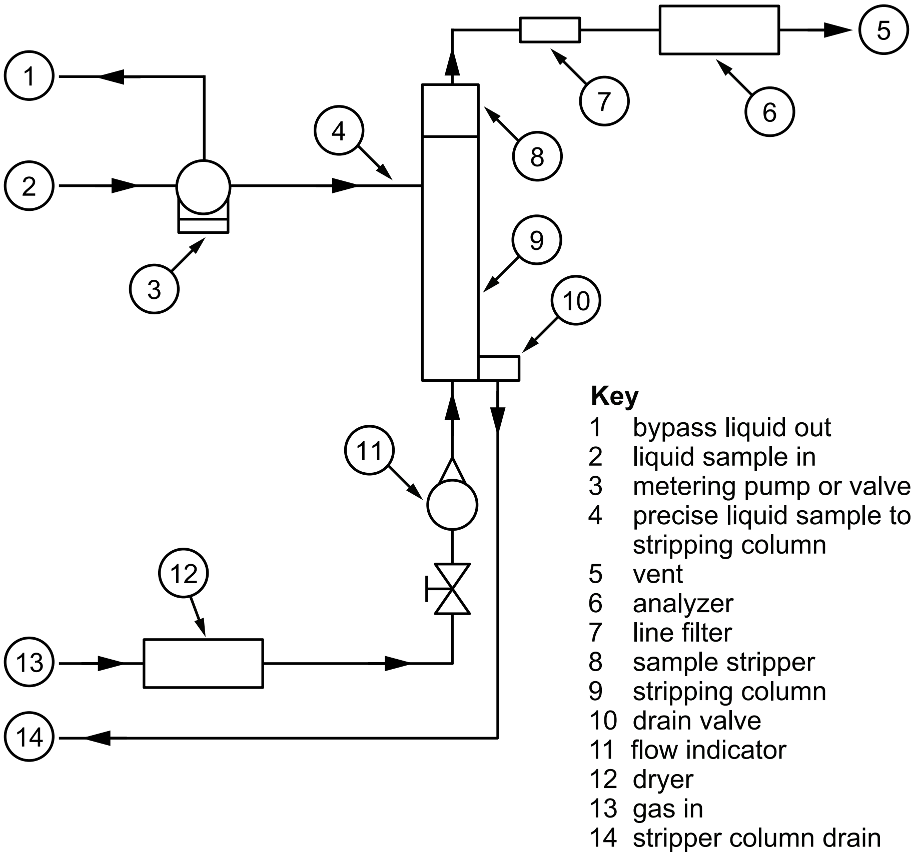
b) Both gas and liquid streams can be analyzed.



Key

1 hygroscopic material
2 vent
3 sample cell
4 gas sample
5 readout

Figure 18-2—Electrolysis Instrument



Key
1 bypass liquid out
2 liquid sample in
3 metering pump or valve
4 precise liquid sample to stripping column
5 vent
6 analyzer
7 line filter
8 sample stripper
9 stripping column
10 drain valve
11 flow indicator
12 dryer
13 gas in
14 stripper column drain

Figure 18-3—Liquid Sample Dry-gas Stripping System

The disadvantages of the electrolysis-type instrument include the following.

a) The instrument is sensitive to changes in sample flow rate.

b) Streams containing materials that will react in the cell, such as butadiene or other olefins (resulting in polymerization), cannot be analyzed.

c) Streams containing basic substances, such as ammonia, which will react with the phosphorous pentoxide to form phosphates, cannot be analyzed.

d) Hydrogen-rich streams sometimes cause erroneous readings because hydrogen will react with the oxygen produced by the electrolysis process, resulting in a higher concentration of water than is present in the sample.

e) Streams containing more than 2000 ppm of water will saturate the phosphorous pentoxide, causing a short in the electrodes, or will wash the phosphorous pentoxide from the cell.

f) At water concentrations above 100 ppm, the analyzer exhibits a great deal of hysteresis when a change in the moisture content of the process stream occurs. Therefore, this analyzer may not be suitable where tight moisture control is required.

18.2.2 Infrared and Near Infrared Instruments

Figure 18-4 illustrates an infrared analyzer. Infrared energy from a standard incandescent lamp is directed through a rotating filter wheel containing two narrow band pass filters. These filters allow infrared energy of the wavelength that is absorbed by water and a reference wavelength that is not absorbed by water to alternately pass through the sample cell to the detector. The measurement and reference signals from the detector are amplified and compared in the amplifier control section. The ratio of these two signals is a measure of the moisture content in the sample. This ratio signal is amplified and converted into the output signal to the readout device. Infrared techniques can be adapted to either liquid or vapor phase analysis in concentrations from low parts-per-million to several percent.

The infrared analyzer provides the following advantages.

a) Both liquid and gas samples can be analyzed.

b) A wide range (0 to 2 ppm to 0 to 30%) of concentrations can be detected.

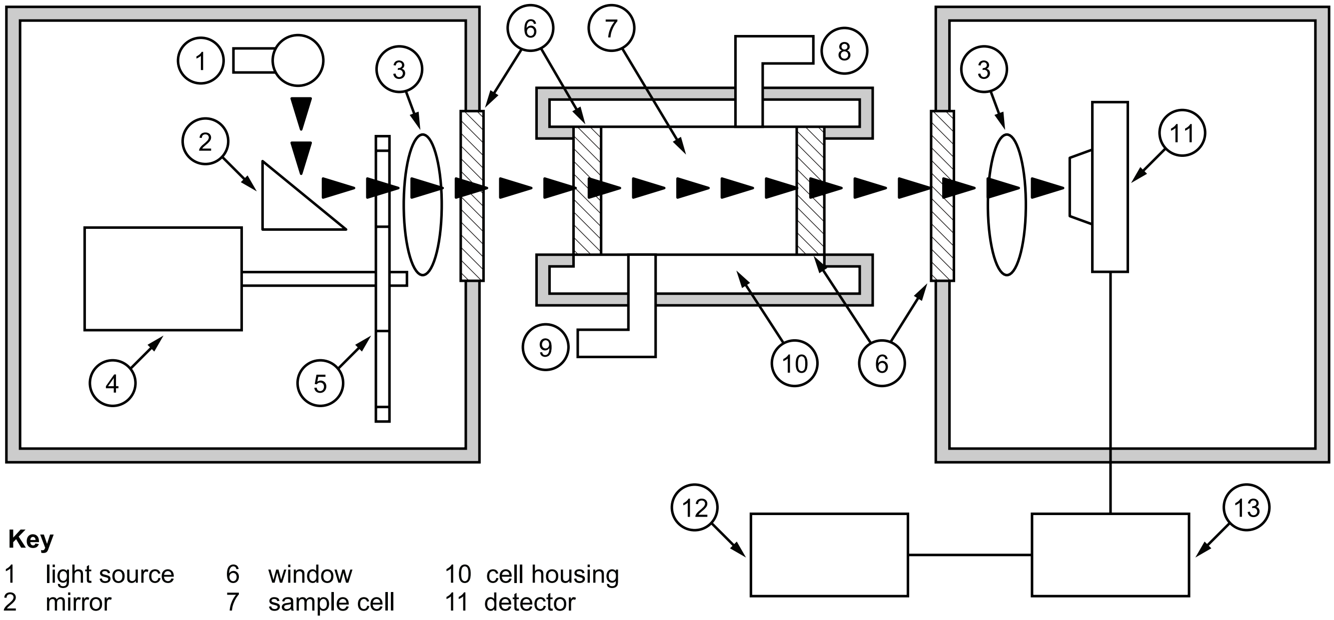
The capability of the infrared analyzer can be compromised by dirty samples deposited in the sample cell resulting in a decrease in the light transmitted to the detector.

Tunable Diode Laser (TDL) analyzers are a specific kind of infrared analyzer that uses a very high resolution diode laser as the source of the infrared beam. The precision of the beam wavelength helps it avoid the cross interferences found with typical infrared analyzers. And since the TDL analyzer's sensing elements never touch the sample (only the laser beam does), there is no concern of the sample causing damage to the analyzer.

18.2.3 Aluminum Oxide Instruments

The aluminum-oxide moisture analyzer employs a sensor probe, Figure 18-5, inserted into a liquid or gaseous slipstream for measuring moisture content. The sensor consists of an aluminum strip that is anodized by a special process to provide a porous oxide layer. A very thin coating of gold is then deposited over this structure. The aluminum base and the gold layer form the two electrodes of essentially an aluminum-oxide capacitor.

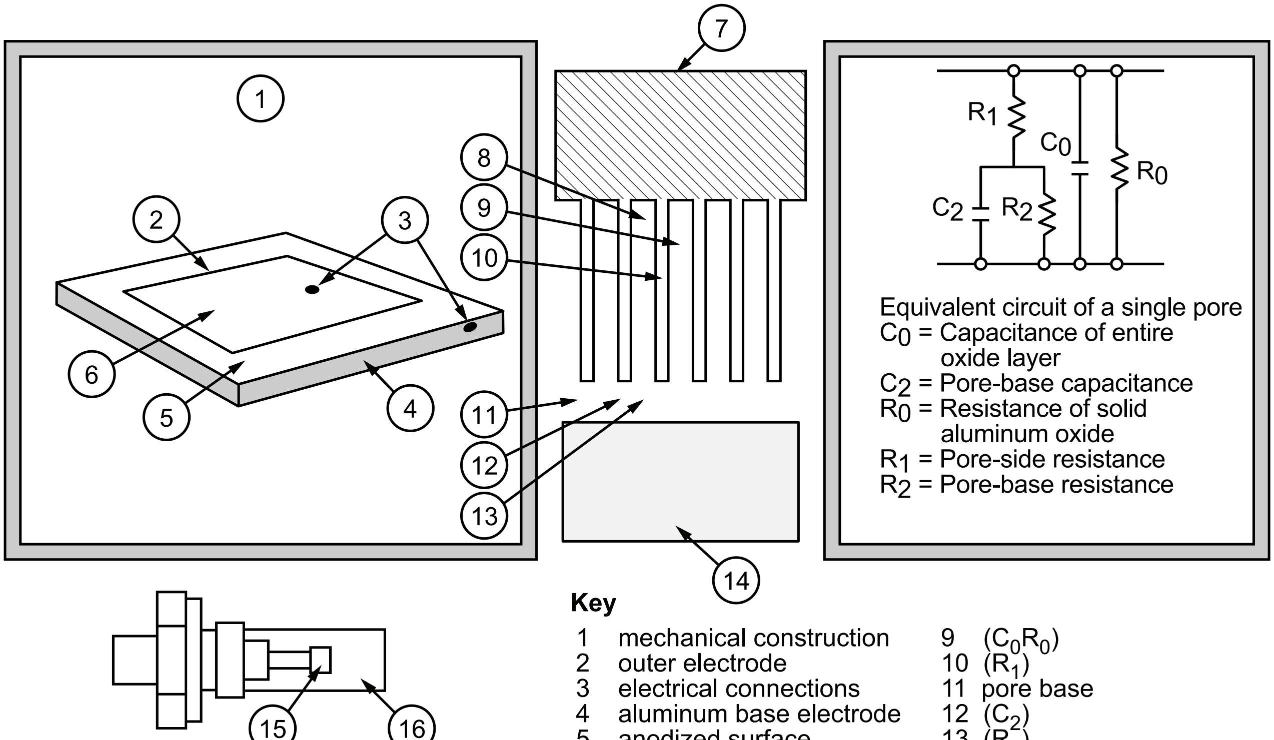
Water molecules transport through the gold layer and equilibrate on the pore walls in a manner functionally related to the moisture content of the sample stream. The number of water molecules absorbed on the oxide structure determines the conductivity of the pore wall. Each value of pore wall resistance provides a distinct value of electrical



Key

1 light source
2 mirror
3 lens
4 motor
5 filter wheel
6 window
7 sample cell
8 out
9 in
10 cell housing
11 detector
12 readout
13 amplifier control section

Figure 18-4—Infrared Analyzer



Key

1 mechanical construction
2 outer electrode
3 electrical connections
4 aluminum base electrode
5 anodized surface
6 metal evaporated over anodized surface
7 outer conductor
8 oxide
9 (C_0R_0)
10 (R_1)
11 pore base
12 (C_2)
13 (R_2)
14 metal
15 sensor
16 sintered stainless steel protection shield

Figure 18-5—Aluminum Oxide Probe

impedance, which is a direct measure of the water vapor pressure in the sample. Each sensor probe has its own calibration curve and is capable of measuring water content of less than 0.1 part per million up to 100,000 ppm in gas service and up to 1000 ppm in liquids. Analysis is limited by the saturation concentration at the probe surface temperature.

Advantages of the aluminum-oxide sensor include the following:

a) Both liquid and gas streams can be analyzed.

b) A wide range of concentrations can be measured.

c) The instrument provides multi-channel capability.

d) The instrument provides a rapid response to changes in moisture content.

e) Probes can be installed in low or high-pressure systems from a vacuum to 5000 pounds per square in. gauge (35,000 kilopascals).

f) A simple sampling system can normally be used.

Disadvantages of the aluminum-oxide sensor include the following:

a) The probe is susceptible to severe corrosion in the presence of certain acids or bases in streams that have a high moisture content.

b) The probe can be poisoned by hygroscopic materials. If such components are present in the stream to be analyzed, the manufacturer should be consulted on the suitability of the analyzer for the application.

c) Exposure to high levels of moisture will result in the sensor being unusable for an extended period.

18.2.4 Vibrating Crystal Type Instruments

In the vibrating crystal analyzer, Figure 18-6, moisture content is determined by comparing the changes in frequency of two hygroscopically coated quartz crystal oscillators which, when dry, vibrate at a nominal 9 megahertz. Water vapor is alternately absorbed and desorbed on the measurement crystal, resulting in a mass difference with a corresponding change in frequency. These changes in the mass of the coating are compared electronically, and the moisture content is indicated on the analyzer readout in parts-per-million by volume. This analyzer can be calibrated to readout in ranges from 0 to 1 ppm full scale to 0 to 25,000 ppm full scale.

This type of analyzer overcomes the problem of measuring dynamic changes of moisture concentration by employing two crystals and a system for flow switching. One crystal is exposed alternately to the moist sample gas and then to a dry reference gas every 30 seconds. The other crystal is kept dry and used as a reference.

The sampling system for the vibrating crystal analyzer must be designed so that liquid cannot be transported to the analyzer because liquid droplets may damage the measurement cell.

The advantages of the vibrating crystal analyzer include the following.

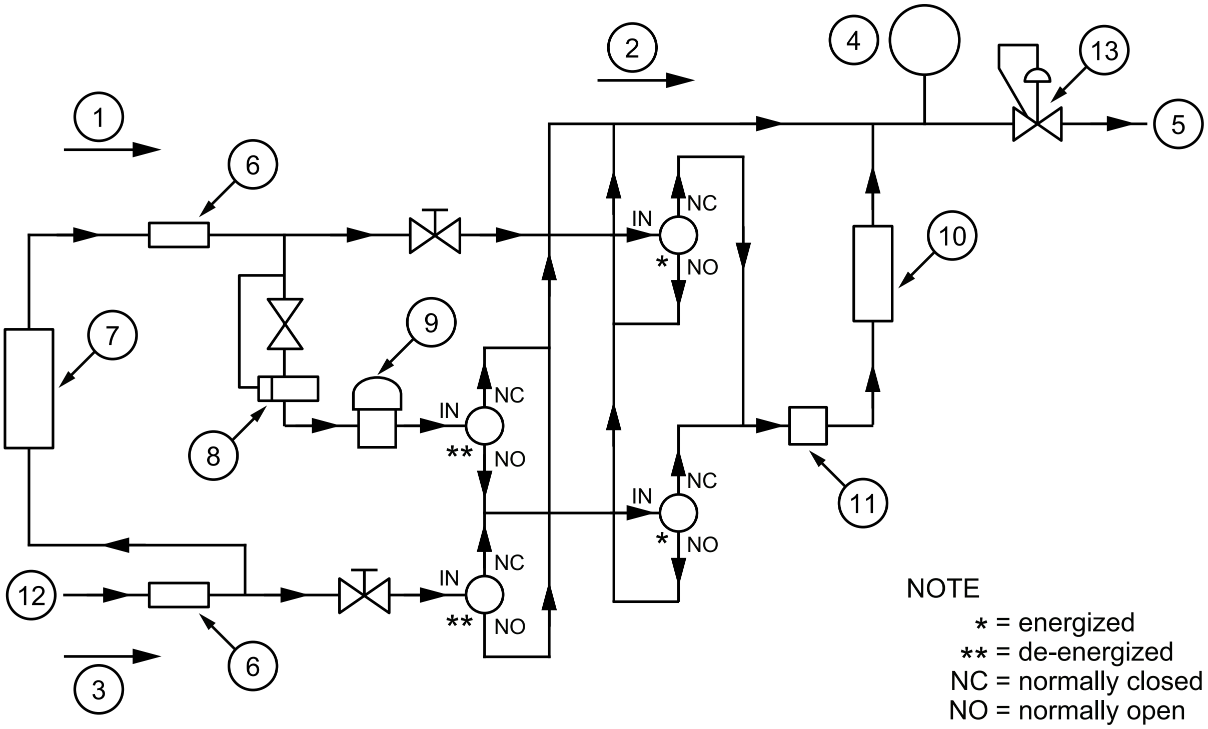
a) The instrument is very sensitive to low concentrations of moisture and to small changes in concentration.

b) The instrument responds rapidly to changes in moisture concentration.

c) Normal sample flow variation does not affect analysis.

d) The instrument needs little maintenance and provides a long life.

e) Very low detection limit (0.02 ppmv).



NOTE
* = energized
** = de-energized
NC = normally closed
NO = normally open

Key

1	reference stream	5	exhaust	9	internal calibrator (optional)
2	exhaust stream	6	filter	10	rotameter
3	sample stream	7	dryer	11	cell
4	0–30 psi	8	flow controller	12	sample in
				13	back pressure regulator (15 psig)

Figure 18-6—Flow Diagram of a Vibrating Crystal Moisture Analyzer

The disadvantages of the vibrating crystal analyzer include the following.

a) It is relatively expensive.

b) The instrument is not directly applicable to liquid samples.

c) The cell can be poisoned by excessive water concentration in the sample.

d) Water droplets can damage the cell coating.

e) The crystal is sensitive to other materials absorbed by the coating.

18.2.5 Other Instruments

There are several analytical instruments other than those mentioned that are capable of determining moisture concentrations. Automated Karl Fischer titration, the mirror dew point type, hygroscopic salt, capacitance, and so forth, and chromatographic analyzers have been used successfully. Because these instruments are generally not used for moisture determination in refinery processes they are not covered in this chapter.

18.3 Sampling Systems

Sample preparation systems must be designed to supply a representative sample to the analyzer. Careful consideration must be given to the design and construction of the sampling system. The designer should know from exploratory analysis the condition, composition, and contaminants of the sample and should design a sampling system with the necessary components to deliver a sample compatible with the analyzer without changing the moisture content of the sample. Special attention must be given to any stream that contains a component which will tend to coat the cell. Additional information concerning good sampling practice is presented in Chapter 4.

18.3.1 Sampling Systems for PPM Analyzers

Proper design and construction of the sampling system are the most important features in the installation of a parts-per-million moisture analyzer. Some of the features the designer should take into consideration are described in this document, and vendor's recommendations should be followed as well.

18.3.2 Moisture Diurnal Effect

Electropolished or silica lined tubing should be used, as well as carefully controlling the sample temperature during transport to minimize diurnal effects in low ppm moisture measurements. Calibration cylinders and pressure reducing regulators should be temperature controlled.

18.3.3 Particle Contamination

The use of sintered stainless steel filter elements will minimize particle contamination. In some installations, it is necessary to install large filters in the main bypass line to remove the bulk of larger particles. Caution should be taken to minimize porous metals that absorb moisture and create a memory effect subject to temperature fluctuations.

18.3.4 Absorption, De-sorption, and Moisture Penetration

The use of stainless steel lines and properly installed (pressure tight) equipment will minimize penetration of moisture from the atmosphere. All components in the system, such as filters, pressure regulators, valves, and flow controllers, should be examined for materials that may absorb moisture from the sample. The use of rubber or plastic diaphragms, oil based pipe dope, and bourdon-type pressure gauges should be avoided.

18.3.5 Vaporizing and Heating

Liquid samples must frequently be analyzed in instruments designed to handle vapors only. It is sometimes necessary to heat the entire sampling system to avoid condensation, which will cause erratic analyzer operation.

18.3.6 Sample Bypass

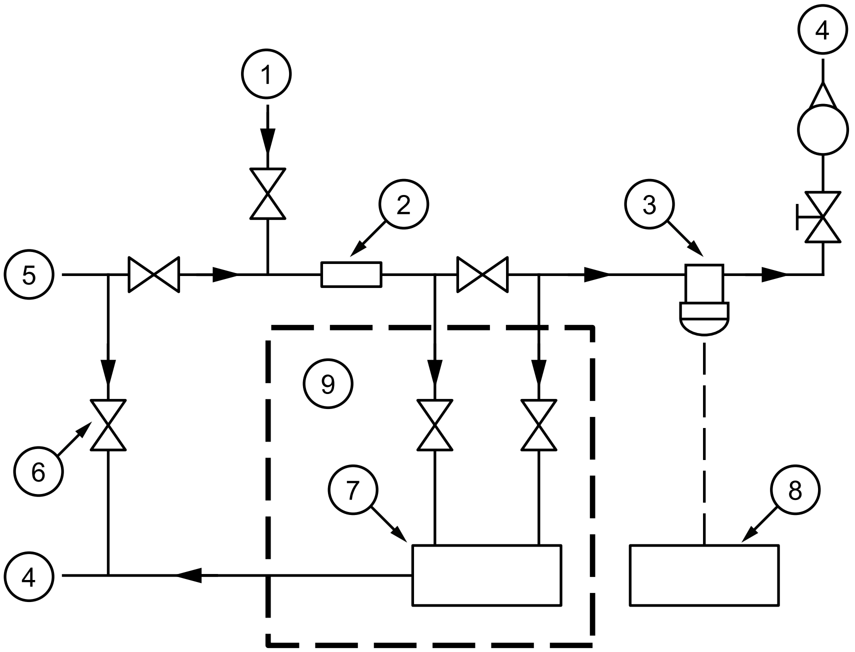
Where conditions periodically occur that could upset or damage moisture analyzers (for example, the catalyst regeneration cycle on a hydrogen reformer), a bypass system can be provided as shown in Figure 18-7 to protect the analyzer. A dry gas purge is recommended to protect the sample cell or probe and to prevent moisture from accumulating in the sampling system while the analyzer is bypassed.

18.3.7 Sample Cell Protection

Cell damage can occur in certain moisture analyzers (such as the electrolysis type) if they are exposed to excessively high moisture content. The manufacturers of these analyzers should be consulted on protection measures to prevent cell damage.

18.3.8 Sampling System Dry Out

After the system has been flushed and purged of contaminating particles and excess moisture, it is necessary to dry out the lines and bring them into equilibrium with the material being sampled. The low parts-per-million sampling system will often require several days to reach equilibrium. Flow through the analyzer cell should not be started until



Key

1	instrument air	4	vent	7	dryer
2	filter	5	sample	8	readout
3	probe	6	bypass valve	9	purge gas drying system

Figure 18-7—Sample Bypass System with Purge Gas Drying

the moisture concentration is less than the maximum scale reading. To assure analyzer availability and reduce dry-down time, it is sometimes necessary to connect a cylinder of dry gas to the system for a day or so of operation.

18.4 Calibration and Startup

Most moisture analyzers require periodic calibration. A moisture generator is usually the most convenient and accurate method for calibrating moisture analyzers. Some analyzers can be calibrated by analyzing a sample from the process stream; however, because moisture tends to absorb or desorb from the walls of a typical gas cylinder, neither method is entirely satisfactory when precise measurements are desired. To avoid this problem, specially coated aluminum cylinders should be used. Problems may also occur while withdrawing a representative sample from the sample containers. In the case of liquid analysis, it is possible to prepare a standard sample if special precautions are taken to dry the sample vessel completely.

18.4.1 Calibrating PPM Analyzers

Some analyzers in the parts-per-million range (for example, the electrolysis type) are not equipped with calibration adjustments. The primary consideration for these analyzers is the precise control of sample flow rate. The actual flow rate can be measured by a soap-film flow technique (timing a soap bubble through a burette) or a wet test meter.

Only trend readings are required in many installations, such as for dryer regeneration, and absolute calibration is not necessary. Some installations will require accuracy checks.

18.4.2 Calibrating Percent-range Analyzers

Standard samples are practical for the calibration of percent-range analyzers. A laboratory analysis of a representative sample withdrawn from the process stream provides satisfactory information for checking calibration.

18.4.3 Moisture Generator

Calibration of an analyzer can be done using a moisture generator. One moisture generator method of calibration is based on the principle of controlled permeation of water through a permeation tube to produce a stream of air or nitrogen at constant moisture.

In the moisture generator illustrated in Figure 18-8, the desired moisture content is obtained by splitting dry gas into two streams: one stream picks up the water vapor emitted at a controlled rate from a permeation tube, and the other steam is a dry gas stream used to dilute the wet gas stream.

The rate of emission of water vapor is controlled by selecting the temperature of the permeation tube and maintaining the tube at this temperature with a high mass heating block. The carrier gas, wet gas, and dry gas flows are controlled by precision flow controllers with micrometer adjustments. This type of moisture generator can provide moisture concentrations from 0.1 to 1000 ppm.

18.4.4 Moisture Blender

Figure 18-9 illustrates a blending-in system used for calibration of moisture analyzers. The entering dry gas is split into two streams: one stream is saturated with water at a known temperature and pressure and the other is a dry steam used for dilution of the wet gas stream. The flow rates of the two streams are precisely measured by rotameters and regulated by metering valves. This permits production of mixtures of gas having water vapor concentrations from 10 ppm to 23,000 ppm. For best accuracy, the water concentrations of the dry gas supply should not exceed 3 % of the generated water concentration.

18.4.5 Humidifier Sample Generator

The humidifier system shown in Figure 18-10 can provide known moisture samples for higher range analyzers. Air is mixed with steam and cooled with water to produce an output stream with a saturation temperature up to 212 °F (100 °C).

18.4.6 Standard Moisture Samples

Another method of calibration is the use of gases with standard moisture contents stored in specially treated aluminum pressurized cylinders. A special lining prevents absorption and desorption of moisture on the cylinder wall so that moisture content remains constant after more than 2 years of storage. Standard samples containing 5 ppm to 500 ppm moisture can be obtained.

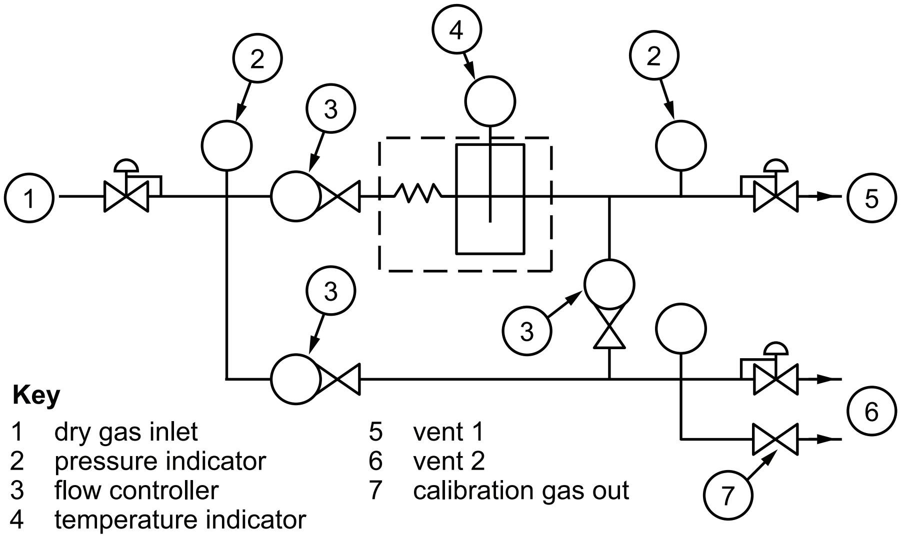
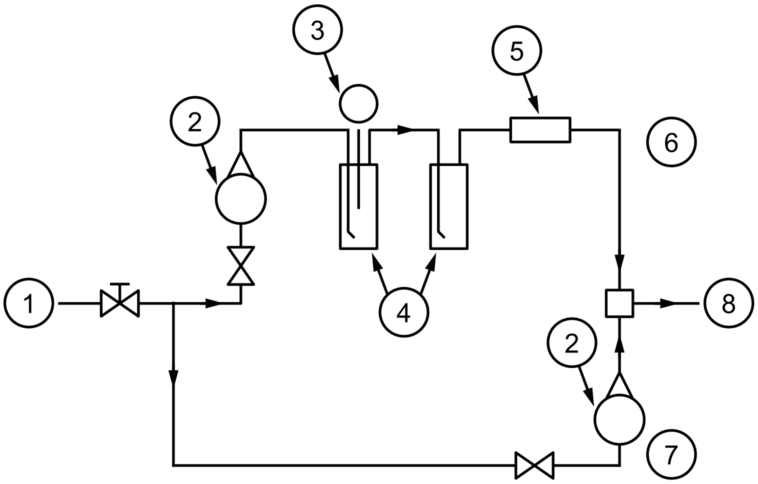


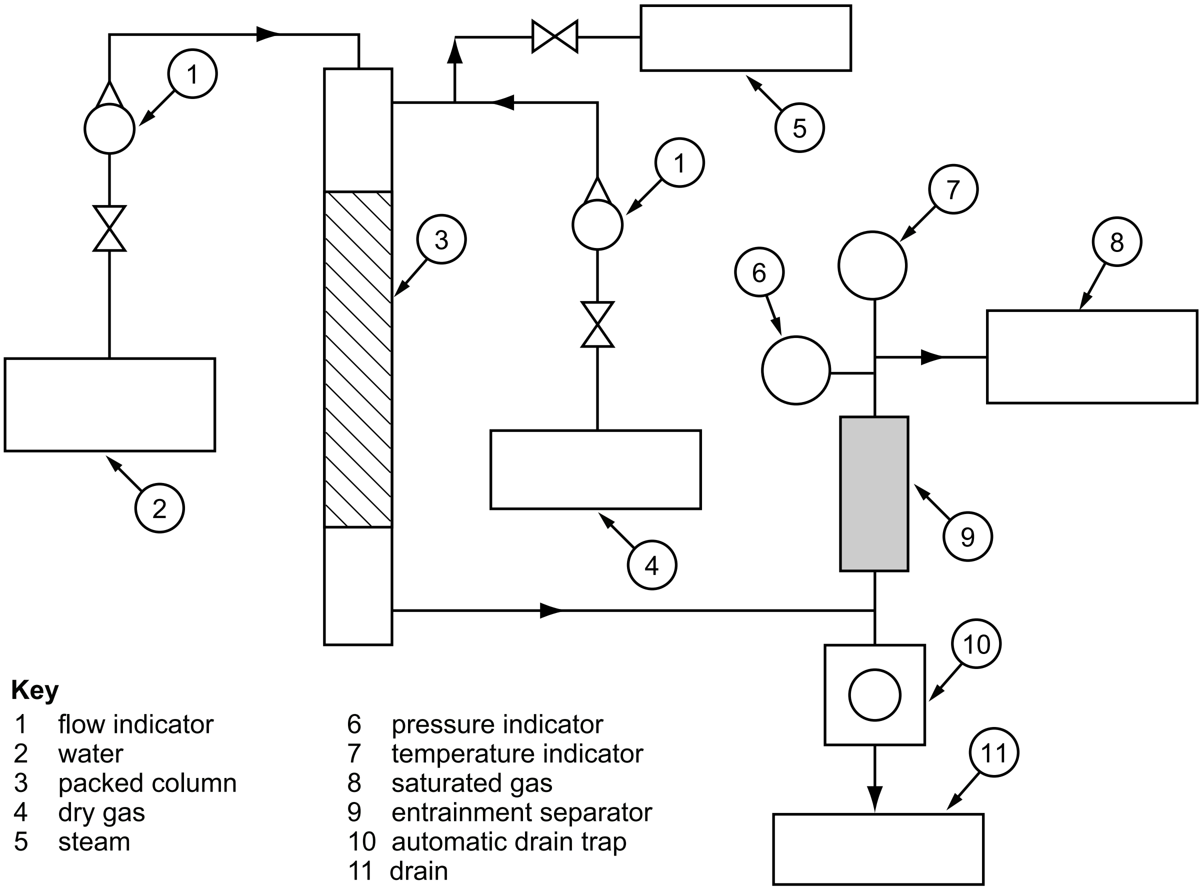
Figure 18-8—Moisture Generator for Calibration Check



Key

1 dry gas in
2 flow indicator
3 temperature indicator
4 saturator
5 filter
6 wet gas
7 dry gas
8 calibration gas out

Figure 18-9—Moisture Blender



Key

1 flow indicator
2 water
3 packed column
4 dry gas
5 steam
6 pressure indicator
7 temperature indicator
8 saturated gas
9 entrainment separator
10 automatic drain trap
11 drain

Figure 18-10—Humidifier System for Calibration Check

19 Oxygen Analyzers

19.1 General

19.1.1 Protecting Personnel

Oxygen analyzers may be used to ensure that sufficient oxygen to support life is available. An accurate and rapid means of sampling and analyzing ambient conditions is required. ANSI Publication Z117.1 provides information on the minimum percentage of oxygen required for life support.

19.1.2 Protecting Equipment

Process conditions frequently require the use of an inert gas to purge or blanket vessels. Oxygen may be a contaminant that would cause degradation of the contents of the vessel or enable an explosive mixture to exist. Continuously monitoring the oxygen content of the purge gas prior to its entering the system may be required. In addition, inadvertent admission of air into the process equipment or vessel may dictate monitoring the blanket gas in the vessel, itself.

19.1.3 Ensuring Product Quality

Product quality is often affected by either the presence or absence of oxygen. Typical applications for oxygen level monitors include the following:

a) catalyst regeneration, to control burning rate;

b) feed, product, and intermediate process streams.

19.1.4 Ensuring Efficient Operations

Excess air is an important parameter in maintaining high efficiency and safety of combustion processes. Flue gas analysis is used to determine the amount of excess air present. This information is then used to control the air-fuel ratio. When the amount of air is optimized, complete combustion and full utilization of the fuel burned is ensured. Unlike most other combustion efficiency indexes, percent of oxygen has a direct relationship to the amount of excess air in the flue gas regardless of the hydrogen-to-carbon ratio of the fuel burned (see Figure 19-1).

19.2 Types of Oxygen Analyzers

There are three basic types of oxygen analyzers currently suitable for refinery process stream applications: the first is based on the electrochemical principle, and the second is based on the paramagnetic principle, and the third is based on laser technology, including Tunable Diode Laser Spectrometer. Other methods of oxygen analysis include gas chromatography, oxygen/combustibles analyzers, and dissolved oxygen analyzers.

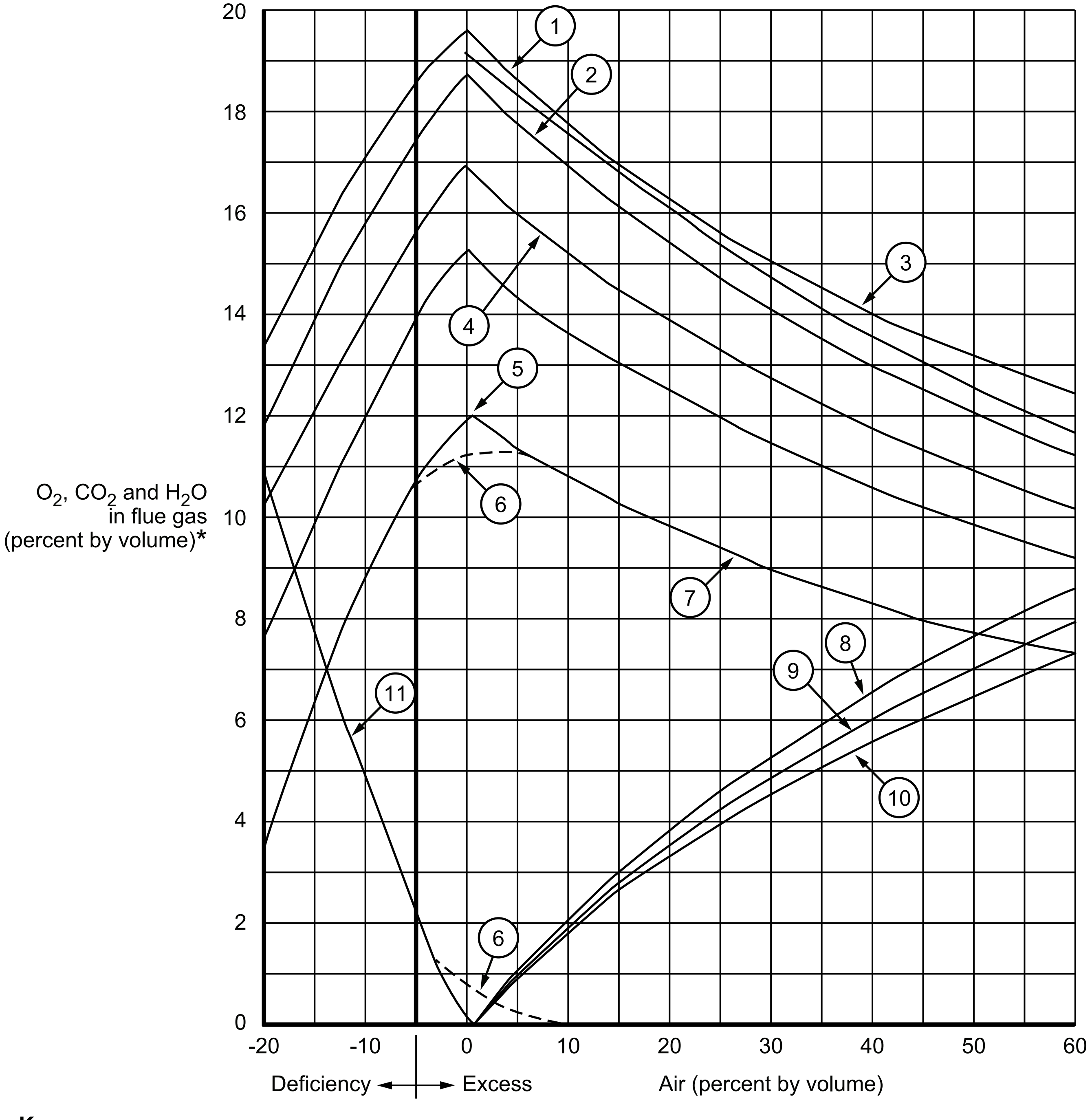
19.2.1 Electrochemical Oxygen Analyzers

19.2.1.1 General

Electrochemical oxygen analyzers consist of at least two metallic electrodes in good electrical contact with an appropriate electrolyte. The chemical reactions occurring in the cell produce an output current or voltage, which is a function of the number of oxygen molecules diffusing into the interface between the electrolyte and the measuring electrode. The various types of electrochemical analyzer cells are conveniently classified by the type of electrolyte used:

a) Aqueous solutions of various metal salts and soluble organic compounds;

b) Zirconia ceramic doped with combinations of calcia, yttria, and scandia.



Key

1 CO_2 coal (anthracite)
2 CO_2 coal (bituminous)
3 H_2O natural gas (wet basis)
4 CO_2 no. 6 fuel oil
5 CO_2 no. 2 fuel oil
6 actual
7 CO_2 natural gas
8 O_2 natural gas/methane
9 O_2 coal (anthracite)
10 O_2 natural gas/methane (wet basis)
11 CO natural gas

* = dry basis except as indicated

Figure 19-1—Distribution of Products from Combustion of Various Fuels

19.2.1.2 Aqueous Electrochemical Type

Figure 19-2 illustrates a typical aqueous electrochemical oxygen analyzer cell. Oxygen molecules diffuse through the membrane to the cathode. At the cathode, they are reduced to OH ions upon acceptance of four electrons produced by an appropriate reaction at the anode. The reactions given below occur in a cell comprised of a platinum cathode, silver anode, and potassium chloride electrolyte. These reactions are typical of those occurring in cells using a noble metal or other non-consumable cathode and a consumable anode as noted in the following:

a) Cathode reaction:

$$O_2+2H_2O+4e^{-} \rightarrow 4OH^{-}$$

b) Anode reaction:

$$4Ag+4KCl \rightarrow 4AgCl +4K +4e^{-}$$

c) Overall reaction:

$$O2 + 2H_2O + 4Ag + 4KCl \rightarrow 4AgCl + 4KOH$$

The materials used in these cells depend upon manufacturers' designs and may be operated in a variety of modes at temperatures between 32 °F and 122 °F (0 °C and 50 °C).

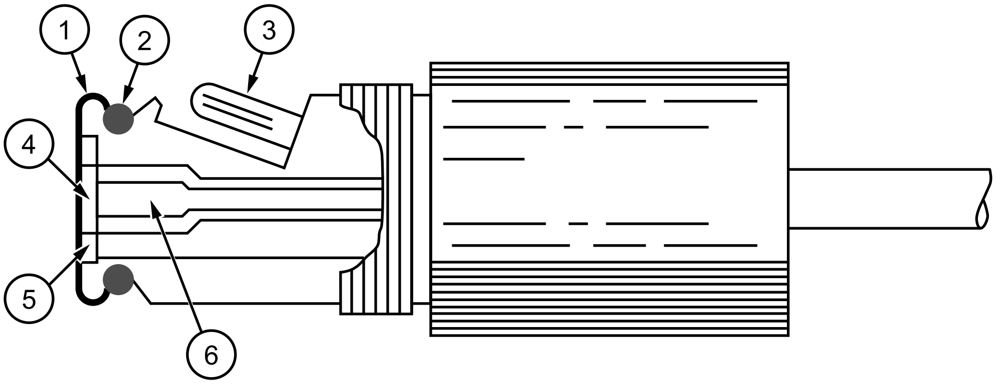
When operated in the potentiometric mode, the open circuit output voltage of the cell is a function of the log of the partial pressure of oxygen in the cathode/electrolyte interface. While nominally responsive to oxygen only, cells also respond in varying degrees to other oxidizing and reducing gases that may be present, such as CO_2, SO_2, H_2S, and NO. Sulfur-bearing gases may poison the electrode if insoluble sulfur bearing compounds form on the electrode surfaces. The output of the cell in the amperometric mode of operation is a current proportional to the number of oxygen molecules reaching and being reduced at the cathode/electrolyte Interface. This mode is subject to the same interferences as the Potentiometric mode. The linear calibration, however, is obtained at the expense of increased sensitivity to the diffusion rate of oxygen molecules to the cathode/electrolyte interface and to the temperature of the cell and the condition of the membrane.

The output of the cell when operated in the polarographic mode is a current proportional to the partial Pressure of oxygen at the cathode/electrolyte interface that flows in the external circuit when a bias voltage is applied between the cathode and anode. This bias voltage is just below the oxidation/reduction potential of the oxygen/electrode system of the cell and suppresses the effects of other electrode reactions with lower oxidation/reduction potentials. Diffusion rate and electrode poisoning are still serious problems. If the sample side of the permeable membrane becomes wet, the cell responds to the oxygen dissolved in the liquid rather than the oxygen content of the sample.

19.2.1.3 Zirconia Electrochemical Type

High temperature zirconia electrochemical cells consist of a thin section of doped zirconia, usually a disk or a tube, whose opposite surfaces are coated with porous platinum electrodes. When operated at a temperature of about 1562 °F (850 °C), the voltage difference between the two electrodes is proportional to the log of the ratio of the partial pressures of oxygen existing at the two electrode/electrolyte interfaces. Figure 19-3 shows a typical arrangement of such a cell with a heated probe.

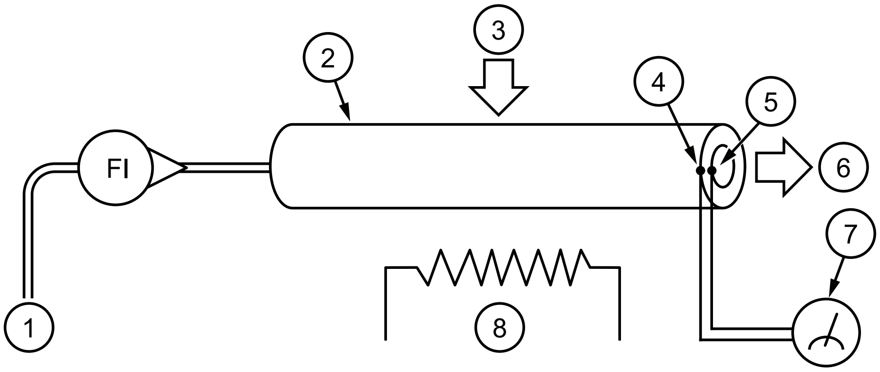
Instrument quality dry air is normally used as the reference gas on one side of the cell, while the other side is exposed to the sample gas. In some models, the temperature of the zirconia must be controlled very accurately if significant errors are to be avoided. Care must be taken to minimize changes of the heat load supplied by the heater. These changes are caused primarily by variations of the temperature and flow rates of the reference and sample gases at the electrode surfaces. An in-situ installation with a heated probe may be limited to maximum flue gas approach



Key

1 teflon membrane
2 "O" ring
3 temperature probe
4 KCl reservoir
5 cathode
6 anode

Figure 19-2—Typical Aqueous Electrochemical Cell



Key

1 sample inlet
2 zirconia sensor tube (850 °C)
3 reference gas instrument air
4 outer electrode
5 inner electrode
6 vent
7 voltmeter
8 heater – 1560 °F (850 °C)

NOTE Voltage output is proportional to the logarithm of the reference and and test gas oxygen partial pressure ratio.

Figure 19-3—Heated Probe-type Zirconia Electrochemical Oxygen Analyzer Schematic Diagram

temperatures from 144 °F to 212 °F (62 °C to 100 °C) lower than the cell operating temperature. High-temperature probes designed for operation in flue gases with temperatures higher than 1400 °F (760 °C) are also available.

These high temperature probes do not have heaters, but a temperature sensor is provided, and the analyzer output is temperature corrected. Any combustible gases present in the sample or reference gases will be burned completely before the gases reach the surface of the electrodes because 1562 °F (850 °C) is well above the ignition temperature of fuel gases. Thus, the partial pressure of oxygen sensed by the zirconia cell will be that remaining after all combustible gases have been burned.

This characteristic becomes quite important when dealing with flue gases containing both excess oxygen and combustible gases, as well as when determining low-residual-oxygen concentrations in inert gases. In the latter case, care must he taken to remove from the sample system all organic contaminants, which will either act as fuel or release oxygen under other than equilibrium conditions. In-situ probe type zirconia analyzers enclose the zirconia cell within a porous ceramic cup through which the sample gas must diffuse. Most other oxygen analyzers using zirconia cells are located immediately outside of the flue and use simple open probes and air aspirators to transport the sample gas over the measuring electrode and back into the stack.

More elaborate sampling systems are used in many instances particularly for dirty, wet applications or when the flue temperature exceeds the temperature limit of the analyzer.

Precautions should be observed when the zirconia electrochemical type analyzer is used on a stack where the combustible content in the stack could reach flammable levels. The cell operating at 1562 °F (850 °C) could present a source of ignition. Refer to 19.4.3 for methods of preventing this from occurring.

19.2.2 Paramagnetic Oxygen Analyzers

19.2.2.1 General

Oxygen molecules are attracted by a magnetic field, thus oxygen is defined as a paramagnetic gas. Gas molecules that are repelled from a magnetic field are called diamagnetic gases. The paramagnetic susceptibility of oxygen is much greater than that of other common gases, most of which are slightly diamagnetic. Other common gases with appreciable paramagnetic susceptibilities (nitric oxide, nitrogen dioxide, and chlorine dioxide) are rarely encountered in significant amounts in refinery and petrochemical operations. Techniques have been developed to use the paramagnetic susceptibility of oxygen to determine the concentrations of oxygen in gaseous mixtures.

19.2.2.2 Magnetodynamic Type

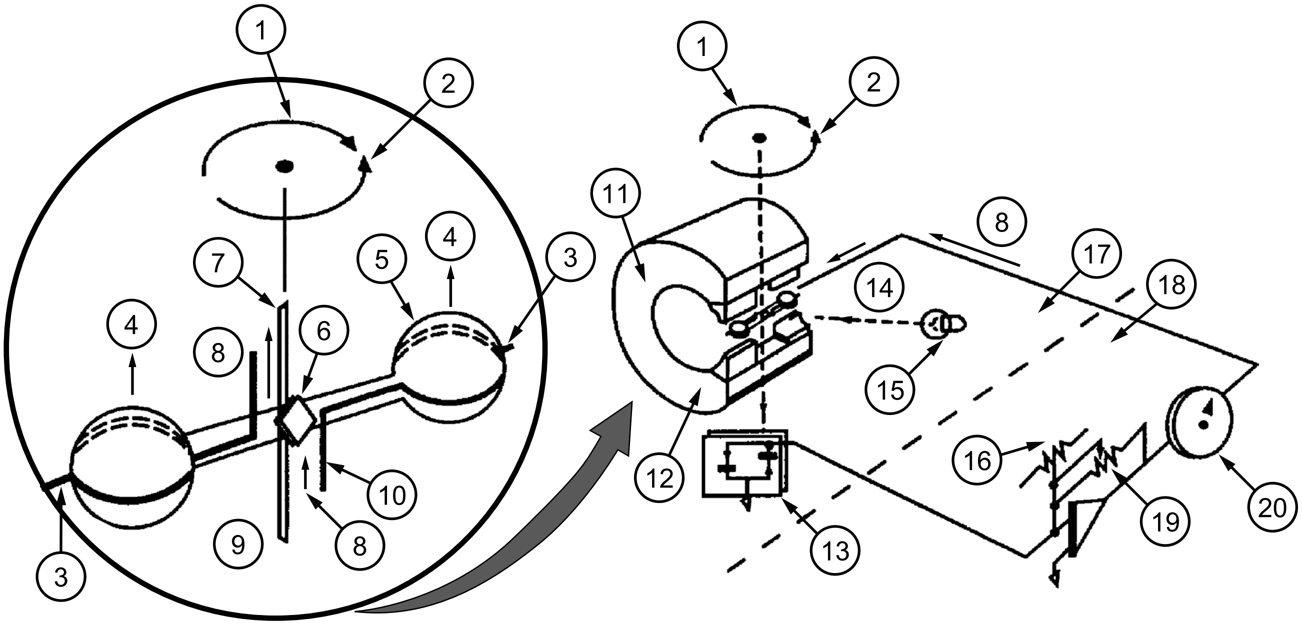
Magnetodynamic oxygen analyzers are based on Faraday's method of determining the paramagnetic susceptibility of a gas by measuring the force developed by a strong non-uniform magnetic field on a diamagnetic test body suspended in the sample gas. The test body is a nitrogen-filled dumbbell, suspended between specially shaped magnet pole pieces by a platinum ribbon. One method is shown in Figure 19-4. The torque tending to displace the dumbbell from its position is a result of the difference between the magnetic susceptibilities of the diamagnetic test body and its surrounding gas. If the gas is paramagnetic, it is drawn into the strongest part of the magnetic field, and the diamagnetic test body tends to be expelled. The magnitude of the torque developed is proportional to the oxygen content of the sample gas when the dumbbell is maintained in a fixed position by one of the various feedback arrangements. The rotational position of the dumbbell is sensed by a light beam projected upon a mirror attached to the dumbbell. The beam is reflected by the mirror to a pair of photocells. The output from these photocells goes to an amplifier whose output is zero when both photocells are illuminated equally.

Another method utilizes the principle of a moving dumbbell. In this case when the dumbbell moves, the amplifier sends its output to the feedback winding, creating a torque equal and opposite to that developed by the oxygen content. This feedback signal is proportional to the oxygen content.

Predictable errors may result when analyzers with a range of 0 % to 2 % oxygen or less are used with samples containing oxides of nitrogen and/or certain hydrocarbon gases whose relative concentrations vary.

19.2.2.3 Thermomagnetic Type

The paramagnetic susceptibility of gaseous oxygen at constant pressure varies inversely with the square of the absolute temperature. The typical configurations used in thermomagnetic oxygen analyzers, shown in Figure 19-5 include two similar heated resistance thermometer elements in contact with the sample gas. Only one resistance element is positioned in the strong magnetic field. When the sample gas contains no oxygen, both resistance thermometer elements lose heat to the sample gas at approximately the same rate. The ratio of the resistances of these elements is sensed in a Wheatstone bridge circuit. When oxygen is present in the sample, the strong magnetic field attracts oxygen molecules into the region of one hot resistance element. The gas in the vicinity of this element becomes heated with a corresponding loss of paramagnetic susceptibility. The colder sample gas entering the



Key

1 displacement torque
2 restoring torque
3 balancing weight
4 electromagnetic axis
5 nitrogen-filled hollow glass test body
6 mirror
7 platinum/nickel alloy suspension ribbon
8 restoring current
9 test body detail
10 titanium wire conductor
11 magnet
12 shaded pole pieces (4)
13 dual photocell BT1.BT222
14 test body
15 surface lamp DS1
16 zero
17 detector magnet assembly
18 control assembly
19 span
20 percent oxygen readout

Figure 19-4—Magnetodynamic Paramagnetic Oxygen Analyzers

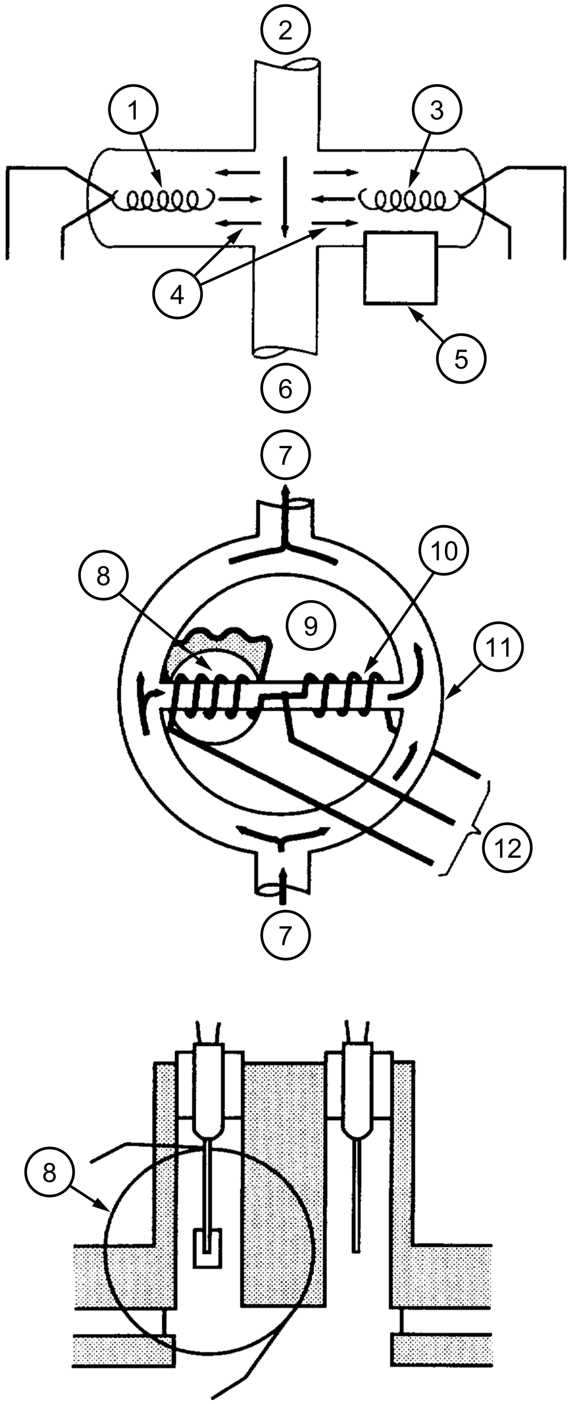
magnetic field thus displaces the heated sample gas giving rise to the phenomena known as the *magnetic wind.* The change in resistance ratio between the two resistance elements is a function of the oxygen content of the sample gas.

Thermomagnetic oxygen analyzers are satisfactory only when the composition of the background gases is relatively constant, since the heat transfer between the hot resistance element and the sample gas is also affected by the heat capacity, thermal conductivity, and viscosity of the sample gas. Errors resulting from changes in background gas composition are not predictable and may be large.

NOTE The surface temperatures of the resistance elements of some thermomagnetic analyzers are above the auto-ignition temperatures of some flammable vapors.

19.2.2.4 Susceptibility Pressure Type

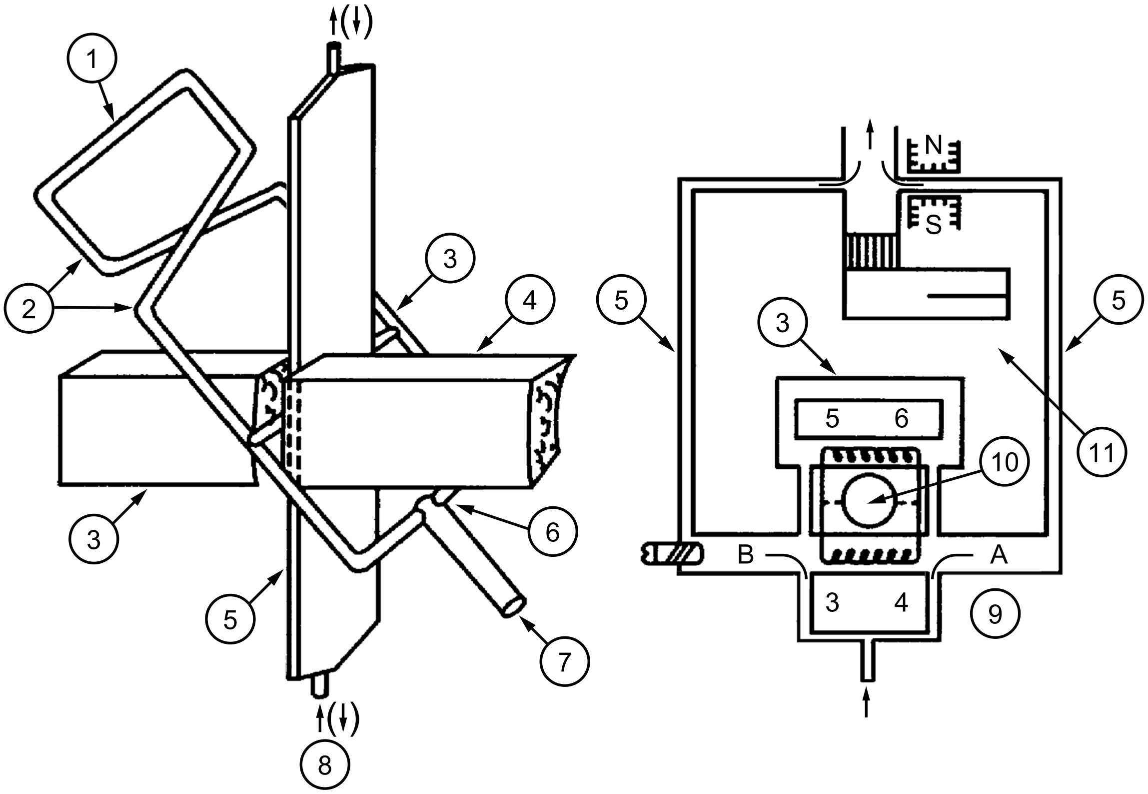
Susceptibility pressure analyzers (Quinke effect) measure the flow rate of a reference gas flowing in a pneumatic bridge circuit, whose balance is altered by the action of a magnetic field on a sample gas containing oxygen. The sample flow in Figure 19-6 is up (or down) through the sample tube. Reference gas is admitted into the pneumatic bridge through the inlet metering orifice. The flow of reference gas in each leg of the bridge is determined by the balancing restrictions. With no magnetic field present, the pressures downstream of the two balancing restrictions will be equal to that in the sample tube, and the flow rate of reference gas in the gas channel containing the flow sensor will be zero. If the sample contains oxygen or other paramagnetic gas, and a magnetic field is applied across the junction of one leg of the bridge and the sample tube, the paramagnetic molecules will be attracted to the magnetic



Key

1 reference element
2 gas in
3 magnetically influenced measuring element
4 diffusion of gas into both cells
5 magnet
6 gas out
7 outlet
8 magnetic pole face
9 windings
10 glass tube
11 ring
12 to remainder of bridge circuit

Figure 19-5—Thermal Paramagnetic Oxygen Analyzers



Key

1 microflow sensor
2 reference gas channel
3 input restriction

4 pole piece
5 measuring chamber
6 main reference gas restriction
7 reference gas

8 analyzed gas
9 nitrogen N_2
10 percent oxygen
11 sample gas

Figure 19-6—Susceptibility Pressure Oxygen Analyzer

field. A pressure gradient develops restricting the flow of reference gas into the measuring cell. Since the total flow rate of reference gas flowing in the system is fixed, some carrier gas must then flow through the gas channel containing the flow sensor and enter the sample tube through the other part. The flow rate past the flow sensor is proportional to the oxygen content of the sample.

The reference gas used is normally an inert gas, such as nitrogen or carbon dioxide; however, when narrow spans are used, the composition of the reference gas should be close to that of the sample.

Isolation of the flow sensor and metering restrictions for the sample gas greatly simplifies the selection of materials of constructions used in the reference channels. A positive flow of reference gas must be maintained at all times or sample gas will enter the reference channel and may damage the restrictions or flow sensor.

19.2.3 Tunable Diode Laser (TDL) analyzers

Tunable Diode Laser (TDL) analyzers are being increasingly used for the measurement of Oxygen. As described in 11.6, TDL analyzers use a diode laser to generate an infrared beam to a highly precise wavelength. Oxygen has a unique infrared absorption in the 750 nm range which is free of any cross interferences.

These characteristics allow a TDL based process oxygen analyzer to measure oxygen reliably. Since the sensor elements of the TDL analyzer never touch the sample (only the laser beam does), sample contaminants have no opportunity to damage the analyzer as might happen with electrochemical or paramagnetic analyzers.

19.2.4 Available Ranges and Limits of Various Methods

a) Electrochemical cells:

  1) Fuel cells, 0 ppm to 2 ppm to 100 % O_2.

  2) Polarographic, 0 ppm to 5 ppm to 100 % O_2.

  3) Coulometric, 0 ppm to 1 ppm to 100 % O_2.

b) Paramagnetic analyzers: 0 % to 1 % to 0 to 25 %.

c) Zirconium oxide: 0 % through 2.5 % to 0 % through 25 %, 0 % through 100 %.

The zirconium oxide method is generally limited to flue gas analysis. The main advantage is that the sample system is reduced to a minimum. Since the temperature of the measurement is high, the gas is well above the dew point, so the analysis is on a *wet* basis; in other words, water vapor is included. Other methods need an extractive sample system including a condensate knock-out, so the analyses are on a *dry* basis.

19.3 Sampling Systems

Continuous-type process analyzers operate most reliably when the sample presented to the sensing element is clean and dry; that is, the sample contains no liquid droplets or particulate matter. Since many oxygen analyzers include sample systems of varying abilities for handling wet and/or dirty samples, the degree of sample preparation required must be evaluated for each installation. Condition of the sample, the ambient temperature, and the nature of the sample system included inside the analyzer should be considered. The design of sampling systems as they pertain to all process analyzers is discussed in Chapter 4. Sampling system problems peculiar to oxygen analyzer systems are discussed in 19.3.1 through 19.3.3.

19.3.1 Flue Gas Sampling

When locating the sample point for flue gas analysis, the possibility of air leakage into the system must be considered. The analyzer should receive a sample of the gases leaving the actual combustion zone, such as in the breaching or firebox sections.

19.3.2 Sampling at Sub-atmospheric Pressure

Sample systems operating at sub-atmospheric pressure present serious operating problems, especially when the sample contains less than about 5 % or more than 95 % oxygen. A small leak located in any sub-atmospheric part of the sample system can easily admit sufficient air to render the resulting determination of oxygen content meaningless. Thus the design of the sample system should minimize the number of possible leaks by limiting the portion of the sample system operating at sub-atmospheric pressure.

The sub-atmospheric portion of the sample system should include the absolute minimum number of pipe and tubing joints, filters, vessel closures, valve stem packings, sample pump head gaskets, and diaphragms. Many small leaks will cause errors as great as a single large leak and will be much more difficult to locate.

Extractive sampling systems, which use water or steam as the driving force and coolers and water wash pots to remove the excess water, must incorporate a temperature controller to ensure operation of these facilities at a constant temperature.

19.3.3 Sampling at High Temperature

Gas samples having high dew points must be maintained at temperatures well above this point to prevent condensation. Many samples are analyzed directly in the process stream at operating temperature. Manufacturers should be consulted for maximum permissible sample temperatures.

19.4 Safety Considerations

Oxygen is extremely reactive when in contact with easily ignited combustible gases and greases. Safety considerations unique to oxygen analysis and the operation of analyzers in refinery environments are discussed in 19.4.1 through 19.4.3.

19.4.1 Venting Span Gas

Clean dry air is a very popular span gas because of its universal availability at very low cost. When the spent sample from an oxygen analyzer system must be vented back to a process, or to a closed vent containing significant amounts of combustible gases or vapors, the means of conducting span gas to and from the analyzer system must be very carefully designed to avoid upsets in the process or explosion hazard. Design and operating techniques for avoiding these hazards include the following:

a) using special gas mixtures with minimum possible oxygen content for the desired operating ranges;

b) minimizing the use of span gas by separating measuring cell gas flow from all bypass flows during calibration operations;

c) switching the analyzer vent from the process or hazardous vent during calibration.

The effects of changing vent pressures on analyzer calibration must also be carefully evaluated in all cases, especially when the measuring cell is switched to different vent systems when in the calibrating and operating modes.

19.4.2 Degreasing

No special cleaning procedures are required for equipment in contact with oxygen concentrations below 21 % by volume. Increasing the oxygen concentration, however, reduces the temperature and energy required for the ignition of flammable materials and at the same time increases the resulting flame temperature. Thus, all equipment in contact with these greater concentrations of oxygen must be free of oil and grease.

Commonly used valves, fittings, and tubing, cleaned for oxygen service by the manufacturer, are readily available through normal commercial channels. Suitable methods for degreasing on-site include flushing with clean organic solvents or hot detergent solutions.

All openings into equipment cleaned for oxygen service must be kept closed until installed in systems to prevent contamination during storage.

19.4.3 Sample Gas Ignition

Where ignition of the sample gas is possible [for instance, when a zirconia electrochemical cell at 1562 °F (850 °C) is left operating in a shutdown heater not free of fuel gas, precautions should be taken to prevent this from happening. Flash arrestors could be installed to prevent back flashing. A safety interlock system that shuts down the analyzer upon flame failure or on other conditions that could let combustible gas reach the measurement cell is a second technique available to the designer. Another option is purge gas flooding of the cell.

Sample streams containing flammable gas or vapors must be vented to a safe location outside of the analyzer enclosure. Consideration should be given to the following:

a) ensuring that normal sample line velocities are in excess of flame velocity;

b) providing the minimum practical sample volume at the ignition source;

c) installing a flame arrestor near the ignition point;

d) providing positive sample dilution below the flammable range.

Each such system requires special consideration and preventive measures.

19.5 Calibration

19.5.1 Calibration Facilities

All oxygen analyzer installations should include facilities for injecting a calibration standard into the analyzer. Calibration facilities for in-situ close-coupled stack gas analyzers should be permanent and preferably operable from grade.

19.5.2 Calibration Gases

Most oxygen analyzers are calibrated by adjusting span and zero when the appropriate calibration mixtures recommended by the analyzer manufacturer are flowing in the analyzer. Because of their convenience and availability, oxygen-free nitrogen or carbon dioxide for zero, and clean, dry air for span are the preferred calibration materials.

Another method of calibration is the use of a standard sample, which can be manufactured or purchased for this purpose. A standard sample gas generally is made up of a given percentage of oxygen in a nitrogen background gas. In cases where the background gases of the process stream differ too greatly from nitrogen in their effect on the analyzer, the standard should be made up from background gases matching the process stream. One suggested procedure is to obtain at least one certified sample bottle with an oxygen content of approximately 75 % of the analyzer range and another bottle with oxygen content at 25 % of the analyzer range. Some authorities prefer that the second sample content be approximately the same as the normally expected sample conditions. When analyzing inert gas, a standard sample gas containing no oxygen is helpful to check analyzer zero. Analyzer manufacturers should submit complete specifications for calibration gases.

19.5.3 Calibration Frequency

The frequency of analyzer calibration will depend upon the type of analyzer used. The manufacturer's recommendation should be followed to determine the maximum time between calibration checks. As a general rule if the application is simple, a monthly check of the calibration is sufficient. If the sensitivity is very high, the frequency should be more often, such as once a week. If the analysis is being made for a government agency, the agency specifies the frequency. Frequent calibration checks can be accomplished by an automatic system.

19.6 Maintenance

In electrochemical sensors of the fuel-cell type, the cell material is consumed, and the cell as a unit must be periodically replaced. Replacement cells must be stored in inert gas sealed packages. Other analyzer types will require periodic servicing such as replacement of membranes, O-rings, and KCl solution. Further installation and maintenance requirements are covered in Chapter 6.

20 Sulfur Analyzers

20.1 General

Sulfur occurs in varying concentrations in much of the world's crude oil deposits, ranging from trace levels to 6% or more by weight. Sulfur content, which remains appreciable through the refining process, is generally an unacceptable contaminant and must be reduced or eliminated from the end product. Sulfur compounds in fuels and lubricating oils corrode engines and boilers, inhibit catalyst activity, and may even destroy the catalyst itself. To minimize pollution, most industrialized countries have adopted laws prohibiting the burning of fuels containing high sulfur concentrations. To meet governmental and user requirements alike, rapid and accurate analysis of sulfur is required in both liquid and gaseous hydrocarbon streams.

20.2 Measurement Techniques

Sulfur and its compounds can be detected and measured in many different ways, depending upon its chemical form and concentration, the physical state of its carrier, and the purpose for which the measurement is to be used. Most sulfur analyzers in common use today use the electromagnetic energy absorption characteristics of the various chemical forms of sulfur. Analyzers employing infrared, ultraviolet, and soft X-ray absorption are available to provide a continuous output of sulfur content. Other instruments sometimes used for sulfur content analysis include the gas chromatograph (see Chapter 17), the mass spectrometer (discussed below), the thermal conductivity analyzer, and various other devices.

20.2.1 X-ray Absorption

Monitors for the detection of sulfur in liquid hydrocarbons are usually based on the absorption of X-rays emitted from radioisotope sources. Although X-ray generators have been used for this purpose, the equipment is expensive, not very easy to maintain, and difficult to use safely in hazardous locations. Radioisotope X-ray sources are generally preferred because they are small, inexpensive, reliable, and safe.

20.2.2 Gas Chromatography and Mass Spectroscopy

The accurate analysis of sulfur compounds in the gaseous state is commonly done with gas chromatography. The separation of the various molecular species within the process stream, particularly if the molecular weight is low (150 atomic units or less), is relatively fast and accurate.

Where heavier components are encountered, or where analysis time must be reduced, the mass spectrometer is sometimes used. Its speed of response, which for heavier molecules is perhaps 500 times faster than that of the chromatograph, coupled with its inherent accuracy and minimal sample conditioning requirements, makes the mass spectrometer another analytical option for measuring sulfur compounds.

20.2.3 Infrared Absorption

The presence of sulfur compounds in gaseous hydrocarbons is generally detected through the use of infrared absorption analyzers. Measurements of this type make use of the fact that all gases (except elemental gases such as nitrogen, oxygen, argon, and the like) absorb infrared radiation in a pattern characteristic of each specific gas. Infrared radiation is radiant energy just below that of visible light in the electromagnetic spectrum. Infrared rays are invisible but can easily be detected by their ability to heat whatever material they strike.

When infrared radiation is transmitted through a gas mixture, each component absorbs radiant energy at specific wavelengths. This pattern of absorption depends on the molecular structure of the gas and distinguishes that component from all others. It is this difference in absorption patterns that enables an infrared gas analyzer to measure one specific gas component in a complex sample stream.

Elemental gases, or those that are formed with two atoms of the given element (such as nitrogen, oxygen, hydrogen, helium, and argon), do not absorb infrared radiation and cannot be measured by this technique. Conversely, however, it is relatively easy to detect low levels of a compound gas against a background of elemental gases (such as clean, dry air) with infrared analyzers.

20.2.4 Ultraviolet Techniques

Monitoring systems for sulfur compounds in waste gas disposal units and stack emissions to meet the need for compliance with state and federal regulations are different from those of process analyzers used in other refinery applications. These differences are due to the low concentrations generally required to be monitored and the characteristics of stack gases. The sulfur components most often monitored in stack emissions are SO_2 and H_2S; however, because of their foul odor, mercaptans, other organic sulfides, and sulfur vapors, have emission limits that are usually quite low. Ultraviolet analyzers are normally used in these applications.

De-sulfurization equipment for sulfur recovery is used to reduce emissions from plant stacks and to provide low-sulfur fuel to comply with governmental restrictions on the use of combustible products. Close control of H_2S/SO_2 relative concentrations, at a 2:1 ratio in the Claus process for sulfur recovery, is required to maximize the yield of elemental sulfur and to minimize the presence of sulfur compounds in tail gases. Continuous on-line ultraviolet analyzer systems that respond to changes in the H_2S/SO_2 ratio are generally used for this measurement. On-line gas chromatographs can also be used to measure the H_2S/SO_2 ratio.

20.3 Application Considerations

In making an analyzer selection for the measurement of sulfur in any application, several factors must be taken into account:

a) Quality and state of the process material must be carefully considered.

b) Instrument location and required measurement accuracy must be determined.

c) Cost trade-offs between anticipated product yield and the installed analyzer cost with proper allowance for servicing and maintenance must be evaluated.

If the material to be analyzed is in the form of a clean, dry gas and is reasonably uniform in composition, direct measurements for various sulfur compounds can often be made using relatively inexpensive infrared or ultraviolet absorption techniques. In many cases, the required sample conditions can be derived with a suitable front end conditioning network. See Chapter 4 for a comprehensive discussion of sample systems. Accuracy of measurements made with infrared or ultraviolet absorption equipment will generally fall within 3 % to 5 % of range with minimum detectable levels down to 10 parts-per-million.

For more accurate measurements of sulfur compounds in a gaseous system, it is often necessary to use the more complex chromatograph. Analysis of process stream content made with this type of instrumentation can be calibrated to very precise levels and is often the best way to obtain the quantitative information needed for proper maintenance of product quality; however, the response time for typical chromatographic measurements may be too slow to control a high-speed process. The special care required for sample preparation and the added maintenance cost of a chromatographic installation need to be considered when selecting such equipment. A more thorough coverage of chromatographs is provided in Chapter 17.

Precise analysis of sulfur content in a process stream, along with all other elements present, is possible through the use of a mass spectrometer. Although it's initial cost may be high, because of instrumentation required and because of added environmental protection needed, its response time is fast and its calibration is very stable. Process control from the analyzer output, together with data collection for laboratory use, make the mass spectrometer suitable for the maintenance of process quality and control.

Determining the type of instrument required for sulfur analysis requires an assessment of the form in which sulfur is to be measured. If the presence of total sulfur is the primary consideration, then an instrument sensitive to sulfur atoms only, apart from the molecular structure in which they are found, should be selected. X-ray absorption can provide the proper selectivity to detect total sulfur in hydrocarbons by appropriate choice of the X-ray energy level. This method is limited to a minimum span of about 0.5% sulfur, however.

When a particular sulfur species, rather than total sulfur, is of interest, radiation at longer wavelengths is required. Energy absorbed at the ultraviolet, visible, and infrared levels is a function of the molecular structure and varies little with differences in atomic composition. Where H_2S or SO_2 is to be measured, as in the analysis of flue gas for atmospheric pollutants, the low cost associated with ultraviolet or infrared absorption equipment is attractive. The measurement of total reduced sulfur, as required in the production of elemental sulfur, is often approximated with the measurement of H_2S.

20.4 Analyzer Types and Applications

20.4.1 Detecting Sulfur in Liquid Hydrocarbons Using X-ray Absorption Analyzers

The detection of sulfur in liquid hydrocarbons by X-ray absorption involves passing an appropriate radiation level through a controlled thickness of the liquid product and comparing the attenuated radiation level with that through an empty cell. The intensity (I) of monochromatic X-rays transmitted through such a cell containing a layer x centimeters thick of a hydrocarbon liquid of density p (rho) grains per cubic centimeter, is given by the equation:

$$I/I_0 = e^{(M_c C_c + M_h C_h + M_s C_s) rx}$$

where

M_c is the mass attenuation of carbon;

C_c is the carbon content;

M_h is the mass attenuation of hydrogen;

C_h is the hydrogen content;

M_s is the mass attenuation of sulfur;

C_s is the sulfur content;

I_0 is the intensity transmitted through an empty cell.

Also:

$$C_c + C_h + C_s = 1 \text{ (the total product)}$$

For X-ray energies in the region of 10 to 30 electron kilovolts, sulfur has a greater attenuation coefficient than do carbon and hydrogen, so that radiation through the sample cell is more sensitive to small variations in sulfur content than to the corresponding changes in carbon and hydrogen makeup.

When the X-rays have an energy of 22 electron kilovolts, the mass attenuation coefficient of carbon is the same as that for hydrogen, and the ratio of carbon to hydrogen becomes irrelevant to the measure of sulfur. C_s, the sulfur content of the hydrocarbon sample, becomes equal to:

$$C_s = (K_1 p) \ell n (I_0, /I) - K_2$$

Where K_1 and K_2 are constants and p is the density of the hydrocarbon. Thus, to obtain an accurate measure of sulfur content in liquid hydrocarbon, only the density of the material and its absorption of 22 electron kilovolt X-rays must be measured.

The sample to be analyzed can be extracted from the main process line and passed continuously through the sampling cell. Temperature of the sample material should be held below 300 °F (150 °C), and its pressure should not exceed 15 bar. Actual limits will naturally depend on the specific equipment used. The sample must be continuously representative of the process stream and also continuously measurable, that is, by this technique the sample must be uniformly in the liquid phase without the presence of gas pockets or other discontinuities. Although the accuracy of measuring radiation attenuation through any material is independent of that material, the conversion of that attenuation into a meaningful measure of sulfur content is dependent upon the sample density, cleanliness, moisture content, and the presence of other foreign materials that can interfere with the computational assumptions of the analyzer's logic (for liquid density measurement, see Chapter 28.)

The best source of 22 electron kilovolt X-ray radiation is from a bead of americium (241) and a silver target. With a half-life of 432 years, this stable source of radiation decays by less than 0.25 % in a 12-month period, making the calibration of equipment using it an infrequent requirement.

The radiation emitted from the americium source bombards the silver target to generate a secondary emission of characteristic X-rays at about 22 electron kilovolts. The X-rays penetrate a shielded barrier and from there travel through the liquid sample cell to reach an ionization chamber. The resulting ionization current, which is a function of X-ray intensity, gives a measure of the attenuated radiation of the X-ray passing through the sample when compared to a reference signal representing zero sulfur content. The output of the detector is first amplified, then converted to a logarithmic function, and finally modified by a signal proportional to sample density to yield the sulfur content of the sample in percent by weight. See Figure 20-1 for a schematic diagram of an X-ray absorption analyzer.

20.4.2 Detecting Sulfur in Liquid Hydrocarbons Using Infrared Absorption Analyzers

The absorption of infrared radiation is a function of the molecular content of the sample rather than of its elemental content.

On-line analyzers are more often designed to utilize all infrared frequencies. The energy from the source consists of electromagnetic waves with all infrared frequencies superimposed. Radiation from the infrared source is usually split into two equal beams, one passing through the sample cell for analysis, the other passing through a reference cell, and both converging to a common detector. Detection involves a differential measurement between these two energy carriers, which are balanced against one another during instrument calibration. This method of detection reduces the effect of variations in the source of infrared radiation.

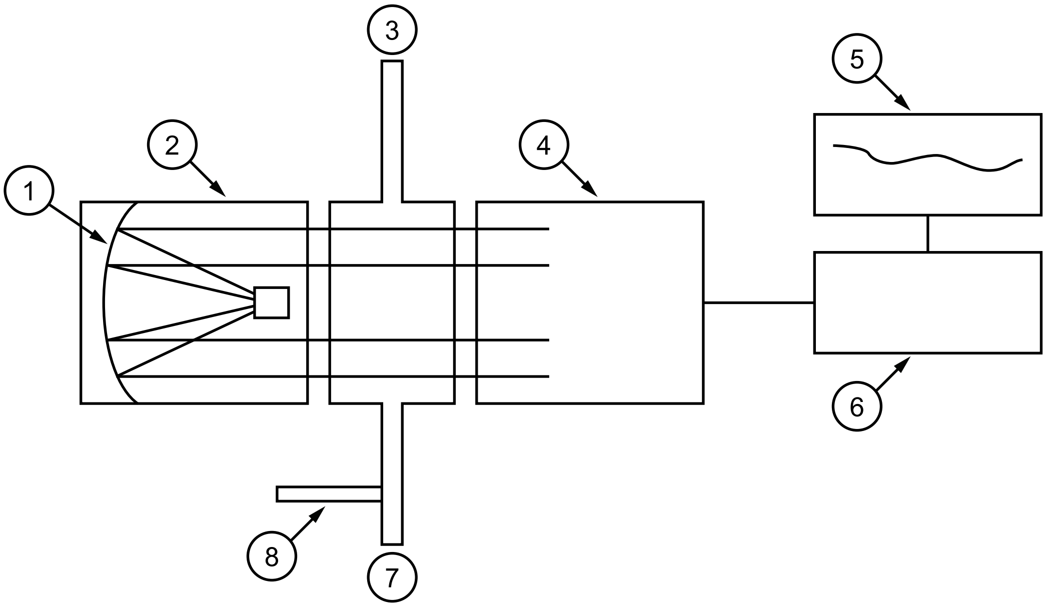
Samples for infrared analysis must be carefully prepared for continuous type processing. Particulates and other foreign matter should be removed from the gaseous samples. Also, moisture should be minimized. Since the infrared analyzer detects any variation in molecular content (other than those within diatomic gases), the product under observation should maintain a high degree of consistency.

20.4.3 Detecting Sulfur in Gaseous Hydrocarbons

20.4.3.1 Infrared Absorption Analyzers

Using infrared techniques to measure sulfur in gaseous hydrocarbons involves a measuring problem similar to that encountered with X-ray analyzers, except that the interpretation of the reading becomes more complex.

When infrared radiation is passed through the sample, certain frequencies are absorbed. These are associated with vibrational changes in the molecules of the substance. The value of this phenomenon lies in the fact that molecules having different bonds have different vibrational frequencies and thus absorb particular characteristic levels of energy from the infrared spectrum. It is this same phenomenon, however, that makes the measurement of total sulfur content



Key

1	silvered reflector	5	recorder
2	radiation source	6	amplifier
3	sample in	7	sample out
4	ionization chamber detector	8	thermocouple

Figure 20-1—X-ray Absorption Analyzer System

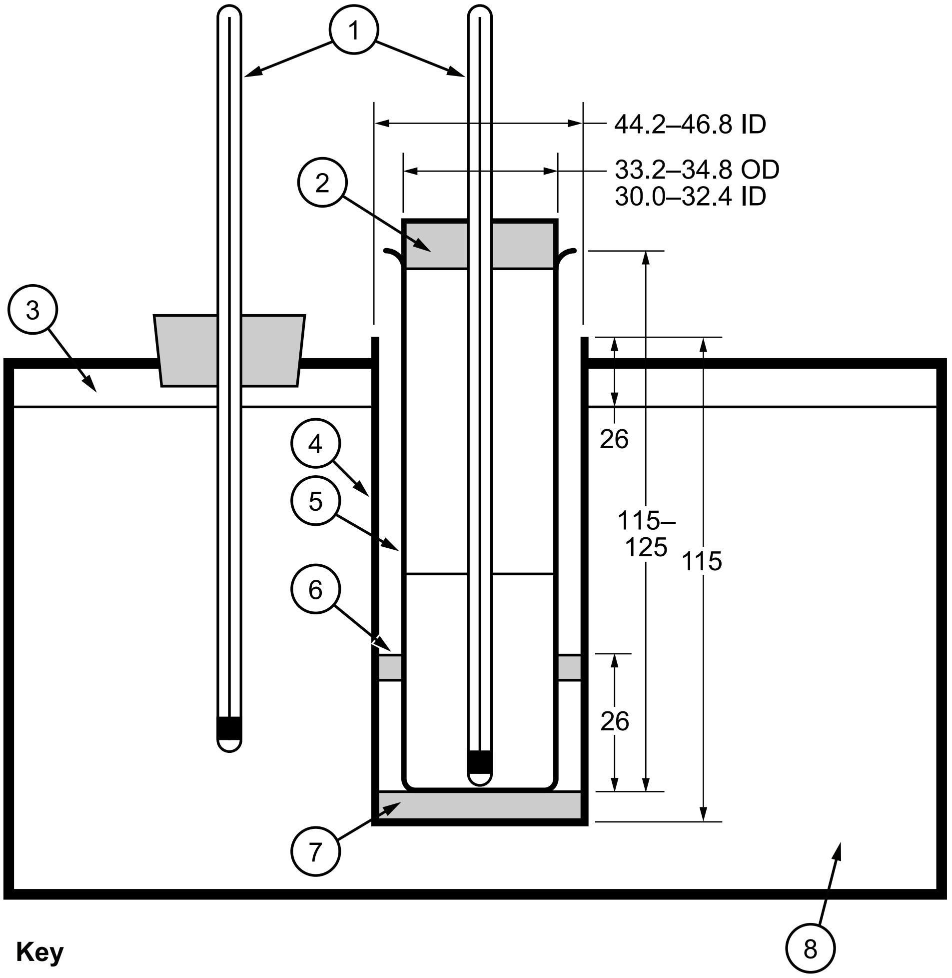
by this method more complex. The absorption of infrared radiation is a function of the molecular content of the sample rather than of its elemental content.

Although laboratory instruments for measuring infrared absorption are generally designed for monochromatic radiation sources, on-line industrial analyzers are more often designed to utilize all infrared frequencies, and thus are considerably more sensitive. The energy from the source consists of electromagnetic waves with all infrared frequencies superimposed. Radiation from the infrared source is usually split into two equal beams, one passing through the sample cell for analysis, the other passing through a reference cell, and both converging to a common detector. Detection involves a differential measurement between these two energy carriers, which are balanced against one another during instrument calibration. This method of detection reduces the effect of variations in the source of infrared radiation (see Figure 20-2).

Samples for infrared analysis must be carefully prepared, whether for batch or continuous type processing. Dirt and other foreign matter should be removed from gaseous samples. Moisture should also be minimized. Since the infrared analyzer detects any variation in molecular content (other than those within diatomic gases), the product under observation should maintain a high degree of consistency. Liquid samples are usually run as thin films between two plates that are transparent to infrared radiation.

The radiation source is normally a heated wire that yields radiation over the analytically useful portion of the infrared spectrum, from 1 micron to 10 microns (millionths of a meter). Analyzers using such a wide range of unordered wavelengths are categorized as nondispersive types. The main requirements for this source are stability of emission and a flat characteristic across the desired wavelengths. Nichrome wire is often used for this purpose.

There are two common detector types for nondispersive analyzers. One of these consists of two gas-filled cells, separated by a diaphragm. As the amount of infrared energy absorbed by the detector gas in one cell changes with respect to the other, the cell pressure changes. This results in movement of the diaphragm, which causes a change in capacitance between the diaphragm and a reference electrode. This change in electrical capacitance is measured as



Key

1 thermometer
2 cork
3 coolant level
4 jacket
5 test jar
6 gasket
7 disc
8 cooling bath

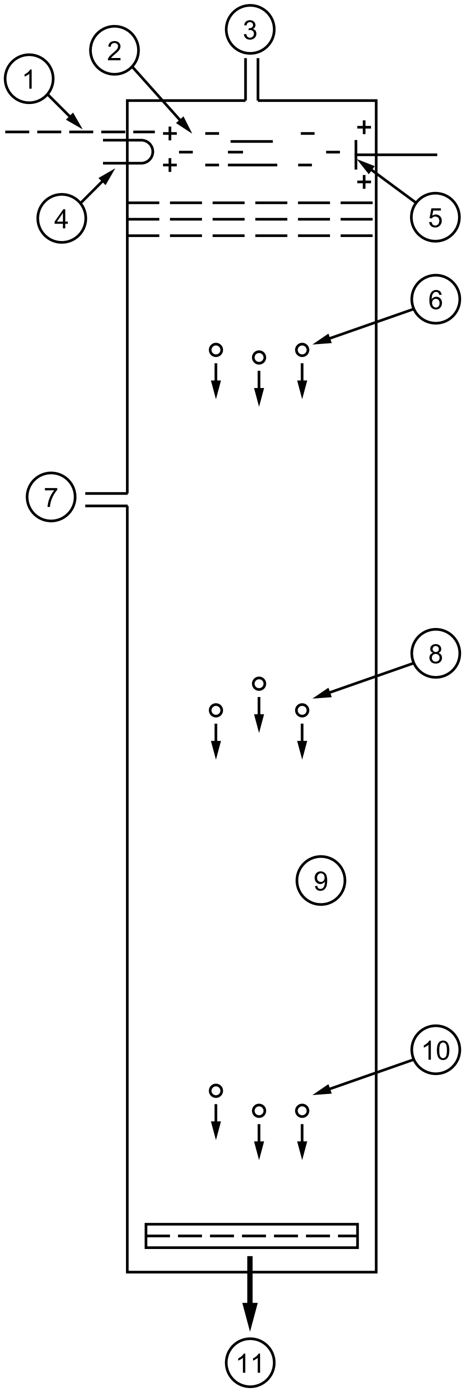
Figure 20-2—Infrared Absorption Analyzer

the output. The second type of detector consists of two thermopiles or temperature-sensitive resistors, one in each of two radiation beams. The infrared radiation absorbed by the sample is measured by a differential thermocouple output or by the unbalancing of a resistance thermometer bridge circuit.

With gas-filled detectors, a chopped infrared beam system is often used. Here, the detector is alternately exposed to the radiating source, first as it is transmitted through the sample and then as it is seen directly. Frequency of this alteration is quite low, only a few hertz. Any absorption by the sample above a calibrated zero-sulfur level is amplified and detected to provide the instrument output.

20.4.3.2 Mass Spectrometer Analyzers

The presence of sulfur compounds and all other components in the process stream can be accurately measured by molecular separation using a mass spectrometer. Substances to be analyzed must be in a gaseous form. Liquids and solids must be vaporizable at the inlet, while gaseous samples are received directly with minimum preparation. When analyzing the sulfur content in liquids, the mass spectrometer is used indirectly because combustion products (usually SO_2), rather than the sample itself, are analyzed. Figure 20-3 illustrates the spectrometer's operating principle[3].



Key

1 electron pulser
2 ionization chamber
3 sample input
4 heater filament
5 electron accelerator
6 heavy ions
7 sample outlet via vacuum pump
8 intermediate ions
9 drift region
10 ion accelerator
11 output pulses to computer

Figure 20-3—Mass Spectrometer

The mass spectrometer consists of five major parts.

1) A vacuum system, as required for an ion accelerator.
2) An inlet system capable of passing pressurized gas into an evacuated region.
3) An ion source, which converts this sample into ionized gas.
4) An accelerator, which separates the ions into various groups according to mass-charge ratios.
5) A detector to measure the abundance of selected ion groups.

To generate a mass spectrum, a small sample of gas is bombarded with electrons of sufficient energy to initiate the ionization process. Where M is the molecule, e is an electron, and M^+ is the molecular ion, the following occurs:

$$M + e^- \rightarrow M^+ + 2e^-$$

Once started, ionization rapidly propagates in the direction of a positively charged anode because of the avalanching effect of the additional electron set free with each electron-molecular collision. The degree of ionization is a function of anode voltage or electron energy[3].

An ionized molecule is normally formed by removing a single electron from a molecule: therefore, the molecular weight and mass of the ionized molecule is essentially the same as that of the original molecule. An ion, which has a positive charge, can be acted upon by an electric force and moved toward a negatively charged target. Ion separation, as a function of molecular weight, occurs when ionized molecules are subjected to an intense electric field. Each positively charged, ionized molecular particle accelerates toward the negatively charged target at a rate proportional to its mass, or molecular weight; therefore, molecules of different molecular weights arrive at the target at different times, and molecules of the same weight will arrive at the target at the same time. Each ion induces a current pulse when it arrives at the target. The size of pulse induced at any particular instant in time is dependent upon the number of ions arriving at that instant. A particular sample containing a mixture of different weight molecules will generate a series of pulses that are indicative of the sample composition.

The analysis of the constituent parts of a gas by means of mass spectrometry is not without its difficulties. The relatively high energy level used to ionize the gas sample is likely to cause the more complex molecules to split apart into smaller fragments. This results in output pulses unrepresentative of the original sample. A reduction in electron energy will reduce this fragmentation since component splitting becomes more probable as the election bombardment is intensified; however, a reduction in electron energy also reduces total ion concentration and impairs the sensitivity of the instrument.

A more practical solution to the problem of fragmentation takes advantage of its predictable occurrence under a given set of sample conditions. The relative level for each of the original process components can be computed from one or more of its characteristic output pulses. This can be done manually but for process analyzers is more often accomplished with a computer. One or more sample mixtures are introduced to the instrument, with corresponding adjustments being made, as required, for a proper reading. The computer makes the necessary internal corrections and will then produce accurate results for a long period of time, measured perhaps in months, before calibration is again required. Execution of this complex logic is normally carried out with the computer directed by a fixed set of instructions that are part of the analyzer's hardware.

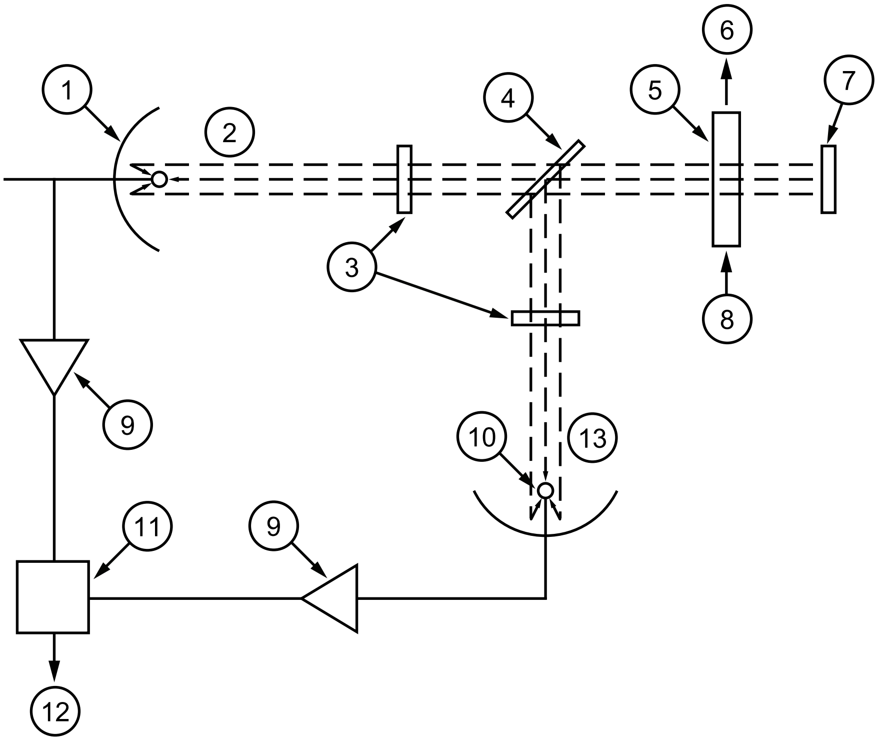
As a process analyzer, the mass spectrometer is in a class by itself. Its cost can, in fact, be several times that of a chromatograph. But where an accurate determination of almost any molecular mix is required on a nearly continuous basis for control of a process or blend, the mass spectrometer may well provide a workable approach not otherwise obtainable.

20.4.4 Detecting Sulfur Dioxide in Stack Gas Emission Using Ultraviolet Absorption Analyzers

Sulfur found in waste gas is normally in the form of SO_2. Sulfur dioxide has a well-defined ultraviolet absorption spectrum, a characteristic exhibited by few of the other gases expected in stack emissions.

A split-beam photometric analyzer, operating in the ultraviolet region, has been one of the most extensively used extractive detectors for SO_2 emission monitoring. In making the measurement, radiation from a mercury discharge lamp passes through a heated sample cell to the photometer, where the beam is divided into two channels. In the transmitted channel, the 280-nanometer mercury line is isolated, and the reflected channel isolates the 578-nanometer line as a reference. Since SO_2 has a strong absorption characteristic for the 280-nanometer mercury line, but practically none for the 578-nanometer line, the difference in the output of the two logarithmic amplifiers fed by the phototube detectors varies directly with the concentration of SO_2. The differential measurement compensates for the light intensity of the lamp and the opacity changes in the optics (see Figure 20-4)[7].

An ultraviolet correlation spectrometer is available as a commercial in-situ gas monitoring system for stack analysis. The source and sensor for this system are mounted in one housing installed on one side of the stack. The reflector is mounted at the end of a probe inserted into the stack. The optics and reflector are enveloped by air purges usually provided by high-volume blowers to keep the surfaces free from particulate matter.



Key

1 measuring channel sensor
2 γ = 280 nanometers
3 optical filters
4 mirror (semi-transparent)
5 sample chamber
6 sample output
7 ultraviolet source
8 sample input
9 logarithmic amplifier
10 reference channel sensor
11 computational unit
12 analyzer output
13 γ = 578 nanometers

Figure 20-4—Ultraviolet Absorption Analyzer

This instrument is a dispersive-type analyzer in which the radiation from a broad band source is dispersed by a grating, much as white light is dispersed by a prism. The radiation is moved or “wobbled” about over the grating in order to create wavelength bands that span the SO_2 absorption band. The grating separates and orders the radiation according to wavelength. A mask or filter, corresponding to that part of the spectrum that lies outside the absorption band, is the key element for the highly selective measurements for SO_2.

A second dispersive-type in-situ analyzer system is designed with the source and sensor on opposite sides of the stack or duct. This system uses a high-resolution spectrometer to provide the required selectivity. Again, air purges are used to shield the optics from direct stack gas exposure.

20.4.5 Detecting Hydrogen Sulfide

20.4.5.1 Hydrogen Sulfide Analyzer Using Lead Acetate Tape Sensor

A technique frequently used for detecting H_2S is based on the reaction of H_2S with lead acetate. Instruments using this technique incorporate a moving tape impregnated with lead acetate. Any H_2S in the gas contacting the tape reacts with the lead acetate to form a black lead sulfide precipitate. The change in the reflection of the tape is measured optically and calibrated for H_2S concentrations. The sample gas must, of course, be flow controlled for accuracy[7].

20.4.5.2 Two-stage Ultraviolet Absorption Analyzers

Although H_2S has a strong absorption in the far ultraviolet, it has no absorption peaks above 200 nanometers where most ultraviolet analyzers operate. Since many other compounds, such as aromatics and sulfur dioxide, also absorb in this region, a selective measurement for H_2S in the ultraviolet region can be difficult to obtain[7].

An ultraviolet photometric analyzer system for monitoring both SO_2 and H_2S is available. The system contains a quartz cell assembly that acts not only as a sample cell but also as a furnace for in-situ conversion of H_2S to SO_2. After purging with clean, dry air, and zeroing, the analyzer is sensitized for SO_2 monitoring. By measuring first the SO_2 level in the sample and then suppressing this reading for a second pass, the H_2S is quickly oxidized into an additional quantity of SO_2 and the difference measured. This method permits the monitoring of low H_2S concentrations in the presence of high concentrations of SO_2. Typical cycling time for this type of instrument is 1 minute to 2 minutes (see Figure 20-5)[7].

20.4.5.3 Split-beam Photometric Analyzer

A split-beam photometric analyzer system uses two ultraviolet analyzers to measure H_2S in the presence of SO_2. One measures the SO_2 concentration using a measuring wavelength of 280 nanometers and a reference of 365 nanometers. At these wavelengths there is no interference from H_2S.

The second analyzer, with a measuring wavelength of 228 nanometers and a reference of 361 nanometers, responds to the H_2S and, to a lesser degree, to SO_2; however, inasmuch as the analyzer outputs are linear with concentration, and the molar extinction coefficients of both H_2S and SO_2 have been established for the 228-nanometer wavelength (122 for H_2S and 66.6 for $S0_2$), the H_2S concentration may be obtained through a simple computation acting upon the signals from this analyzer and the SO_2 analyzer (see Figure 20-6)[8].

20.5 Sample Preparation System

Factors that must be considered in the design of a sample preparation system are covered in Chapter 4. Some special points about sulfur analyzing systems follow.

20.5.1 Materials of Construction

Stack gases can be highly corrosive, particularly if condensation occurs. In combustion sources, stack gas condensate may contain sulfuric, nitric, and sulfurous acids. Ordinary stainless steel construction will often be

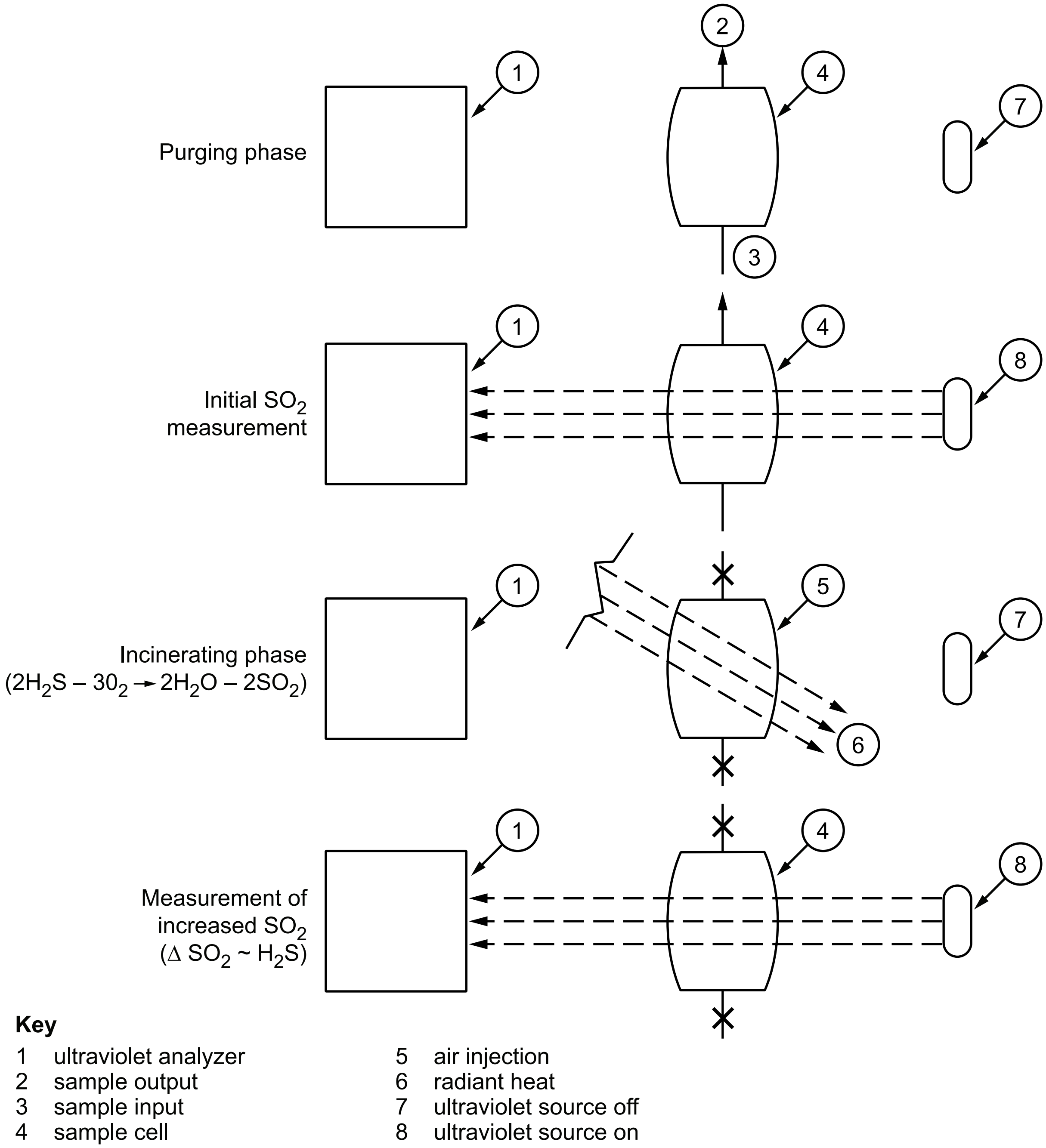
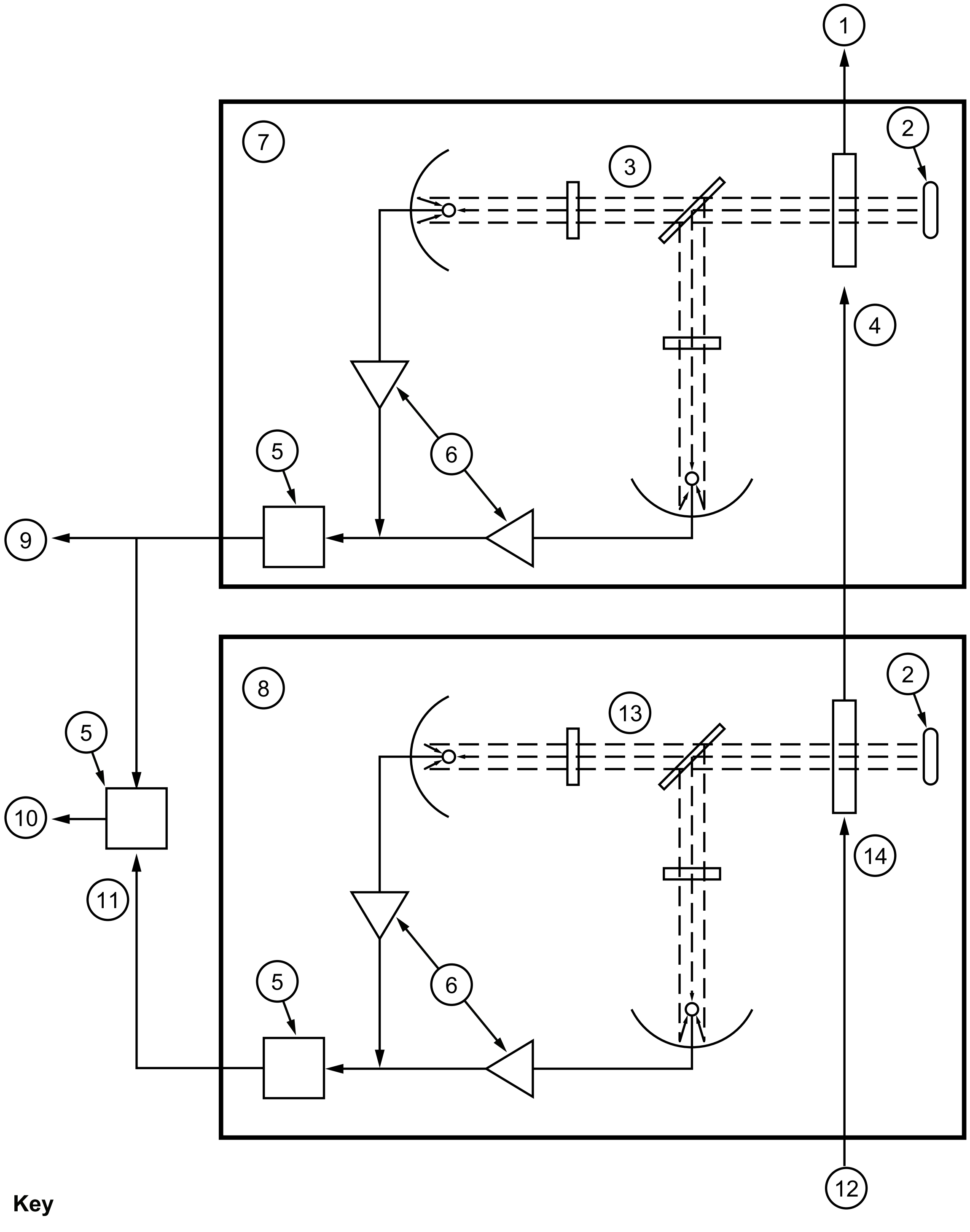


Figure 20-5—Measurement of H_2S in the Presence of SO_2

attacked by these compounds, particularly at the liquid-gas interface. Despite an initial high cost, the use of corrosion-resistant materials in sample system components will, in the long run, pay off by increasing reliability and reducing maintenance time. Components made of materials such as Hastelloy C or fluorocarbon resins may be fairly expensive, but they have proven to be highly resistant to corrosion in many stack gas applications[7].

20.5.2 Sample Point

Tail gas sampling from sulfur recovery plants often requires the entire system to be steam jacketed for high reliability. If installed as recommended, the sample is extracted at the top of the tail gas line or coalescer through a vertical pipe.



Key

1	sample output	6	log amp	11	f (B) H_2S kSO
2	light source	7	analyzer A	12	sample input
3	γ = 280 nanometers	8	analyzer B	13	γ = 228 nanometers
4	355 nanometers	9	SO f (A)	14	361 nanometers
5	computation module	10	H_2S f (A, B)		

Figure 20-6—Measuring H_2S in the Presence of SO_2 Using Two Ultraviolet Analyzers

The pipe is jacketed with low-pressure steam, which is used as a coolant to minimize sulfur vapor. Information supplied by the vendor should be consulted for the temperature levels required[7].

Stack gas samples are usually gathered through a probe mounted directly in the stack. To minimize sampling problems, the probe is designed to minimize the introduction of solids, thus the probe often includes a filter. Experience has shown, however, that the filter element must be shielded from direct impact of the stack gas flow where particulate loading is of consequence. A relatively coarse filter for those elements of about 20 microns or more is usually adequate for a photometric analyzer system to compensate for particulate matter. However, finer filtering at the sample point or later in the system is often required for many of the other types of systems[7].

When stack gas is cool and close to the dew point, heating of the probe assembly within the stack may be required to avoid sample condensation and all the corollary problems often associate with the probe itself. The system design must be modified to handle anticipated plant upsets. High temperatures and steam blow-back will help keep the analyzer on line[7].

Liquid products can often be extracted directly from process lines without any special requirements, although care must be taken to ensure that the sample is truly representative of the product being measured. When environmental conditions are severe, the sample line will require tracing for proper operation. Fast loops to cut “dead time” in the delivery of a sample from the point of extraction to the point of analysis are often required. Considerations involved are discussed in Chapter 4.

20.5.3 Automatic Blow-back

When particulate matter is prevalent in gaseous sample lines, automatic blow-back through the line and probe on a periodic basis with hot clean air or steam is usually necessary to maintain reliable system operation. Lines carrying liquid product are generally easier to maintain, but periodic flushing is sometimes required if the material is contaminated by solid matter or highly viscous residues. Frequency of such periodic cleaning operations is a matter for careful study and evaluation, and cleaning should be adjusted to match the prevailing process conditions. For additional information, refer to Chapter 4.

20.5.4 Other Considerations

Because SO_2 and H_2S monitoring equipment are frequently located in hazardous areas. pneumatic operators are normally used for valves and other system control devices. Aspirators should normally be selected over other sample moving methods to ensure the accuracy of their listed contents[7].

20.6 Calibration and Maintenance

The accuracy of a stack monitor is only as good as the primary calibration standard, and calibration standards may present more problems than the instrument itself does. Most knowledgeable users distrust standard cylinders of gases less than 1000 parts-per-million. Although the use of treated aluminum cylinders for low levels of standard gases is promising, all cylinders should be stored at fairly constant temperatures and should be checked frequently in the laboratory to ensure the accuracy of their listed contents.

Another source of SO_2 calibration gas is found in permeation tubes, which are constructed entirely of glass and tetra fluoroethylene resin materials. Maintained under optimum conditions in temperature controlled ovens, this calibrating source is often used with chromatographs.

Calibration checks for ultraviolet radiation analyzers are normally made with special ultraviolet absorption filters inserted in the radiation path of the instrument[11].

Since a reaction between SO_2 and H_2S occurs, these two gases cannot be stored in one cylinder. Flow dilution systems with gas cylinders containing each component may be used for dynamically blending SO_2 and H_2S when a blended test mixture is required[4].

In every case, the detailed instructions supplied by the vendor for instrument calibration should be carefully followed for maximum analyzer performance.

The maintenance of analyzer equipment plays a critical part in its proper use. Failure to keep this type of equipment in proper operating condition at all times will lead to user mistrust of the data it supplies and will eventually eliminate its usefulness. Chapter 6 provides a general review on maintenance activities and the need to pay close attention to maintenance procedures outlined in the manuals supplied with analyzer instrumentation.

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Section E—Physical Property Analyzers

E.1 Scope

Instruments covered in this section are used in refineries to duplicate certain ASTM laboratory tests that formerly could be made only in the laboratory. These process stream analyzers are connected to a process by a permanently installed sample system. Devices used in control rooms or operating areas for occasional quality control tests on samples obtained by the operators are sometimes known as access testers. Those devices in which the operator initiates the sample injection manually are known as batch-type analyzers and are not covered in this section.

Since these instruments employ a different technique than the lab instruments they are compared against, they must be “correlated” to the off-line method. This often requires adjustments to be made so that the instrument’s output agrees with the lab method’s results.

To avoid repetition, selected topics normally covered in individual chapters will be detailed in this “overview” of Physical Property Analyzers when the information is applicable and common to the majority of these instruments (sample handling, calibration, etc.).

Analyzers covered in this section include the following:

Chapter 21	Pour Point
Chapter 22	Cloud and Freeze Point
Chapter 23	Distillation and Boiling Point
Chapter 24	Flash Point
Chapter 25	Vapor Pressure
Chapter 26	Octane
Chapter 27	Viscosity
Chapter 28	Density
Chapter 29	Color

E.2 Terms and Definitions

E.2.1
pour point instruments
Devices that determine the temperature at which a hydrocarbon becomes too viscous to flow.

E.2.2
cloud point instruments
Devices that determine the temperature at which crystals first appear as the sample is cooled.

E.2.3
freeze point instruments
Devices that determine the temperature at which crystals disappear as the sample is heated.

E.2.4
vapor pressure instruments
Devices that determine the pressure exerted over the sample within specified conditions of temperature and in the presence or absence of other gases.

E.2.5
octane instruments
Devices that measure the "knock" value of blended gasoline.

E.2.6
viscosity instruments
Devices that measure the viscosity of selected hydrocarbon streams. Viscosity is a measure of the resistance of a fluid to flow or movement.

E.2.7
density instruments
Devices that measure the density of process streams. Density is a measure of the mass per unit volume (normally expressed as gm/cm^3 in CGS system or lb/ft^3 in the English system).

E.2.8
color instruments
Devices that measure the intensity of color of process streams on one of several color scales in the visible portion of the electromagnetic spectrum.

E.3 General

Some of the instruments described in E.2 continuously measure the desired property of the sample producing an unbroken output signal or curve. This signal may be used directly as an input to a controller. Other instruments, such as the semi-continuous type, operate on automatically sequenced, discrete quantities and produce sawtooth, spike, or bar records from which the desired values are read from the peaks or valleys. The intermittent signal from these instruments must be stored (or "held" at the last value) in order to be useful as a controller input.

E.4 Safety Considerations

E.4.1 Sample Material Problems

Many physical property analyzers require large volumes of sample in the fast loop or bypass stream, or in the conditioned sample slipstream. A small leak in these systems may result in significant quantities of hydrocarbon release, some of which may result in citations or fines as recordable regulatory releases. Many of the materials analyzed by physical property analyzers are also flammable and have low flash points, which make them particularly susceptible to ignition if released to the atmosphere. If a sample is taken from a process line carrying material at relatively high pressure and at a temperature above its auto-ignition temperature, the slightest leak in the sample line can be the cause of a fire. Even though the sample material does not flash as it emerges from a leak, it may vaporize and create a potentially explosive atmosphere. The sample is often analyzed in a case or housing which contains the electrical equipment of the analyzer and where it is possible to have a source of ignition. Therefore, sample lines and all connections must be made leakproof. Hot sample lines, in addition to being leakproof, should also be insulated or shielded for personnel protection. Sample coolers, where used, should be equipped with automatic over-temperature shutoff valves in the sample line.

E.4.2 Electrical and Mechanical Considerations

All electrical wiring should be installed in accordance with the *National Electrical Code* as well as applicable national, state, and local codes. Electrical sample heaters should be of the low-watt density type and should be equipped with overheat protection.

Pumps and piping are the prime sources of mechanical leaks. Where pumps are used, provision for disposal of leakage should be considered when designing the installation. If an analyzer is equipped with its own pumps, the proper provision for collecting and draining leakage should be an integral part of the apparatus. Where pumps are installed separately, good-quality leak-proof pumps, such as “canned” pumps, will help to ensure a tight system. The use of screwed joints should be minimized to avoid piping leaks. Tubing and high-quality tubing fittings should be used wherever practicable.

E.5 Analyzer Location

The ideal location for an analyzer is seldom found; therefore, a compromise is nearly always necessary. The following considerations affect the decision as to where to place the instrument.

a) Proximity to the sample tap is desirable. Most analyzers furnish either an electrical or pneumatic output that can be transmitted to the control room.

b) The analyzer should be installed in a non-hazardous area if practicable. Even though the analyzer, or any part of it, is built into an explosion-proof housing and is perfectly safe during operation in *National Electrical Code* Class I areas, unsafe conditions could exist during maintenance and electrical calibration because the electrical and electronic elements must be exposed. Soldering of components should not be done in locations where hydrocarbon vapors may be present. If the analyzer cannot be located in a non-hazardous area, the analyzer or faulty plug-in type of units should be removed for soldering or for checking (refer to Chapter 7*)*.

c) The control room is the least desirable location for an analyzer because of the necessity of piping the sample to it. It is generally not permissible to pipe hydrocarbons into the control room.

d) In their present stage of development, many analyzers must be maintained and calibrated in place and therefore should be enclosed in a walk-in type of housing. In areas of cold winters, heating of the shelter is required for the benefit of maintenance personnel even though some instruments are capable of operating under extremes of ambient temperature. In hot areas, protective shading should be provided for the instrument as well as for personnel. Additionally, air conditioning should be considered in areas where ambient air temperatures could exceed the operating temperature limits of the analyzer. In all other areas, rain protection at a minimum is necessary. Proper ventilation of analyzer shelters should always be considered. The analyzer environment must be adequate for the analyzer performance to meet the manufacturer’s specifications.

E.6 Sampling Systems

E.6.1 Sample-Point Location

E.6.1.1 General

The location of the sample tap is important. Refer to the discussion in Chapter 4 for general considerations.

A representative sample must be obtained. This requires special care where the sample point is in the overhead vapor line from a fractionator because under some conditions liquid may be condensing on the pipe wall. In such instances, a sample probe extending into the pipe should be used. Adaptations of the ASTM and American Society of Mechanical Engineers (ASME) steam-sampling nozzles may be used (see Chapter 4). The openings in the probe should be so oriented that impinging droplets will not be picked up. For volatility-type instruments, however, the sample is usually liquid as it is withdrawn from the process, thus, a horizontal tap in the side of a horizontal line is preferable. Taps into the top of a line should be avoided because of the possibility of withdrawing non-condensable components or vapor. Also, taps into the bottom of a line should be avoided because of the possibility of withdrawing water or sediment. Free water is especially troublesome in a distillation type of instrument. It is usually better to withdraw the sample from a flowing line rather than from a vessel; however, if it is necessary to withdraw the sample from a vessel, the same precaution should be observed as for sample taps in piping. In addition, regions of stagnation should be avoided.

E.6.1.2 Pressure and Temperature Considerations

Pressure and temperature conditions at the sample point must be selected in order to give a manageable sample. For liquids, the pressure should be high enough and the temperature low enough so that there is no danger of flashing in the sample line. If the sample must be taken at or near its bubble point, it should flow through a small cooler to prevent flashing when the pressure is reduced. In some analyzers the pressure ahead of the inlet pumps must be low enough to avoid uncontrolled flow through the pumps yet high enough to afford positive suction. In addition, the temperature must be reduced enough to prevent vaporization of the sample in the suction side of the pump.

E.6.1.3 Sample System Lag (Dead Time)

In many cases, improper selection of the sample point can introduce as much lag as excessively long sample lines. Sample-point location is discussed in detail in Chapter 4. The consideration of lag becomes more important if the analyzer is to be used as a control instrument or its information is transmitted to a process control computer.

E.6.2 Sample System Piping Design

It is necessary to design the sampling system piping so that it has small volume, minimum length, and sufficiently high flow rate to keep the distance/velocity lag reasonably short. In general, the excess flow must be circulated back to the process line. Usually sufficient pressure differential for satisfactory sample loop circulation is available across a control valve or a pump. Pumps are preferred over control valves. There is very little differential flow when a control valve is wide open and sample is bypassing a control valve that is closed for process reasons.

Practical velocities in small-diameter liquid systems are much lower than for gas systems. For example, $^1/_2$-in. steel pipe or $^1/_2$-in. OD stainless steel tubing are good choices for liquid sample lines. At a flow of 2 gallons per minute of a hydrocarbon with 0.7 specific gravity and 1 centipoise viscosity, the pressure drop is about 7.5 psig per 100 ft of straight run pipe and the velocity is approximately 5 ft per second.

If the viscosity under these same conditions rises to 9 centipoise, the pressure drop rises to 13 psig per 100 ft; therefore, in some cases, it may be necessary to heat the line to reduce the viscosity. It is frequently necessary to use smooth drawn tubing or a larger size pipe for the sample loop in order to achieve the desired velocity. Pressure reducers and visual flow indicators are generally needed to maintain the required sample flow into the analyzer.

If a sample line containing liquid must be heated to maintain a lower viscosity for better flowing conditions, precautions must be taken to prevent upsetting the analyzer temperature control or overheating and vaporizing volatile components (when these are to be measured). If steam heating is used, the steam pressure may be reduced and/or proper spacing of the tracer line from the sample line may be chosen to maintain the required temperature of the sample.

Electric heating is often used because of its flexibility and other inherent advantages. Sometimes satisfactory temperature regulation can be achieved by selecting heating cable with proper voltage and resistance characteristics. If closer temperature regulation is required, a thermostatic control or an appropriate modulating controller may accomplish it.

E.6.3 Sample Conditioning

A fine mesh strainer to remove particles, such as pipe scale, from the sample stream may be sufficient for most instruments; however, if the sample must pass through capillaries or other small restrictions, or if deposits of fine particles may be detrimental to the performance of the instrument, a suitable filter of small volume should be installed ahead of the analyzer. Some instruments require the sample stream to enter the analyzer section at a temperature that is within certain prescribed limits. If sample preheating or pre-cooling is required, the heater or cooler may be furnished separately or as part of the instrument. In either case, appropriate utilities must be furnished. If the heater or cooler is furnished separately, installation of a temperature control system to maintain the proper sample temperature may be necessary.

Coolers can be a source of considerable trouble. Sample and effluent coolers are usually so small that fouling becomes a problem. Small, self-contained recirculating coolant systems are now available that overcome these cooler problems; however, these systems require electrical power. Plant drinking water should never be used for sample conditioning due to the possibility of drinking water cross-contamination. It is advisable to use water filters if plant cooling water or cold condensate is used for cooling purposes. The water temperature in the cooler should not be allowed to rise above the point at which mineral deposits tend to accumulate. In general, this maximum temperature is several degrees lower than that allowed for larger heat exchangers using the same water supply. If liquid water is present in the sample, it must be eliminated. Removal of entrained liquid is discussed in Chapter 4. It may be necessary to remove other undesirable components, such as corrosive materials from the streams. For suggested installations of sample conditioning systems, see Chapter 4.

E.6.4 Connections For Standard Sample

If the instrument calibration is to be checked by means of standard samples, piping provisions must be made for introducing the standard sample into the instrument either manually or automatically, as required.

E.6.5 Effluent Disposal

Sample disposal is a problem common to all analyzer installations whether the sample is unchanged, vaporized, or distilled and condensed. The end products in any case must be disposed of to a safe location. Practices for hydrocarbon drains in the particular refinery should be followed. Overhead vapors may be condensed and disposed of as a liquid. Bottoms should be cooled, if required, for disposal.

Liquids that are virtually unchanged in the analyzer (such as gasoline in the vapor pressure instruments) or liquids that will cause no contamination (such as fractionated liquids and bottoms) may be pumped back to the process line. Sample systems containing liquids that cannot be returned to the process line should be pumped to a safe disposal point. Relief valves in the sampling system or at pumps should be piped to vent or drain (not to the atmosphere).

The low-back-pressure discharge requirements for most analyzers can be met by installing a vented receiver with a level controller and pump. The level controller can be arranged to automatically start and stop a pump that has sufficient head to deliver the liquid into the process line. Such an arrangement is shown in Figure 4-11. With some boiling point analyzers, the effluent can be returned to the process by an eductor included in the sample conditioning package.

E.7 Readout

The readout from most distillation devices is temperature. The same precautions must be observed as for any other temperature-recording installation with additional attention to sensitivity and accuracy. Flash point instruments also read out in values of temperature, usually producing sawtooth chart curves. To provide a continuous readout a suitable sample-hold module may be added to the analyzer output.

Vapor pressure instruments usually read out in pressure. Generally, the principles for the installation of pressure instruments apply to the readout end of the vapor pressure instruments as well.

E.8 Checking and Calibration

E.8.1 Use of Standard Samples

Almost any analytical instrument can be checked by means of a standard sample; however, the practicality of standard samples for high flow rate analyzers should be considered. This is a basic check that is analogous to checking a micrometer with a gage block. The assistance of laboratory personnel is generally required to develop the standard sample necessary to achieve the optimum calibration.

E.8.2 General Practices

The practices generally followed in checking a plant stream analyzer are listed here.

1) A sample should be obtained which corresponds closely in measured properties to the normal plant stream. Such a sample may be a quantity of the plant stream or may be obtained from other sources. A 55 gallon-drum quantity is an appropriate size sample. Several laboratory analyses, according to the appropriate ASTM method, should be run on the sample. The statistical average of these analyses should be taken as the comparison value for the instrument, if the instrument is to duplicate the method.

2) The sample should be kept under conditions that will not cause changes in the analyzed properties. These values can change because of evaporation, polymerization, stratification, contamination, and so forth. Storage conditions should be selected for each particular type of sample. This is especially important if standard samples are used to check volatility measuring instruments that are calibrated for high volatility. It may be necessary to heat and/or stir a captured process sample prior to introducing it into the analyzer, to ensure it has not stratified.

3) The sample should be admitted into the instrument for the proper interval of time and the results compared with the value that should be recorded for the sample.

4) If the recorded value differs from the predicted value, proper adjustments should be made. Some such adjustments may be made in the recording or transmitting instrument; however, it may be necessary to clean or replace faulty parts of the analytical section of the instruments.

5) After adjustments are made and the instrument is lined out on the process stream, the standard sample should be readmitted and the actual and predicted readings again compared.

6) If it is impossible to obtain agreement between an instrument reading and a standard sample (and if agreement has been obtained previously), it is best to obtain a new standard sample.

Standard samples may be admitted to the plant stream analyzer by pressurization from a suitable vessel with a suitable gas, usually nitrogen, or by pumping into the unit with a sample pump.

E.8.3 Comparison With Laboratory Analyses

If the use of a standard sample is impractical or impossible, the recorded reading of the analytical instrument may be checked against laboratory analysis. For a check of this type, at least three separate portions of the same sample should be submitted and the statistical average of the sample results should be used for comparison of the results recorded by the instrument. If the agreement is beyond tolerances and if it seems reasonable that the instrument is out of calibration, adjustments should be made. After appropriate adjustment or maintenance, or both, are performed and the instrument is lined out, a recheck should be made against another set of laboratory results. This method works best under conditions in which the properties of the sampled stream are changing slowly. Recognized, accepted procedures for obtaining and handling laboratory samples should be followed.

Many plant stream analyzers are designed to correlate with tests based on specified ASTM methods (refer to ASTM D2891, *Validation of Results of Process Distillation Analyzers* and ASTM D2984, *Test for Validation of Results of Process Vapor Pressure Analyzers).* Where this is the case, it is essential to use the proper ASTM method for checking the grab sample or for certifying a standard sample.

E.8.4 Calibration By Means of Temperature

Temperature checks may be used on some instruments in which the readout is directly dependent upon temperature measurement. These checks may include putting a simulated signal into the system, checking the temperature sensor in a standard bath, or replacing the sensor with a certified replacement.

E.9 Special Precautions

It should be determined whether the plant stream contains or may contain any contaminants that will adversely affect the analyzer. The instrument manufacturer should be advised of contaminants that may be present in the sample. Such contaminants may include corrosive agents (such as chlorides, caustics, hydrogen sulfide, sulfur dioxide, and sulfur trioxide) as well as dyes, salts, or residues that cause deposits. If the analyzer design is such that these contaminants cannot be tolerated, or if suitable materials of construction are not available, it will be necessary to remove the undesirable materials from the sample stream. For suggested installations for sample conditioning, see Chapter 4.

In some cases, it may be impossible to arrive at an ideal solution, and periodic cleaning, inspection, and part replacement will be required.

E.10 Startup

The manufacturer's instructions should be followed in startup; however, regardless of the make of instrument, the following points must be observed.

a) Check all connections for tightness. Visually trace all sample lines from sample point to sample disposal. Check for continuity, proper slope, and absence of pockets.

b) Check out all utility and power supplies for proper connections, correct voltages or pressures, and for safety.

c) Check the analyzer circuit for loose connections and for function. Make certain that all field connections have been made in accordance with the manufacturer's appropriate wiring diagram.

d) Start flow through the sample loop and establish proper pressures and flow rates. Make certain that there are no leaks. Open valve in the sample conditioning system only after sufficient time to thoroughly flush the sample fast loop.

e) A sampling system should never be connected to the instrument until repeated tests assure that the sample is clean, representative, and measurable.

f) Admit sample to analyzer. Establish proper flow rates, pressures, and levels.

g) Check all controls for operability and stability. Check all valves for operability.

h) Turn on heaters. It is advisable to watch the instrument closely during this warm-up period. Observe the instrument at frequent intervals until equilibrium seems to have been established.

i) After operation seems satisfactory and stability has been achieved (this may be hours or even days) the results may be checked by the appropriate method selected (see E.8.1).

j) Blow down all instrument air lines if appropriate.

E.11 Shutdown Procedures

Shutdown should be made in accordance with the manufacturer's instructions. The following steps should be observed, where applicable.

a) Turn off power to heaters.

b) Allow sample to flow until analyzer is cool.

c) Shut off sample at source.

d) Drain analyzer and flush out if required.

e) Take precautions to prevent freezing in cold weather by heating or flushing with a light oil.

f) Lock the door of the analyzer housing.

21 Pour Point Analyzers

21.1 General

This section covers process analyzers used to measure the Pour Point of refinery products.

Pour Point measurements relate to flow characteristics of refinery products as defined by ASTM Method D97-66 and IP15-67. Process pour point analyzers are cyclical in operation and the cycle time is generally related to the cooling requirements of the sample to reach the pour point. Typical cycle times vary from 5 minutes to 60 minutes, programmed by the user.

21.2 Applications

Pour point analyzers may be used for the determination of products specification and pour point characteristics of products such as middle distillates, lube oils, synthetic gasoline, diesel fuel, light gas oil, crude oil, and other refinery products. Pour Point analyzers are used for measuring pour points of products in the range of –50 °C to +38 °C (–58 °F to +100 °F) to control the addition of additives to meet product specifications and to assure flow characteristics of the product.

Typical on-line repeatability on the same sample is ± 0.5 °C (± 1 °F). Typical on-line measurement accuracy is ± 6.0 °C (± 11 °F).

21.3 Principles of Pour Point Measurements

In the laboratory ASTM D97 or IP15 Method, a sample is preheated to a specific temperature above the pour point without stirring. The sample is cooled at a fixed rate by a jacketed bath. At intervals of 5 °F (3 °C) the test jar is tilted to see whether there is a movement of liquid within a set time period of 5 seconds. The pour point temperature is reported to be +5 °F (3 °C) above the detected or indicated pour point temperature of the sample.

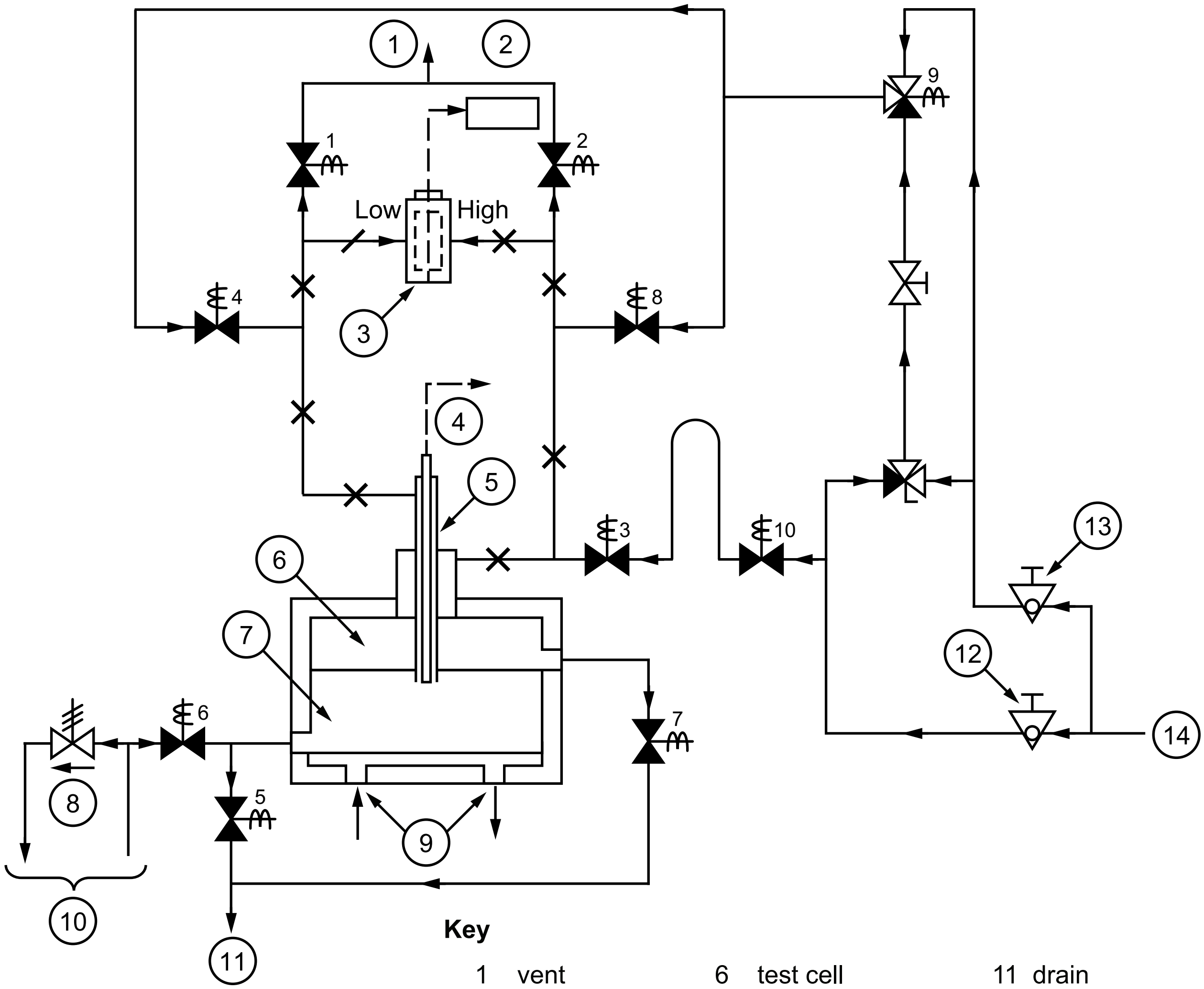
Process pour point analyzers closely follow an automated procedure similar to the laboratory method, but with differing detection methods. Results are correlated to ASTM D97, or IP15 for reproducibility comparisons to off-line methods.

21.4 Operating Methods

There are two types of pour point analyzers as follows:

21.4.1 Pressure Sensing Method

One type of analyzer as shown in Figure 21-1 has a test cell, into which a sample is introduced and cooled. A sensor probe is submerged in the sample. The sensor probe and the test cell are simultaneously vented to atmosphere, while a low pressure air reservoir is tapped upstream of the test cell. The sensor probe and test cell are sealed, then the low pressure air reservoir is discharged into the test cell and into the high pressure side of a differential pressure transmitter, generating a momentary pressure pulse. The compression of air in the sensor probe is a function of the flow of the liquid sample into the probe and is sensed by a reduction in differential pressure across the transmitter. This sequence of venting and pressurization continues until the differential pressure transmitter senses an imbalance, which indicates a no-flow condition of the sample in the sensor probe. The temperature of the liquid below the sensor probe at this time is measured as pour point temperature. The test cell is heated and flushed prior to the next measuring cycle.



Key

1	vent	6	test cell	11	drain
2	logic circuits	7	T/E module	12	LP regulator
3	D/P sensor	8	10 psig (69 kPa)	13	HP regulator
4	thermocouple	9	coolant	14	air in
5	sensor probe	10	sample fast loop		

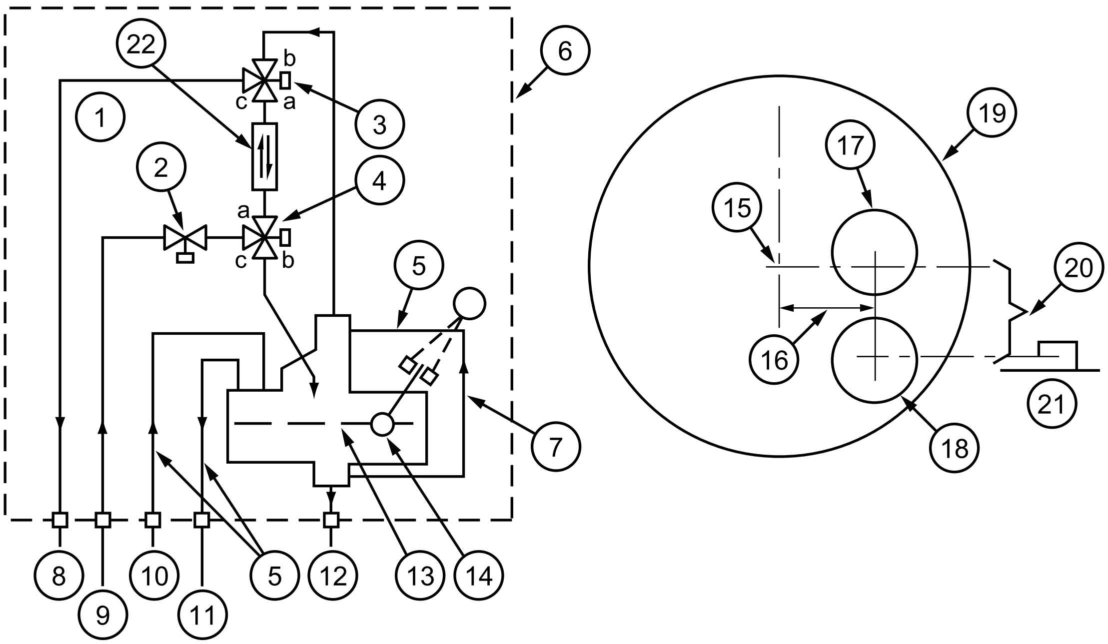
Figure 21-1—Pressure Sensing Pour Point Analyzer

21.4.2 Motion Sensing Method

A second type pour point analyzer is shown schematically in Figure 21-2. Sample flows through a reservoir to flush the previous sample and at a set time the sample is trapped and heated in the reservoir. The sample drops into the test cup. The cooling cycle is initiated while the test cup slowly rotates. A ball is suspended in liquid sample in the test cup. A thermocouple brazed to the ball's surface measures the sample temperature. As the temperature of the sample decreases, its viscosity increases, thereby increasing the drag force exerted on the ball. When the drag force is sufficient to displace the ball, it trips an optical detector. The temperature noted when this occurs is the pour point. The sample cup is heated after the measurement and drained prior to the next analysis cycle.

21.5 Sampling Systems

The cyclic operation of the analyzers requires that a fast loop sample system be incorporated. The sample must be free of entrained water and any particulate matter. Care must be taken to heat the spent sample drain line to assure that no build-up occurs to plug the drain line.



Key

1	heated reservoir
2	SV2
3	SV1B
4	SV1A
5	nylon
6	optical detector
7	vent
8	sample out
9	sample in
10	water in
11	water out
12	sample drain
13	test cup
14	ball
15	center of cup
16	8 mm (0.314 in.)
17	approximate ball position at detection
18	ball position at start
19	inner wall of test cup
20	ball displacement
21	pivot axis of ball bar
22	23 ml

Figure 21-2—Motion Sensing Pour Point Analyzer

Typically, the sample must at least 10 °C (18 °F) above the pour point temperature, but no more than 55 °C (131 °F) higher at the inlet to the analyzer. Typical sample flow rates are 0.2 to 1.0 liters/minute (0.05 to 0.25 gallons/minute), with a viscosity no greater than 750 cST at 38 °C (100 °F). Maximum allowable pressures are typically 200 psig (14 kg/cm^2), with a minimum pressure of 30 psig (2.1 kg/cm^2). If there is significant downstream pressure on the return line, the minimum differential (supply to return) is 30 psig (2.1 kg/cm^2).

For low temperature applications, normal process water may be utilized to cool the sample. For higher temperature streams, a 50/50 mixture of glycol/water in a re-circulating bath may be required. Sample coolers are typically available from the manufacturer as an option.

For additional sample conditioning details, refer to Chapter 4.

21.6 Installation and Calibration

Pour point analyzers should be mounted in an analyzer shelter. Some general considerations are:

The analyzer should be installed as close to the sample point as possible to minimize sample response time. The sample line should be provided with pressure and temperature gauges to indicate proper sample conditions.

A fast loop sample pump should be installed if the minimum available pressure is inadequate to provide a differential pressure of 30 psig (2.1 kg/cm^2) through the analyzer.

Proper sample conditioning should include a filter and a coalescer (or other means of removing uncoagulated water particles).

Reynolds Constants of 4000 or greater ensure the sample is adequately mixed (i.e., not laminar).

The sample system should provide a means to introduce a standard (or captured process sample of known pour point). It may be necessary to stabilize the temperature of the captured sample and to mix it, prior to introducing it into the analyzer. A sample pump is typically required to introduce the sample. Alternately it may be possible to force a captured sample through the analyzer by pressurizing a DOT-rated cylinder with Nitrogen.

For additional installation, calibration, start-up and maintenance, see manufacturer's instructions and refer to the section overview.

22 Cloud Point and Freeze Point

22.1 General

This section covers the application, installation, and operation of the commonly used instruments for the continuous on-line measurements of cloud point and freeze point. Instruments used in this section are used in refineries to simulate certain ASTM tests.

Supplemental information on safety, sample system design, sample conditioning, installation, maintenance, and additional reference documentation may be found in Chapter 4 and Chapter 6.

22.2 Definitions

The freezing point is defined as the fuel temperature at which solid hydrocarbons crystals, formed on freezing, disappear when the temperature of the fuel is allowed to rise. The freezing point of an aviation fuel is the lowest temperature at which the fuel remains free of solid hydrocarbon crystals that could restrict the flow of fuel through filters if present in the fuel system. ASTM D2386-88 Freeze Point measurement are applicable to the determination of the temperature below which solid hydrocarbon crystals may form in aviation turbine fuels and aviation gasoline.

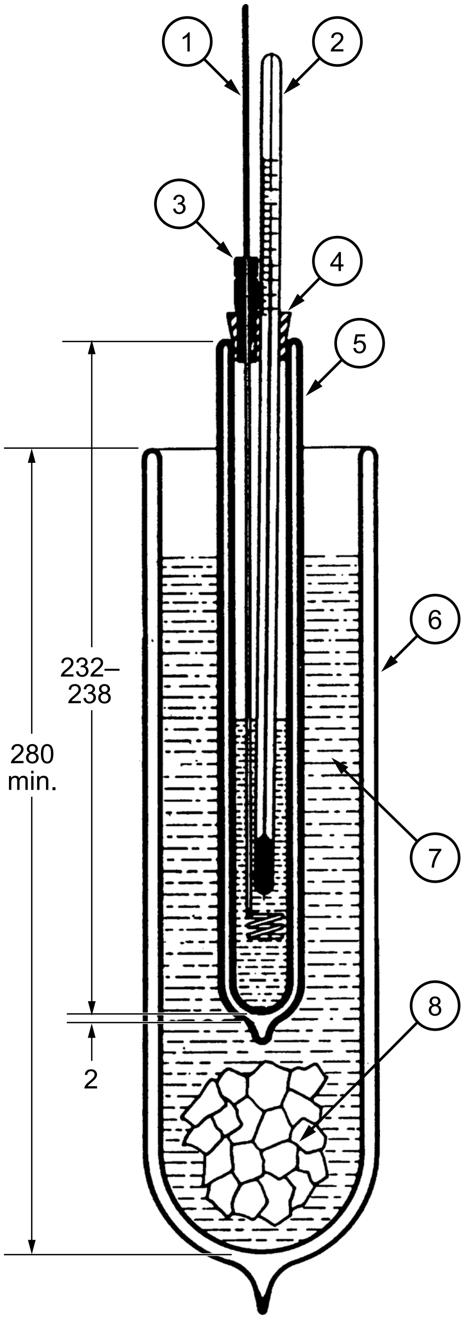
The cloud point is defined as the temperature at which crystals first appear (usually as a haze) as the temperature of the sample is lowered at a defined rate. ASTM D2500-91 Cloud point measurements are applicable only to petroleum products that are transparent in layers 40 mm in thickness, and which have a cloud point of less than 49 °C (or 120 °F).

The on-line measurement techniques and results are based on a correlation to the laboratory methods and a "correlation" must be developed in each application.

22.3 Cloud Point General

ASTM Standard Test Method D2386-88—The laboratory test is carried out in double-walled unsilvered vessel, in which the space in between is filled with dry air or nitrogen at atmospheric pressure (see Figure 22-1). The test begins with the addition of 25 milliliters ±1 of the process sample. The vessel is lowered into a slightly larger vessel filled with a suitable refrigerant (acetone, isopropyl alcohol, ethanol, or methanol). Dry ice is added to the refrigerant and the sample stirred. The temperature at which a small cloud of crystals forms at the bottom of the test vessel is recorded (as the Cloud Point). The sample vessel is removed from the refrigerant and the sample is stirred as it is allowed to warm up. The temperature at which the crystals disappear is recorded as the Freeze Point. The test is repeated if the difference between the two recorded values is greater than 3 °C (~5 °F). The measured value is reported to the nearest 0.5 °C.

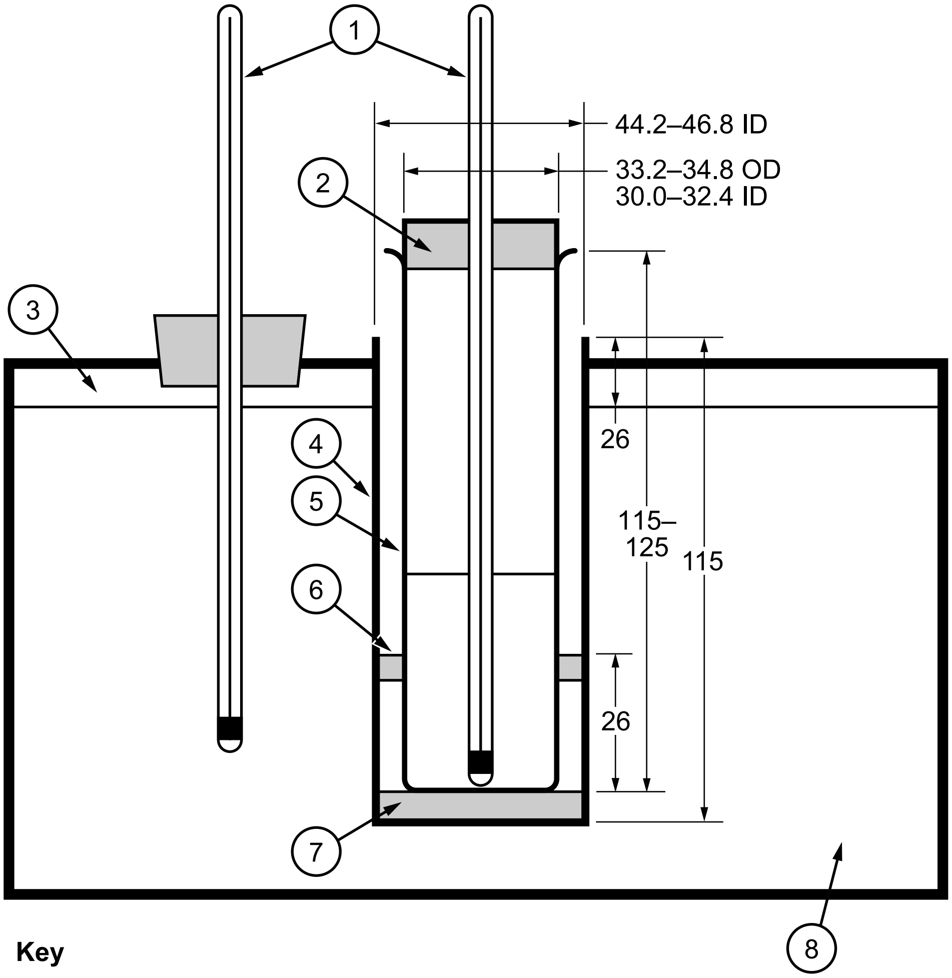
ASTM Standard Test Method D2500-91 for Cloud Point—The apparatus described in the test method is functionally the same as in D2386-88 with the same basic procedures and materials (see Figure 22-2). Whereas the freeze point method merely uses the cloud point as a reference point to stop cooling and begin heating the sample, the cloud point method is designed to optimize the detection of the cloud point temperature.



Key

1 brass stirrer rod
2 thermometer IP specification 14 °C
3 brass packing gland
4 cork stopper
5 jacketed sample tube
  outer tube – 30.00 x 26.10
  inner tube – 22.00 x 18.10
  space between inner and outer tubes to be filled with dry nitrogen or air at approximately atmospheric pressure
6 unsilvered vacuum flask 70 ID min.
7 refrigerant
8 solid carbon dioxide

Figure 22-1—ASTM D2500 Freeze Point Apparatus



Key

1	thermometer	5	test jar
2	cork	6	gasket
3	coolant level	7	disc
4	jacket	8	cooling bath

Figure 22-2—ASTM D2386 Cloud Point Apparatus

The repeatability of the Freeze Point test with the same operator and same apparatus is such that the value should not be greater than 1.0 °C only in one case in twenty. There is no known bias because the Freeze Point is only defined by this method.

The repeatability of the Cloud Point test with the same operator and same apparatus is such that the value should not be greater than 2 °C for distillate oils and 6 °C for other oils, only in one case in twenty. There is no known bias because the Cloud Point is only defined by this method.

22.3.1 On-line Cloud Point Measurements

Cloud Point monitors measure the temperature at which a haze of hydrocarbon crystals form as the temperature of the sample is lowered. On-line monitors typically provide measurements ranging from –80 °F to +77 °F (–62 °C to +25 °C) with a repeatability of ±1 °F (±0.5 °C), and an accuracy that is correlated to the lab results of ASTM D2500-91.

Solenoids isolate a fixed quantity of the sample stream in a detection cell and a beam of monochromatic light is passed through the transparent sample (see Figure 22-3). A coolant stream, in conjunction with thermoelectric coolers mounted on the sample cell, then cools the sample at a pre-determined rate.

Light absorbed at the detector (typically a photocell) is constant until crystals begin to form, scattering some of the light away from the detector. Several measurement methods exist. Early monitors recorded the temperature in the sample cell at a pre-determined decrease in detector response (output voltage). Recent monitors employ a dual polarizing filter system, one on the light source and another perpendicular to the first in front of the detector. Only scattered light from crystal formation is absorbed at the detector and the temperature is recorded at a sufficient detector output. In another monitor the detector is mounted perpendicular to the light source and the scattered light is detected, with the same threshold recording of sample temperature (see Figure 22-4). Most monitors employ a new baseline on each measurement to minimize the effect of sample deposits in the sample cell.

After the cloud point is determined, the solenoids allow the warm process sample to flush the detector cell in preparation for the next sample. The basic cycle time may vary from 2 minutes to 10 minutes. A sample/hold module maintains a constant output to the control or process monitoring equipment. Microprocessor-based monitors also provide a serial communications link that can also be used for remote adjustments to the analyzer. The basic calibration, mechanical and electrical setup, and correlation of Cloud Point monitors are performed at the factory. Final calibrations and adjustment to the correlation factor may be required in the field. If parts are replaced or significant maintenance or overhaul is performed, a new calibration will be required. Calibration is discussed in Section 22.8.

Monitors are available that offer three modes of operation, including a slow cooling mode that attempts to mirror the slow cooling method of the ASTM laboratory test, and a high-speed cooling mode that shortens the overall cycle time. A third mode is also be provided that is a combination of the slow and fast cooling modes. In this mode, a slow cooling cycle is performed once in a pre-determined number cycles. Based on the results, adjustments are made in the monitor to optimize the cooling rate near the Cloud Point value for the remaining analyzer cycles to be run in the fast mode.

22.3.2 On-line Freeze Point Measurements

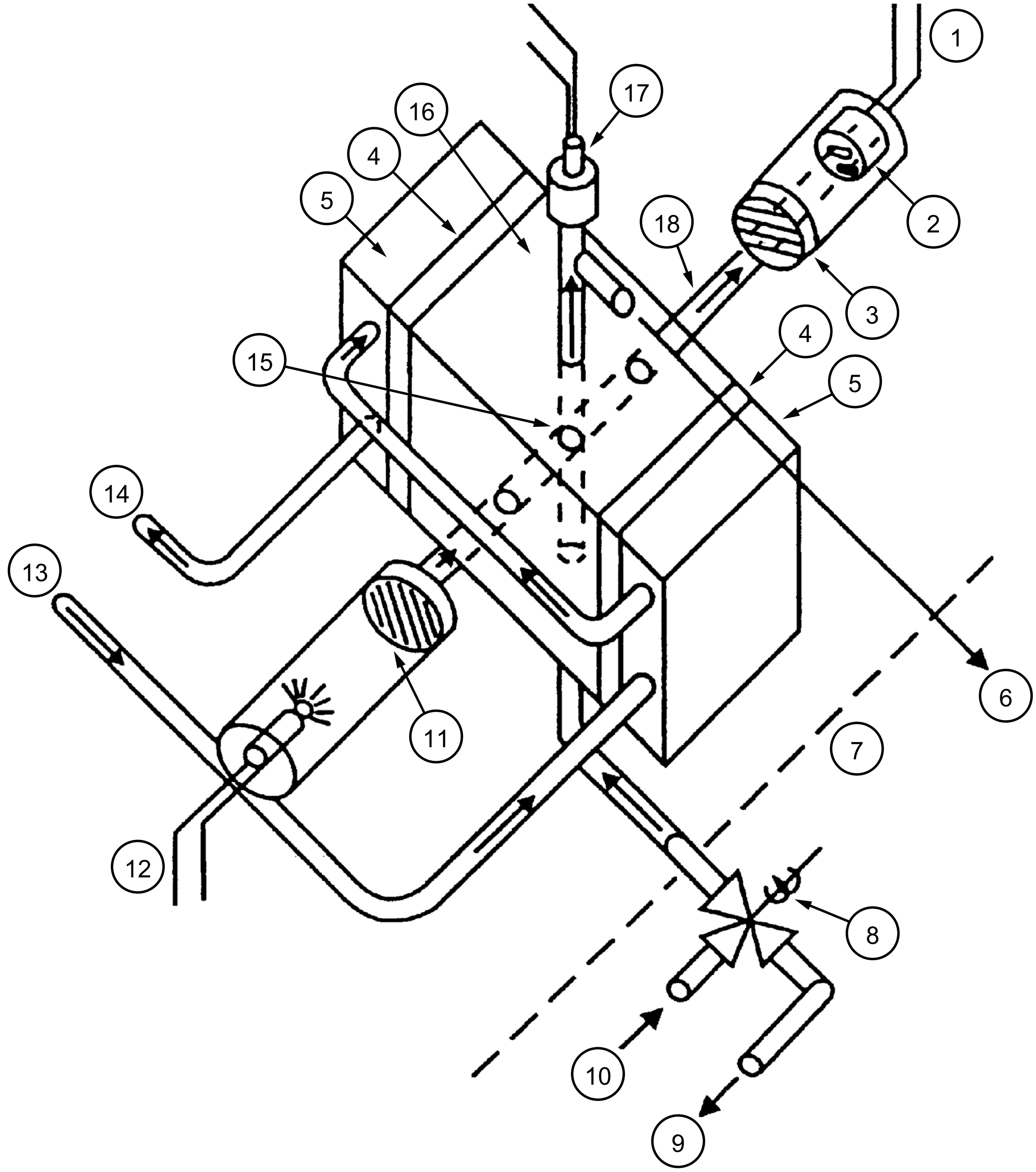
The hardware required for Freeze Point measurement is almost identical to the Cloud Point system described previously. Freeze Point measurements typically range from –80 °F to +77 °F (–62 °C to +25 °C) with a repeatability of ±1 °F (±0.5 °C), and an accuracy that is correlated to lab results of ASTM D2386-88.

In practice, a captured sample is cooled past its Cloud Point and then heated until the crystals that are formed during the cooling step disappear. Since the equipment employed is different than the laboratory equipment and method, and a hardware related set of factors affect crystal formation, a correlation to the laboratory Freeze Point analyzer must be made (see Figure 22-5). The basic cycle time may vary from 2 minutes to 10 minutes.

The basic calibration, mechanical and electrical setup, and correlation of Freeze Point monitors are performed at the factory. Final calibrations and adjustment to the correlation factor may be required in the field. If parts are replaced or significant maintenance or overhaul is performed, a new calibration will be required. Calibration is discussed in section 22.8.

22.4 Safety Considerations

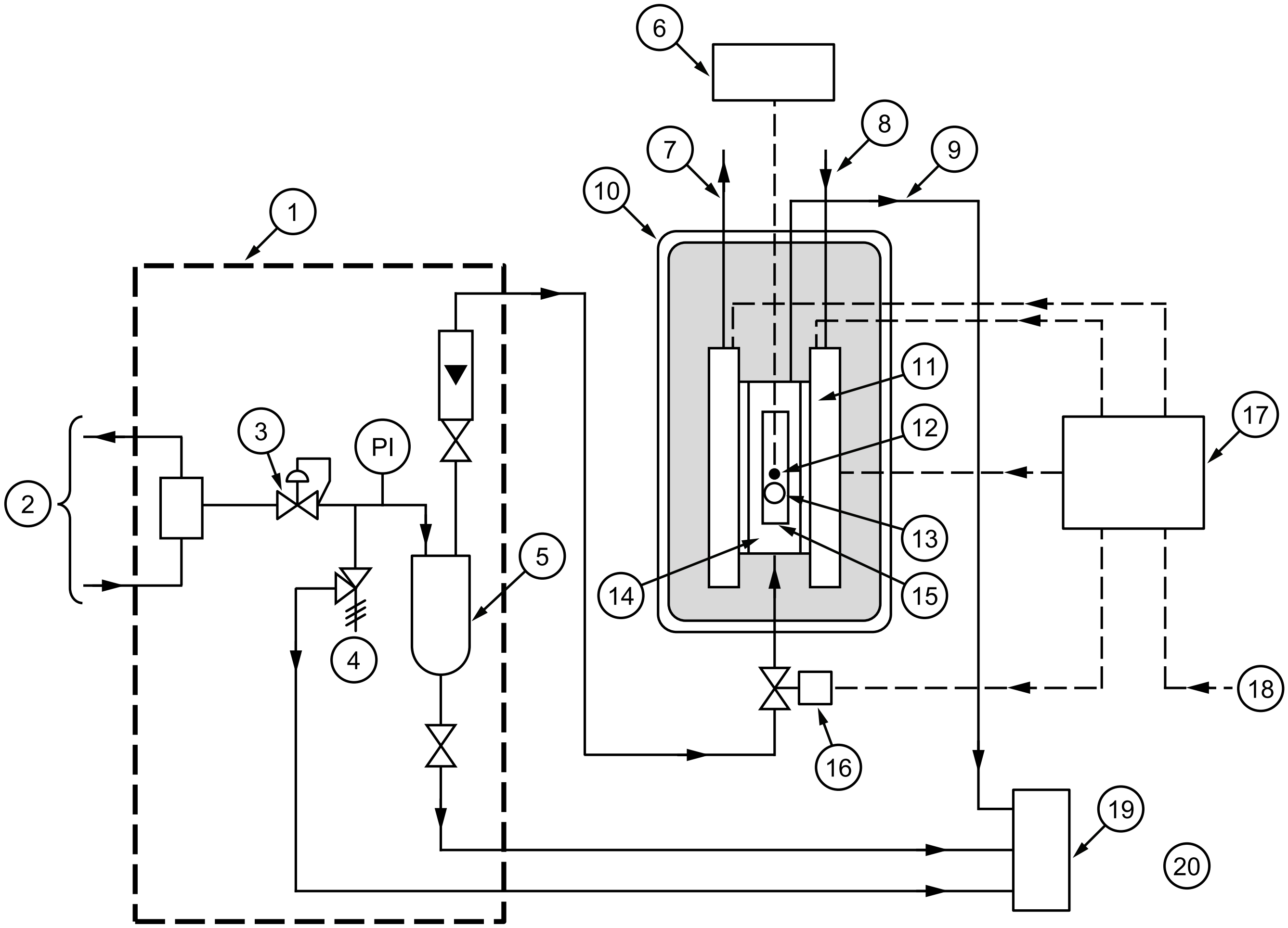
Streams commonly analyzed by Cloud Point and Freeze Point analyzers are volatile fuel-type hydrocarbons, and significant quantities of hazardous materials may be present in the sample system and analyzer section. Prior to the initial startup of these monitors, the analyzer system hardware and the routine maintenance procedures must be reviewed to ensure that personnel are not exposed to significant and potentially hazardous concentrations of liquid or vapors.



Key

1 detection circuit
2 photocell
3 adjustable polarizing lens
4 thermoelectric module (measurement circuit)
5 heat exhanger
6 spent sample out
7 outside explosion-proof box
8 solenoid valve
9 recirculated sample out
10 sample in
11 fixed polarizing lens
12 measurement circuit lamp
13 coolant in
14 coolant out
15 point of measurement
16 test cell
17 thermocouple
18 light path

Figure 22-3—On-line Cloud Point Sample Cell Schematic



Key

1 sampling system
2 process sample fast loop
3 pressure regulator
4 relief valve
5 filter coalescer
6 temperature recorder
7 cooling water out
8 cooling water in
9 sample out
10 measuring cell
11 heat sink
12 thermocouple
13 lamp source
14 thermo-electric cooler
15 photocell lens
16 solenoid valve
17 control and power supply units
18 power supply
19 drain manifold
20 atmospheric drain

Figure 22-4—Cloud Point Schematic Diagram

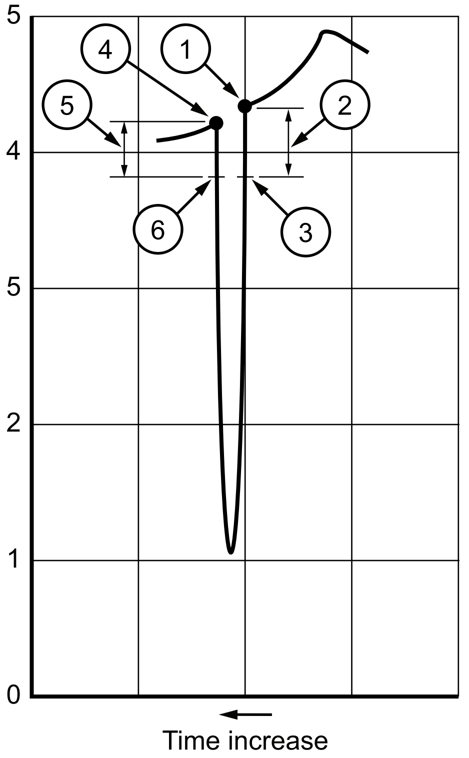
Typical items for safety considerations include.

a) Safety relief valves, if present in the sample system, should be piped to an approved disposal system.

b) Sample systems handling large quantities of volatile hydrocarbon streams should be located on the outside wall of an analyzer shelter.

c) Sample systems containing significant quantities of hydrocarbons should be designed to allow flushing of the system with nitrogen prior to opening it up for maintenance (for part replacement, cleaning of filters, etc.).

d) Nameplates should warn of any unusual hazards associated with routine operation and maintenance.



Key

1 lab cloud
2 cloud point sensitivity (programmable)
3 on-line unit cloud point
4 lab freeze
5 freeze point sensitivity (programmable)
6 on-line unit freeze point

NOTE Typical for jet, kerosene and JP-4/Military.

Figure 22-5—On-line Freeze Point Analyzer Output

22.5 Analyzer Location and Installation

The following information is common to both Cloud and Freeze Point Monitors.

Monitors should be located as close to the process sample point as possible to minimize sample lag time as this must be added to the basic measurement cycle time. Sample probes are recommended, along with sample line linear velocities of 2 ft/sec to 5 ft/sec (or 0.5 m/sec to 1.5 m/sec) to ensure uniform mixing. A sample pump may be required at the sample point to obtain the recommended linear velocity. Filtering and coalescing of the sample are also recommended. If there is a possibility that process upsets could result in entrained water in the sample, then a conductivity probe should be installed in the sample line. The probe should operate a valve to divert the stream until the process recovers.

Generally, these monitors should be located in level, vibration-free areas preferably in shelters with floor drains for disposal of accidental spillage or leaks.

Sample recovery systems may be required if the sample return point pressure does not allow the recommended pressure differential, or disposal of the bypass sample, the coalesced sample, and the spent sample from the monitor.

Monitors should be protected from the elements (rain, wind, direct sun, etc.) typically in shelters that provide a minimum temperature of 5 °C (41 °F) and a maximum of 38 °C (100 °F). Maximum performance and reliability is obtained in a climate-controlled shelter with a minimum temperature of 65 °F (18 °C) and a maximum of 90 °F (32 °C). Shelter heaters and air conditioners may be required in certain climates.

Monitors are typically configured in explosion-proof housings suitable for operation in classified areas.

22.6 Utility Requirements

The following information is common to both Cloud and Freeze Point Monitors.

Filtered, dry (– 40 °F or – 40 °C) nitrogen or air, hydrocarbon and oil-free (typically at 30 psig to 60 psig or 2 kg/com^2 to 4.2 kg/cm^2) is required to purge the detector housing to prevent condensation. Typically 1.5 SCFM (or 42 l/min) are initially required to purge out the cabinets prior to operation.

Glycol mixtures (50/50 with water) with a chiller/re-circulation system are typically used as the sample coolant medium. Typical coolant pressures required are 150 psig (or 10.5 kg/cm^2). Filtered, de-mineralized water may also be used if the temperature can be maintained at less than 100 °F above the expected sample Cloud Point temperature. A once through coolant system will require a minimum pressure differential (between supply and return) of 40 psig (or 2.8 kg/cm^2). A chiller/re-circulation system will be required for very low Cloud Point measurements (less than – 80 °F or – 62 °C).

Typical power requirements are less than 600 watts.

22.7 Sampling Systems

The following information is common to both Cloud and Freeze Point Monitors

For Cloud and Freeze Point measurements, the sample pressure and temperature must typically be preconditioned prior to entering the analysis section.

Typical maximum sample pressures are 150 psig (or 10.5 kg/cm^2), and minimum sample pressure differentials (difference between the supply and return pressures) are 20 psig or (1.4 kg/cm^2).

The sample temperature typically must not be less than 10 °C (50 °F) and at least 10 °C (50 °F) above the expected Cloud Point. A sample cooler is required if the sample temperature is greater than 37 °C (100 °F) as this may adversely affect the analyzer hardware and the time required to cool the sample.

Typical sample flow rates through the analyzers are 0.2 GPM to 0.4 GPM (or 0.8 liters per minute to 1.6 liters per minute). As these monitors are correlated to the ASTM D2386-88 and D2500-91 laboratory tests, the sample must be transparent and its color must not exceed ASTM 8 in color and water concentrations below 5000 PPM are recommended (to prevent water crystallization interference). Coalescing filters may be required to remove free water.

22.8 Checking and Calibration

Microprocessor-based monitors have numerous built-in alarm functions, both local visual alarms, and contact closures that may be brought back to process monitoring locations.

Calibrations employing captured process samples may be accomplished if a calibration point is built into the sample system. Typically, a significant quantity (5 gallons or 19 liters) of the process is captured in a suitable container, an off-line measurement is made of Freeze Point and/or Cloud Point, and the sample is introduced into the sample system just prior to the analysis section. This calibration reference sample may be pumped through the analyzer, or the container may be pressurized with an inert gas (typically at 15 psig or 1.05 kg/cm^2) and the sample forced through the detector section. Some monitors provide programming or circuitry that identifies calibration or reference samples and utilizes the values obtained to adjust the output circuitry accordingly.

22.9 Typical Applications

Cloud and Freeze Point are important specifications in the formulation of fuels for jet engines, marine and automobile diesel engines, and residential heating equipment. They are measures of the lowest temperatures at which fuels can be utilized without risk of pumping or plugging filters problems. These analyzers are applied mainly in the petroleum industry, to optimize yields, profitability, and to ensure that these product specifications are met in blending operations for aviation fuels, kerosene, and diesel fuels. Accurate measurements reduce off-spec product and allow more economic use of valuable feedstock streams.

23 Distillation

23.1 General

Distillation instruments are devices which operate on a liquid (or condensed vapor) sample by volatilizing and, usually, condensing part or the entire sample. Distillation instruments may be used to analyze mixtures of liquids (or gases) if the components differ at least in vapor pressure and are not decomposed by heat.

Distillation-type instruments may be of the continuous, semi-continuous, or batch type. Most of these devices correlate with ASTM D86 *Test for Distillation of Petroleum Products*, or ASTM D1160 *Test for Distillation of Petroleum Products at Reduced Pressures*.

The D86 procedure is a laboratory method developed to provide atmospheric distillation information on numerous hydrocarbon samples. In this method, 100 milliliters of the sample is placed in a round bottom flask and heated at a controlled rate. The vapors boiled off pass through a water-cooled condenser and are collected in ice-bathed flask. The temperature at which the first drop is collected is considered to be the initial boiling point of the sample and conversely the last drop is the final boiling point. Temperatures are recorded at fixed volumes distilled over and a curve is plotted based on the temperature versus volume collected. An inherent problem in the method is the loss of volatile species that escape from the collection flask. The final numbers therefore must be adjusted to account for the actual volume collected.

The range of hydrocarbons that can be measured by this method is limited, as some hydrocarbon tend to "coke" or undergo an oxidation/polymerization of the high boiling fraction at atmospheric pressure vaporization temperatures. These streams may be analyzed by applying a vacuum to the distillation to lower the temperature required for vaporization.

Some manufacturers have developed off-line instruments that automate these laboratory methods by utilizing optical means to determine the number of liquid drops distilled over and recording the temperature at fixed volume intervals. On-line instruments are frequently correlated to these off-line methods.

Types of on-line distillation analyzers are (a) initial boiling point, (b) end point, (c) other boiling points, such as 50 % point, and (d) thin film evaporative type and vacuum distillation analyzers.

Simulated Distillation (SimDis) is a Gas Chromatograph-based application that provides an alternative method to determine the boiling distribution in a hydrocarbon stream. Chromatographic columns are selected that are known to separate hydrocarbons according to their boiling point. In a post run analysis, each measured component's retention time is compared to the retention times of a calibration set of pure hydrocarbons. The percent area of each component is then determined from the total integrated area. Since the GC detectors employed are "carbon counters," the SimDis method provides weight percent determinations that can/must be correlated to the volume percent values obtained from physical boiling point determinations (as described in this chapter). The SimDis technique is described extensively in Chapter 17.

23.2 Applications

Distillation analyzers are most commonly found in refinery fluid catalytic cracking units and in gasoline blending units. Other applications include analysis of streams in crude distillation units and product specification (jet fuel, heating oil, etc.).

23.3 Types of Boiling Point Analyzers

23.3.1 Initial Boiling Point

The initial boiling point analyzer automatically controls a continuous distillation of a sample so that it is split into a constant ratio of overhead vapor fraction to bottoms liquid fraction. The vapor temperature in the top of the distillation tower is measured and can be correlated with ASTM D86 distillation data. An initial boiling point analyzer is illustrated schematically in Figure 23-1.

A preconditioned stream sample passes through a pre-heater coil in the boiling pot and enters the top of the tower through a variable inlet valve. A float in the boiling pot which responds to liquid level changes controls the volume of sample as it enters the analyzer. The sample flows through the float guide tube to the feed zone of the tower and to the boiling pot. As fractionation progresses, the sample feed is split into overhead and bottoms cuts. Overhead vapor exits at the top of the tower. Bottoms liquid exits from the boiling pot and is combined with overhead vapor. A ball-type check valve in the bottoms outlet line prevents overheads from flowing back into the boiling pot. Pressure in the process line and tower is controlled by the pressure control system.

An orifice in the overhead line and an “equivalent orifice” in the bottoms line maintains the overhead to bottoms ratio. Overhead flow is restricted by the orifice; the “equivalent orifice” creates resistance to flow, thus the ratio remains constant. Vapor temperature of vapor in the top of the tower is measured and represents a readout temperature that can be correlated with ASTM D86 distillation data.

A fixed wattage heater provides necessary heat to the boiling pot. Heat input requirements are based on the boiling range of the sample. Proper heater wattage is determined by the manufacturer, based on the customer’s sample distillation data. Heater selection is made in the range of 800 watts to 3200 watts. Putting enough energy into the sample to vaporize a large fraction of the sample on a continuous basis often results in the formation of “coke”. Removal of the coke is difficult, dirty, and time-consuming and often results in extended downtime for the analyzer. This has been overcome somewhat by the introduction of smaller boiling pots that require less energy to boil the sample (see Figure 23-2).

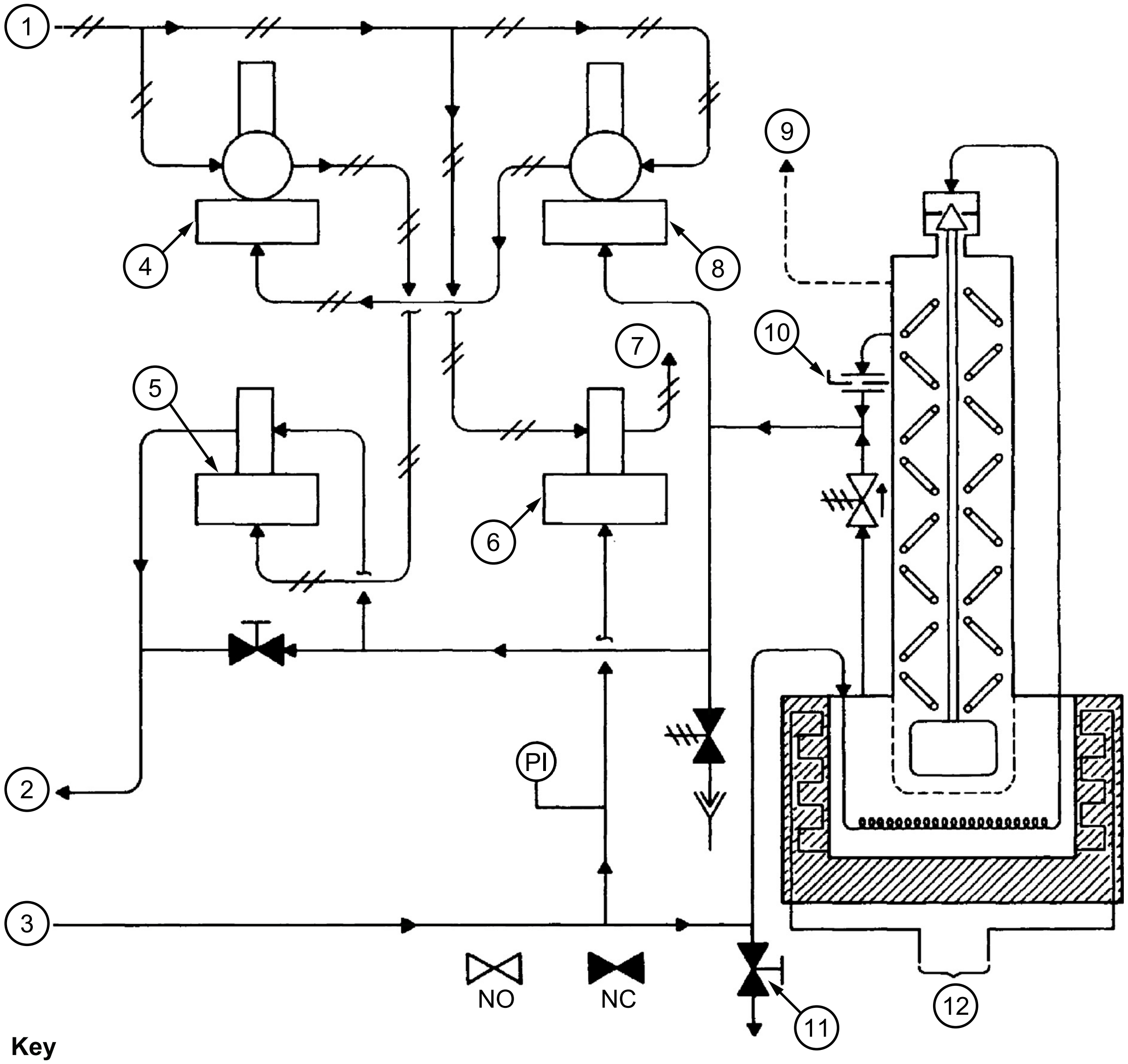
23.3.2 End Point Instruments

The end point analyzer automatically controls continuous distillation of a sample so that it is split into a constant ratio of overhead vapor fraction to bottoms liquid fraction. The bottoms boiling temperature is measured and can be correlated with ASTM D86 distillation data. The end point analyzer is illustrated schematically in Figure 23-3.

The operation of the end point analyzer is basically similar to the initial boiling point analyzer with a few minor exceptions. The major difference in operation lies in the fact that in the end point analyzer the split between overhead and bottoms cuts is accomplished with the orifice in the bottoms line, and the temperature monitored is the bottoms boiling temperature.

23.3.3 Vacuum Distillation

For very high boiling point applications, vacuum operation may be required (see Figure 23-4). The same basic technique is employed under vacuum conditions.



Key

1	air in	5	sample valve	9	thermocouple out
2	sample out	6	pressure switch amplifier	10	overheads orifice
3	sample in	7	to pressure switch	11	sampling valve
4	amplifier no. 2	8	amplifier no. 1	12	115/230 VAC

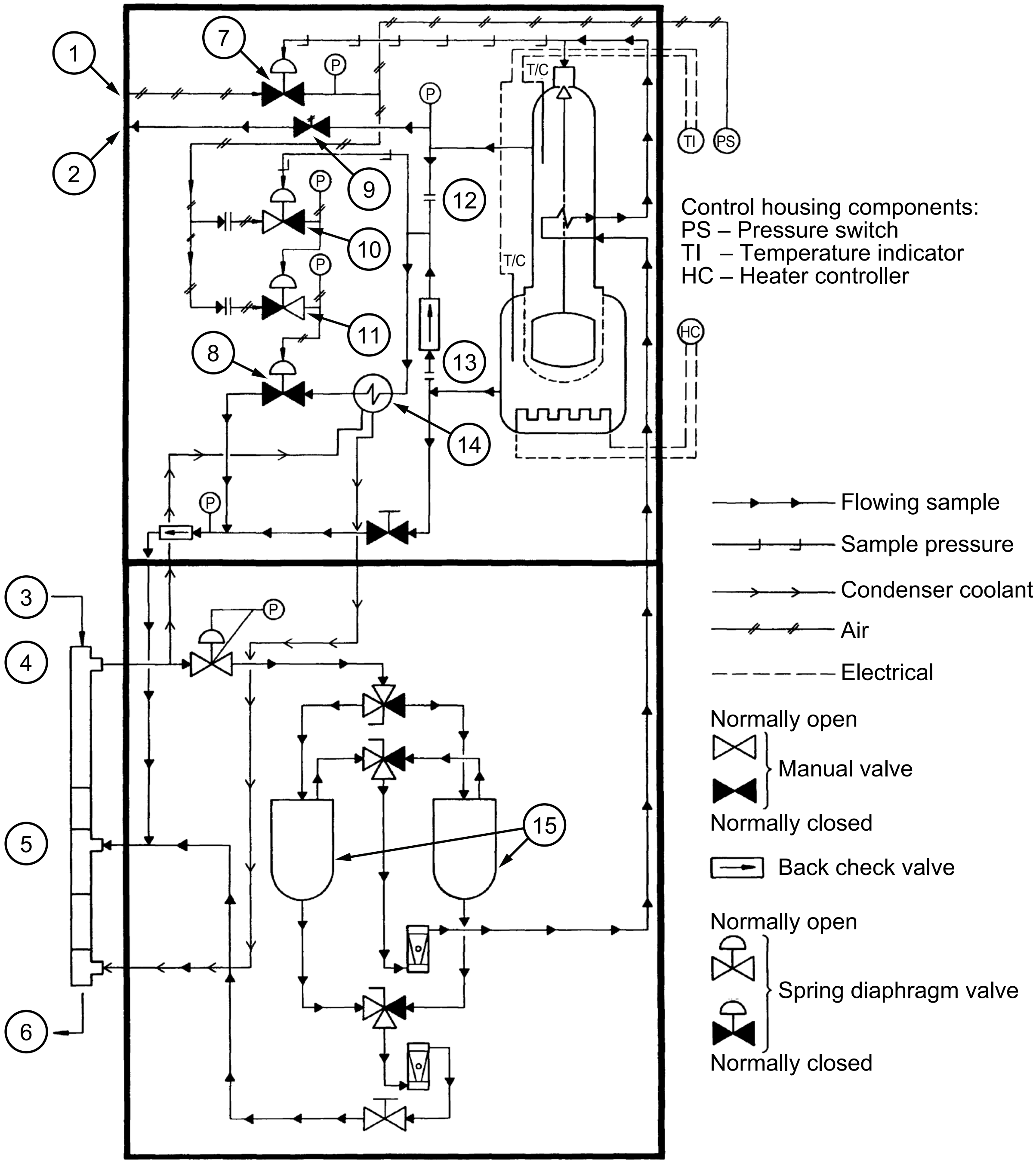
Figure 23-1—Initial Boiling Point Analyzer

23.3.4 Other Boiling Point Instruments

Additional points on the distillation curve are usually obtained by adapting the initial boiling point or end point instruments. The only modification required in these cases is to change the orifice size and possibly the heater wattage. Changing the orifice size will change the overhead to bottoms ratio and, in this way, will change the operating point.

23.3.5 Thin Film Boiling Point Analyzers

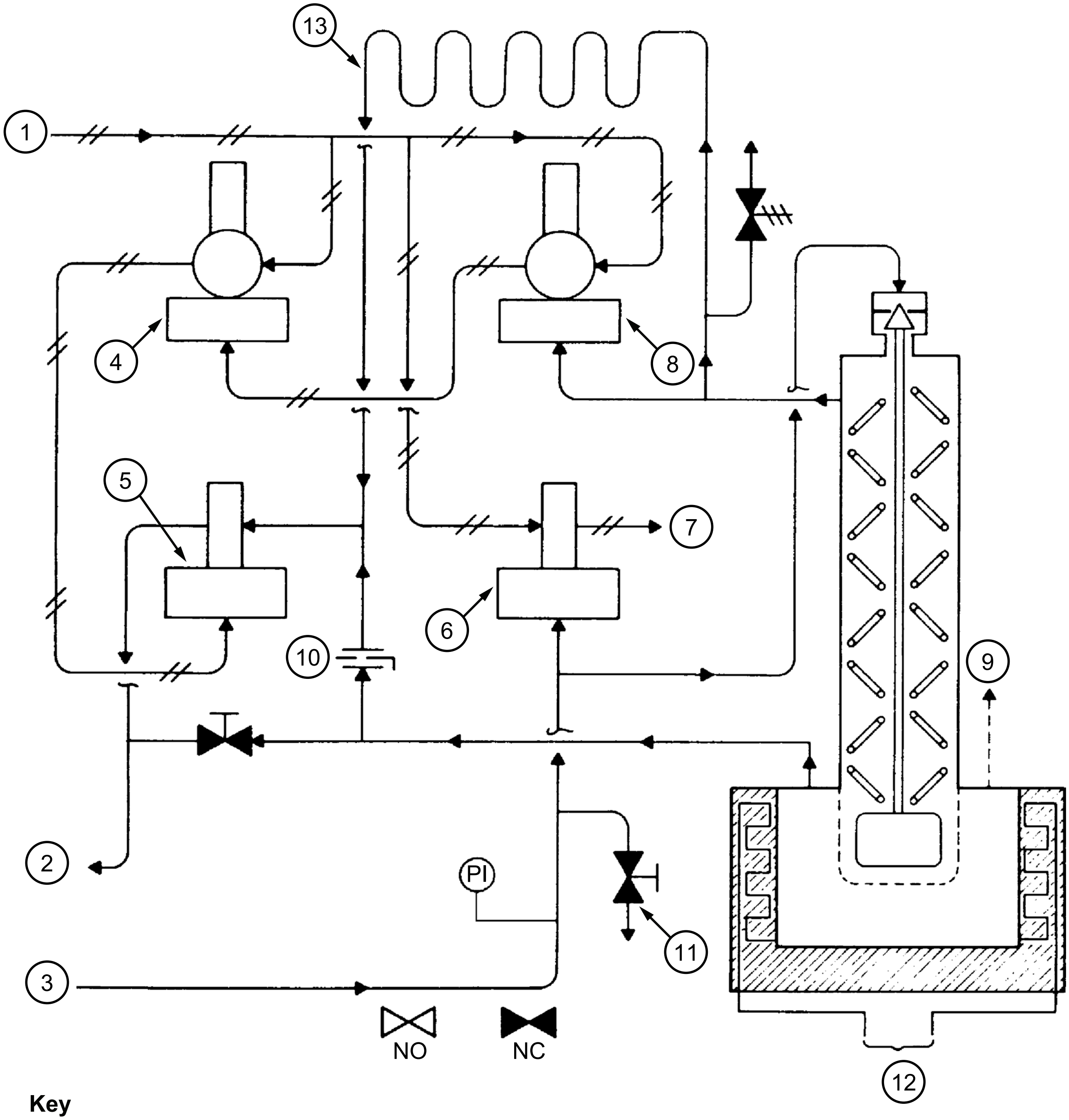
This technique differs from conventional “boiling pots” in that the sample flows as a “thin film” over a vertical distillation column that requires much less energy to vaporize the sample (see Figure 23-5). This greatly reduces the potential for “coking” of the sample (and therefore the annual manhours required for maintenance).



Key

1	air supply	9	30 PSIG
2	safety out	10	no. 1 amplifier
3	sample in	11	no. 2 amplifier
4	strainer	12	overheads orifice
5	eductor	13	bottoms orifice
6	sample out	14	condenser
7	sample pressure valve	15	filter coalescer
8	sample outlet valve		

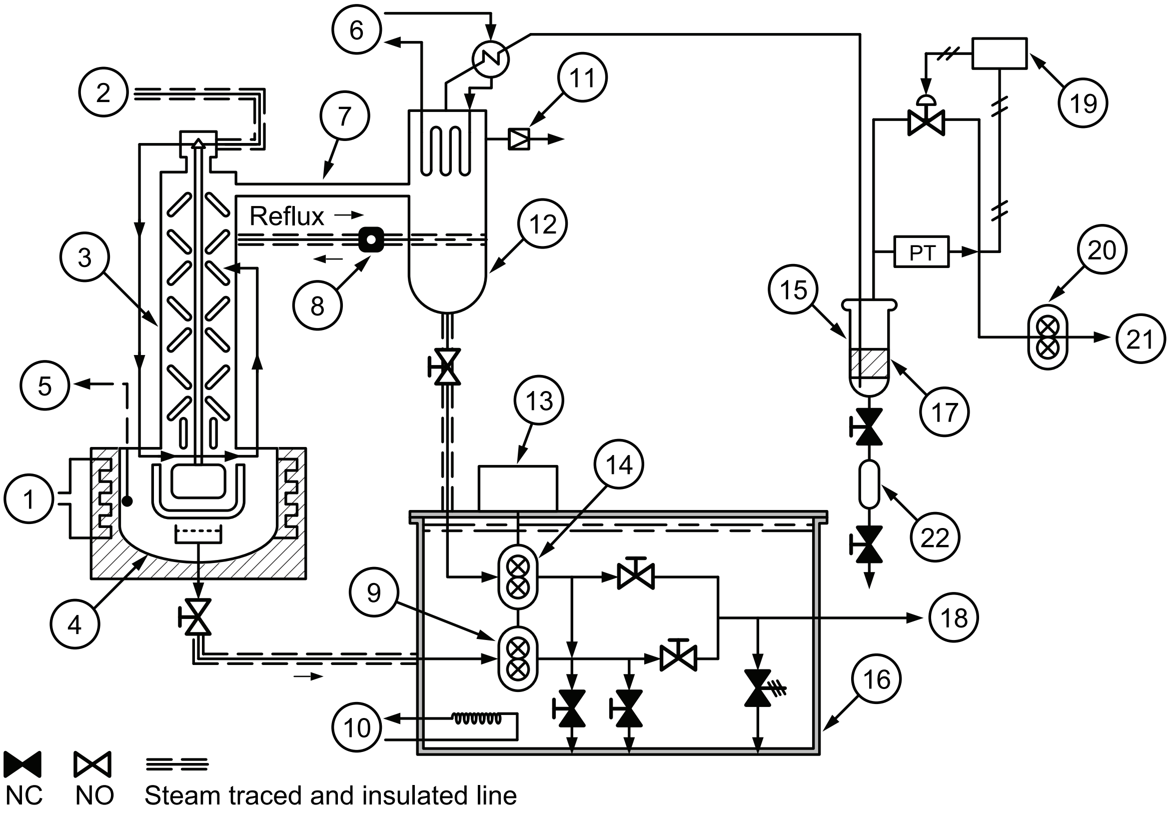
Figure 23-2—Boiling Point Analyzer with a Smaller Boiling Pot



Key

1 air in
2 sample out
3 sample in
4 amplifier no. 2
5 sample valve
6 pressure switch amplifier
7 to pressure switch
8 amplifier no. 1
9 thermocouple out
10 bottoms orifice
11 sampling valve
12 115/230 VAC
13 condenser

Figure 23-3—End Point Analyzer



Key

1	230 VAC
2	sample in
3	distillation tower
4	reboiler
5	thermocouple out
6	coolant
7	overheads
8	sight glass
9	bottoms pumps
10	steam
11	rupture disc
12	condenser
13	motor
14	overhead pumps
15	condensate recovery vessel
16	oil-filled bath housing
17	demister screen
18	sample out
19	pressure controller
20	vacumm pump
21	to atmosphere
22	blowdown tank

Figure 23-4—Vacuum Distillation Analyzer

23.4 Typical Boiling Point Analyzer Specifications

Sample system complexity:	average to complex
Typical analysis spans:	37 °C to + 370 °C (100 °F to + 700 °F)
Typical analyzer outputs:	local indicator, Thermocouple, 4 mA to 20 mA
Manufacturer’s listed accuracy:	± 1 % of sample boiling range
Typical analysis precision:	correlates to ASTM D86
Typical analysis time:	continuous, 10 minutes to 15 minutes

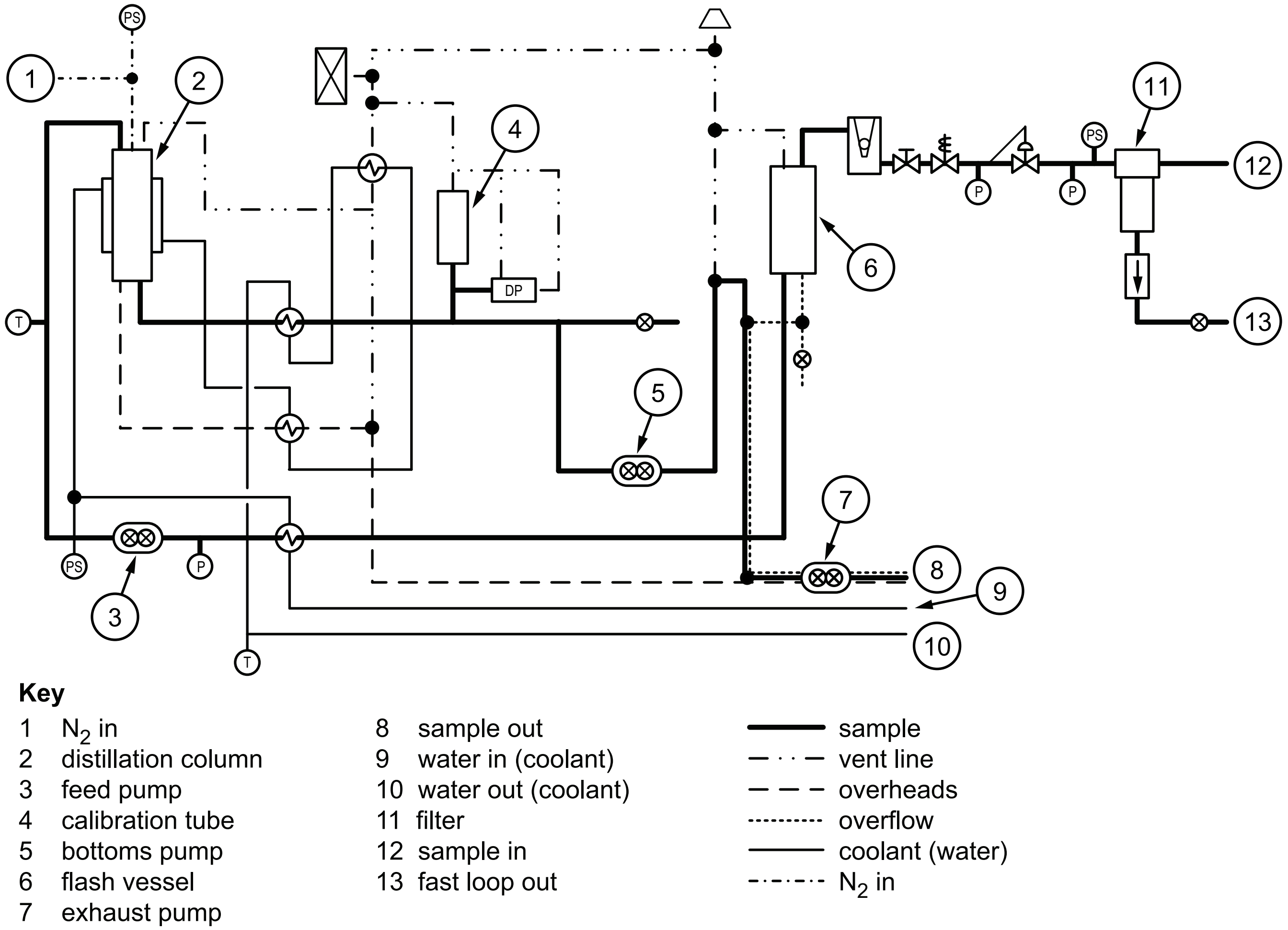


Figure 23-5—Thin Film Boiling Point Analyzer Flow Schematic

Typical on-stream time:	< 95 %
Relative installed price:	$80K up
Relative maintenance frequency:	0.5 man-hour/day or less
Average startup:	3 man-days
Typical refinery applications:	CCU units, gasoline blending, gasoline
Sample temperature limits:	– 20 °C to 150 °C (– 4 °F to 302 °F)
Sample flow rate:	0.2 gph (11 liters/min)
Sample pressure:	1.4 to 28.1 kg/cm^2 (20 psig to 400 psig),
Sample temperature:	5 °C (40 °F) below IBP (275 °F, 135 °C max)

23.5 Sampling Systems

Typically, the sample must at least 5 °C (40 °F) below the Initial Boiling Point, but no more than 135 °C (275 °F) at the inlet to the analyzer. Typical sample flow rates varying according the type, model, and manufacturer but vary between are 0.2 l/min to 2 l/min (0.05 gal/min to 0.5 gal/min) as a minimum flow. Maximum allowable sample pressures typically range from 20 psig to 400 psig (1.4 kg/cm^2 28.1 kg/cm^2). If there is significant downstream pressure on the return line, the minimum differential (supply to return) is 30 psig (2.1 kg/cm^2).

For low temperature applications, normal process water may be utilized to cool the sample. For higher temperature streams, a 50/50 mixture of glycol/water in a re-circulating bath may be required. Sample coolers are typically available from the manufacturer as an option. A typical sample system is shown in Figure 23-6.

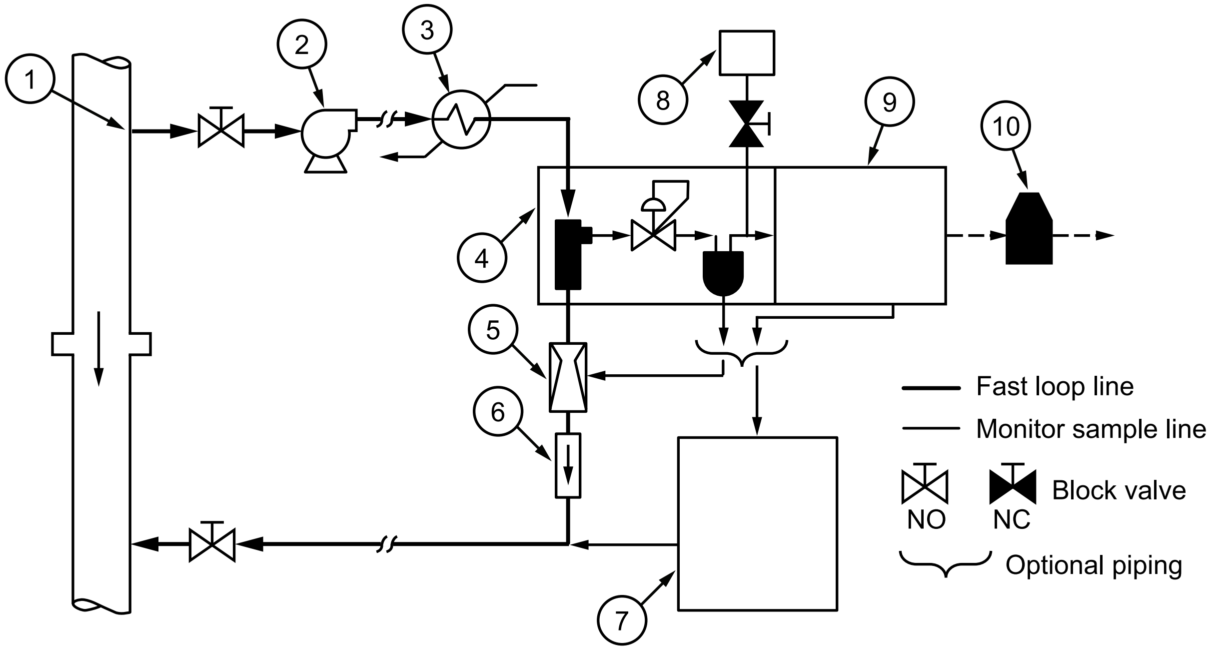
For additional details, refer to Section 4.

23.6 Installation and Calibration

Boiling point analyzers are generally located in rain/sun shelters. Some general considerations are:

The analyzer should be installed as close to the sample point as possible to minimize sample response time. Valves should be provided to isolate the sample cell from the process. It is often advisable to provide pressure and temperature gauges in the sample line to indicate proper sample conditions. The sample pressure to the analyzer inlet must be regulated.

Sample conditioning should adequately remove all particulate matter from the sample stream to avoid plugging small orifices. Free or entrained water should also be removed by a suitable coalescer.



Key

1 sample point
2 sample pump (if required)
3 sample cooler (if required)
4 sample conditioning
5 eductor (if required)
6 check valve
7 sample recovery system (if required)
8 calibration system
9 monitor
10 transmitter

Figure 23-6—Typical Boiling Point Analyzer Installation

Calibration is often accomplished with captured process samples, generally in 5 gal (19 liters) DOT rated tanks, that have been analyzed in the refinery laboratory.

For additional installation, calibration, start-up and maintenance, see manufacturers instructions and refer to Section 4 and Section 6.

23.7 Sample Material Problems

Many of the materials analyzed by distillation analyzers are highly flammable and have low flash points, which make them particularly susceptible to ignition if released to the atmosphere. If a sample is taken from a process line carrying material at relatively high pressure and at a temperature above its auto-ignition temperature, the slightest leak in the sample line can be the cause of a fire. Even though the sample material does not flash as it emerges from a leak, it may vaporize and create a potentially explosive atmosphere. The sample is analyzed in a case or housing which contains the electrical equipment of the analyzer and where it is possible to have a source of ignition. Therefore, sample lines and all connections must be made leak-proof.

Hot sample lines, in addition to being leak-proof, should also be insulated or shielded for personnel protection. Sample coolers, where used, should be equipped with automatic over-temperature shutoff valves in the sample line.

With some boiling point analyzers the low back-pressure effluent can be returned to the process by an educator included in the sample conditioning package.

Pumps and piping are the prime sources of mechanical leaks. where pumps are used, provision for disposal of leakage should be considered when designing the installation. If an analyzer is equipped with its own pumps, the proper provision for collecting and draining leakage should be an integral part of the apparatus. Where pumps are installed separately, good-quality leak-proof pumps, such as “canned” pumps, will help to ensure a tight system.

The use of screwed joints should be minimized to avoid piping leaks. Tubing and high-quality tubing fittings should be used wherever practicable.

23.8 Effluent Disposal

Sample disposal is a problem common to all analyzer installations whether the sample is unchanged, vaporized, or distilled and condensed. The end products in any case must be disposed of to a safe location. Practices for hydrocarbon drains in the particular refinery should be followed. Overhead vapors may be condensed and disposed of as liquid. Bottoms should be cooled, if required, for disposal.

Liquids that are virtually unchanged in the analyzer, or liquids that will cause no contamination (such as fractionated liquids and bottoms) may be pumped back to the process line. Liquids that cannot be returned to the process line should be pumped to the blowdown system or other safe disposal point. Relief valves in the sampling system or at pumps should be piped to vent or drain.

The low-back-pressure discharge requirements for most analyzers can be met by installing a vented receiver with a level controller and pump. The level controller can be arranged to automatically start and stop a pump that has sufficient head to deliver the liquid. (See Figure 4-11.)

24 Flash Point Analyzers

24.1 General

This section covers process analyzers used to measure the flash point of refinery products. The flash point is the lowest temperature at which a liquid will produce sufficient vapors to ignite, if exposed to an ignition source.

Flash Point analyzers continuously monitor the flash point temperature of hydrocarbon samples in correlation with ASTM procedure D56-79 (Tag Closed Cup), ASTM procedure D92-78, IP 36-67 (75) (Cleveland Open Cup), or ASTM procedure D93-80, IP 34-75 (Pensky-Martens Closed Cup).

It should be recognized that the three procedures referenced above have some overlap and that, generally, Pensky-Martens and Cleveland tests are used at higher flash point temperatures and on more viscous fuels.

24.2 Applications

Flash point analyzers are most frequently used to determine the flash point temperatures of heating oils and jet fuel. There are applications in pipeline service for interface detection or for the detection of hot spots in commodity transfer.

24.3 Methods Of Operation

For on-line flash point analyzers there are two testing methods used for detection of the flash point. One measures the temperature of ignition of a heated sample that is mixed with a constant flow of air; the other relates the temperature of a catalytic reaction using a catalytic detector that correlates to the flash point temperature. Both analyzer methods correlate to ASTM procedure D56-79.

24.3.1 Flash Point Detection By Ignition

There are two kinds of analyzers that utilize this method of detection.

24.3.1.1 As illustrated in Figure 24-1, this type of flash point analyzer, which measures ignition temperature, introduces a controlled flow of fuel and air into a flash chamber while raising the temperature of the mixture at a constant rate. Vapors are exposed to a high voltage spark at regular intervals until ignition occurs. Ignition can be detected by monitoring vapor temperature rise, or by monitoring flash chamber pressure for the pulse that occurs at ignition. At the moment of ignition the temperature of the fuel-air mixture entering the flash chamber represents the flash point temperature.

This type of analyzer is cyclic, and on ignition, shuts off the spark and the sample heater, returns the heater control to its initial level, and utilizes the fuel-air mixture to reduce flash chamber surface temperature sufficiently to prevent auto-ignition at the end of the cooling cycle.

Analyzers of this type are generally operated over temperatures from 50 °F (10 °C) – 250 °F (121 °C). They are limited to light distillate products having a viscosity below 215 CS @ 100 °F (1000 SUS @ 37.8 °C), and correlate to ASTM procedure D56-79 (Tag Closed Cup Method).

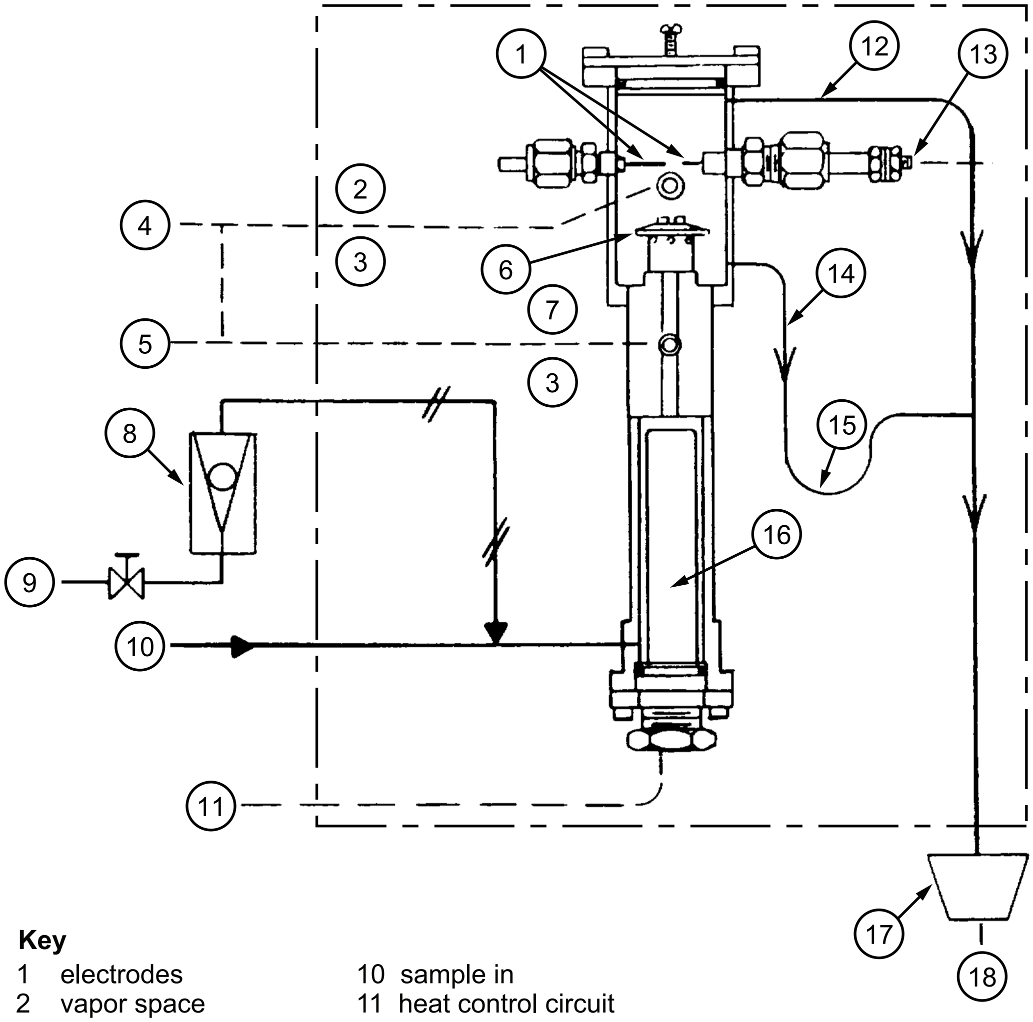
24.3.1.2 A second type of flash point analyzer which utilizes ignition for detection of flash point has been designed to minimize coking at higher temperatures, and therefore, correlates to all three ASTM procedures previously referenced due to its ability to measure heavy fuels as well as lighter distillates. It is illustrated in Figure 24-2.

In this analyzer, air is preheated before being introduced into the fuel. The fuel is heated by a low watt heater element, designed to minimize coking in the reaction chamber.

The unit utilizes a motor-driven potentiometer to establish a temperature control set point. The controller monitors fuel temperature as the controlled variable and varies voltage to the heater on a ramp basis, increasing heater voltage during heating cycles and reducing heater voltage during cooling cycles. By maintaining continuous heat, coking tendencies are limited. Ignition is detected by a pressure pulse, which initiates a cooling cycle of less than half a minute.

Temperature set point is lowered, spark circuits are turned off, and a purge solenoid valve is energized, directing a large volume of air into the flash chamber to cool internal surfaces, blow soft coke off the electrode, and exhaust spent gases. A motorized filter protects the exhaust pump from coke particulate matter that may carry over from the flash chamber.

This type of analyzer is suitable for flash point temperatures up to 600 °F (315 °C) and sample viscosity up to 2000 CS @ 100 °F (9300 SUS @ 37.8 °C).



Key

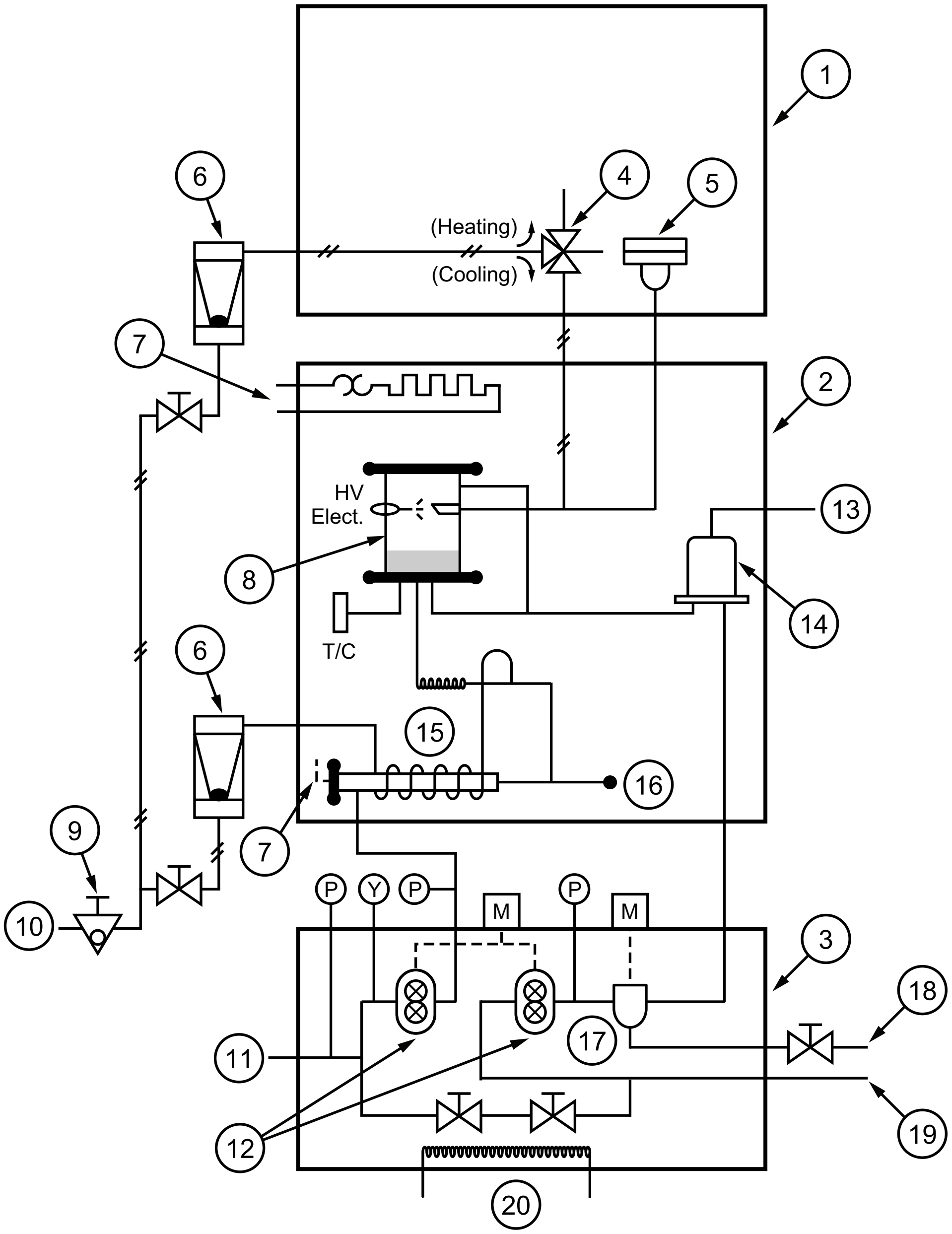
1	electrodes	10	sample in
2	vapor space	11	heat control circuit
3	thermocouple	12	vapor vent
4	detection circuit	13	high voltage spark circuit
5	measuring circuit	14	liquid drain
6	splash shield	15	liquid trap
7	liquid	16	cartridge heater
8	flowmeter	17	flame arrester drain
9	instrument air in	18	atmospheric drain

Figure 24-1—On-line Ignition Type Flash Point Analyzer

Analyzer output is constant at flash point temperature once the analyzer achieves equilibrium. The cooling cycle is too brief to affect the measuring thermocouple that is immersed in the liquid at the base of the flash cup.

24.3.2 Flash Point Detection by Catalytic Reaction

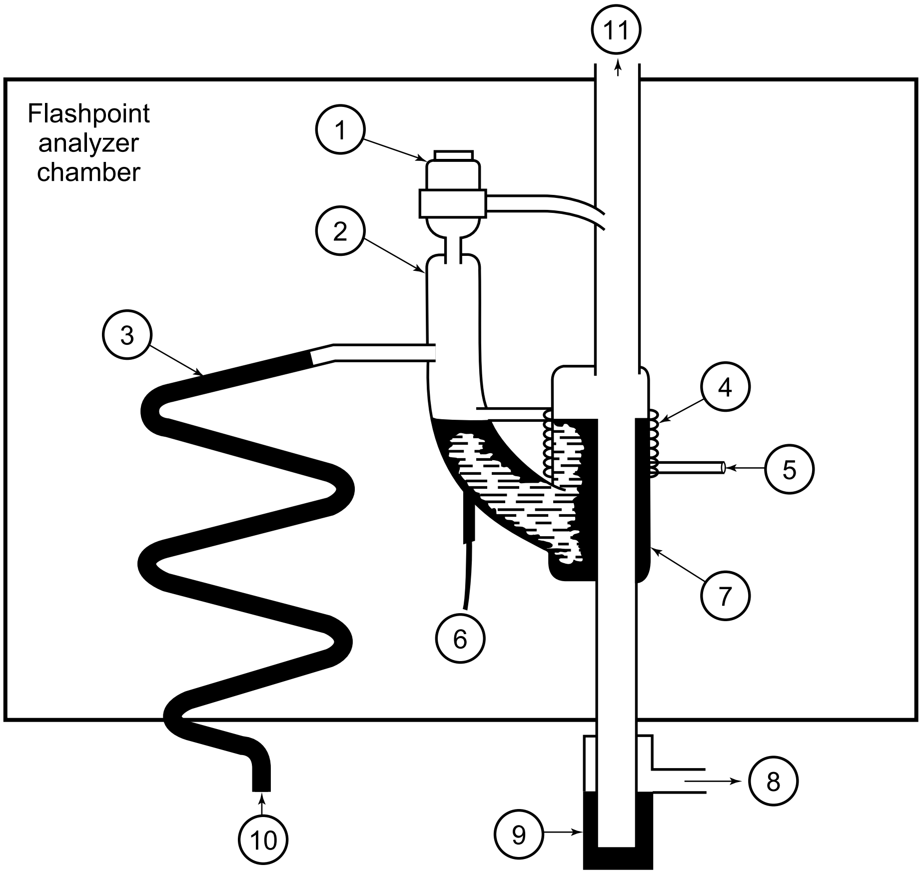
As illustrated in Figure 24-3, the catalytic detection type flash point analyzer continuously introduces a heated fuel and air mixture into a measuring chamber containing a platinum/palladium catalytic element. The surface temperature of this element varies with hydrocarbon vapor concentrations. The critical vapor concentration of given products and their corresponding influence on the surface temperature of the element has been empirically determined. Vapor concentrations are maintained at critical levels through regulation of sample temperature. A RTD in the heated liquid sample continuously measures the inferred flash point temperature in correlation to ASTM procedure D56-79.



Key

1	control chassis	11	sample in
2	measuring chassis	12	pump
3	pump assembly	13	vent
4	solenoid valve	14	separator
5	pressure switch	15	sample heater
6	F1	16	RTD
7	115 VAC	17	filter
8	flash cup	18	drain
9	pressure regulator	19	sample out
10	air supply	20	LP steam

Figure 24-2—Flash Point Detection by Ignition—High Temperature, Anti-coking Design



Key

1 catalytic detector
2 air and fuel mixing chamber heater
3 sample heater
4 air preheaters
5 air in
6 flashpoint thermocouple to amplifier
7 overflow chamber
8 sample drain
9 flame trap
10 sample in
11 vent to safe height

Figure 24-3—On-line Catalytic Reaction Flash Point Analyzer

24.4 Sampling Systems

It is imperative that all possible moisture be removed, both from the sample and from the air supply. Flow rates of fuel and air must be regulated to permit reproducible analyzer performance. As fuel and/or air is used to cool these analyzers, temperature control of these components is required to prevent auto-ignition and to keep cooling cycle times at a minimum.

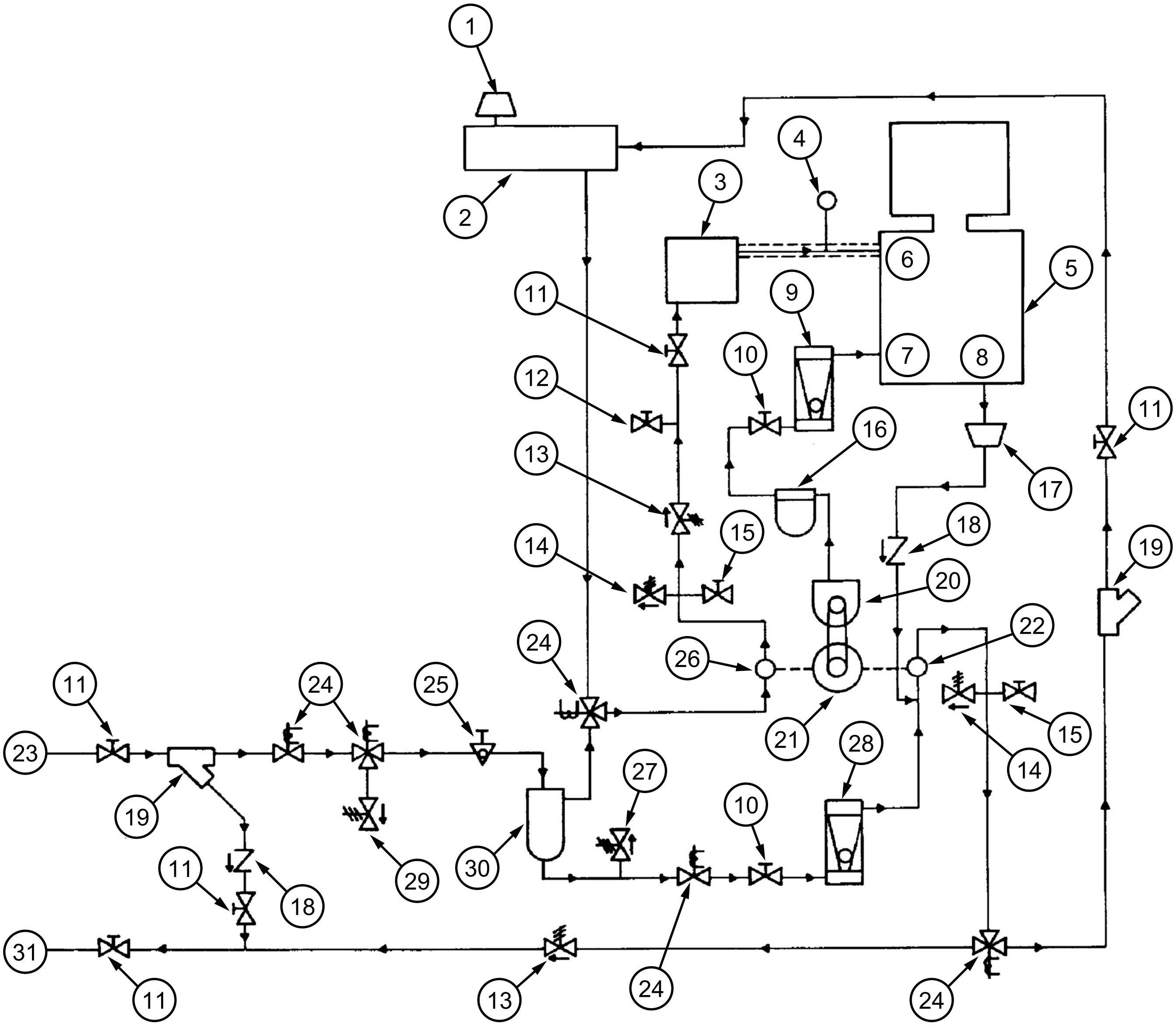
Manufacturer’s recommendations regarding sampling system should be considered.

For further information on sample systems, see Chapter 4.

24.5 Installation

Spent sample from the analyzer should be cooled. Flame arrestors are recommended for vent and drain lines. Back pressure on vent lines will affect the discharge of spent gases and the fuel-air ratios of the test sample. Heating of vent lines may be required to prevent blockage caused by sample condensation. A typical installation is shown in Figure 24-4.

Refer to the manufacturer for specific recommendations regarding installation, and to Chapter 6.



Key

1	vent	12	calibration	22	exhaust pump
2	sample calibration reservoir	13	125 psig (8.79 kg/cm^2)	23	sample in
3	mechanical refrigeration	14	500 psig (35.16 kg/cm^2)	24	solenoid valve
4	sample temperature	15	air bleed	25	pressure regulator
5	flash point monitor	16	air filter	26	feed pump
6	sample in	17	vent flame arrester	27	75 psig (5.27 kg/cm^2)
7	air in	18	check valve	28	sample flow meter
8	sample out	19	Y-strainer	29	800 psig (56.25 kg/cm^2)
9	air flow meter	20	air compressor	30	filter coalescer
10	adjusting	21	motor	31	sample out
11	shut off				

Figure 24-4—On-line Flash Point Analyzer—Typical Installation

24.6 Safety

Flash point analyzers must be considered as hazardous because sample is heated and ignited. Explosion-proof flame arrestors, shielding of hot surfaces, and hazardous warning signs are recommended for safe operation. Allow adequate time for cool-down before maintenance.

Refer to analyzer manufacturer for specific safety recommendations**.**

25 Vapor Pressure Analyzers

25.1 General

Vapor pressure instruments are usually the continuous type. The product is pumped, without interruption, through the instrument yielding a continuous output signal that is recorded or used as an input to a controller, or both.

25.2 Applications

Reid Vapor Pressure (RVP) analyzers are most often used in gasoline blending applications. The output of the monitor is used to control the setpoint of the butane flow controller to maximize the addition of butane to gasoline without exceeding the RVP specification. Techniques for measuring the Reid Vapor Pressure include both continuous and batch-mode methods.

25.3 Types of Reid Vapor Analyzers

Instruments which determine Reid vapor pressure (see Figure 25-1) are built to simulate the procedure described in ASTM D323 *Test for Vapor Pressure* of *Petroleum Products (Reid Method)* wherein the sample is brought to equilibrium with air in a constant-temperature chamber. The pressure in the chamber is the signal to the recorder, which is calibrated in pounds of Reid vapor pressure.

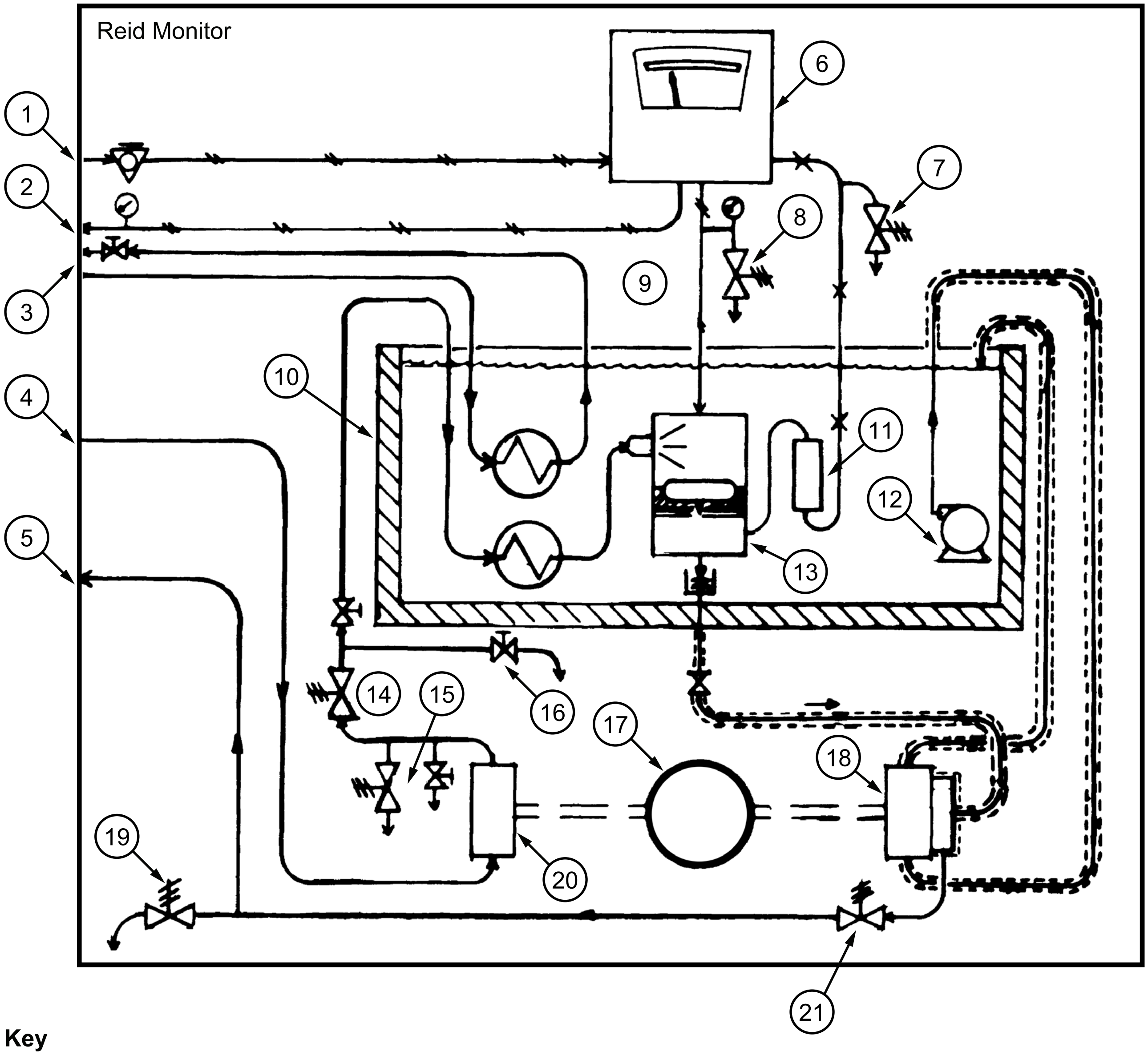
An alternative to the continuous measurement method exists in ASTM D2551 *The Micro Method of Reid Vapor Pressure*. A sample cell is maintained at 100 °F in a chamber designed to provide a 4 to 1 vapor-to-liquid ratio. Using solenoids, sample is introduced slowly through a capillary tube until the appropriate level is obtained in the sample cell. The sample is then allowed to come to equilibrium for a predetermined period. The vapor pressure above the liquid is measured and the sample is dumped and the cell and chamber flushed several times with air prior to the start of the next cycle. Typical cycle times are less than 10 minutes (see Figure 25-2).

25.4 Kinetic Vapor Pressure Analyzers

Another type of vapor pressure analyzer makes use of an ejector-type nozzle. The ejector device works on the principle of increasing the kinetic head until the static head at the nozzle discharge reaches the vapor pressure of the liquid (see Figure 25-3). When the pressure at the tip of the nozzle attains the vapor pressure of the fluid being educted at the stream pumping temperature, a cut-off or cavitation limit occurs which determines the maximum quantity pumpable for a given suction condition. To take advantage of this, the sample is forced through the nozzle of the analyzer at a preset constant high pressure and at a corresponding velocity so that the existing liquid velocity will be large. Under these conditions, pressure in the diffuser chamber will approach and be limited by the vapor pressure of the sample. This pressure is measured at the vapor chamber surrounding the nozzle tip and is identical to that in the diffuser chamber. The analyzer can be calibrated for either absolute or Reid vapor pressure monitoring.

25.5 Safety Considerations

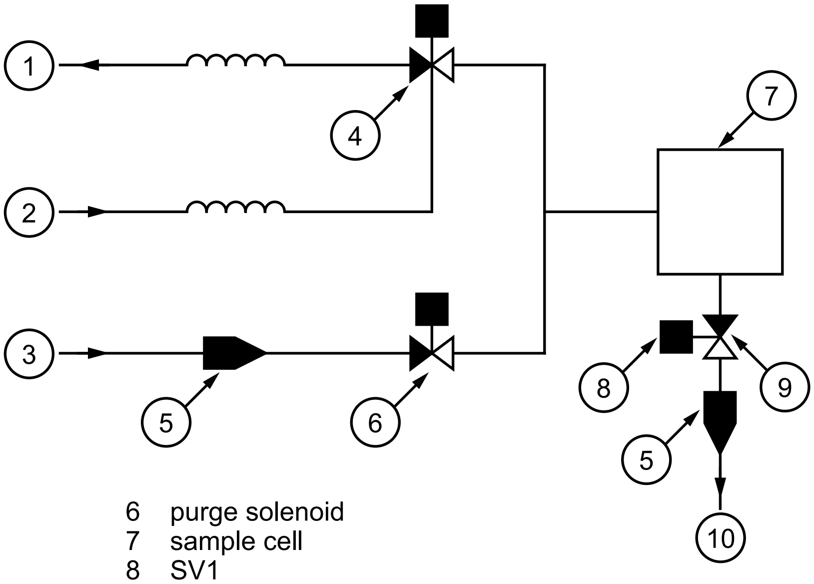
Safety considerations applicable to vapor pressure analyzers are covered in the Section E overview document, and in Chapter 7.



Key

1 20 psig air supply	12 circulation pump
2 3–15 psig	13 saturation chamber
3 output coolant	14 125 #
4 sample in	15 400 #
5 sample out	16 calibration valve
6 pressure transmitter	17 pump motor
7 10 #	18 exhaust pump
8 25 #	19 75 #
9 0.3–14.8 psig feedback	20 feed pump
10 oil bath	21 20 #
11 seal pot	

Figure 25-1—Continuous Reid Vapor Analyzer



Key

1 sample purge
2 sample in
3 purge nitrogen
4 sample solenoid
5 flameproof breather
6 purge solenoid
7 sample cell
8 SV1
9 drain solenoid
10 sample drain

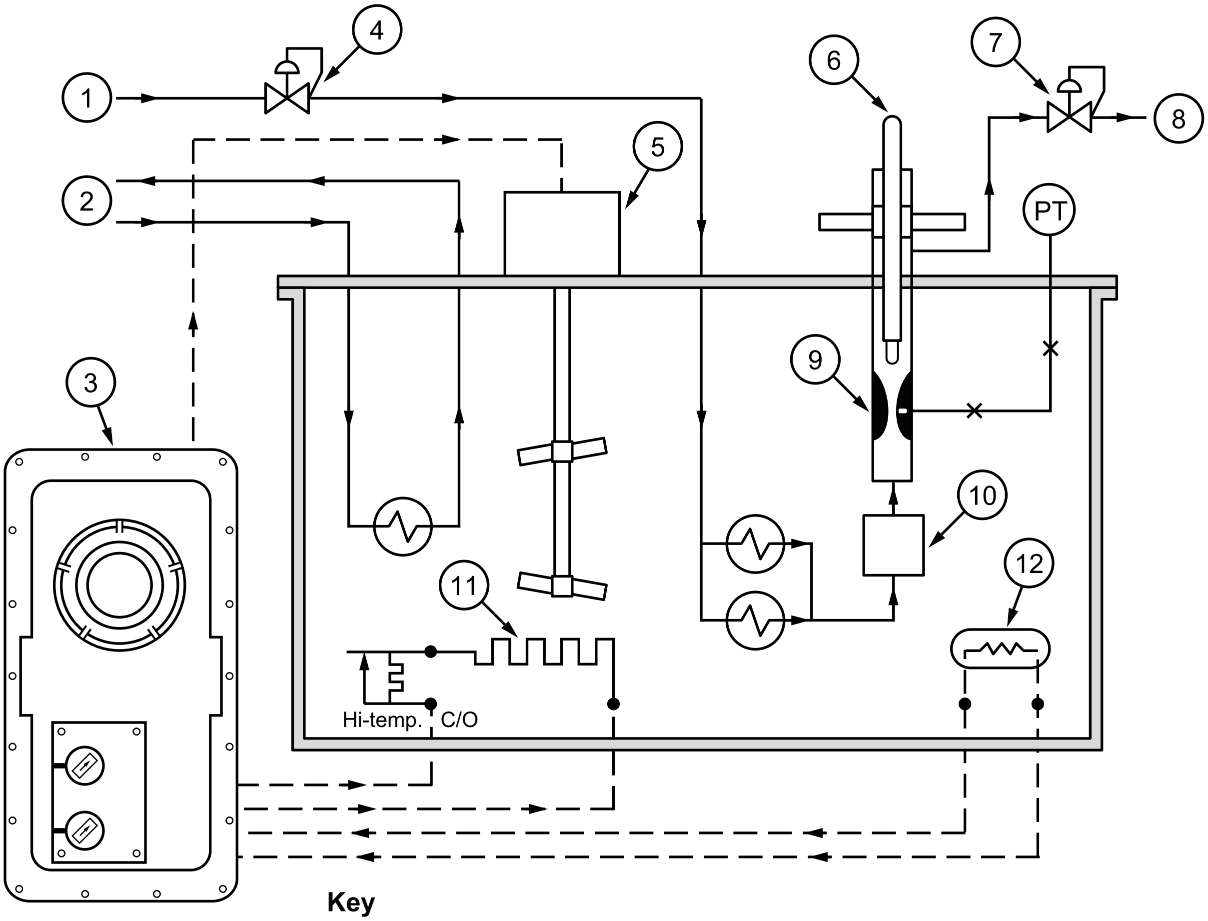
Figure 25-2—Micro-method Reid Vapor Analyzer

25.6 Analyzer Location

Reid and kinetic vapor pressure analyzers are usually located in a shelter or house near the gasoline blending operation.

25.7 Typical Reid Vapor Pressure Analyzer Specifications

Sample system complexity:	average
Typical analysis spans: 3 psig to 15 psig output	0 to 20 RVP (indication),
Typical analyzer outputs:	local meter, 4 mA to 20 mA
Manufacturer’s listed accuracy:	±0.1 to 0.2 RVP
Typical analysis precision:	±0.1 RVP
Typical analysis time:	continuous, less than 10-minute cycle
Typical on-stream time:	85 % to 95 %
Relative installed price:	$50 K up
Relative maintenance frequency:	1 to 1.5 man-hour/day
Average startup:	< 3 man-days
Typical refinery applications:	gasoline blending
Sample temperature limits:	50 °F to 110 °F (10 °C to 43 °C)
Sample flow rate:	100 cc/min (continuous method)
Sample pressure:	10 psig to 100 psig



Key

1 sample in
2 coolant
3 temperature controller
4 inlet pressure regulator
5 stirring motor
6 ASTM thermometer
7 back pressure regulator
8 sample out
9 ejector assembly
10 filter
11 bath heater
12 RTD

Figure 25-3—Kinetic Vapor Pressure Analyzer

25.8 Typical Kinetic Vapor Pressure Analyzer Specifications

Sample system complexity:	average
Typical analysis spans:	0 to 20 PSIA to 0 to 200 PSIA
Typical analyzer outputs:	local meter, 4 mA to 20 mA
Manufacturer’s listed accuracy:	± 5 % of span
Typical analysis precision:	± 5 % of span
Typical analysis time:	continuous
Typical dead time:	25 seconds

Typical response time:	43 seconds
Typical on-stream time:	95 %+
Relative installed price:	$50 K up
Relative maintenance frequency:	< 1 man-hour/day)
Average startup:	< 3 man-days
Typical refinery applications:	light distillates
Sample temperature limits:	70°F to 120°F (21°C to 49°C)
Sample flow rate:	10 to 50 GPH (38 to 190 LPH)
Sample pressure:	75 psig to 500 psig (5.3 kb/cm^2 to 35 kg/cm^2)

25.9 Sampling Systems

Key elements in the design of the sample system include the following.

a) Samples taken from process lines greater than 3 in. are extracted with a sample probe to ensure a representative sample is taken.

b) For optimum response a fast loop sampling system is employed to minimize overall system response (there typically is a minimum lag time of a minute through most vapor pressure analyzers). Fast loop sample and return lines should be sized and routed to ensure a linear flow rate of 2 ft/sec to 5 ft/sec (0.5 m/sec to 1.5 m/sec) to ensure the sample is well mixed (non-laminar). A pump may be required if an adequate flow rate cannot be established by normal pressure drops.

c) A sample slipstream conditioning system should be provided which regulated the pressure, filters the sample, and removes entrained water (during upset conditions).

d) A captured process sample, which has been analyzed in the laboratory, should be a key element in the design of the sample system. A water displacement system is often used to ensure the integrity of the captured sample (i.e., it does not lose its light components). Water displacement systems are readily available from the analyzer manufacturer.

e) If the sample return back-pressure exceeds the analyzer’s limits, it may be necessary to install a liquid sample recovery system. These are briefly described in the section overview and are also available from the analyzer manufacturer.

25.10 Startup

This topic is addressed adequately in the section overview. The manufacturer’s instructions should be followed in startup. See Chapter 6 for additional information on installation and startup of analyzers.

25.11 Shutdown Procedures

This topic is addressed in the section overview. Exact procedures should be obtained from the manufacturer.

26 Octane Analyzers

26.1 General

Laboratory Standard ASTM 2699/2700 describes procedures that evaluate the expected performance of gasoline in internal combustion engines using a rating system known as the octane scale. The octane scale is defined as a tendency of a fuel to “knock” in a special internal combustion engine called a knock engine. The assigned octane number scale is defined by the pure hydrocarbon, iso-octane (2,2,4-tri-methylpentane) as 100 octane number and n-heptane at an octane number of 0. Mixtures of these pure compounds are known as primary reference fuels (PRF). The octane number of any fuel can be defined as the percentage of iso-octane in a known mixture that knocks at the same compression ratio and at the same knock intensity as the fuel under test.

The ASTM Manual of Test Methods includes the standards and procedures for the ASTM-CFR (Cooperative Fuel Research) Engine. Knock intensity is measured by a detonation and intensity meters. The octane number of the sample is calculated by interpolation between the two reference fuels (PRFs) for lab engines, and by comparison to a proto-fuel for on-line knock engines (see ASTM 2885).

On-line octane monitors are based on ASTM-CFR engines or correlative techniques.

Manual and automatic knock test engines are available in a compression ratio, octane comparative or knock intensity systems. These engines are mechanically complex, require frequent and significant maintenance, and are very expensive to install.

Alternative Correlative techniques determine an octane number by partial oxidations that proceed at elevated temperatures without an ignition source or, alternatively, by the correlation of octane number with multivariate analysis of Near Infrared (NIR) spectroscopy.

26.2 Correlative Combustion Techniques

26.2.1 Theory of Operation of Combustion Techniques

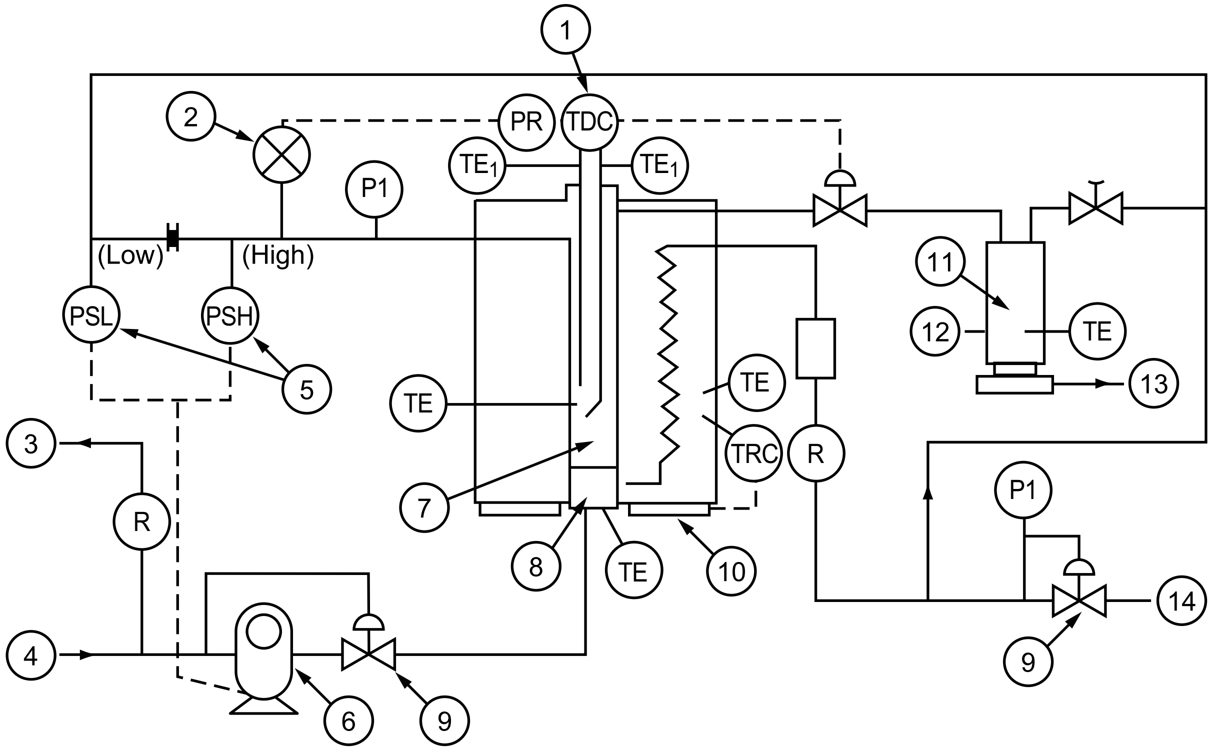
Correlative techniques attempt to relate combustion properties of hydrocarbons that correlate resulting temperature or pressure changes with octane. They are relatively simple relative to an octane engine and have been used for process stream analysis. These techniques have not replaced CFR octane engines for blenders because of the relatively poor accuracy that they provide, and the need to re-calibrate if the sample changes significantly. These techniques have been described extensively by Clevett.[1]

The method developed is based on the premise that the partial oxidation of hydrocarbons, which proceeds at elevated temperature without a source of ignition or catalyst, can be related to octane. The measurement system basically consists of a hot reactor tube. Sample flows through the tube where an exothermic partial oxidation takes place. This results in an maximum temperature at an octane dependent distance down the reaction tube. In practice the maximum temperature point is kept constant by varying the reactor pressure. The required reactor pressure is then calibrated against octane. See Figure 26-1.

Another developed technology is referred to as “cool flame.” In this system a small precisely measure amount of sample is injected into a constant temperature reactor along with a continuous flow of air. The temperature of the exothermic reaction is measured and is correlated with octane.

26.2.2 Applications

Both techniques have been used for octane analysis in process units such as reformers where use of a CFR engine is impractical because of the high maintenance required. These techniques have largely been supplanted by use of NIR that is lower in maintenance and can operate over a wider range of process conditions without re-calibration.



Key

1 temperature differential controller
2 pressure transmitter
3 sample bypass loop
4 sample inlet
5 pressure switches
6 metering pump
7 reactor chamber
8 preheater
9 pressure controller
10 bath heater
11 afterburner
12 flow controller
13 vent to stack
14 instrument air

Figure 26-1—Cool Flame Octane Analyzer

26.2.3 Materials of Construction

Sample system components should be stainless steel, and gaskets and filters should be appropriate for hydrocarbon service.

26.2.4 Safety Considerations

Both units are designed for use in hazardous conditions. Both use high temperature reactors. Maintenance practices may require bringing the unit to ambient temperature to avoid situations hazardous to the facility or to service personnel.

26.2.5 Sample Disposal Considerations

Effluent from these systems is a gaseous oxidation product which can be vented to a small stack on the instrument house. The cool flame system effluent is a combustion product vented through a flame arrestor and a small amount of condensed liquid hydrocarbon that is collected in a drip pot.

26.2.6 Calibration and Startup

For the “hot reactor” analyzer, a calibration curve must be developed describing the relationship between octane and the reactor pressure. This is done using three primary reference fuels and a proto-fuel. Two of the primary reference fuels should bracket the expected octane, and the third should have the same octane as the proto-fuel. The reactor temperature is varied until the pressure obtained for the reference fuel with the same octane as the proto-fuel gives the same reactor pressure. The three reference fuels are then used to calibrate the analyzer.

For the “cool flame” analyzer the correlation between octane and maximum temperature must be determined for the chosen reactor temperature using a set of proto-fuels which span the expected octane and which are chemically similar to the expected product.

26.2.7 Maintenance

Routine maintenance is typical of sample systems, such as measuring flows and changing filters. A proto-fuel should be re-run periodically to assure accurate performance. Additionally, re-calibration is required if the sample octane or composition changes significantly.

26.3 Analytical Type—NIR

NIR octane model based analyzers employ optical spectroscopy as the basis for octane measurement. The principles of infrared spectroscopy are described in Chapter 11; however, unlike the analyzers described there, NIR octane analyzers are “full spectrum” analyzers which examine a broad continuous spectrum rather than one or a few wavelengths. Several optical configurations are used including Fourier transform interferometers (FTNIR), moving gratings, acoustic optical tunable filters, and fixed gratings with diode array detection.[2] These analyzers are being used both in blenders, as alternative to high maintenance octane engines, as well as in refinery process units where engines are not used and the alternative correlative methods are less accurate and more maintenance intensive.

26.3.1 Theory of Operation NIR/FTNIR Octane Analysis

Near infrared light is transmitted through the hydrocarbon sample and absorbed by the sample molecules. The amount of light absorbed at a given wavelength depends on the chemical composition of the sample and the concentrations of the various components. When light absorbance is plotted as a function of wavelength, a spectrum is produced. A typical spectrum is shown in Figure 26-2.

The spectrum represents the average chemical composition of the sample. Since octane is dependent on this composition, the octane can be derived from it by mathematical correlation with octane engine values. The mathematical correlation techniques used are diverse but are grouped under the general term “Chemometrics”. Chemometrics is the use of statistics and mathematical techniques to extract the chemically relevant information from a set of chemical data and develop calibrations using numerical data. Typical techniques include Partial Least Squares (PLS), Principle Component Regression (PCR) and Multiple Linear Regression (MLR).

26.3.2 Applications

Research Octane (RON) and Motor Octane (MON) can in principle be obtained for nearly any single phase liquid hydrocarbon stream. Gasoline, reformate, and alkylate are the most commonly analyzed streams to date. Road octane (RON+MON)/2 is generally determined via separate calibrations for RON and MON rather than direct calibration. In addition it is common to determine additional parameters with the same NIR data, but not necessarily limited to parameters such as distillation points, benzene, total aromatics, total olefins, total aliphatics, and oxygenates such as Methyltert-butyl Ether (MTBE), Tert-Amylmethyl Ether (TAME), methanol or ethanol.[3]

26.3.3 Materials of Construction

The system is typical of liquid hydrocarbon sample system components. The sample cell or probe should be constructed of stainless steel, with windows constructed of a suitably compatible, optically transparent material such as Near Infrared quality amorphous quartz, barium fluoride, or sapphire. Cell or probe gaskets or other seals should be made of materials appropriate for hydrocarbon service at process sample temperatures and pressures.

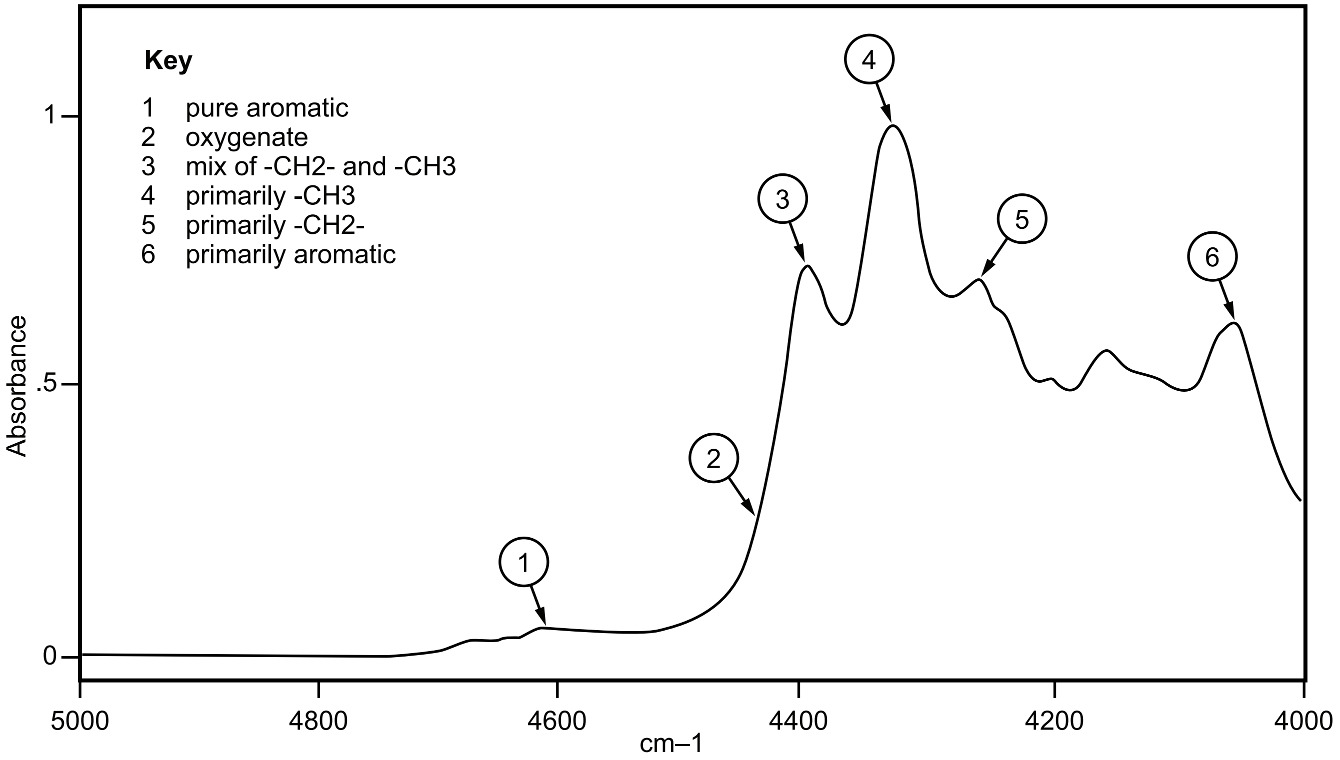


Figure 26-2—Typical NIR Spectrum of a Reformulated Gasoline

26.3.4 Sampling Systems and Installation

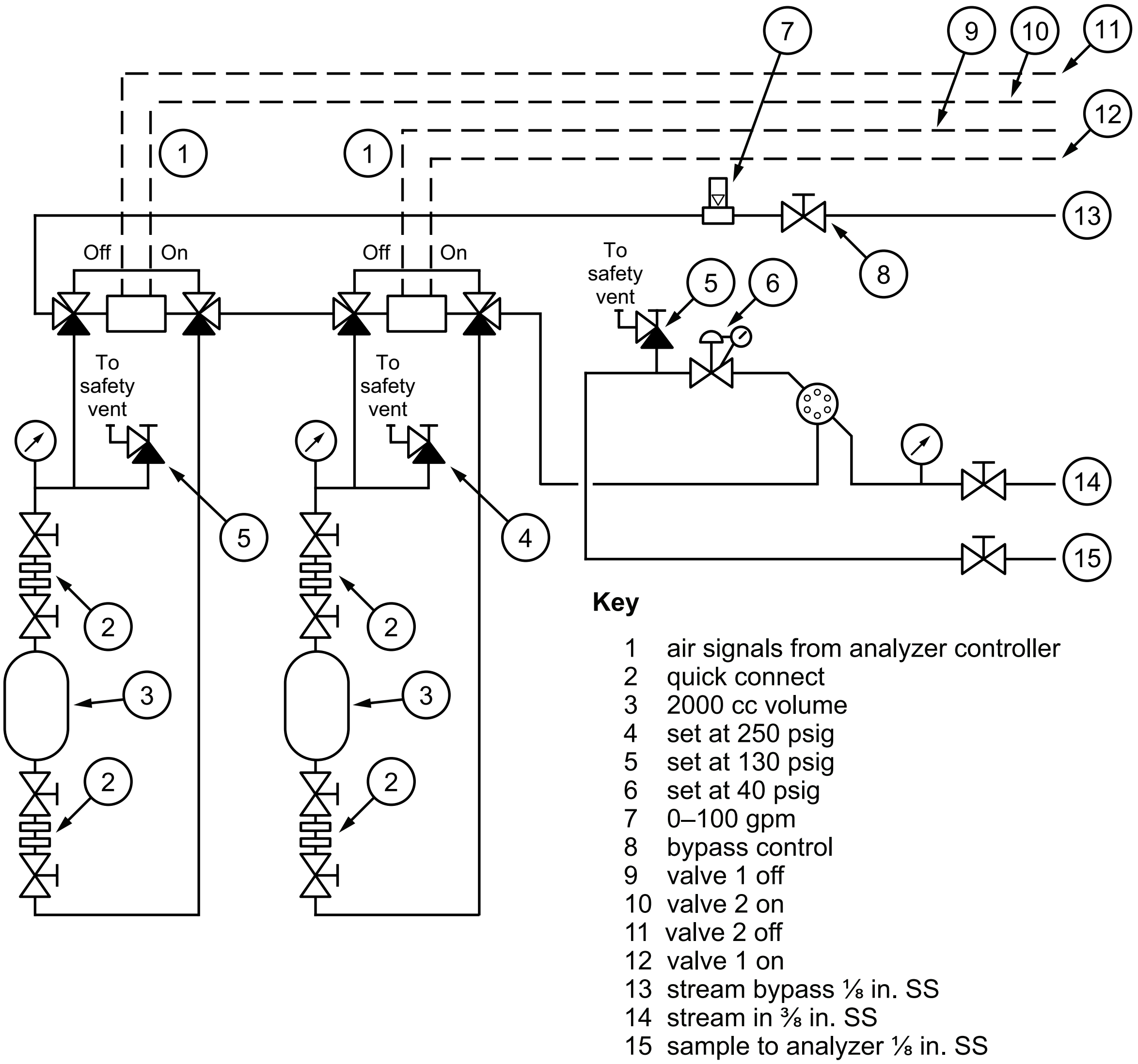
Two types of systems are typically used for NIR/FTNIR octane model-based analyzers, extractive sampling systems and in-situ probes.

It is important to assure that anything in the sample that might cause light scattering is minimized or removed by filtering the sample before analysis. This includes particulate, emulsions (such as from water), or bubbles. Likewise care must be taken to assure that pressure drops do not cause bubbles in the sample system.

NIR/FTNIR spectra change with sample temperature. It is advisable to control the sample to a constant temperature. An increase in sample temperature decreases the intensity of the spectrum due to a sample density decrease, and temperature-related spectral shifts that broaden peaks in the spectrum. A density change can be corrected by scaling, but the broadening and shifting phenomenon is complex. For gasoline and other light-to-intermediate streams, a suitable temperature control must be provided which minimizes bubbles from volatile components and the condensation of ambient water vapor which might occur at lower temperatures. Alternatively, some systems minimize the sensitivity to sample temperature change by appropriate processing of the spectrum during calibration and prediction.

Extraction sampling systems can serve multiple functions including sample extraction from the process; filtering; sample temperature control; switching of multiple sample streams; a maintenance wash cycle; the introduction of reference fluids; and importantly, proper flow of the sample through a sample cell.

An extractive sample system can be used to switch a wash solvent into the sample cell. Toluene is often used for both reference and wash solvent but the material chosen will vary with the analyte. The sample system can also be used to wash and dry the cell so that an empty cell “zero” can be obtained. Figures 26-3 and 26-4 show an extractive sample system with two grab sample bottles, and a switching system which conditions the temperature of the sample and selects between sample, wash solvent, reference solvent and nitrogen gas.



Key

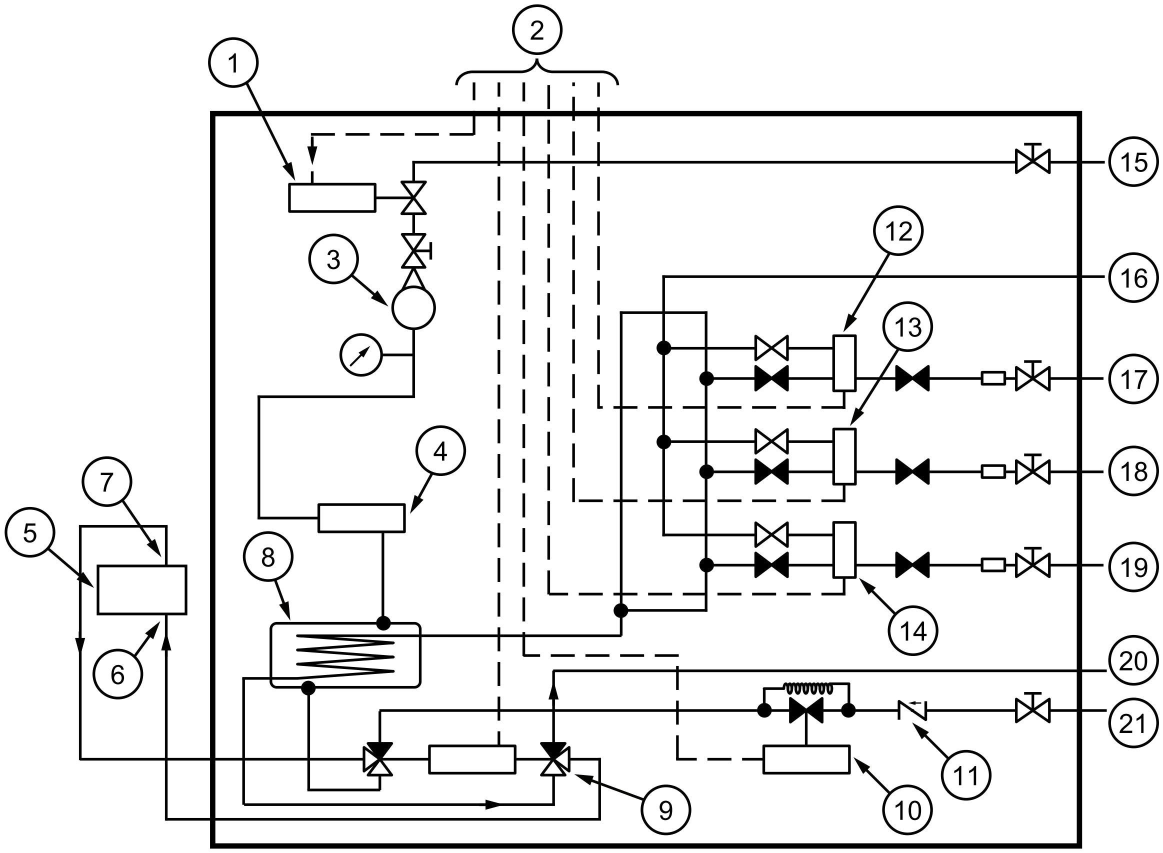
1 air signals from analyzer controller
2 quick connect
3 2000 cc volume
4 set at 250 psig
5 set at 130 psig
6 set at 40 psig
7 0–100 gpm
8 bypass control
9 valve 1 off
10 valve 2 on
11 valve 2 off
12 valve 1 on
13 stream bypass ⅛ in. SS
14 stream in ⅜ in. SS
15 sample to analyzer ⅛ in. SS

Figure 26-3—Single Stream Sample System with Two Grab Sample Bottles

Since ambient air contains NIR absorbing chemical species including water, the optical path must be purged with dry nitrogen or purified air. Requirements will depend on the specifics of the analysis, but a Dew Point of – 40 °F (– 40 °C) is typical.

In-situ systems of fiber optic cable and cell or probe are used directly in the process or preferably in a process bypass line, remote from the spectrometer. Figure 26-5 is a typical installation of an in-situ probe system. The use of fiber may not completely remove the need for some sample preparation. If optical fiber is used, care in materials selection and proper installation must be taken so that the optical signal is not affected by vibration, temperature, temperature gradients, bending, ambient light, or hydrocarbon coatings.

On probe systems, cell washing and zeroing is usually handled by manual removal of the probes from the system. In some systems a short term zero is obtained by obtaining a spectrum through a blank fiber loop or through a second path through the probe itself. These approaches allow compensation for spectrometer changes but do not compensate for changes in the probes. Such changes should typically be detected, when they occur, during calibrations or when comparisons are made of the spectrums obtained.



Key

1 sample shut-off valve
2 air signals
3 flow controller
4 flow switch
5 sample cell
6 sample in
7 sample out

8 heat exchanger
9 N2 & REV
10 high N2 flow
11 check valve
12 process
13 wash
14 reference

15 sample return ⅛ in. tubing
16 select valve vent
17 sample in
18 NC5 wash in
19 reference in
20 N2 out ¼ in. tubing
21 N2 in ¼ in. tubing

NOTE All lines are ⅛ in. SST unless otherwise noted. Air signal lines are also ⅛ in. SST.

Figure 26-4—Stream Switching and Sample Conditioning System

26.3.5 Safety Considerations

NIR and FTNIR systems contain electrical components and a hot light source that must be packaged properly to meet area safety requirements. Some systems may include a low powered internal laser.

Caution—Safety notices on the instrument should be followed carefully.

Fiber optic cable is not yet accepted as being intrinsically safe. Fiber optic cable use must be in accordance with the safety codes specified in the areas of installation.

26.3.6 Sample Disposal Considerations

NIR/FTNIR is a non-destructive technique. The extractive systems require sample return and there may be small volumes of hydrocarbon wash or reference solvents, which will also have to be disposed of. Generally the wastes can

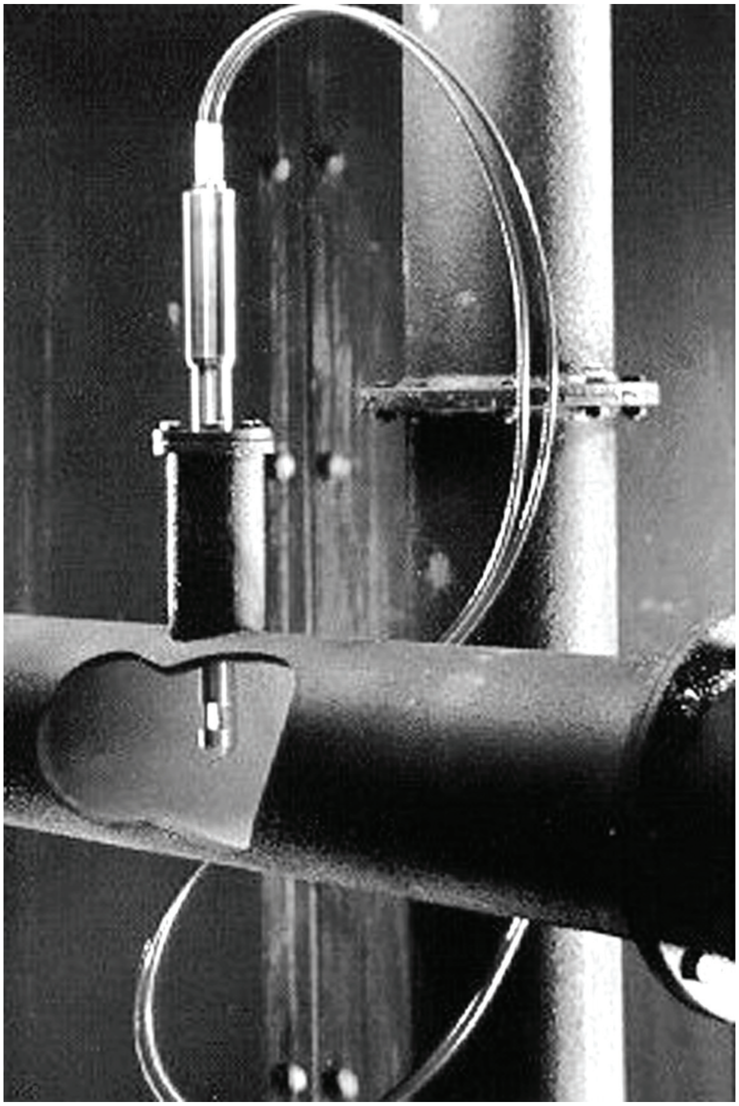


Figure 26-5—Typical Installation of In-situ Probe/Fiber Optic System

be returned harmlessly to the process, to a flare, or to a hydrocarbon sewer. If chlorinated wash solvents are used, alternative disposal may be required. In-situ probes may not have a return or sample disposal consideration in normal operation.

26.3.7 Calibration and Startup

Because the actual octane values obtained are correlational, calibration of a NIR octane analyzer is unique. Startup and calibration should be considered to consist of two separate components—a determination that the spectroscopic hardware is operating according to specifications, and the correlational calibration and its subsequent validation.

Methods of characterization of NIR hardware are described in ASTM methods[4] for FTNIR and for diffraction grating or prism based NIR's[5]. In general, tests could include a determination of signal-to-noise ratio, spectral stability, wavelength accuracy, wavelength precision, stray light, and detector linearity. In addition, for purposes of calibration maintenance and transfer, it is critical to demonstrate that an instrument will give precisely the same spectrum after optical maintenance (such as a light source replacement) as the original instrument, as well as other instruments of the same type in the laboratory.

The actual octane calibrations are generally either provided by the hardware vendor or by a corporate R&D group. Generally the calibration requirement on the end user is to assist in obtaining accurate CFR Engine octane values and NIR spectra of the samples needed for calibration. The samples required for calibration are a set of samples that represent both the span of octane, as well as compositional variation that will be observed by the NIR analyzer. A typical calibration scheme is shown in Figure 26-6.

Since the calibration depends on the use of CFR engine data, it is imperative that this data be of high quality and that the procedures recommended for sample handling and analysis be followed. A review of current laboratory procedures is recommended before collection of calibration data begins. Additionally, procedures for all phases of data collection should be documented and personnel involved should be trained and qualified in their use.

Only process samples should be used for development of calibration models. Artificial blends, such as those used for CFR engines, should not be used as they have limited spectral correlation with process samples. Generally, the best strategy to collect calibration samples is to follow the same schedule of sample analysis that is currently followed for the CFR analyses of the particular stream to be calibrated. Unusual samples such as might be obtained during a process startup or shut down are particularly valuable. If the particular stream has periodic variations such as season specification changes, then several calibration periods will be required.

An important requirement for an adequate data set is that the span of the octane values be 5 to 10 times the error in the CFR octane measurement. That is, the span should be at least 3 octane numbers without gaps in the calibration curve. This is sometimes problematic since a given sample stream will likely be controlled tightly to one or a few target values (Figure 26-7). A solution to this is to use calibration samples from a multi-refinery database (Figure 26-8). This allows filling in the gaps in the calibration data, as well as providing a more robust model that will operate under unusual process conditions.

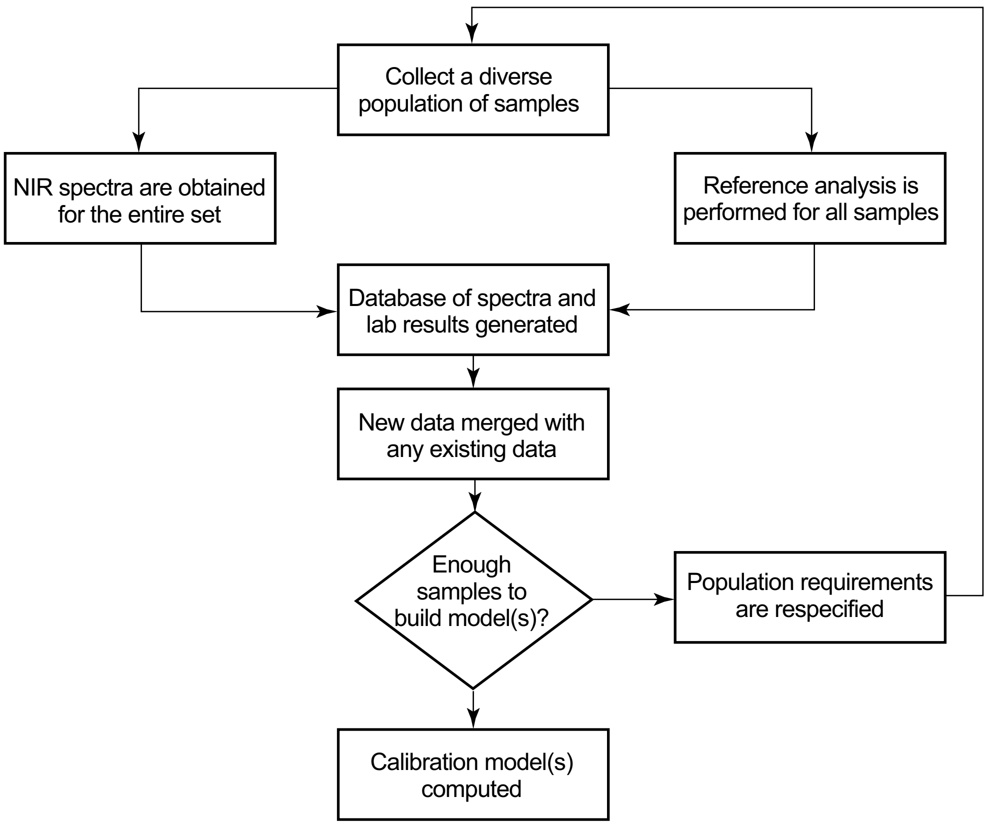


Figure 26-6—Typical Calibration Procedure

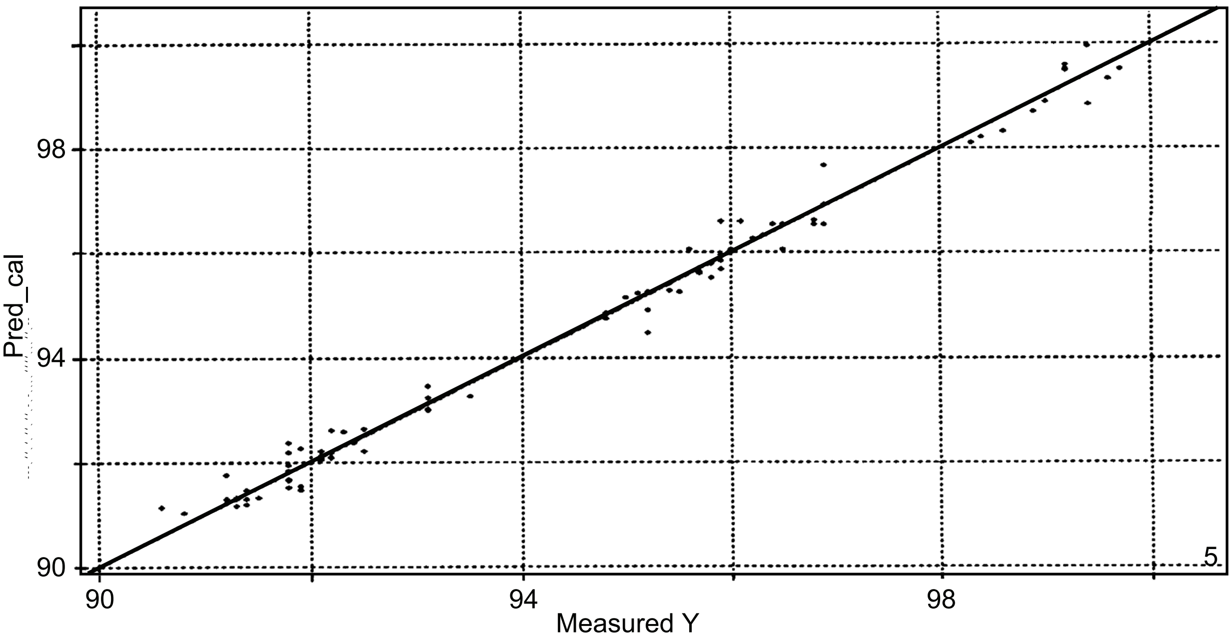


Figure 26-7—Typical Distribution of Calibration Data from a Single Refinery

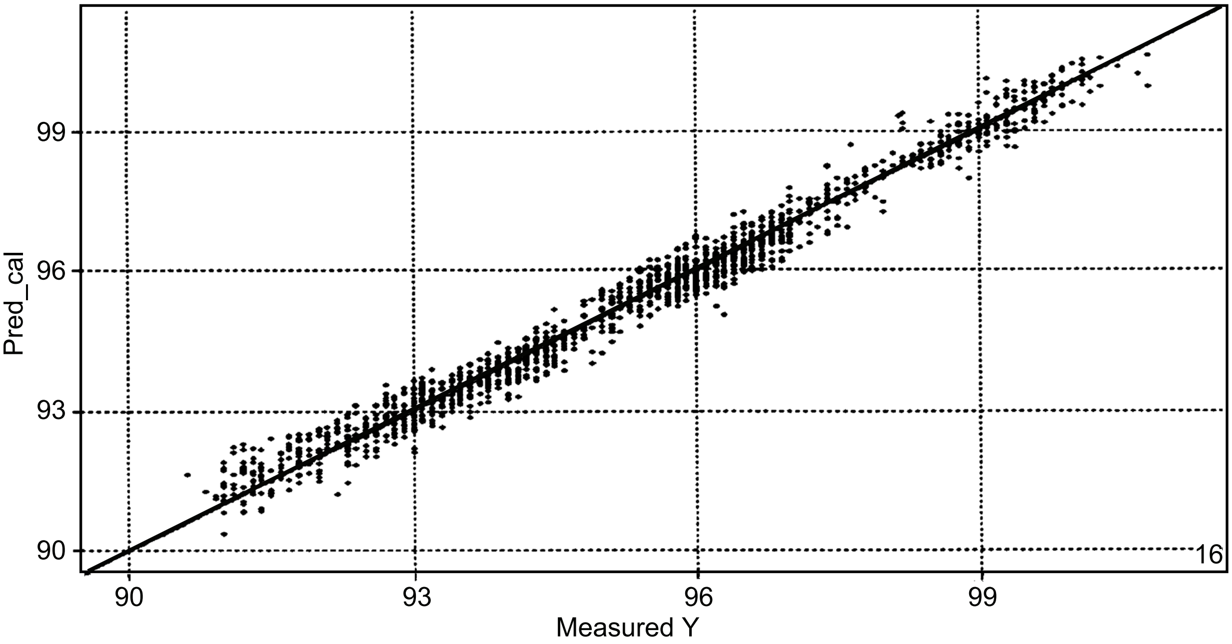


Figure 26-8—Calibration Data from Multiple Refineries

Calibration techniques used include multiple linear regression (MLR), principal component regression (PCR), partial least squares regression (PLS), and locally weighted regression (LWR). PLS is the most widely used and accepted technique. MLR is only applicable to very simple streams and, in general, has been superseded by the other approaches. LWR is appropriate for situations where the relationship between the NIR spectra and octane is expected to be very non-linear, and where the error in the engine octane values is small relative to the octanes between samples in the calibration data set. Detailed descriptions of calibration technique are given in ASTM standards E1655[6] and a pending method.

In addition to calibration, it is necessary to develop discrimination rules that determine whether a particular sample can be properly analyzed. This is necessary because chemometric models will, on their own, predict the research octane of anything. The discrimination rules are generally developed in parallel with the calibration models. The discrimination rules can also be used to select between calibration models when two or more models are present for different streams or different octane ranges.

After the calibrations and discrimination rules have been developed, the calibration scheme should be validated via the analysis of additional samples not in the calibration set. (A pending ASTM 2885 method describes a recommended procedure in detail). Minimally, this should involve the analysis of perhaps 30 different samples. A typical validation procedure is shown in Figure 26-9.

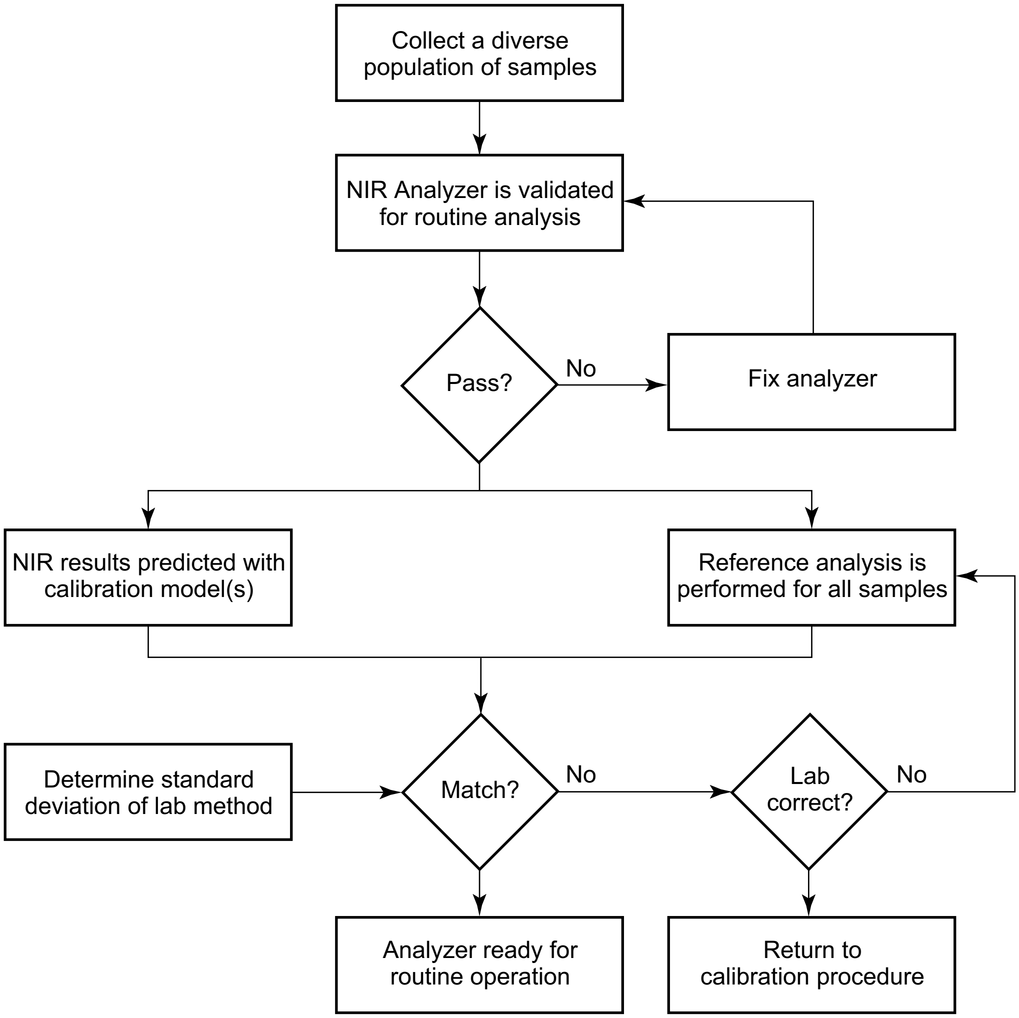


Figure 26-9—Typical Calibration Validation Procedure

26.3.8 Maintenance

Routine sample system maintenance consists of monitoring adequate sample flows, and sample pressure, and assuring particulate filter cleanliness. NIR hardware maintenance could also include assuring that cell or probe windows are clean, that the optical purge gas is water-free, and that the spectrometer performance, such as wavelength calibration signal-to-noise, baseline stability, and light source intensity, are within specifications. NIR specific parameters can be monitored automatically by some instruments and can alarm on faults.

Scheduled maintenance should include light source replacement, and laser replacement at the interval recommended by the vendor.

Calibration maintenance is generally required under two circumstances. In the first, an analyte is produced by the process that is not represented in the calibration model. This is identified as an “outlier” with regard to the model set. In this case it is necessary to obtain a process sample, the corresponding NIR spectrum, and a laboratory engine octane value. For sample systems with grab sample capability, the collection of the sample and the spectrum can be automated to occur on outlier detection, and trigger an alarm. Typical alarm logic is illustrated in Figure 26-10. This sample then must be entered into the calibration. Figure 26-11 shows a typical re-calibration.

The second circumstance requiring re-calibration occurs when the hardware changes sufficiently such that the NIR spectrum obtained on the same sample is no longer the same as that obtained on the instrument, when the calibration data was taken. Wavelength drift and band shape can be affected by source movement or replacement requiring re-calibration. This re-calibration can involve either the rerunning of all calibration samples, or running a set of standards samples and using these to either adjust the original calibration spectra or to adjust new spectra obtained for the prediction model.

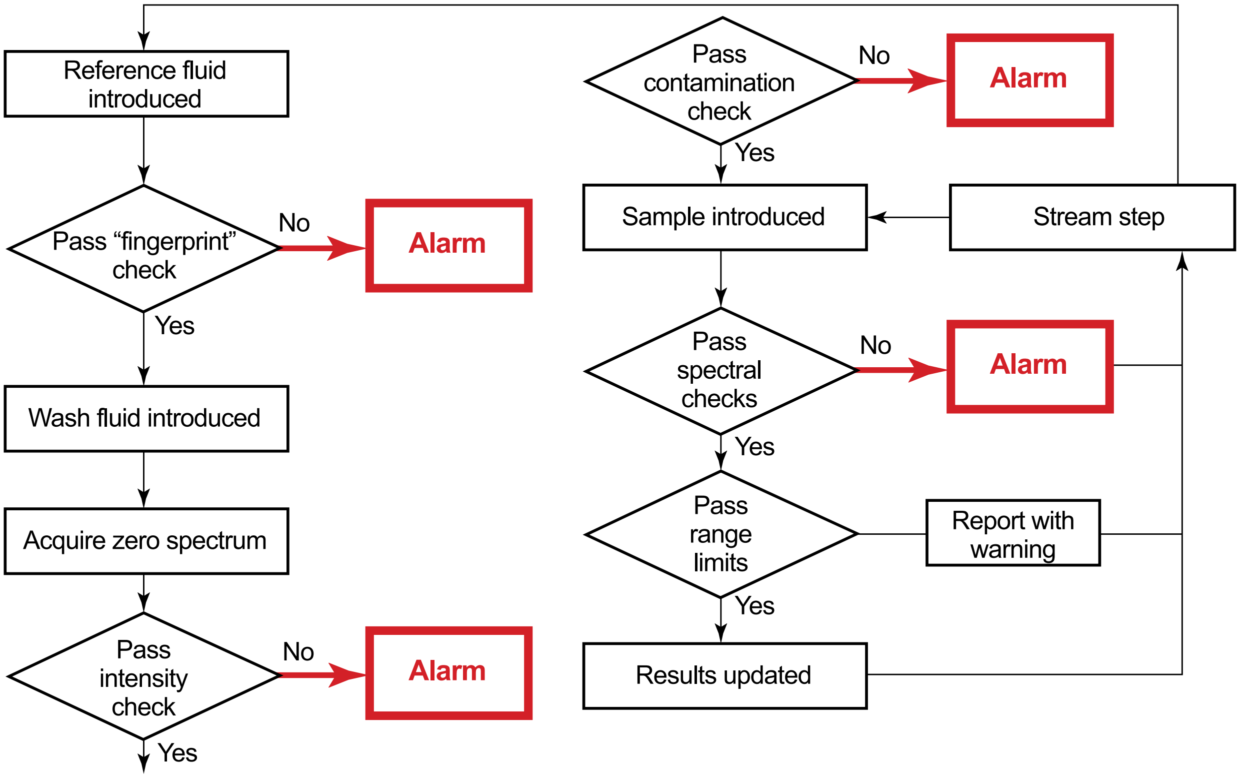


Figure 26-10—Typical Routine Analysis Cycle

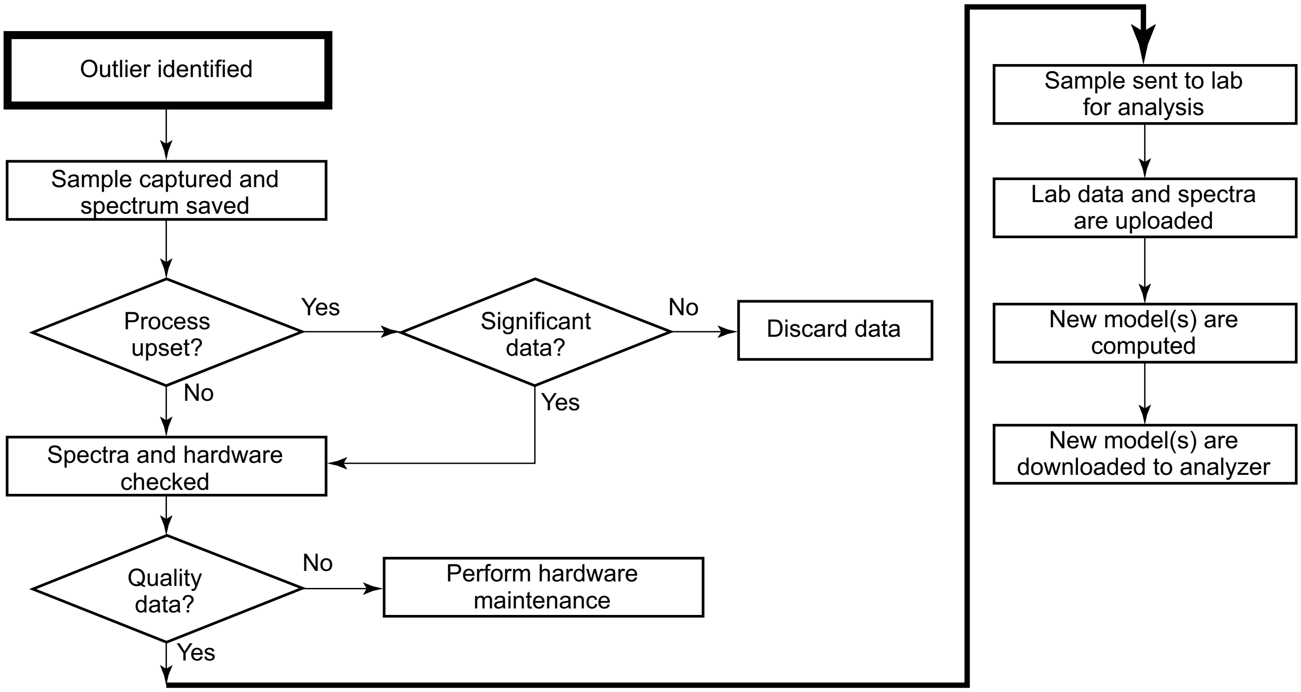


Figure 26-11—Typical Calibration Update Procedure

27 Process Stream Viscometers

27.1 Scope

This section covers the installation of the more commonly used instruments for the continuous measurement of liquid viscosity.

27.2 Basic Principles Of Viscosity Measurement

Viscosity can be defined as the internal friction of a fluid. It is the reciprocal of fluidity. When a fluid passes between two parallel plates of unit area and unit distance apart and the plates are moved in opposite directions at a given rate (rate of shear), a certain force must be applied to overcome the shearing stress of the fluid. The ratio of the shearing stress to the rate of shear is an expression of the viscosity.

The first intelligent definition of viscosity is credited to Isaac Newton. He assumed that the force required to maintain a difference of velocity between two planes in a liquid is proportional to their relative velocity divided by the distance between them, that is, the velocity gradient. If, for example, a plane of area A square centimeters is situated parallel to and at a distance of d centimeters from a fixed plane which is at rest and the space between the planes is completely filled with a fluid, the force F in dynes required to move the plane area A at a velocity v centimeters per second in its own plane relative to the fixed plane is given by Formula 1.

$$F = \mu A(v/d) \tag{1}$$

where

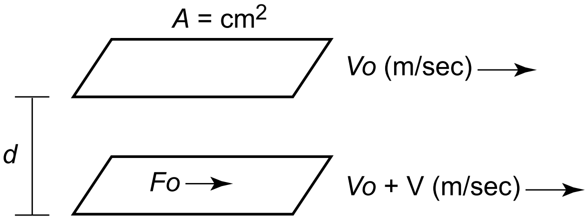
F is the force, in dynes;

μ is the coefficient of viscosity of the fluid between the planes, in poises;

A is the area of plane, in square centimeters;

v is the velocity, in centimeters per second;

d is the distance from fixed plane, in centimeters.



A more practicable definition is that of Hagan-Poiscuille who described viscosity in modern terms as the ratio of shearing stress to the rate of shear at the wall of a tube. Mathematically viscosity may be expressed as in Formula 2.

$$\mu = \frac{\pi \Delta P R^4}{8QL} \tag{2}$$

where

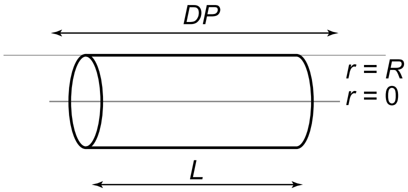
μ is the viscosity, in poises;

ΔP is the pressure drop of fluid through tube in dynes per square centimeter;

R is the radius of tube, in centimeters;

Q is the flow rate by volume, in cubic centimeters per second;

L is the length of tube, in centimeters.



In the centimeter-gram-second system, μ is given in poises, the absolute unit of viscosity, where 1 Poise = 1 dyne-sec/cm^2. Centipoise is more commonly used for convenience, for example the viscosity of water at 68 °F is one centipoise. Closely related are the kinematic viscosity units of stoke and centistoke, the viscosity obtained by expressing Q in mass flow. Hence, centipoise equals centistoke times density. Unfortunately, these relationships apply only to simple Newtonian Liquids, in which the viscosity is a constant at any given temperature. Fortunately, most petroleum products such as lubricating oils where viscosity is a factor, are Newtonian. Notable exceptions are certain lube oils with additives, greases, tars, asphalts, and certain residuum fuels. These latter products are said to be thixotropic. A thixotropic substance possesses an internal structure which breaks down (that is, the viscosity decreases) when the substance is subjected to shear but will rebuild itself in time if allowed to rest.

The majority of laboratory viscosity-measuring devices are the kinematic type, and results are usually calibrated in time units rather than in units of either absolute or kinematic viscosity.

A few of these relative or inferential scales are in general use today: the Saybolt scales in the United States, the Redwood scales in Great Britain, and the Engler scales in Europe. All three of these scales, based on Poiscuille's law, indicate the time of efflux under given conditions of fixed volume of fluid through a specific capillary or aperture. The viscosity of a specified oil, for example, might be expressed as 105 Saybolt Universal Seconds (SUS) at 130 °F. In this case, 105 seconds is the time required for 60 milliliters of the specified oil under its own head at 130 °F to flow through the orifice in a Saybolt Universal viscometer. The viscosity of lubricants is usually reported at Saybolt Universal Seconds at 100 °F, 130 °F, or 210 °F and Saybolt Furol seconds at 122 °F or 210 °F.

Kinematic viscosity, v, may be determined from various scale values by means of an empirical formula in the form of the following:

$$v = \mathrm{A}t - (\mathrm{B}/t) \tag{3}$$

where

v is the viscosity, in stokes,

A and B are the constants applicable to the measuring apparatus (viscometer),

t is the fluid efflux time, in seconds (scale time).

If the fluid density at the temperature of the test is known, absolute viscosity may then be calculated. Commonly accepted values for A and B in Formula 3 are listed in Table 27-1.

All of the continuous-process types of viscometers measure viscosity in absolute units but are usually calibrated to read out in time units in order to correlate with the laboratory instruments. Inasmuch as absolute viscosity is equal to kinematic viscosity multiplied by density, this calibration is valid as long as the density of the material being measured is constant.

The density of most lubricating oil streams will not vary more than ± 1 % so that variations in calibration accuracy as a result of density changes are negligible. In measuring the viscosity of heavy fuels; however, large variations in density could occur which may necessitate plotting several calibration curves for the expected variation in density. In some extreme cases it may be necessary to implement an on-line density analyzer to input into a computer algorithm to correct for density variations.

Table 27-1—Constants Applicable to Viscometers

Viscometer type	Efflux Time (seconds)	A	B
Saybolt Universal	32 to 100	0.00226	1.95
	> 100	0.00220	1.35
Saybolt Furol	25 to 40	0.0224	1.84
	> 40	0.0216	0.60
Redwood No. 1	34 to 100	0.00260	1.79
(Standard)	> 100	0.00247	0.50
Redwood No. 2	32 to 90	0.0246	1.00
(Admiralty)	> 90	0.0245	—
Engler	—	0.00147	3.74

27.3 Types of Process Viscometers

Several types of continuous viscometers are available. All may be mounted in conjunction with one or a combination of remote or close coupled, continuous recording, indicating, or controlling devices, thus lending themselves to automatic process control.

27.3.1 Capillary Type

If a fluid of constant density is forced to move at a constant volumetric rate through a fixed constriction, the differential pressure across the restriction is a measure of the viscosity.

In viscometers based on this principle, the constriction ordinarily is a short tube or capillary of a cross-sectional area appropriate to the viscosity range to be measured. The constant volumetric rate is maintained with a positive displacement pump, and the differential pressure is measured with an instrument of the same type as is used for flow measurement. The sample temperature is controlled by immersing the sample transport tubing and measuring capillary in a constant temperature oil bath that is maintained with heat exchange equipment. The most common measuring temperature is 100 °F (38 °C). Hot samples are normally pre-cooled to less than 100 °F (38 °C) with a water-based heat exchanger prior to entering the viscometer.

Usually, only a small flowing bypass sample of the process stream is pumped through the instrument. Each viscosity range will require a specific selection of constriction and temperature. This type of viscometer has been used successfully for streams with a viscosity of up to 2500 centipoise with an accuracy of ± 1 % of span. Typical applications include fuel oils, hydraulic oils, lubricating oils, and various grades of asphalt.

27.3.2 Ultrasonic Probe

The dampening effect of a surrounding fluid on the vibrations of a probe is a function of the viscosity of a constant-density fluid. In one such device based on this principle, the sensing probe is a metal blade a little over two in. long, a fraction of an in. wide, and a few thousandths of an in. thick. The blade is magnetostrictively driven in a longitudinal direction with periodic pulses of 28 kilohertz. The rate of decay of the dampened oscillations is electronically measured and is a function of the product of the viscosity times the density of the fluid film in contact with the blade. A temperature bulb can be inserted in the fluid under test and connected into the electronic circuit so that the viscosity referred to some specific temperature may be directly indicated, recorded, or controlled.

The ultrasonic viscometer is generally available in five ranges, 0 to 5, 50, 500, 5000, and 50,000 (centipoise) in grams per cubic centimeter. Accuracy of the system is about ± 2% of full scale for Newtonian fluids of low viscosity (below 2000 centistokes). The ultrasonic probe viscometer is finding applications in fuel oil and asphalt blending, continuous asphalt conversion, and vacuum tower bottom fraction separation.

27.3.3 Rotational Type

The drag on a rotating cylinder is a function of the viscosity of the surrounding fluid. In one viscometer employing this principle, the cylinder is turned at a constant speed and the drag develops an electronically detected displacement of a spring section of the driving shaft. There are several other methods of measuring this drag. In a process viscometer application, the sample is continuously replaced and is subjected to a constant shear rate; thus measurement of apparent viscosity of non-Newtonian fluids is possible as well as measurement of absolute viscosity of Newtonian fluids. This instrument can operate within any range from 0 to 10 centipoise to 0 to 50,000 centipoise with an accuracy of ± 1 % full scale for ranges greater than 0 to 100 centipoise.

27.3.4 Float Type

The plummet of a variable-area flowmeter (rotameter) normally is designed to minimize the effect of viscosity. If, on the contrary, the plummet is designed to maximize the effect of viscosity, and the flow rate through the tapered tube is maintained constant, the position of the viscosity-sensitive plummet becomes a measure of viscosity. Based on different applications, there are three types of float viscometers: single-float, two-float, and concentric.

The single-float viscometer is a direct reading viscosity instrument for continuous measurement. The constant sample flow is provided by a positive displacement pump. This type of an instrument can be used with non-Newtonian fluids with a viscosity of less than 400 centipoise and Newtonian fluids up to 10,000 centipoise. Expected accuracy is ± 4 % of the reading.

The two-float viscometer incorporates a second float sensitive to fluid flow rate. This instrument is available for local indication only, and the flow rate must be adjusted manually to a predetermined value. This instrument is used for Newtonian fluids with a viscosity of between 0.3 and 250 centipoise. The accuracy is ± 4 % of the reading for a viscosity of greater than 35 centipoise and ± 2 % of reading for a lower viscosity.

The concentric viscometer is a variable area flowmeter with a viscosity-sensitive float and a differential pressure regulator. The flow rate of fluid past the viscosity sensitive float is held constant by the differential pressure regulator. This viscometer is commercially available in all metal construction with an extension coupled to the float and a magnetic pickup for display recording or control. The concentric viscometer can measure viscosity in the range of 0.5 to 550 centipoise with an accuracy of ± 2 % of reading for a viscosity of less than 35 centipoise and ± 4 % of reading for higher viscosity streams.

27.3.5 Piston Type

The length of time required for a weighted piston to fall into a cylinder filled with fluid is a function of the fluid viscosity. Viscometers based on this principle raise and drop a measuring piston at 1 or 2-minute intervals and measure the time of drop by electrical means. The falling piston viscometer can be used for Newtonian and non-Newtonian fluids with a viscosity ranging from 0.1 to 106 centipoise. The accuracy of this type is about ± 1 % of full scale.

27.4 Temperature Compensation

The variation of viscosity with temperature for petroleum materials is sufficiently great so that either the temperature of the sample measured must be held precisely constant or compensation of some sort must be provided. This compensation is generally provided by a temperature-measuring device which electrically, pneumatically, or mechanically applies a correcting factor to the indicated viscosity. This factor must be predetermined experimentally for the material being measured. Since accurate compensation is only possible over a narrow temperature range, temperature control of some sort is usually needed. This is especially true if the viscometer is to be used for automatic control to some viscosity related to a specific temperature.

For in-line blending of oils having known characteristics, the need for precise temperature control may be avoided through the use of a captive sample of the required blend. In the case of the ultrasonic probe viscometer, a captive sample (providing that the oils are not thixotropic) can be inserted in the flowing stream with one sensing element inserted in the captive sample. The other sensing element is inserted directly into the flowing stream and connected so that the electronic circuitry compares the two signals and transmits the difference or error signal to the appropriate control valve. The same thing can be accomplished with most viscometers provided that two sensing elements are used and that both the captive and the flowing samples are kept at the same temperature regardless of what that temperature might be.

27.5 Safety Considerations

27.5.1 Sample Material Problems

Most viscometers require a small bypass stream from the process to the measuring element. This stream may be quite hot and the normal precautions should be taken to insulate sample lines and equipment for personnel protection. Where the material is extremely hot and sample coolers must be used to prevent damage to the viscometer, automatic over-temperature safety shutoff valves should be installed in the sample line to function in the event of cooling water failure.

For sample disposal, very small amounts of non-toxic materials can be discharged to convenient process sewers. Larger quantities can be returned to some low-pressure vessel or line or pumped to a high-pressure vessel or line. Toxic materials must be returned to some low-pressure vessel or line or pumped to a high-pressure vessel or line.

27.5.2 Electrical Precautions

Viscometers are not generally used with particularly volatile or hazardous materials, but the normal electrical requirements for handling hydrocarbons should be followed.

All viscometers may have some electrical equipment associated with their operation either in the measuring circuit, temperature compensating circuit, or transmission system. The electrical system should be studied to determine whether it is intrinsically safe or what degree of hazard it might present.

The area classification of the equipment should also be reviewed for the desired location. The controller portion of some viscometers may only be located in a General Purpose area which may be quite some distance from the measuring unit. The manufacturer's specification should state the maximum distance allowable between the controller and measuring unit. In some cases, it may be necessary to locate a general purpose controller in a Z-purged enclosure in a rain/sun shelter near the measuring unit.

27.6 Location and Housing Requirements

It is desirable to locate the viscometer so that sample lines are as short as possible. At the same time, the viscometer must be readily available for maintenance. This usually means that some sort of compromise must be made. Where a number of viscometers are to be installed in the same operating unit, it may be desirable to locate them adjacent to each other, especially if they are to be mounted in a walk-in type of enclosure.

27.7 Sampling Systems

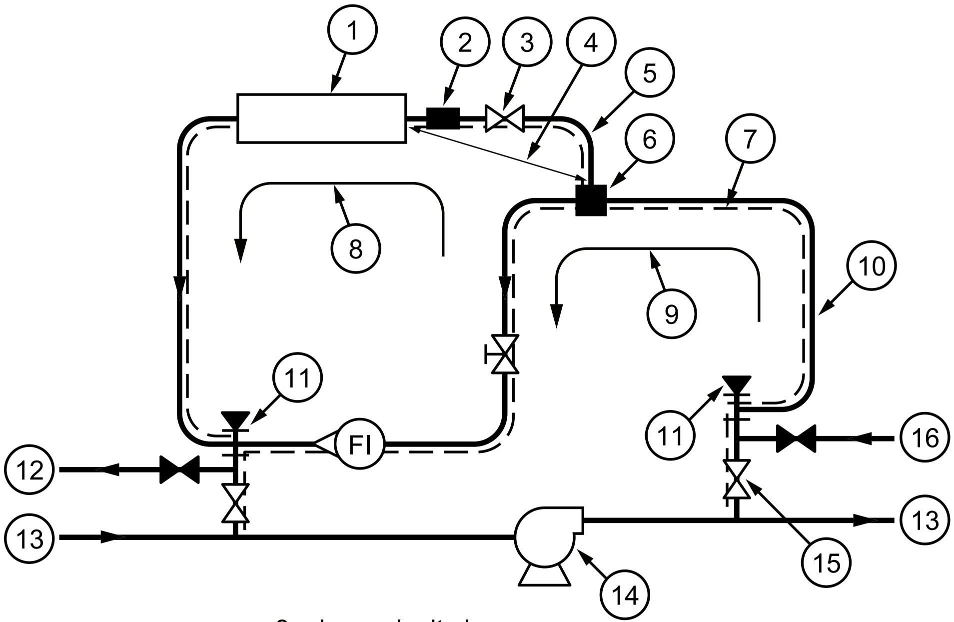
27.7.1 General Design Issues

Basically, sampling systems for viscometers may be divided into two types: one for sampling dirty materials of high viscosity, such as tars, asphalts, and heavy residual fuels; the other for sampling clean lubricating oils in the low to medium-high viscosity range.

A typical sampling system for high-viscosity liquids is shown in Figure 27-1. Note the use of a Y-type of strainer or rotating-disk filter connected into the high velocity sample loop in such a manner as to continuously flush the filter face clean of entrained material. It may also be desirable to install a small in-line filter in the sample slipstream line. All sample lines are connected to the sample taps on the process lines through the side connections of tees. This installation permits reaming out of the sample taps. In extreme cases, an automatic rod-out apparatus may be required to keep the sample point from plugging from catalyst fines or other solids in the process sample.

Viscometers and all piping, equipment, and so forth should be heat traced or cooled as required. Plugging of sample lines when the viscometer is shut down for a prolonged period of time can be minimized by the installation of wash oil connections for flushing out the system with a lighter oil. (Some processes, such as vacuum distillation units, have a wash oil system incorporated in their design.) If the wash oil cannot be returned to the process line, it may be necessary to install a wash oil effluent line.

A typical sampling system for measuring the viscosity of clean, light oils is shown in Figure 27-2. In those sections of the country where winter temperatures fall as low as 32 °F (0 °C), it may be desirable to heat trace all sample lines. Line sizes shown in Figure 27-1 and Figure 27-2 are minimum. Actual line size would be determined by desired sample loop speed of response, type and temperature of material handled, and operating practices in the particular refinery in which the installation is located.



Key

1	viscometer	8	low-velocity loop
2	small volume in-line filter (80 to 100 mesh)	9	high-velocity loop
3	¼ in. gate valve	10	½ in. min. sample loop
4	keep distance between these point as short as possible	11	bull plug
5	¼ in. min. sample line	12	wash oil effluent
6	"Y"-type strainer of rotating-disk filter (80 mesh)	13	process line
7	heat trace, as required	14	existing process pump
		15	¾ in. min. gate valve
		16	wash oil line

Figure 27-1—Typical Sampling System for High-viscosity Liquids

27.7.2 Specific Sampling Systems

Specific sampling systems vary with the type of viscometer selected and the material that is to be sampled. Five common types of viscometers are included in this discussion: the capillary, ultrasonic probe, rotational, float, and piston.

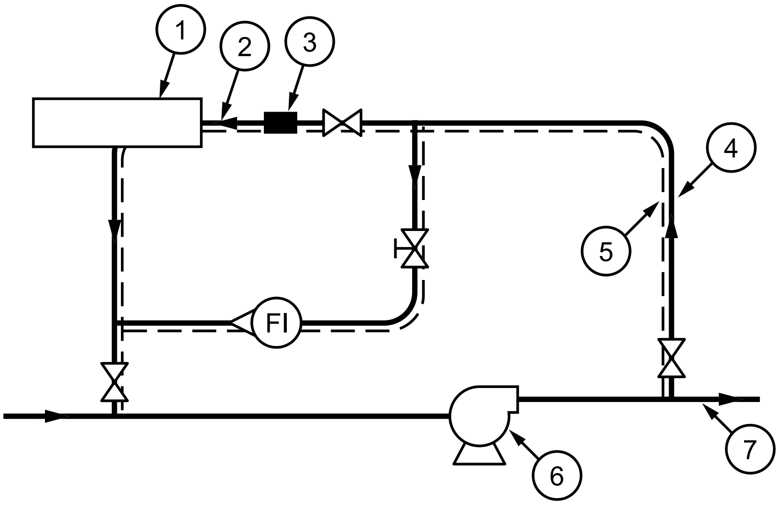
27.7.2.1 Capillary Type Sample Systems

The rate of sample flow through capillary-type viscometers is so small that unless the viscometer can be mounted within 10 ft of the process line, a controlled bypass sample loop should always be used. Figure 27-3 shows a typical installation of a capillary-type viscometer.

It is necessary to have a good filter in the sample line of capillary-type viscometers. Filtering can become a problem when measuring the viscosity of dirty material or material with suspended solids, such as tar, since the filter will plug up very rapidly. A cleanable disc-type filter is recommended (which in very dirty service may be motor driven to automatically rotate the movable discs). As an alternative, a dual filter system may be used (connected in parallel and valved to allow one filter to be cleaned while the other is in service).

A Y-type filter with 60-mesh screen may be installed in the sample line followed by an additional 60-mesh screen installed ahead of the capillary system.

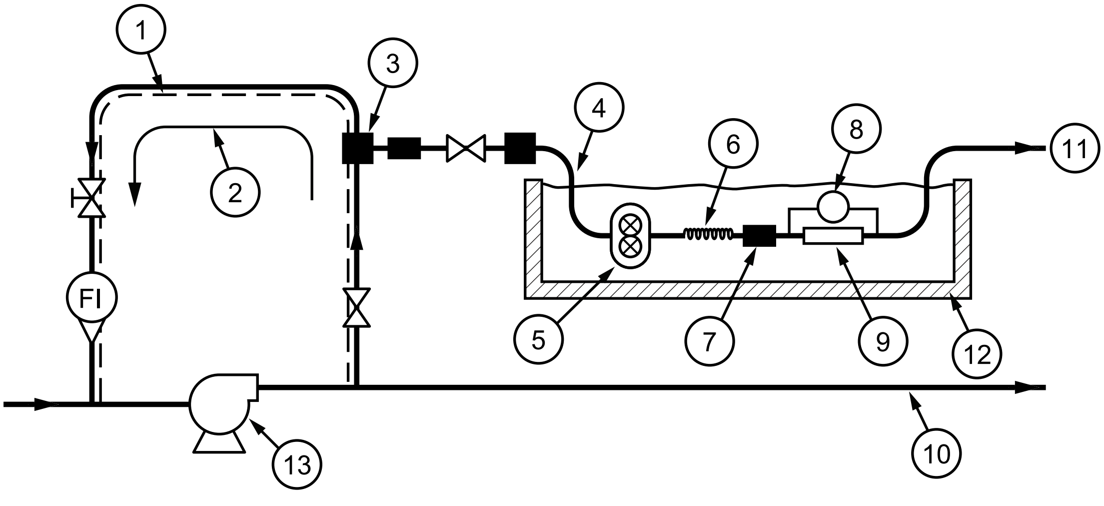
The capillary filter screen may be omitted when using the larger diameter capillary tubes usually required for narrow range measurements of stream with a high viscosity.



Key

1	viscometer	5	heat trace, as required
2	¼ in. min. sample line	6	existing process pump
3	small volume in-line filter	7	process line
4	½ in. min. circulating loop		

Figure 27-2—Typical Sampling System for Clean, Light Oils



Key

1	heat trace, as required	7	optional filter
2	controlled bypass sample loop	8	pressure sensing element
3	filter	9	capillary tube
4	distance should be kept to a minimum	10	process line
		11	effluent to sample return
5	positive displacement pump	12	constant temperature oil bath
6	heat exchange	13	existing process pump

Figure 27-3—Typical Installation of a Capillary-type System

27.7.2.2 Ultrasonic Probe Type Sample Systems

Although the ultrasonic type of viscometer employs a probe as a sensing element, which can be inserted directly in process lines in about the same manner as a thermocouple or thermometer, generally it is advantageous to insert the probe in a circulating sample loop for several reasons:

a) Temperature compensation is available over a limited range, so it is also usually necessary to control the temperature of the sample surrounding the probe.

b) The rate of flow can be controlled in a sample loop. The probe is not excessively sensitive to flow rate but does show some reaction to wide variations.

c) There is less exposure to the process when It becomes necessary to remove the probe for cleaning or replacement from a sample loop than it is from a process line. (Some materials tend to deposit out on the probe necessitating cleaning the probe to restore calibration.)

d) It is possible to design a flush system to clean the probe without actually removing it from the process, which can reduce maintenance manhours. Automation of the flush system followed by a calibration step is possible further reducing required maintenance manpower.

A typical installation of the ultrasonic probe viscometer is shown in Figure 27-4.

27.7.2.3 Rotational Type Sample Systems

The rotational type of viscometer may be mounted directly in a vessel, or it can monitor viscosity in a flowing line. In either case, it is necessary to use a purge gas, such as instrument air, nitrogen, or carbon dioxide, to prevent corrosive fumes or explosive vapors from entering the upper chamber of the viscometer. A rate of 0.5 ft^3 per minute or greater and a positive pressure differential of 3 psi are recommended. If viscosity is to be referred to some specific temperature, it is necessary to precisely control the temperature of the material being monitored by the viscometer or to compensate for the temperature changes.

Figure 27-5 shows a typical installation in a vessel where a definite liquid level is maintained in the vessel.

This type of viscometer can also be used to monitor viscosity in flowing lines through the use of a sample chamber suitably connected to the flowing stream. The piping arrangements for connecting the sample chamber to the flowing line are shown in Figure 27-6. Unless long sample lines are necessary or the material is extremely dirty, no strainers are required in this installation.

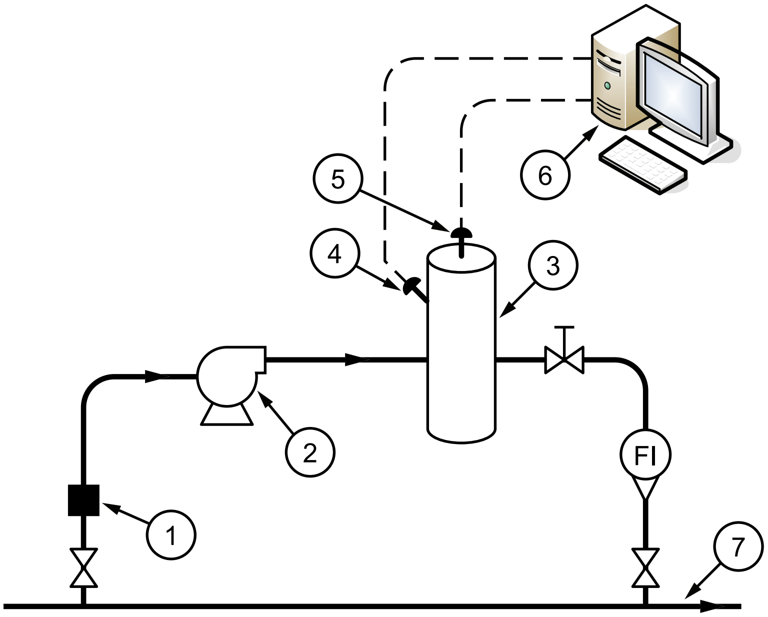
The installation, as shown in Figure 27-6, can be used to directly indicate viscosity referred to a specific base temperature. If this type of analysis is required, precise temperature control of the material in the sample chamber is necessary.

As shown in Figure 27-5 and Figure 27-6, it is desirable to include a flow indicator (FI) in the purge gas line. When handling explosive materials, even though the electrical system is intrinsically safe, it may be desirable to install a pressure switch to automatically de-energize the electrical circuits if the purge gas pressure drops below a safe level.

27.7.2.4 Float Type Sample Systems

The float viscometer can only be used to continuously monitor viscosity in a flowing stream. Temperature compensation is available on this model, but the sample stream should be temperature controlled if variations in temperature of greater than ± 10 °F (± 5 °C) can occur.

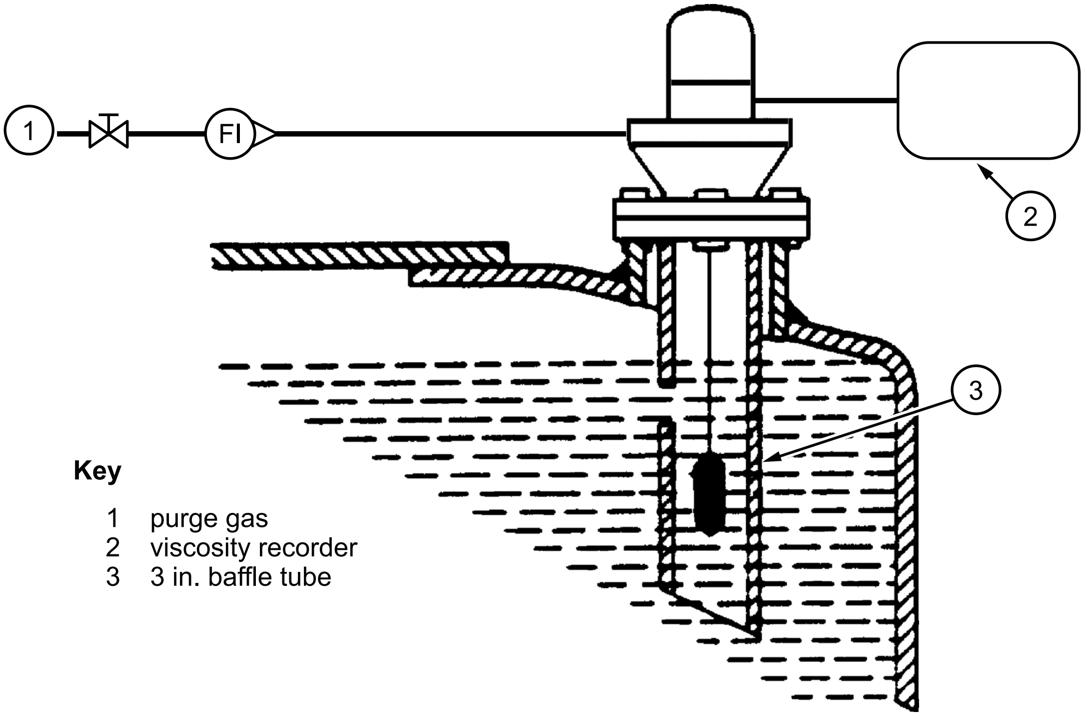
It is important that the flow rate be kept constant in float-type viscometers. The various sampling arrangements to obtain constant flow rate are shown in Figure 27-7 and Figure 27-8. The sampling system shown in Figure 27-7 uses a precision positive displacement pump to ensure constant flow rate through the viscometer. A strainer, located in the sample line ahead of the pump, is an absolute necessity as any amount of solids entrained in the flowing liquid



Key

1 filter
2 sample pump
3 temperature-controlled pot
4 resistance thermometer
5 viscometer probe
6 viscometer computer
7 process line

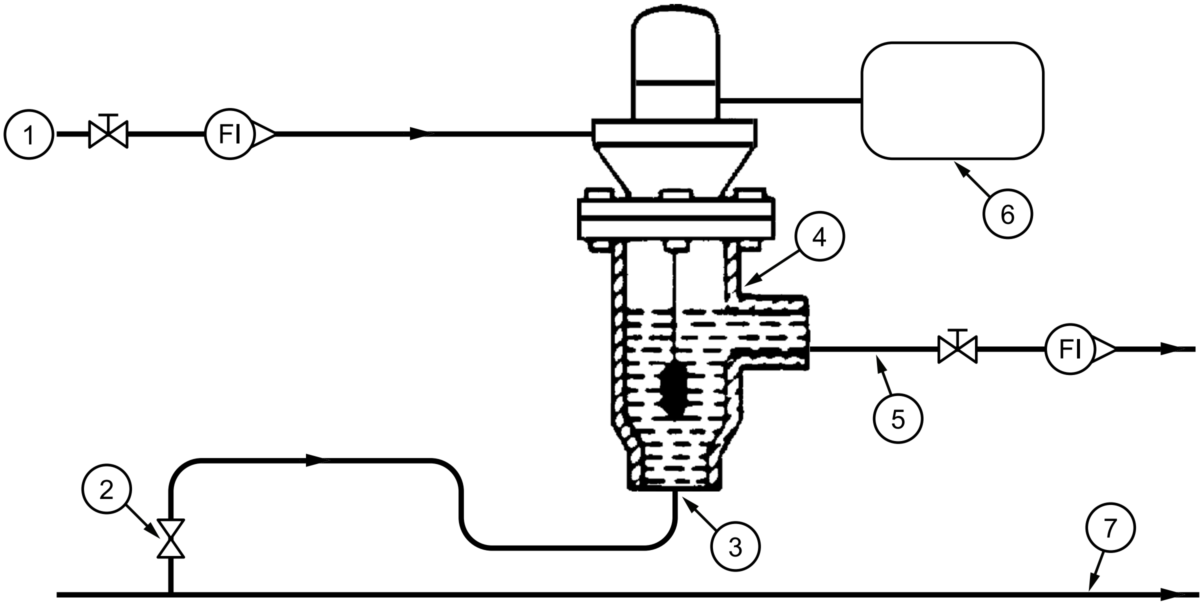
Figure 27-4—Typical Installation of an Ultrasonic Probe Viscometer



Key

1 purge gas
2 viscosity recorder
3 3 in. baffle tube

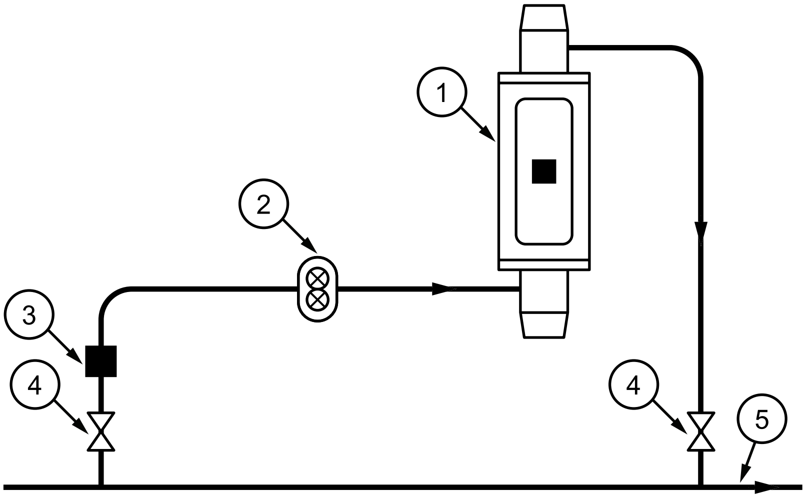
Figure 27-5—Tank Mounting for a Rotational Viscometer



Key

1 purge gas
2 ½ in. needle valve
3 ½ in. inlet
4 sample chamber
5 2 in. effluent to LP vessel
6 viscosity recorder
7 process line

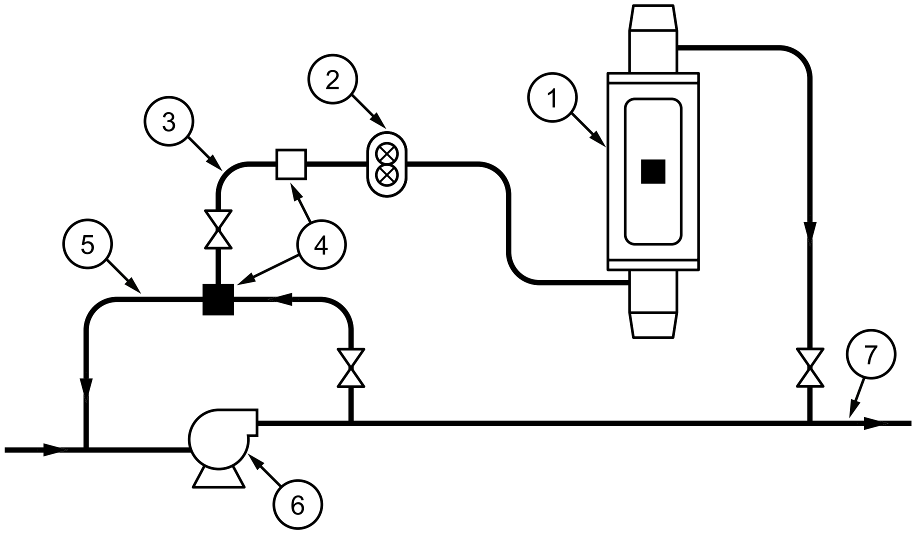
Figure 27-6—Flowing Line Installation for Rotational Viscometer



Key

1 viscometer
2 precision positive displacement pump
3 strainer
4 isolating valve
5 process line

Figure 27-7—Viscometer Located Close to the Process Line



Key

1 viscometer
2 precision positive displacement pump
3 ¼ in. sample line
4 strainer
5 2 in. sample loop
6 existing process pump
7 process line

Figure 27-8—Viscometer Sample Line from Circulating Loop

would destroy the close clearances essential for the operation of the pump. This sampling system is applicable where the viscometer can be conveniently located close to the process line. Where it is not convenient to locate the viscometer near the process line, sampling time or transportation lag can be reduced by installing a relatively high velocity sample loop as shown in Figure 27-8.

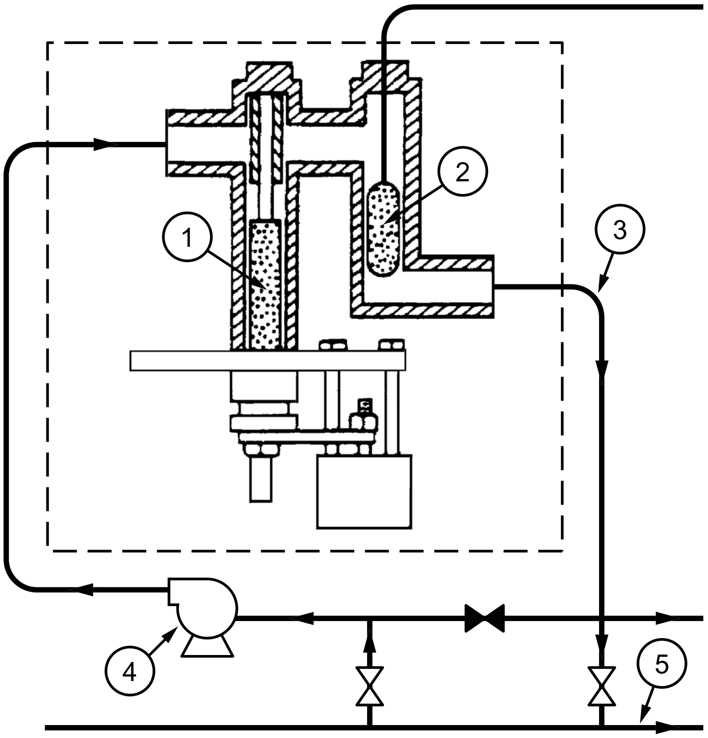
If it is not practical to connect the sample loop around an existing process pump, as shown in Figure 27-8, an orifice in the process line or an existing control valve can be used to create a pressure drop to force the fluid through the sample loop. If pressure drop is not available, it may be necessary to use a sample pump. Sample line size is shown as $^1/4$ in., but line size and viscometer size will vary with the viscosity range of the material to be measured.

Use of the concentric viscometer eliminates the need for a positive displacement metering pump since flow rate of fluid past the viscosity sensitive float is held constant by maintaining a constant pressure drop across the viscometer tube.

27.7.2.5 Piston Type Sample Systems

The sample flow rate through a piston type of viscometer, as shown in Figure 27-9, is not critical, and a simple sample pump normally is satisfactory. The normal flow for the sample (see Figure 27-9) is from the process line through Valve 1, the pump, and then into the viscosity measuring tube. From the measuring tube, the sample flows through the temperature bulb chamber and then back to the line through Valve 2. The bypass line is used to calibrate the viscometer and adjust the temperature compensator. During this procedure, Valve 3 is opened and either Valve 1 or 2 is closed. For complete information on calibration, refer to manufacturer’s literature.

Filters or strainers are not essential in the sample line unless the material to be measured is known to be dirty or contain solids. If the viscometer cannot be mounted close to the process line, it may be desirable to install a sample loop as illustrated in Figure 27-8. One manufacturer claims that temperature compensation is effective over a range of ± 15 °F (± 7 °C). Any variations in temperature greater than this will require temperature control of the sample. Use of the piston type of viscometer should be avoided where vibration is expected or where fast response time (less than 1 minute) is required.



Key

1 piston
2 temperature compensator
3 ¼ in. sample lines
4 sample pump
5 process line

Figure 27-9—Installation of Piston-type Viscometer

27.8 Calibration Requirements

Calibration of viscometers in lubricating oil service does not present any problems since lubricating oils are usually stable and nonvolatile. Furthermore, the following items should be noted during viscometer calibration.

a) The viscometer can be calibrated from control laboratory analyses of a representative sample taken near the viscometer or a standard sample can be run through the analyzer. (The control laboratory should be alerted that the samples to be analyzed are for viscometer calibration and where possible the laboratory analyzer should be operated at the same temperature as the process analyzer.)

b) Viscometers can sometimes be calibrated from standard samples which are available commercially.

c) A chart should be marked when a sample is taken for calibration.

The calibration of viscometers measuring materials such as residual fuels, which exhibit some non-Newtonian characteristics can be quite difficult. These materials tend to be thixotropic. A chemist in the control laboratory or the manufacturer should be consulted as to the method used to analyze samples of such materials.

Check the calibration daily at first, decrease the number of checks as reliability is established. Refer to the manufacturer's literature for calibration methods.

27.9 Readout

All of the viscometers described in this section can be adapted to read out on most of the standard pneumatic or electrical indicating or recording instruments for measurement or control. Refer to manufacturer's literature for special adaptations of peak-picking devices for batch-type viscometers.

27.10 Startup

Typical startup procedures for the continuous measurement of liquid viscosity are as follows.

1) Turn on the heat tracing of the sample lines (if required).

2) Circulate the sample. (In the rotational type of viscometer, it is necessary to turn on the purge gas and note that it is at the correct pressure before circulating the sample.)

3) Check for sample leaks.

4) Place the heat exchangers, coolers, temperature controls, pressure controls, and so forth in operation and check for stability.

5) Apply a step change and check for the appropriate speed of response.

6) Calibrate per the manufacturer's instructions.

28 Densitometers

28.1 General

This chapter covers the installation of the more commonly used instruments for the continuous measurement of fluid density or specific gravity. Excluded from the discussion are those instruments or devices primarily used in laboratory analysis of given samples.

Various methods are used for the determination of fluid density or specific gravity. It is the intent of this section to cover only those methods that are more commonly employed with remote or close coupled, continuous recording, indicating, and/or controlling devices; thus lending themselves to automatic process control. Densitometers are available for measurement of both liquids and gases. The two types will be covered separately in this discussion.

28.2 Density and Specific Gravity Definitions

The density of a material may be defined as the weight per unit volume at given conditions of temperature and pressure. Generally, it is expressed in pounds per cubic ft, pounds per gallon, or grams per cubic centimeter.

28.2.1 Liquid Service

The specific gravity of a liquid is the term indicating its density with reference to water. The specific gravity of water is usually defined as 1.0 (at 60°F or 15°C in the Petroleum Industry), and atmospheric pressure.

28.2.2 Gas Service

The specific gravity of a gas is the weight of a cubic ft of gas compared to the weight of a cubic ft of dry air under the same pressure and temperature conditions. The dry reference air is defined as base 1.0 at 60 °F and 1 atmosphere (14.676 psi absolute, or 760 mm of mercury absolute).

28.3 Liquid Densitometers—Basic Operation

28.3.1 Balanced Flow Vessel

In this method of determining liquid density, a fixed volume vessel through which the sample flows is balanced by a scale beam (see Figure 28-1 and Figure 28-2). The displacement of the scale beam caused by a change in weight of the fixed volume of sample is proportional to density.

28.3.2 Balanced Flow Tube

Another version of the fixed-volume vessel instrument (see Figure 28-3 and Figure 28-4) employs either a straight or U-shaped hollow beam. In operation, fluid is circulated through the hollow beam which is attached to a null-balance system. Changes in weight of the fluid are frequently transmitted in the form of a pneumatic signal which can be used to record, indicate, control, or a combination of these functions. No interpolation or indirect measuring is involved. Density is read directly, and errors which result from velocity, viscosity, pressure, and product composition are precluded. The relatively large flow rate through the hollow tube permits such materials as slurries, drilling mud, and cement-water to be measured.

28.3.3 Industrial Specific Gravity Displacer

With the industrial specific gravity displacer (see Figure 28-5 and Figure 28-6), the sample is passed through a chamber containing a completely submerged, externally counterbalanced float. The change in buoyancy of the float, with change in density of the liquid within the chamber, is proportional to density. The signal may be transmitted by pneumatic, mechanical, or electrical means. This instrument is similar to the widely used displacement types of level controls except that sample connections to the chamber are made in such a manner as to minimize velocity effects.

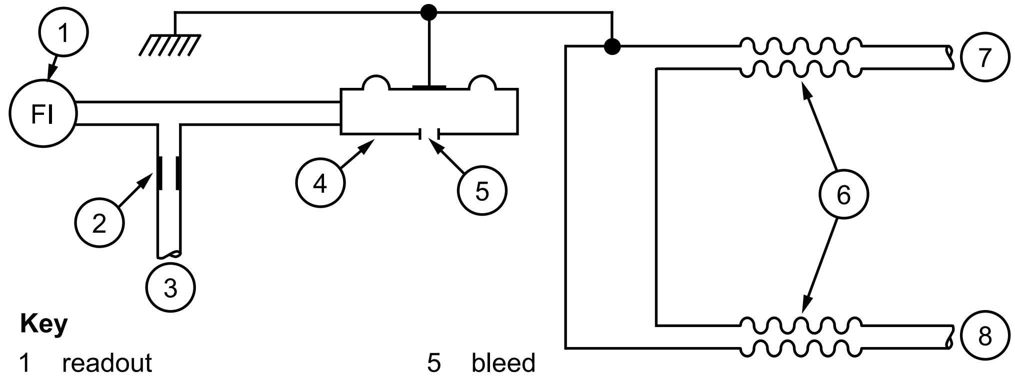
28.3.4 Chain-balanced-float Density Instrument

With the chain-balanced-float density instrument (see Figure 28-7 and Figure 28-8), a float in a continuous flow chamber is weighted to carry half the weight of a light chain when submerged in medium-density liquid at midpoint in its range. The chain is attached to the bottom of the float and to the vessel wall at half height. Any increase in density causes the float to rise, supporting more chain; any decrease in density causes the float to sink, supporting less chain. The float position is transmitted by a differential transformer.

28.3.5 Gamma-ray Density Gauge

In the gamma-ray density gauge (see Figure 28-9), a gamma-ray source, such as a radium salt or radioisotope, is arranged so that the gamma rays pass through the pipe or vessel walls and through the fluid to a radiation detector. The detector is mounted on the outside of the pipe or vessel. The source may be located on the opposite side of the line or vessel, inside the line or vessel, or arranged to traverse a diagonal or longitudinal portion of the line or vessel. The selection of the proper arrangement depends upon the ratio of gamma-ray absorption by the fluid and metal through which the rays pass. The manufacturer should be consulted as to the most desirable type to use for adequate results.

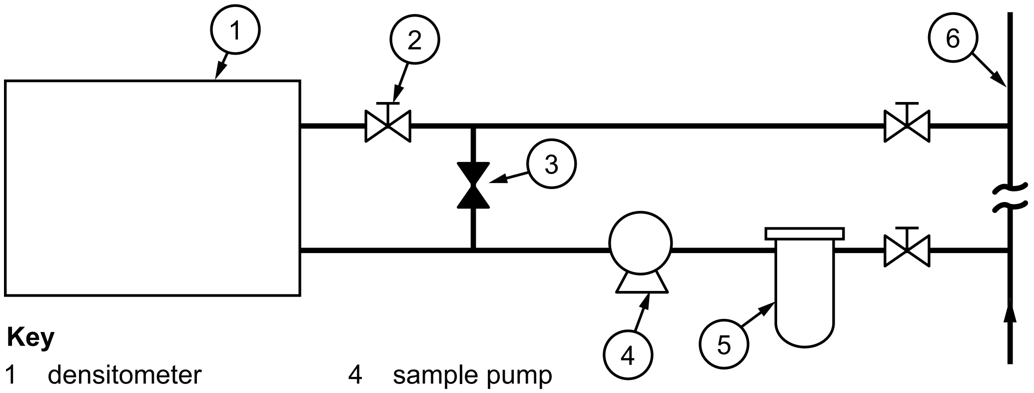
In a commonly used arrangement, the radioisotope source is located on one side of the line and the radiation detector is located on the other side of the line. This type, illustrated in Figure 28-9, is supplied as an assembly and bolts in place around the section of line. Any material passing through the pipe or contained in the vessel will absorb part of the gamma rays from the source. The amount of energy reaching the detector varies inversely with the density of the process stream. The gamma-ray density gauge may be used to take continuous density measurements of solutions, liquids, slurries, or divided solids. It requires no sampling system as the radiation source and the detector may be mounted directly on the outside of the process line. Consult with the manufacturer regarding positioning on insulated pipe. It can be used to indicate, record, or control, or for a combination of these functions.



Key

1 readout
2 restriction
3 air supply
4 force-balance transmitter
5 bleed
6 flexible connections
7 fluid out
8 fluid in

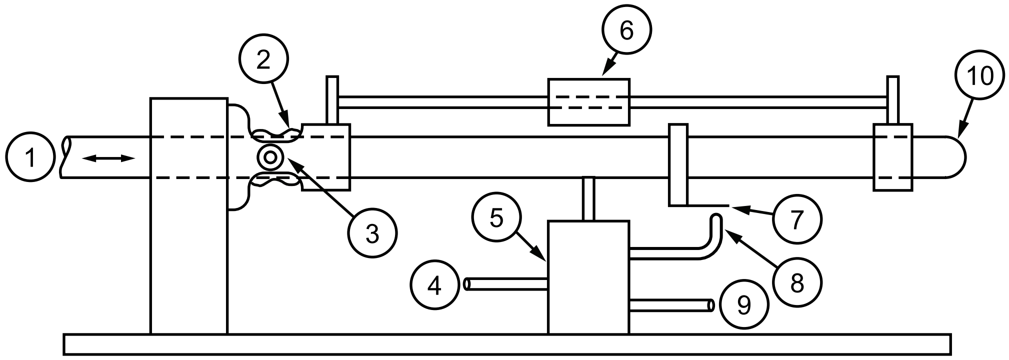
Figure 28-1—Balanced Flow Vessel



Key

1 densitometer
2 gate valve drilled disk (restriction orifice)
3 globe valve
4 sample pump
5 strainer
6 line

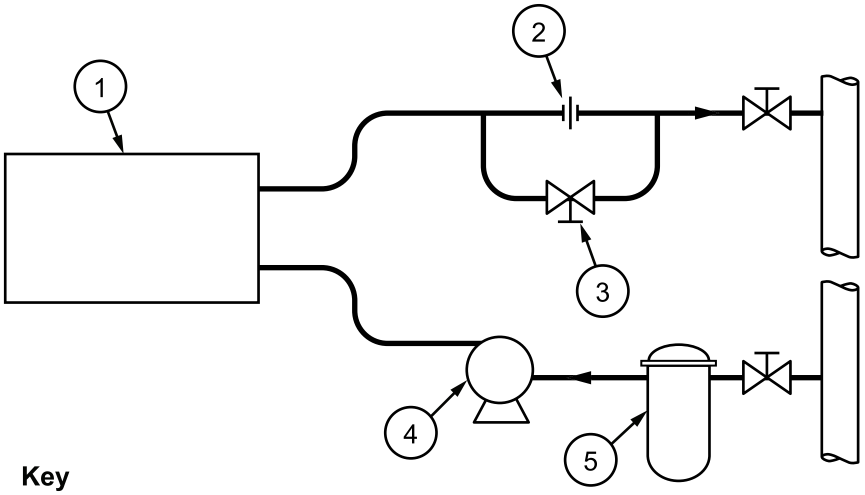
Figure 28-2—Typical Liquid Densitometer Sampling System



Key

1 sample
2 flexible seal
3 pivot
4 air supply
5 force-balance
6 adjusting weight
7 flapper
8 nozzle
9 to readout
10 horizontal U-tube

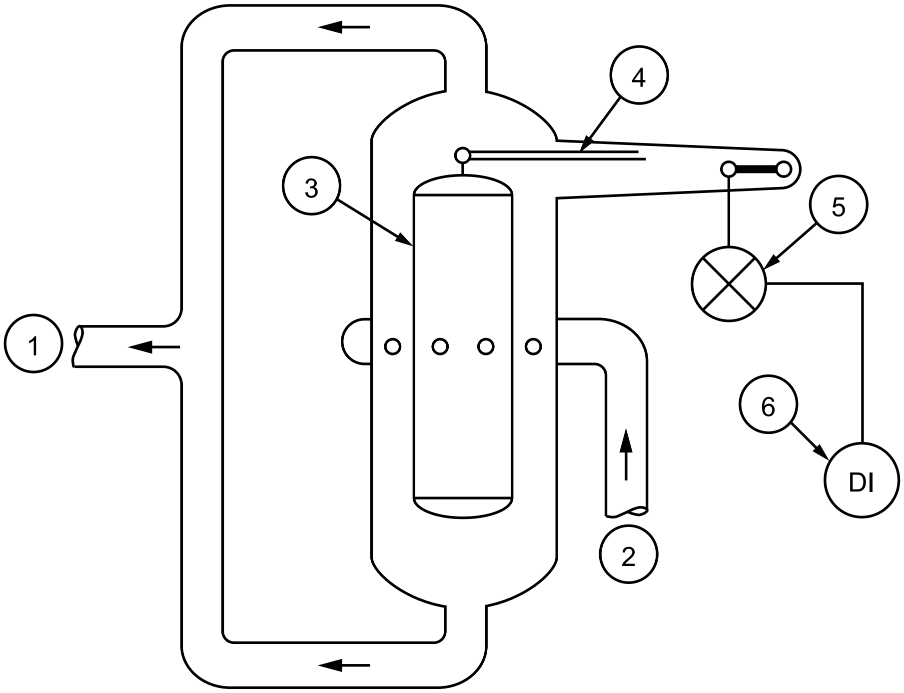
Figure 28-3—Balanced Flow Tube



Key

1 densitometer
2 restriction orifice
3 fast flush valve
4 centrifugal sample pump
5 filter

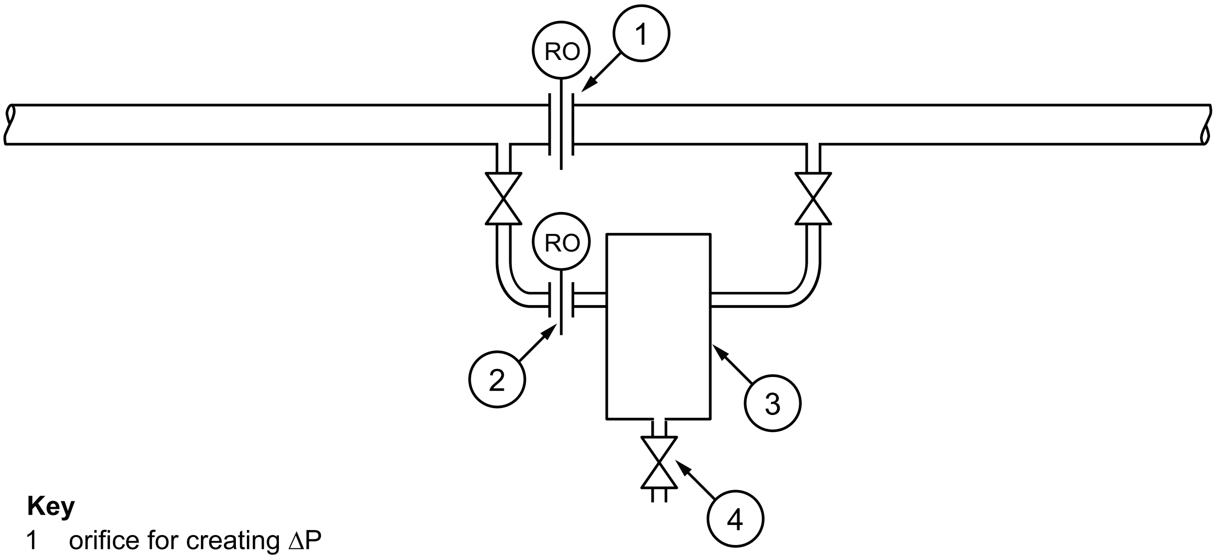
Figure 28-4—Typical Sampling System for Balanced Flow Tube



Key

1 sample out
2 sample in
3 displacer
4 torque arm
5 transmitter (electric or pneumatic)
6 receiver

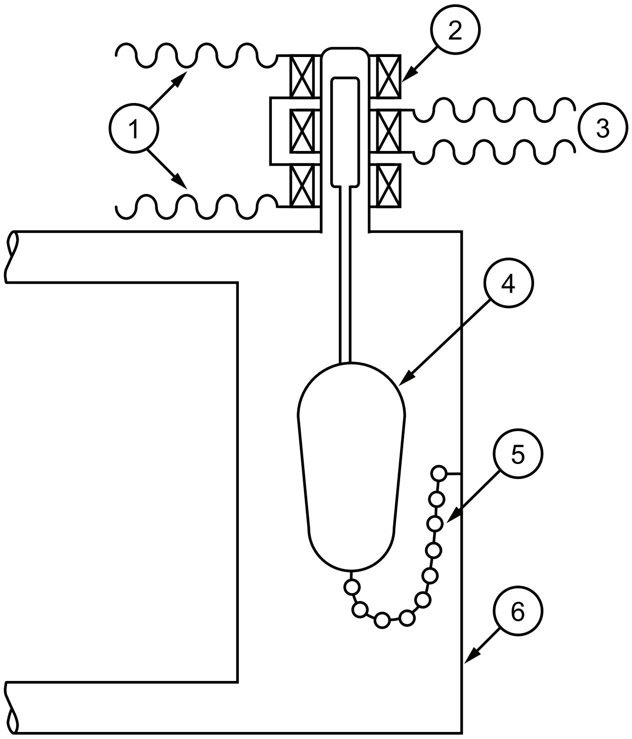
Figure 28-5—Industrial Specific Gravity Displacer



Key

1 orifice for creating ΔP
2 orifice restriction
3 densitometer
4 drain valve

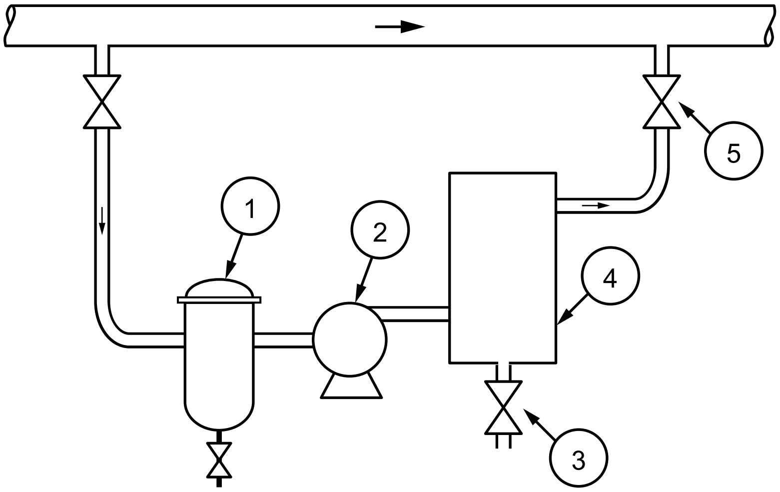
Figure 28-6—Typical Hookup for Industrial Specific Gas Displacer



Key

1 AC power
2 differential transformer
3 variable output to bridge
4 plummet
5 chain
6 flow vessel

Figure 28-7—Chain-balanced-float Densitometer

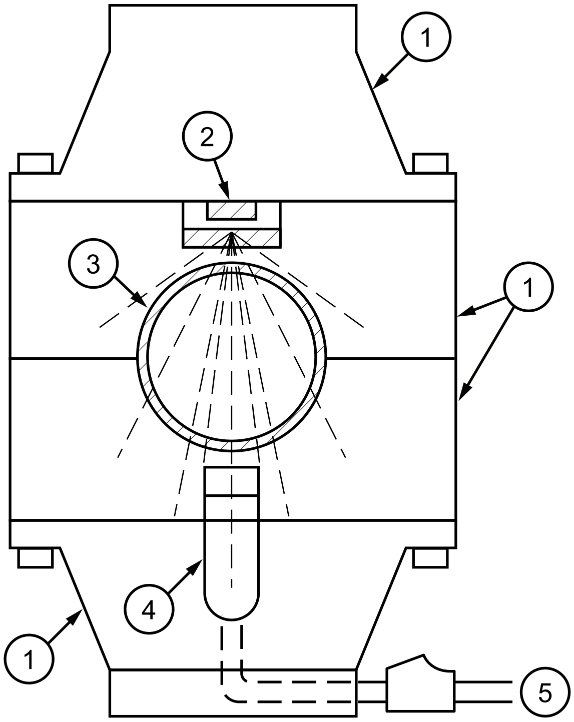


Key

1 strainer
2 centrifugal sample pump
3 drain valve
4 densitometer
5 globe valve for regulation of sample rate

NOTE The hookup shown in Figure 27-6 may not be used.

Figure 28-8—Typical Hookup for Chain-balanced-float Density Instrument



Key

1 lead shielding
2 radioisotope source
3 process line
4 radiation detector
5 to recorder, etc.

Figure 28-9—Gamma-ray Density Gauge

28.3.6 Vibrating Probe Liquid Densitometer

In one form of vibrating-probe densitometer (see Figure 28-10), a detector consists of a driver end connected through a vibrational path to a paddle and returned to a pickup end, thus completing a loop through the liquid to be tested. The driver coil receives 60 Hz AC input and produces 120 Hz vibrations in the loop. The pickup end contains a permanent magnet and coil that generate an output signal proportional to the amplitude of the paddle vibration. The electromotive force of this output signal is nominally 500 millivolts. Inasmuch as changing liquid density will increase or decrease the amplitude of the paddle vibration, the output signal will also increase or decrease, thus becoming a measure of the liquid density. A temperature element may be connected into the electrical output circuit for temperature correction.The detector may be installed directly in the flow line or vessel and is adaptable to a wide range of liquids or slurries (see Figure 28-11). If normal process pressure, temperature. or velocity do not exceed manufacturer's recommendations, no special sample handling system is required.

28.3.7 Vibrating-tube Liquid Densitometer

This twin-tube densitometer is designed to provide continuous on-line measurement of liquid density. The operation of the system can be compared to that of a tuning fork. Two parallel tubes carrying the process liquid are maintained in mechanical vibration by an electromagnetic coil placed centrally between them. This causes the tubes to vibrate at their natural frequency that is a function of the density of the liquid they contain. Then the output frequency is detected and converted to a direct density reading, by a frequency-to-current converter. If desired, a temperature sensor is used to enable the output reading to represent the density at a specific temperature.

This instrument is immune to vibration and can be mounted at any angle. Vertical mounting is preferred as this prevents solids from precipitating onto the tube walls and air bubbles from being trapped.

28.3.8 Vibrating-spool Density Meter

Another type of density meter incorporates a vibrating, thin-wall cylinder or spool (see Figure 28-12). The spool is maintained in circumferential oscillation by an electromagnetic field. The frequency of oscillation depends only upon the density of the fluid surrounding the spool and is independent of temperature, viscosity, and static pressure effects. Measurement of this frequency allows determination of the fluid density. This type of density meter is suitable for liquids, gases, or cryogenic fluids.

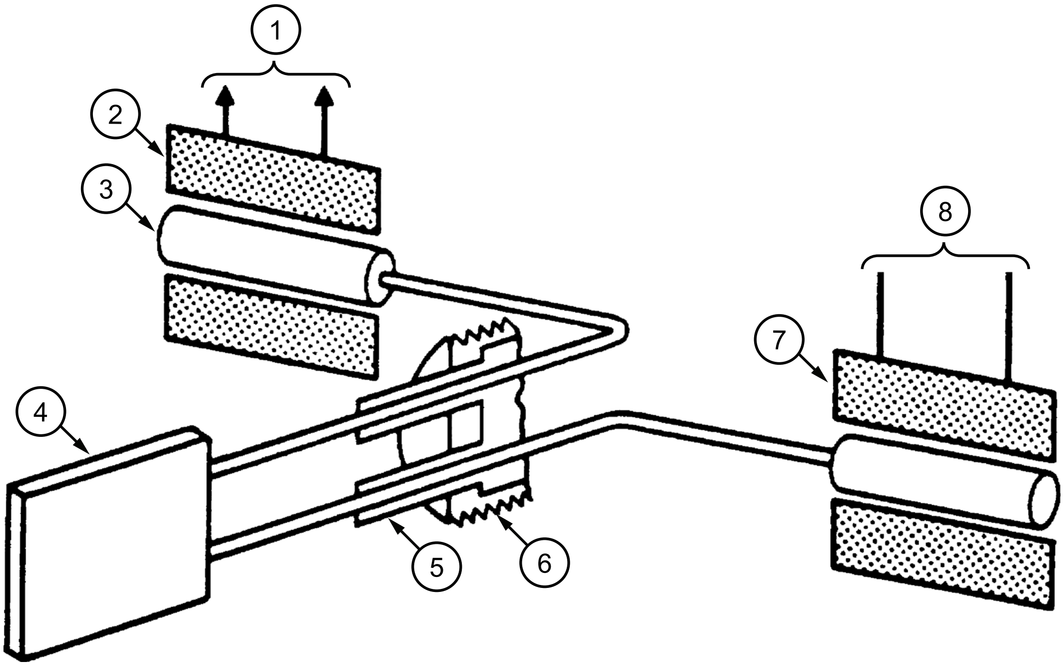
28.3.9 Sonic Liquid Densitometer

Sonic liquid densitometers measure the density of a liquid by determining the time required for sound at a specific frequency to traverse through the liquid over a fixed distance (see Figure 28-13). For example, sound at 122 kHz will travel 1500 meters/second through water, but only 1150 meters/second in gasoline (~25 % slower). One major advantage of this type of measurement is the ability to distinguish very small differences in density. For example, sonic densitometers have been used to detect the interface between different grades of gasoline as they traverse down a pipeline. Another major application involves the measurement of density of concentrated acids or bases. Since these instruments are not affected by vibration, and most have an internal compensation for temperature, they may be located remotely on process piping or pipelines.

28.4 Gas Densitometers—Basic Operation

28.4.1 Gas Specific Gravity Balance

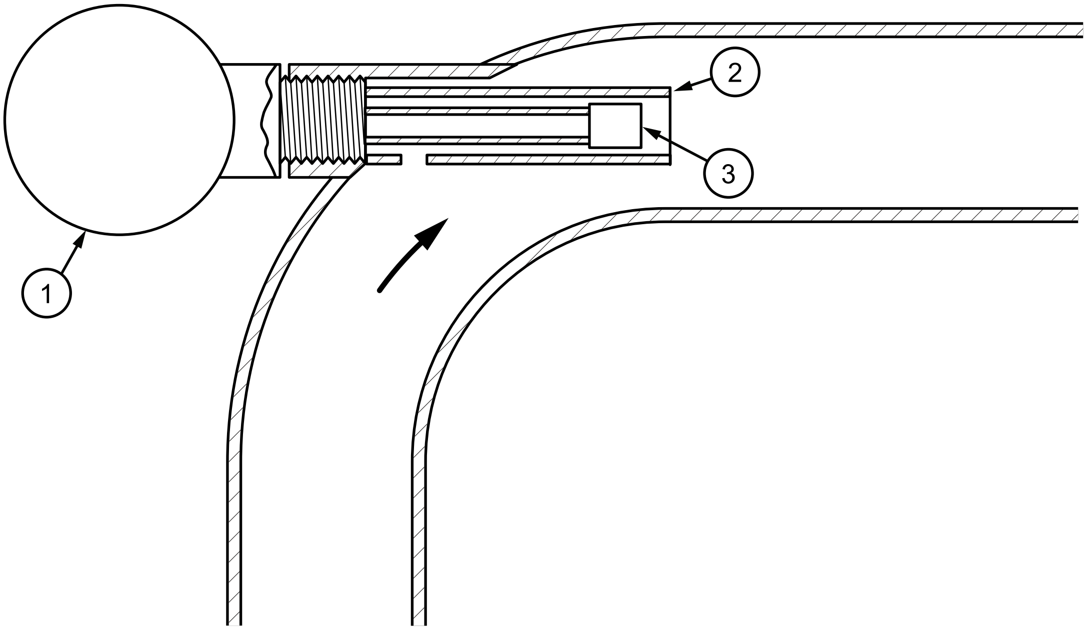
The gas balance densitometer (see Figure 28-14 and Figure 28-15) is comprised of a test chamber with a tall vent stack or column inside of which is a floating, liquid-sealed bell. The floating bell is scale or force-balanced. Gas, which is admitted to the test chamber at atmospheric pressure, fills the chamber and exits at the top of the vent stack. The column of gas acting on the outside of the floating bell is thus weighed against the air acting against the inner side of the floating bell. The resultant vertical movement of the floating bell is, therefore, proportional to the specific gravity of the gas compared to the specific gravity of air.



Key

1 to amplifier
2 pickup coil
3 magnet
4 probe
5 flexible seal
6 housing
7 driver coil
8 115 VAC

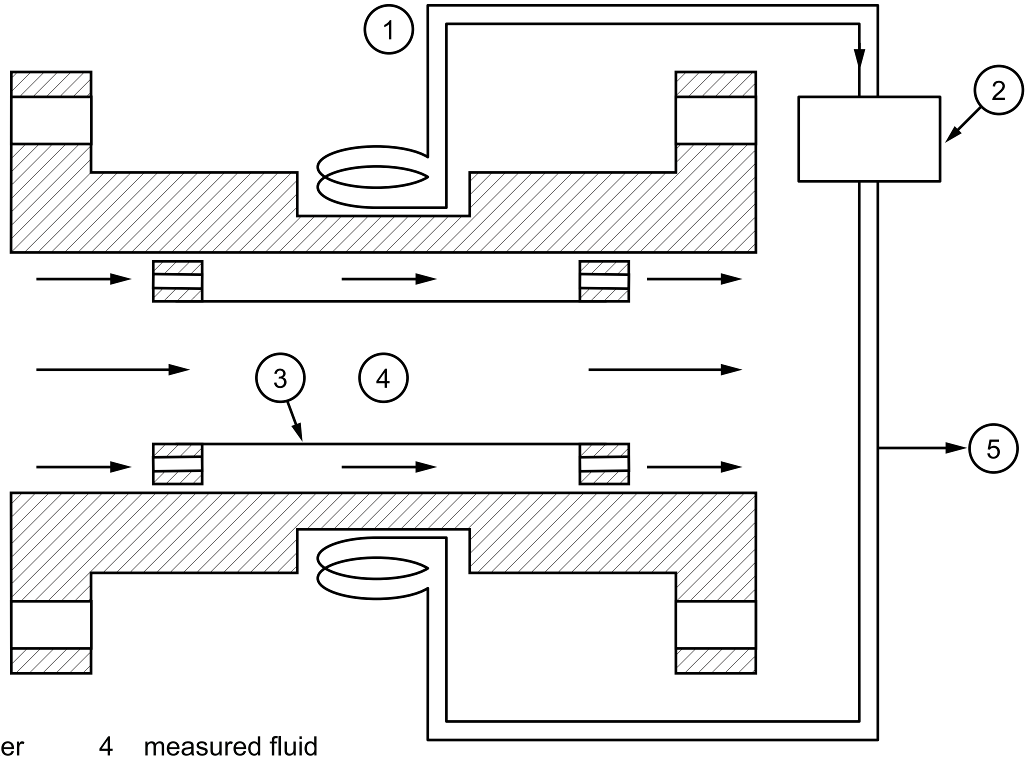
Figure 28-10—Vibrating Probe Densitometer



Key

1 probe head
2 flow guard
3 probe

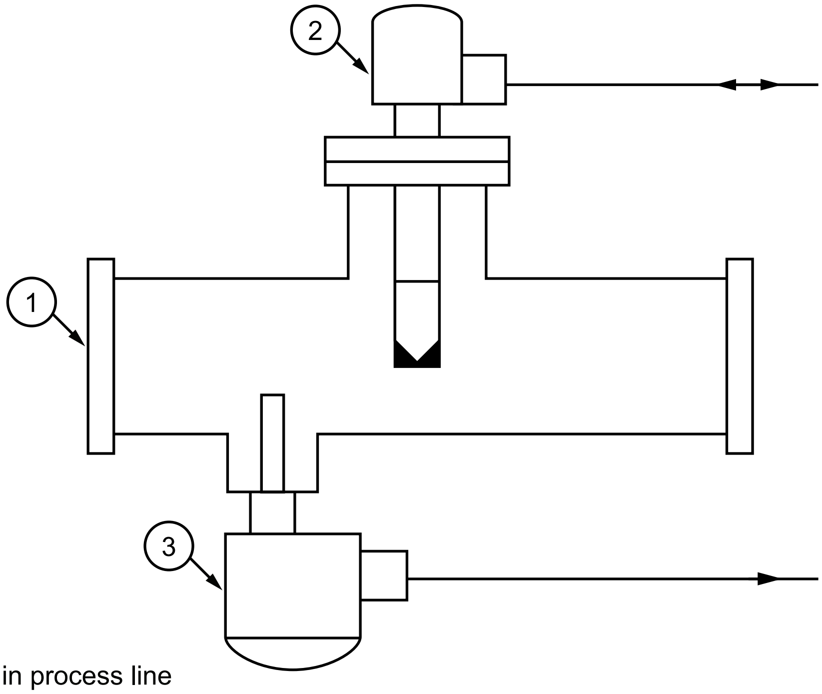
Figure 28-11—Typical Line-mounted Vibrating Probe



Key

1	density meter	4	measured fluid
2	amplifier	5	output
3	vibrating spool		

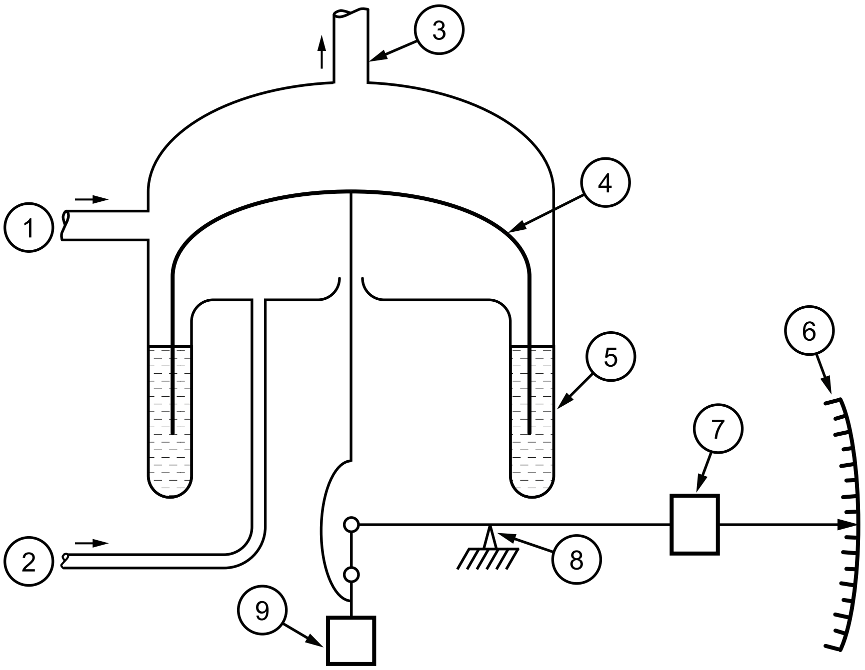
Figure 28-12—Vibrating Spool Principle



Key

1 T-piece in process line
2 receiver
3 transmitter

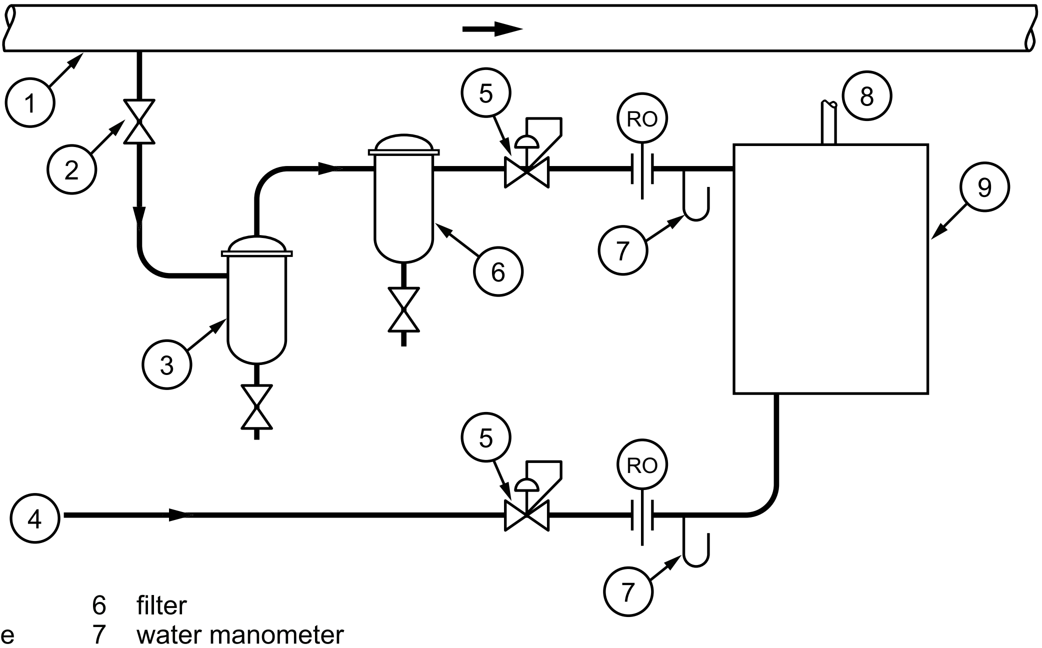
Figure 28-13—Sonic Liquid Densitometer



Key

1 sample in
2 dry air (for reference)
3 gas column
4 floating bell
5 oil seal
6 may be pneumatic or electric transmission
7 counterweight
8 pivot
9 weight

Figure 28-14—Gas Specific Gravity Balance



Key

1 gas line
2 block valve
3 drip pot
4 dry air
5 PCV
6 filter
7 water manometer
8 vent
9 gravity balance

Figure 28-15—Typical Hookup for Gas Specific Gravity Balance

28.4.2 Gas Density Balance

The gas density balance instrument (see Figure 28-16 and Figure 28-17) is of the electrical null-balance type. The gas density is measured by the buoyancy of one ball of a dumbbell as compared with the other. The reference ball is punctured; therefore, it is not subject to the buoyancy effects. Rotation of the dumbbell about a horizontal suspension produces an electrostatic force between electrodes and the suspension. A light source is arranged to project a beam of light onto a small mirror mounted on the dumbbell. This light beam is reflected by the mirror to a prism which divides it into two beams which fall on two identical phototubes in a bridge circuit. Balancing potential is obtained and measured by the amount of light received by each of the phototubes. The rebalance potential nulls the balance and is recorded as specific gravity relative to air. The instrument is compensated for barometric pressure changes. Calibration is made with a known reference gas. Narrow spans may be obtained.

28.4.3 Fluid-Drive Gas Gravitometer

With the fluid-drive gas density meter (see Figure 28-18 and Figure 28-19). two opposing fluid drives develop a torque which is proportional to fluid density. The difference in the opposing torques aligns a pointer which indicates specific gravity.

28.4.4 Blower-type Gas Densitometer

In the blower-type gas densitometer (see Figure 28-20 and Figure 28-21) a constant-speed rotating element in a bypass line produces a differential pressure which is proportional to the gas density. A differential pressure transducer connected between the inlet and the outlet of the rotating element measures the differential produced and sends signals to indicate, record, or control. This instrument does not require correction for gas compressibility and may be used in conjunction with a gas volume flowmeter as a mass flow device.

28.4.5 Vibrating-probe Gas Densitometer

The vibrating-probe liquid densitometer, described in 28.3.6 and shown in Figure 28-10, may also be adapted to the measurement of gas density. Two models are available. The first employs a single probe. The second uses two probes, one of which is immersed in a reference gas at the same temperature and pressure as the sample. The latter type is usually more stable and more easily calibrated.

28.4.6 Thermal Conductivity Gas Densitometer

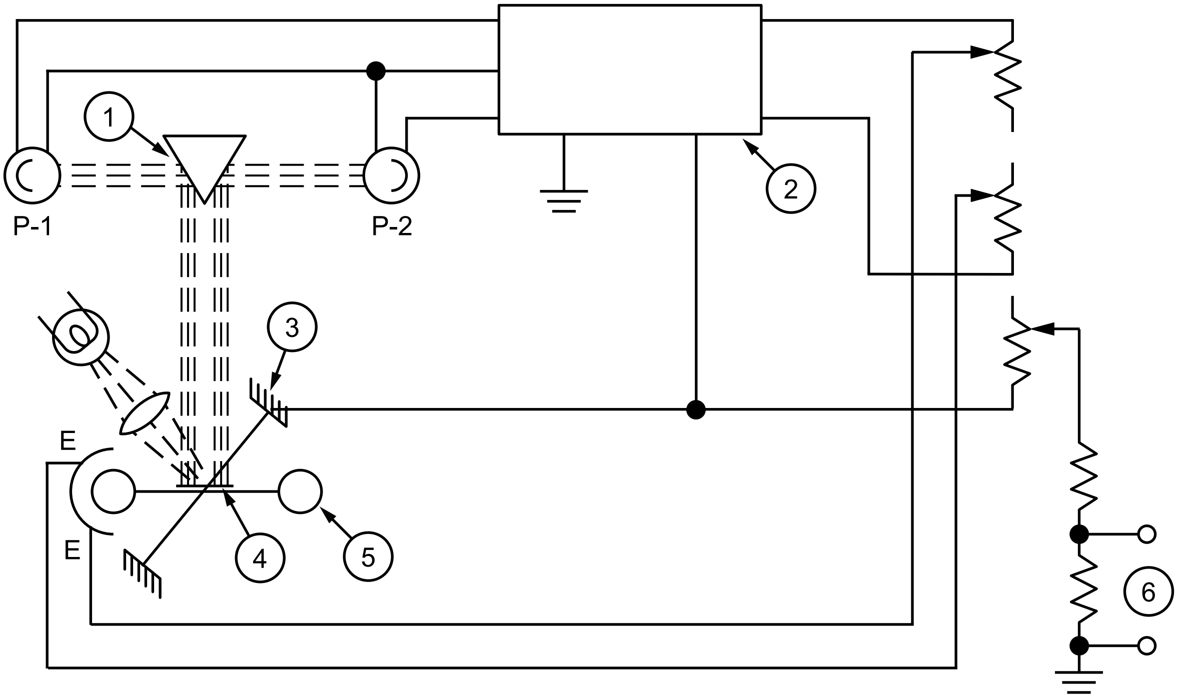
The thermal conductivity gas densitometer (see Figure 28-22) consists of a pneumatic Wheatstone bridge mounted in the vertical plane. The difference in molecular weight between the reference gas and sample gas will cause an unbalanced flow past the two thermistors. The temperature difference between the two thermistors is a measure of the sample gas molecular weight which is correlated to density. Alternating the sample with air will give results which can be correlated to specific gravity.

The reference gas is selected for having sufficient difference in density from the sample and is preferably of high molecular weight, high heat capacity, and low viscosity. Nitrogen, argon, and carbon dioxide tend to satisfy these requirements. The sample flow is maintained at about 10 cubic centimeters per minute while the reference flow is set at about ten times that to avoid back-diffusion.

The main advantage of this design is that the sample gas never comes in contact with the detectors and, therefore. they cannot become coated, coked, or contaminated by the sample. Another desirable feature is that the cell contains no moving parts. Variations in ambient temperature can introduce errors and, therefore, the cell temperature is normally controlled within 1 degree Fahrenheit.

28.4.7 Sonic Gas Densitometers

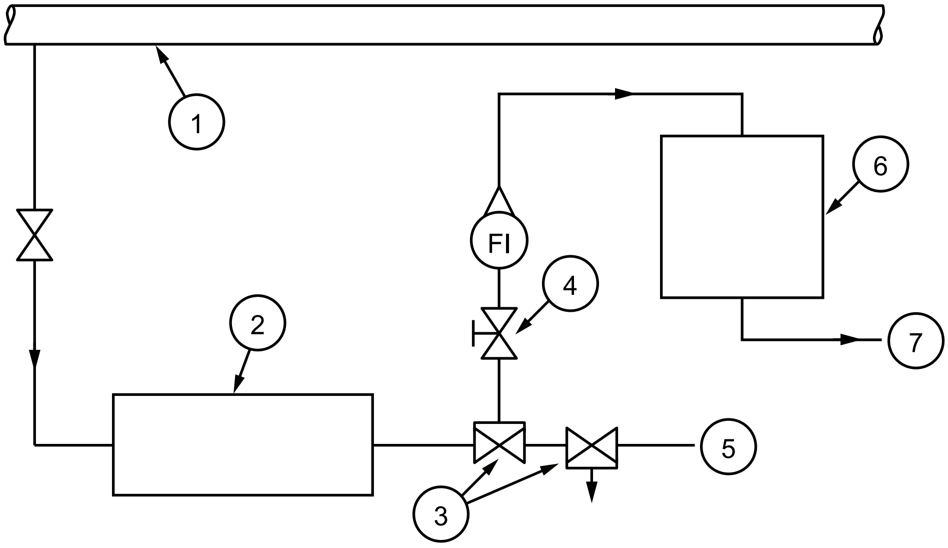
Sonic gas densitometers measure the density of a gas by measuring the velocity of sound in a tube containing the gas (see Figure 28-23). The velocity is calculated by the time required for sound to travel through the gas from the transmitter to the detector, in what is often referred to a “time-of-flight” densitometer. To improve accuracy a two-tube



Key

1	prism	4	mirror
2	power supply and amplifier	5	dumbell
3	suspension	6	to receiver

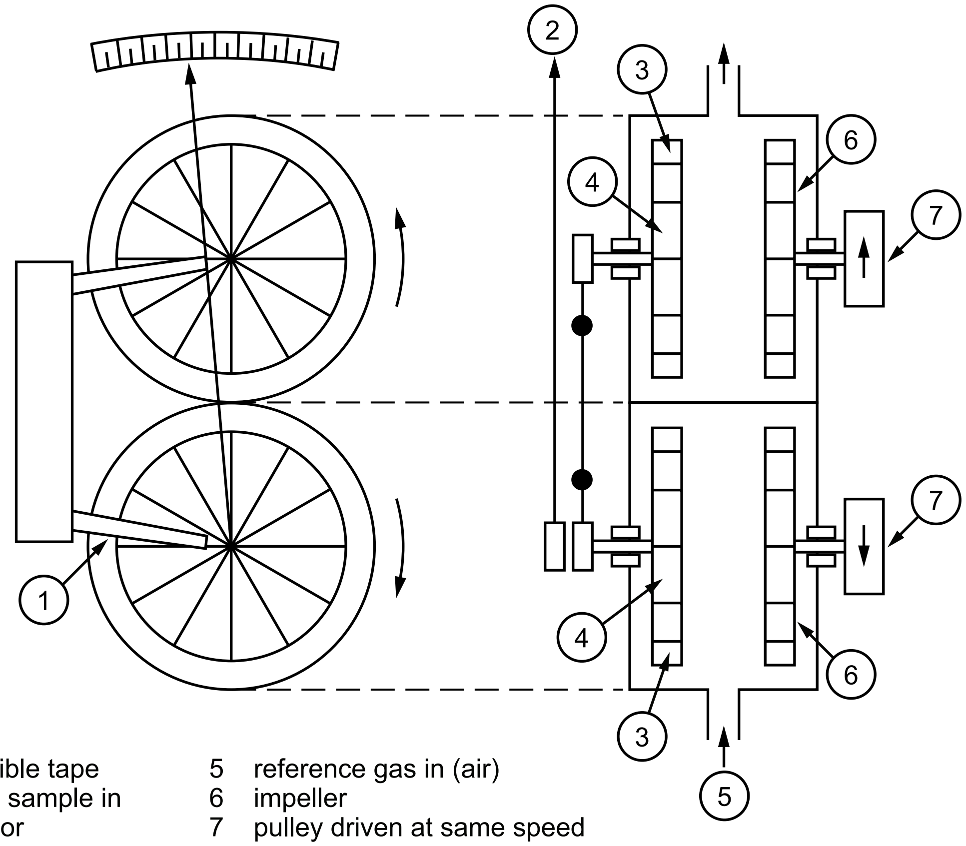
Figure 28-16—Gas Density Balance



Key

1	sample slipstream (if possible, to reduce time lag)	4	needle valve
		5	reference gas
2	sample preparation	6	gas density balance
3	selector valves	7	vent to closed system

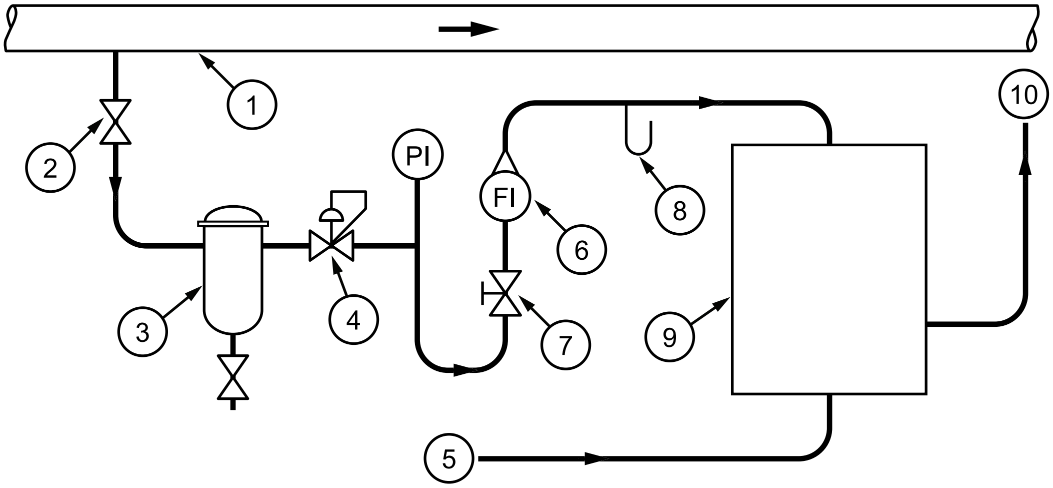
Figure 28-17—Typical Gas Densitometer Sampling System



Key

1 flexible tape
2 gas sample in
3 stator
4 implulse wheel
5 reference gas in (air)
6 impeller
7 pulley driven at same speed

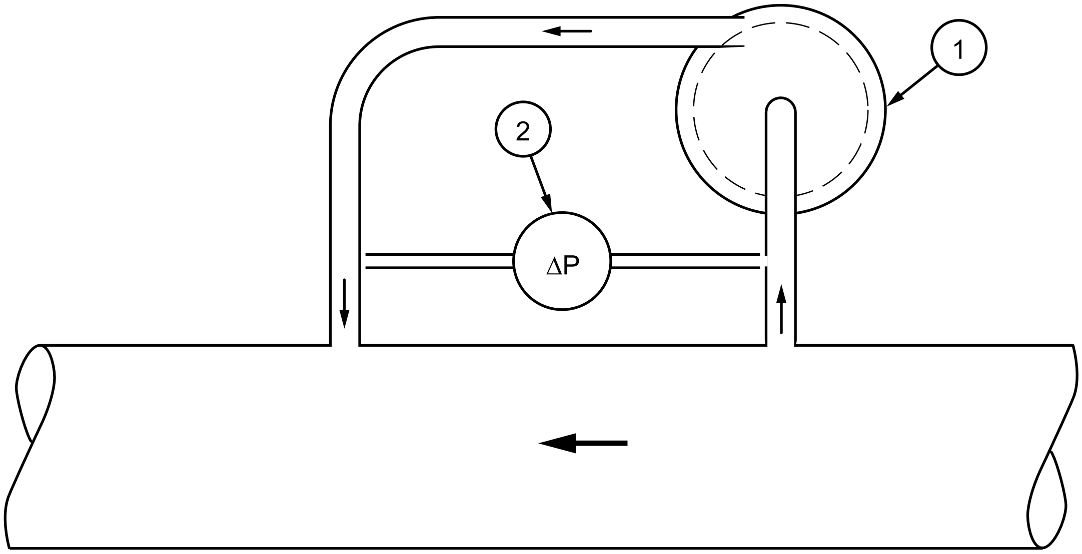
Figure 28-18—Fluid Drive Gas Gravitometer



Key

1 gas line (under pressure)
2 block valve
3 filter knockout
4 PCV
5 reference air
6 flow meter
7 needle valve (10–25 CFH)
8 manometer
9 gravitometer
10 vent to closed system

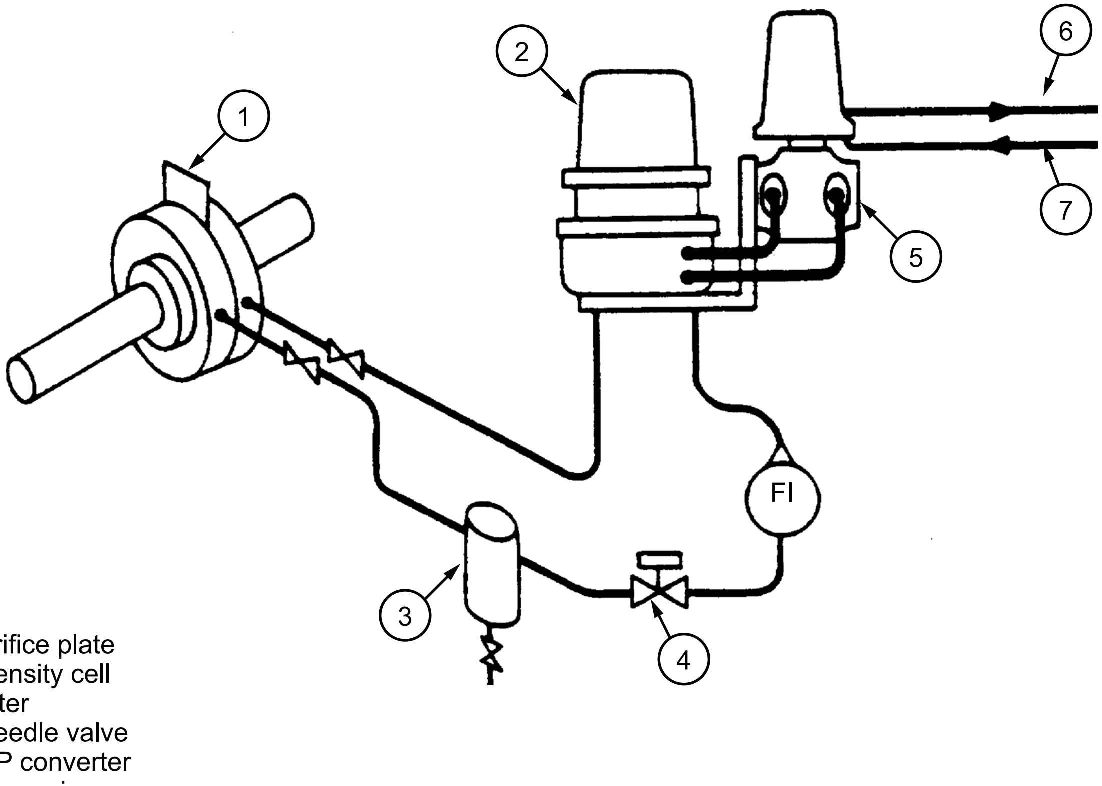
Figure 28-19—Typical Sampling System for Gas Under Pressure



Key

1 Rotating element at constant speed
2 transmitter

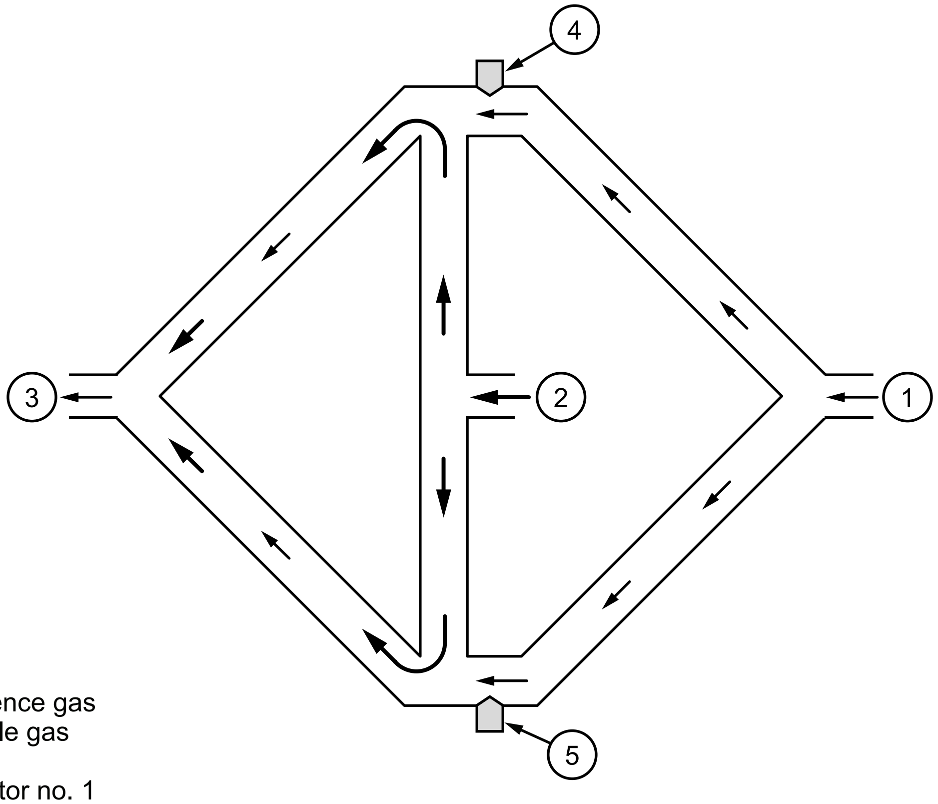
Figure 28-20—Principle of the Rotating-element Type of Gas Densitometer



Key

1 orifice plate
2 density cell
3 filter
4 needle valve
5 ΔP converter
6 to receiver
7 air supply

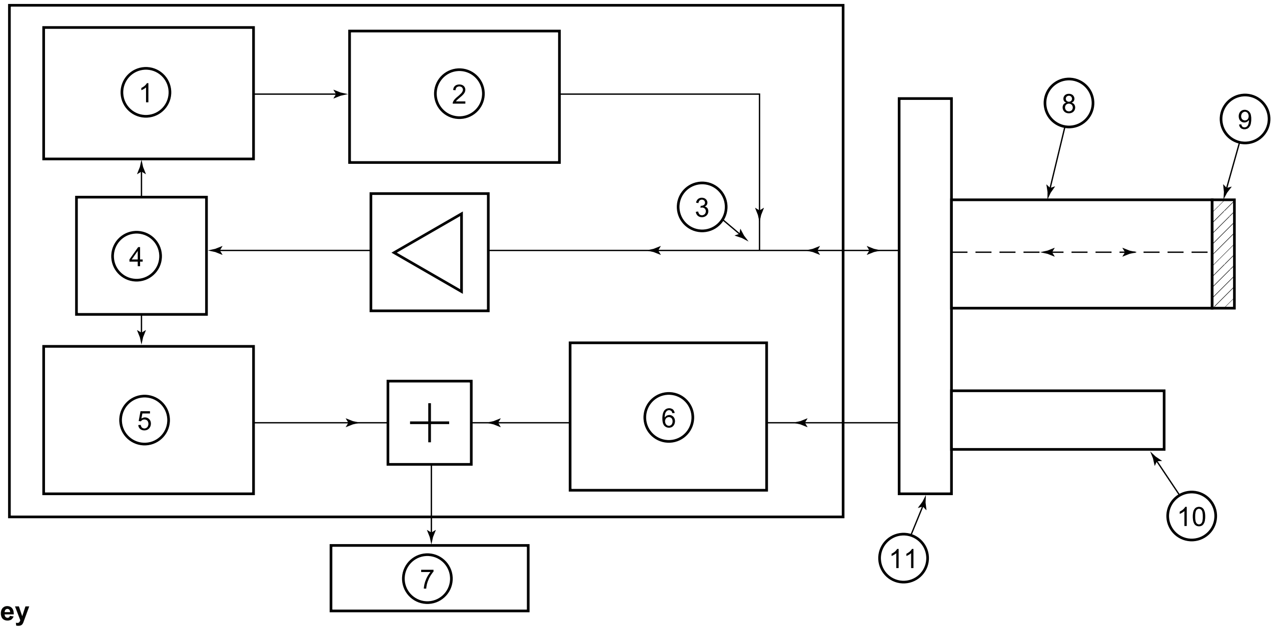
Figure 28-21—Typical Hookup for One Form of Rotating-element Densitometer



Key

1 reference gas
2 sample gas
3 vent
4 detector no. 1
5 detector no. 2

Figure 28-22—Thermal Conductivity Gas Densitometer



Key

1 auto sensitivity adjustment
2 pulse generator
3 sing-around circuit
4 threshold detector
5 F/V converter
6 temperature compensation
7 recorder
8 electro-acoustic transducer
9 reflector
10 resistance thermometer
11 mounting flange

Figure 28-23—Sonic Gas Densitometer

time-of-flight differential system is used in which the time required to transverse a reference gas is compared to the process. The density of the reference gas is used along with the ratio of the two times to calculate the density of the process. The signal must be corrected for temperature variations.

28.5 Compensation for Factors Affecting Accuracy

28.5.1 Pressure Compensation

Where dissolved gases have no effect, liquid densitometers usually require no pressure compensation. Where dissolved gases are present in such quantity as to affect accuracy, a careful study should be made prior to installation to determine the type and extent of corrective steps required to minimize their effect.

28.5.2 Temperature Compensation

On liquids where variation in the temperature of the liquid at the measuring instrument does not exceed 10 °F (~5 °C), no temperature compensation is normally employed. For high accuracy, temperature compensation must be provided when temperature variations exceed this value.

The change in density of gases with change in temperature is significant and must be corrected by employing a suitable means of temperature compensation. On most densitometers, temperature compensation can be obtained by providing a temperature-measuring device that electrically, mechanically, or pneumatically acts upon the primary signal from the density-measuring element to correct for the effect of temperature variation.

28.5.3 Effects of Deposits, Moisture, and Foreign Materials

The accuracy of all liquid densitometers may be adversely affected by the deposit of foreign materials in the measuring chamber or on the displacer or float. If deposits or buildup are likely to occur, a system of flushing or cleaning will aid in obtaining the desired accuracy. With the gamma-ray instruments, a decrease in thickness of the pipe or vessel wall will adversely affect the instrument.

The gas specific gravity balance of Figure 28-13 will give inaccurate results if dust, dirt, or other foreign materials are allowed to accumulate on the floating bell.

Gas densitometers of the types shown in Figure 28-13, Figure 28-15, and Figure 28-17 are affected by the moisture content of the air used as a reference. For this reason the reference air must be thoroughly dried before introduction to the instrument or both the gas and reference air streams must be saturated.

The viscous-drag gas gravitometer (see Figure 28-17) can be supplied with a built-in, two-compartment humidifier through which the gas and air sample pass before entering the impeller chambers. If it is desirable to obtain the density of the gas on a dry basis, the reference air must pass through suitable drying equipment prior to its entry into the instrument.

28.6 Safety Considerations

28.6.1 Sample Material Hazards

With the exception of the balanced flow vessel described in 28.3.1, the liquid densitometers covered here-in are usually mounted in the line or vessel or very close to the line or vessel. With this type of installation, the connecting lines are relatively large and mechanically strong. The same precautions should be followed as when installing other equipment handling the fluid involved.

The liquid densitometer described in 28.3.1 is used most often for pipeline sampling of crude oil and refined oil products. Temperatures are near ambient and no special precautions other than those normally observed when handling hydrocarbons at line temperatures and pressures are involved.

Gas densitometers like other gas sampling instruments may handle gases that are flammable, toxic, or irritating to the eves or mucous membranes, or both. Precautions should be taken to vent such gases to a safe location-either sufficiently high, so that they will readily disperse in the atmosphere, or to a convenient, low-pressure line, vessel or stack.

28.6.2 Electrical Hazard

Liquid or gas densitometers may be used with volatile and other flammable materials. Generally, some electrical equipment is associated with their operation, either in the measuring circuit, temperature compensating circuit or transmission system. The electrical system should be studied to determine what degree of hazard it might present. The scope of electrical precautions necessary is outlined in 7.3.

28.6.3 Potential Radiation Hazards

Densitometers using radium salts or radioisotopes to present an additional hazard because of the possible exposure of personnel to radiation. Before installing or using a device of this type, all maintenance personnel should be thoroughly familiar with state and federal regulations which may be applicable. The manufacturer will usually assist in obtaining license application forms and copies of other pertinent information. It is desirable that personnel servicing equipment of this type be provided with film badges or dosimeters. These devices are essential for monitoring and maintaining within safe limits the radiation dosage received by service personnel.

28.7 Installation Considerations

28.7.1 Location Considerations

Sampling problems may be minimized by locating the densitometer as close as practical to the sample point. In some cases, it is essential to locate the densitometer right at the sample point with the minimal practical sample line length. The various components should be protected from nearby hot equipment, severe ambient temperature changes, shock, vibration, and other mechanical damage. This is not difficult in an existing plant, but in a new plant proximity to heavy reciprocating equipment and locations near highways, and railroads. Shock mountings should be used where vibration is unavoidable.

Many densitometers require weekly maintenance, and in some cases daily when extremely dirty sample streams are measured. Good installation practices can save man-hours and improve reliability.

The densitometer measurement cell should be conveniently accessible, whether at grade or some elevated point. Accessibility may be provided by allowing space for portable platforms or by installing permanent platforms. Avoid installations where a ladder would be necessary.

28.7.2 Housing Considerations

In most cases, it is desirable or even mandatory to house the densitometer to protect it from the weather and to maintain the ambient temperature within reasonable limits. Even in the most benevolent climate, a roof over the instrument is justified to protect service personnel from thundershowers, process and water spills, falling objects, and sunlight. Normally housing requirements increase with climate severity. In some installations, lighted, heated, and ventilated housings, preferably of the walk-in type, will be desirable.

Walk-in analyzer buildings (housings) should be provided with exits so located as to permit safe evacuation in the event of an emergency within the process area.

Material selected for the construction of an analyzer house should be of a type that will not cause operational difficulties, nor create a safety hazard.

For example, a house constructed of sheet aluminum can absorb enough heat on a hot sunny day to raise the temperature of the enclosure higher than the setpoint of the thermostatic control point in the densitometer, thus causing false readings and malfunctions.

Fiberglass housings are recommended for corrosive atmospheres resulting from leaks in process equipment, or by the location of the equipment near bodies of salt water.

It is recommended that the instruments shown in Figure 28-1, Figure 28-3, Figure 28-12, Figure 28-14, and Figure 28-16 be enclosed in weatherproof housings. The instruments shown in Figure 28-5, Figure 28-7, Figure 28-9, and Figure 28-10 generally are mounted in the line or vessel and require no housing. The readout equipment should be located in the control room or at some protected location.

28.7.3 Effects of Vibration

The densitometers shown in Figure 28-1, Figure 28-3, Figure 28-10, Figure 28-13, and Figure 28-15 can all be adversely affected by vibration. Precautions should be taken to locate the instrument and arrange the process piping so that vibration will not be transmitted to the device. Shock mounts may also reduce the effect of vibration for densitometers that cannot otherwise be located away from areas of vibration.

28.8 Sampling Systems

It is safe to assume that process stream samples will contain contaminants. Some samples must be chemically treated to remove or inactive contaminants, however, this may cause other problems from the reactants. Some materials may polymerize or react when heated. When gas pressure is sharply reduced some samples may freeze, deposit ice, or form hydrates due to the refrigeration effect. Frequently, both the sample and densitometer temperature and pressure require close regulation. Usually the sample flow rate, or sampling quantity and frequency, must be closely controlled. Neglect by the installation designer of any one of these requirements may result in erroneous analysis or no analysis at all.

Most refinery streams are water saturated, therefore, some method of removal is necessary and must be provided. Entrainment coalescers or separators will remove water droplets. Where saturated vapor samples are transported through an area where ambient temperature is lower than the temperature at the sample inlet point, the sample line should be heat traced or jacketed to avoid formulation of condensate.

Bubbles can also affect a densitometer's accuracy. Generally, the detection section should be positioned such that the process sample flow rises vertically through it.

Densitometers differ from other types of process stream analyzers. Most types of densitometers use much larger samples and some may be mounted in the line or vessel. Also densitometers may handle material such as slurries. In order to give a better understanding of the specific sampling system required this discussion will be referenced to the appropriate figure numbers.

1) Figure 28-1: The balanced flow vessel design generally is used for crude oil and refined products. The sample connections to the flow vessel are relatively small. The sampling system auxiliaries should be designed to deliver a reasonably clean stream to the instrument. The sample should be free of solid or foreign material which might plug or coat the connections or settle out in the balanced vessel, thus contributing to false information. The sample is usually supplied by a small-volume displacement pump. A restriction orifice in the main line can sometimes be used to promote sample flow.

2) Figure 28-3: The balanced flow tube may be obtained with a tube diameter of $^3/_4$ in. or larger. It can be used on any liquid and is suitable for measuring slurries. No special sampling system is required. If the process line is small. the instrument may be installed directly in the line; suitable block valves and a bypass must be provided so that the instrument may be taken out of service for maintenance.

3) Figure 28-5: The industrial specific gravity displacer has large sample connections and no special sampling system is required. A valve or restriction orifice should be provided on the outlet for regulating the flow rate so that the velocity of the flowing stream will not affect the displacer. Location of the valve or restriction on the inlet is not advisable due to possible partial vaporization across the restriction when used on some types of liquids.

4) Figure 28-7: The chain-balance-float densitometer requires the same precautions as the balanced flow tube (see Item 2 and Figure 28-3).

5) Figure 28-9: Inasmuch as the gamma-ray density gauge is entirely external to the line and has no contact with the fluid, no sampling system is required. It is suitable for interface detection or for use on any material which can be moved through a line; for example, liquids, divided solids, or slurries. Coaxial cable is used from the radiation detector to the remotely located amplifier. Refer to Chapter 30—pH Analyzers for precautions to be followed when using coaxial cable.

6) Figure 28-10: The vibrating-probe densitometer may be mounted on the line or vessel or in a slipstream. It employs no sampling system and may be used on numerous liquids and some slurries. As this instrument is somewhat sensitive to flow effects, it should be provided with a sleeve-type guard around the probe.

7) Figure 28-13: The gas specific gravity balance is suitable for clean, dry gases such as natural gas. It is not suitable for gases that contain dust, dirt, or other impurities which would settle out on the floating bottom or on the surface of the sealing liquid. The sample must be supplied at near atmospheric pressure; therefore, a suitable pressure reducer and filter are required in the sample supply line.

8) Figure 28-15: The gas density balance is probably one of the most accurate instruments available and is capable of measuring very low gas densities; however, it is one of the most delicate instruments and requires the most sophisticated sampling system. The sample must be extremely clean and dry and must be only slightly above atmospheric pressure. Refer to Chapter 4 for details of sample preparation and handling systems.

9) Figure 28-17: The fluid drive gravitometer is a rugged instrument requiring minimum maintenance. This type of densitometer has been successfully used on gases, such as flue gas, sulfur dioxide. nitrogen, hydrogen sulfide, and hydrogen recycle gas. Ambient air is generally used as a reference gas. To prevent errors in measurement and to avoid damage to the instrument, the gas sample may require a sample conditioning system. Gas should enter the instrument at essentially atmospheric pressure (within $^1/_2$ in. of water column) or at a flow rate of 10 to 25 ft^3 per hour. If the sample is at high pressure, a primary reducing valve should be used followed by a differential pressure regulator with a rotameter for final pressure reduction. With non-corrosive gases, a simple filter should be installed in the sample line along with a knockout pot to remove free water. For use on non-corrosive gases, the instrument has a built-in, double-compartment humidifier through which both the sample gas and reference air pass before entering the measuring chambers. The temperature of the sample gas should be ambient. Usually if the sample piping is 15 ft or more in length, the sample will reach ambient temperature before reaching the instrument and no auxiliary cooling or heating devices are necessary. If the gas sample is corrosive, it is usually measured on a dry basis, and reference gas dryers as well as dryers for the sample must be provided. Since this sample cannot be disposed of to a flare or other potentially pressurized systems, it may be necessary to provide a sample recovery system if local regulations do not permit the venting of the sample gas.

10) Figure 28-19: One form of the rotating-element densitometer is installed directly on the line and no sample handling equipment is required. A typical sampling system for another form of the densitometer is shown in Figure 28-20. Measurement is density at line conditions.

11) Figure 28-21: The thermal conductivity gas densitometer requires a clean, dry sample only slightly above atmospheric pressure. Refer to Chapter 4 for details of sample preparation and handling systems.

28.9 Calibration

With so many different types of densitometers currently available, no attempt will be made to detail the methods of calibration. Calibration may be in terms of API gravity or specific gravity, as desired. Refer to the manufacturer's instruction manuals for this information.

28.10 Readout

All of the densitometers described in this section can be adapted to read out on most of the standard pneumatic or electrical indicating or recording instruments for. measurement or control. Refer to manufacturer's literature for special adaptations.

28.11 Startup

Startup procedures are discussed in Chapter 6. For additional information, refer to manufacturer's instruction manuals.

29 Color Analyzers

29.1 General

This section covers process analyzers used to measure the color of refinery products.

Color measurements relate to flow characteristics of refinery products as defined by ASTM Method D1500 and Saybolt (ASTM D156). Process color analyzers typically employ solid state electronics, are continuous in operation, and have no moving parts. A typical color analyzer is shown in Figure 29-1.

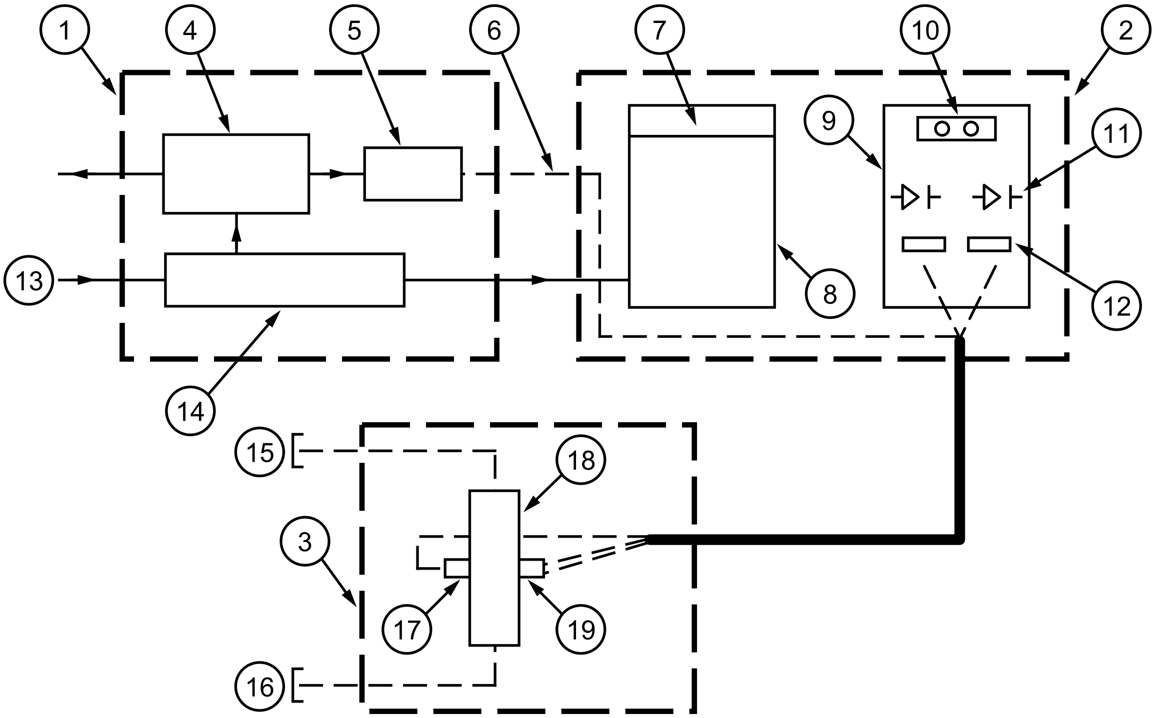
29.2 Applications

Color analyzers may be used for the determination of products specification and characterization of products such as kerosene, lubricating oils, gasolines, heavy gas oils, and other similar refinery products. Color analyzers may be calibrated for ASTM D1500, Saybolt (ASTM D156) or other quality scales. Allowable ambient range of operation is generally 0 °C to 55 °C (32 °F to 131 °F).

Typical on-line repeatability on the same sample is 2 % of scale.

29.2.1 Typical Color Analyzer Specifications

Sample system complexity:	simple
Typical analysis spans:	correlates to ASTM D1500 or ASTM D156
Typical analyzer outputs:	local meter, 4 mA to 20mA
Manufacturer's listed accuracy:	complies with ASTM D1500 or D156
Typical analysis precision:	2 % of scale
Typical analysis time:	continuous
Typical on-stream time:	95 %+
Relative installed price:	$20 K up



Key

1 power/alarm module
2 control/display module
3 flow cell enclosure
4 alarm relay (2)
5 lamp
6 fiber optic source
7 display
8 digital PCB
9 analog PCB
10 4/20 mA
11 photodiodes
12 optical filters
13 AC
14 power supply
15 sample out
16 sample in
17 source
18 flow cell
19 detector

Figure 29-1—Typical Color Analyzer

Relative maintenance frequency:	0.5 man-hour/day or less
Average startup:	< 1 man-day
Typical refinery applications:	kerosene, lubricating oils, gas oils, gasoline
Sample temperature limits:	– 20 °C to 150 °C (– 4 °F to 302 °F)
Sample flow rate:	200 cc/min to 300 cc/min
Sample pressure:	10 bar to 100 bar (147 to 1470 psig),
Sample temperature:	– 20 °C to 150 °C (– 4 °F to 302 °F)

29.3 Color Measurements

A dual wavelength, dual detector ratiometric system is employed to reduce the effects of bubbles, dirt, haze, and coatings on the detector optics. Newer models employ fiber optics to carry the light from a visible light source (typically a halogen lamp) to the measurement cell and return back to the detector cell. This allows the sample cell to be remotely located from the analyzer optics and electronics section. A sample cell could be located on the fast loop sample cell to minimize size and sample tubing runs.

29.4 Sampling Systems

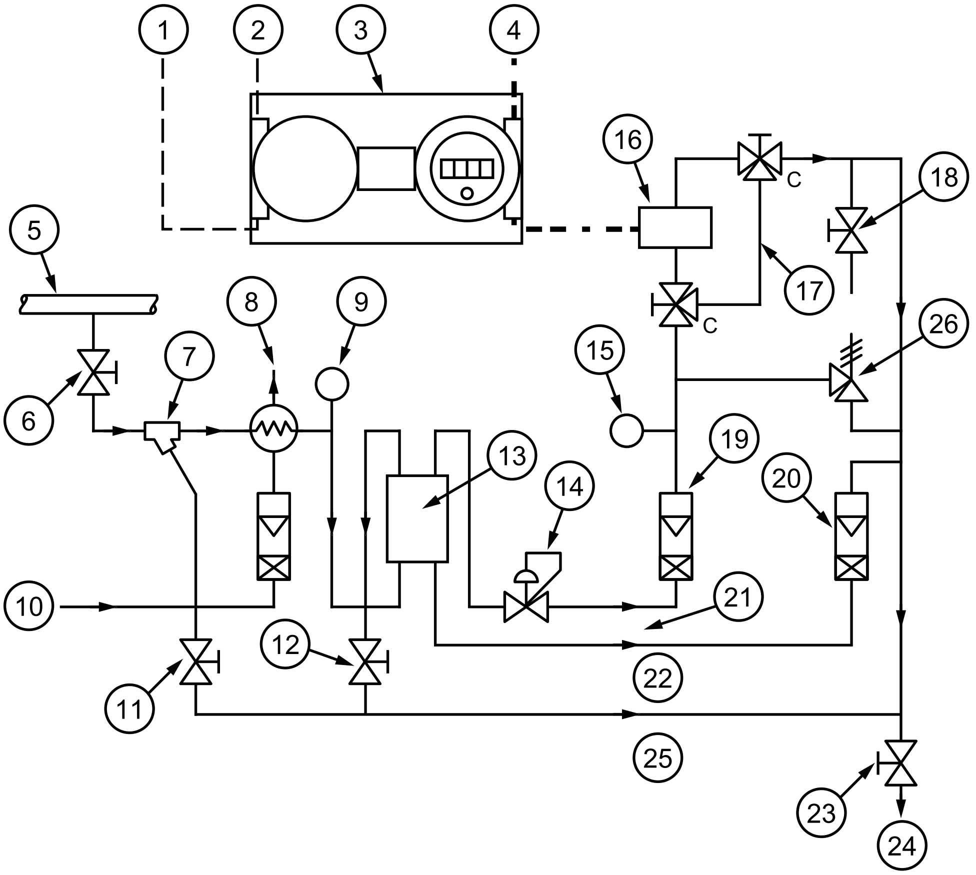
The sample must be at least 10 °C (18 °F) above the pour point temperature, but no more than 55 °C (131 °F) higher at the inlet to the analyzer. Typical sample flowrates are 0.2 l/min. to 1.0 l/min. (0.05 gal/min 0.25 gal/min.), with viscosities no greater than 750 cST at 38 °C (100 °F). Maximum allowable pressures are typically 200 psig, with a minimum pressure of 30 psig. If there is significant downstream pressure on the return line, the minimum differential (supply to return) is 30 psig.

For low temperature applications, normal process water may be utilized to cool the sample. For higher temperature streams, a 50/50 mixture of glycol/water in a re-circulating bath may be required. Sample coolers are typically available from the manufacturer as an option. A typical sample system is shown in Figure 29-2.

For additional details, refer to Chapter 4.

29.5 Installation and Calibration

The optics and electronics portion of color analyzers are typically mounted in an analyzer shelter. Some general considerations include the following.



Key

1	alarm relay output
2	power 115/230 VAC 50/60 Hz
3	continuous colormeter
4	4–20 mA output
5	process line
6	shutoff valve
7	strainer
8	sample cooler
9	temp. ind.
10	cooling water in
11	sweepstream throttle
12	throttle valve
13	filter coalescer
14	press reg.
15	press ind.
16	cell
17	by-pass
18	sample tap
19	sample flow
20	by-pass flow
21	water-free sample
22	coalesced water plus sample
23	sample out
24	sewer or process line
25	sweepstream
26	relief valve

Figure 29-2—Color Analyzer System Diagram

The analyzer should be installed as close to the sample point as possible to minimize sample response time. Valves should be provided to isolate the sample cell from the process. It is often advisable to provide pressure and temperature gauges in the sample line to indicate proper sample conditions. The sample pressure in the measuring cell must be regulated.

Sample conditioning should adequately remove all particulate matter from the sample stream to avoid a physical blockage of the light path. Removal of all particles greater than 5 microns is recommended. Free or entrained water should also be removed by a suitable coalescer.

Calibration is often accomplished with pre-calibrated filters that are mechanically inserted into the light path.

For additional installation, calibration, start-up and maintenance, see manufacturer’s instructions and refer to Chapter 6.

Annex E—References

Manufacturer’s Literature

Chapter 21—Pour Point Analyzers

ASTM D97-66 IP15-67, American Society for Testing Materials, Philadelphia, Pennsylvania, 1980.

Manufacturer’s Literature

Chapter 24—Flash Point Analyzers

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ASTM D93-80, IP 34-75 *Standard Test Methods for Flash Point by Pensky-Martens Closed Tester.*

ASTM D3764-80, *Standard Practices for Validation of Process Stream Analyzers.*

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Chapter 26—Octane Analyzers

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Process Measurement and Analysis, Lipt‡k, BŽla G., Chilton Book Company, 1995.

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Liptak, Bela G., *Instrument Engineers' Handbook 1*, Chilton Book Co., Philadelphia. Pa., 1994.

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Manufacturer's Literature

Section F—Chemical Property Analyzers

F.1 Scope

This section covers the selection and installation of liquid stream process analyzers for continuous measurement of electrochemical properties. Gaseous stream analyzers, and laboratory analyzers are not covered in this section. Common liquid electrochemical measurements include hydrogen ion concentration (pH), oxidation-reduction potential, and electrolytic conductivity.

This section also covers the characteristics, application, selection, and installation of water quality analyzers. Aqueous effluent and water treatment type analyzers that provide on-line analyses are discussed. Some of the on-line analyzers, due to their high initial and maintenance cost, are used as laboratory analyzers.

The detection of regulated contaminants in wastewater streams is becoming more important as regulatory agencies promulgate and enforce standards for effluent quality. Rapid detection of contaminants in wastewater is necessary so that a stream may be diverted before large quantities of contaminants are released. Continuous monitoring may be necessary for documentation of compliance to permitting requirements.

Some analyzers (measuring dissolved oxygen, pH, conductivity, and specific ions) used in water quality applications are described in more detail in other sections, and are mentioned only briefly in this section.

Wastewater analyzers are generally grouped into two main types: the aqueous effluent types, which are used to measure total carbon, total organic carbon, total oxygen demand, turbidity, residual chlorine, hydrocarbons in water, hydrogen ion concentration, and dissolved oxygen; and the water treatment types, which include conductivity, specific ion, titration, and other wet chemistry analyzers. Some analyzers, though listed under only one of the two main types, may be suitable for both. Wastewater analyzers are discussed in detail in Section A.

30 pH Measurement

30.1 General

Ionization is the basis for the measurement of pH, electrolytic conductivity, and oxidation-reduction potential (ORP). In an aqueous solution, when water is bound together in the molecular form, it is often referred to as *associated*. When a molecule is separated or *dissociated,* two or more ions are formed. One of these ions is called a hydrogen ion and is designated H^+. The other, the hydroxyl ion, is designated OH^-.

A solution conducts electricity only when ions are present to carry electrons from one electrode to another. Conductive solutions are called electrolytes. *Strong* electrolytes are highly dissociated; that is, a significant number of its molecules will form ions in an aqueous solution. The degree of dissociation will vary depending on the composition, concentration, and temperature of the solution (see Figure 30-1).

The hydrogen ion (H^+), sodium ion (Na^+), and ammonium ion ($NH4^+$) are some of the common positively charged ions. Common negatively charged ions are the hydroxyl ion (OH^-), the sulfate ion (SO_4^{-2}) and the chloride ion (Cl^-).

Positive and negative ions can be joined to form molecules with uniquely different properties. For example, the hydrogen ion (H^+) combines with the chloride ion (Cl^-) to form hydrochloric acid (HCl). The OH^- hydroxyl ion joins with the NA^+ sodium ion to form a strong base known as sodium hydroxide (NaOH). All acids contain the hydrogen H^+ ion, and all bases contain the hydroxyl OH^- ion.

If an acid is added to water, more hydrogen ions will be present than basic ions. The more concentrated the acid solution, the greater the number of H^+ ions. Adding a base to water causes the OH^- content to increase. Pure water forms very few ions. The ionization constant of water has been determined to have a value of 10^{-14} moles per liter at 22°C. A solution is deemed to be neutral when both the H^+ and the OH^- concentrations are approximately equal (see Figure 30-2).

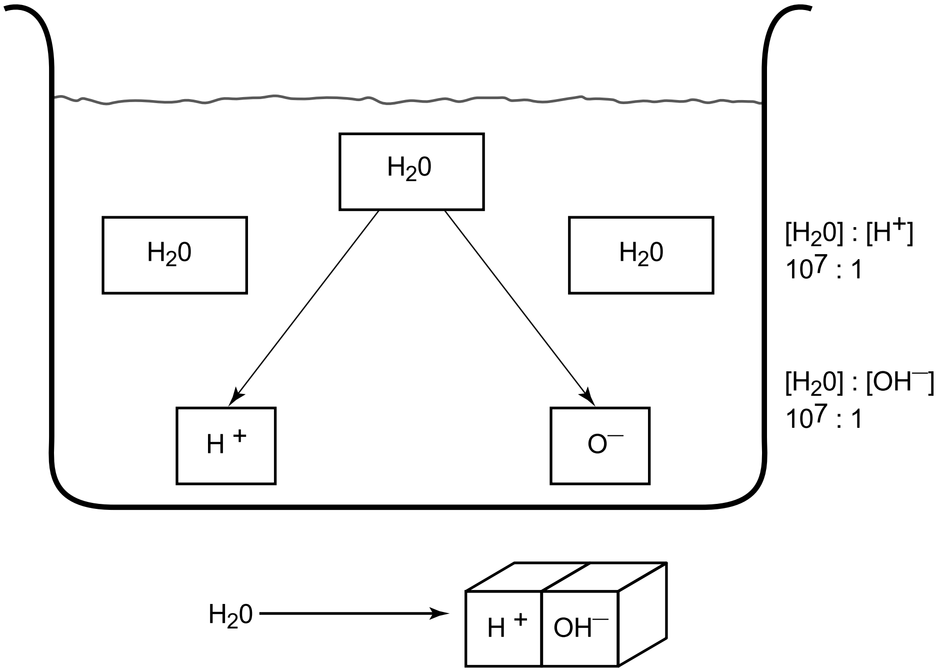


Figure 30-1—Ionization

Adding an acid to water causes $[H^+]$ to increase and $[OH^-]$ to decrease so that $[H^+]\ [OH^-] = K_d$

Example:

$[H^+] =$ 0.00001 = 1 x 10^{-5}

$[OH^-] =$ 0.000000001 = 1 x 10^{-9}

$[H^+]\ [OH^-] = 1 \times 10^{-14}$

Adding a base to water causes $[H^+]$ to decrease and $[OH^-]$ to increase so that $[H^+]\ [OH^-] = K_d$

Example:

$[H^+] =$ 0.000000001 = 1 x 10^{-8}

$[OH^-] =$ 0.000001 = 1 x 10^{-6}

$[H^+]\ [OH^-] = 1 \times 10^{-14}$

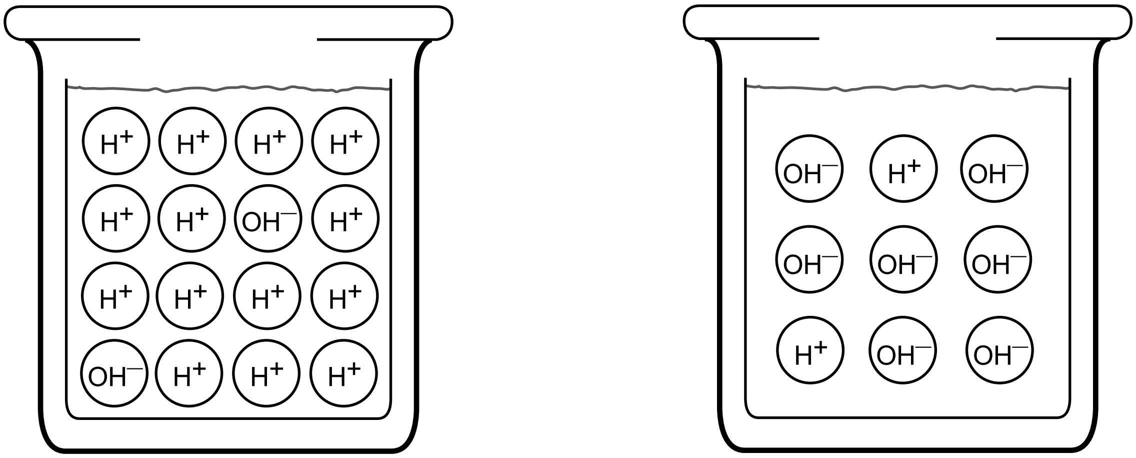


Figure 30-2—Ion Content in Water Solutions

To avoid cumbersome representation for H^+ ions in terms of fractional or exponential notation, the value of pH is commonly expressed as the minus log of the H^+ ion. A different form of the same expression is $H^+ = 10^{-pH}$. Figure 30-3 shows a typical pH scale. A pH of 7 indicates a neutral solution with equal concentrations of H^+ and OH^- ions. All solutions with pH values from 0 to 7 are acidic. The lower the pH number, the stronger the acid solution. From pH 7 to 14, the solution becomes increasingly basic or alkaline.

30.2 Applications

pH is a measure of the hydrogen ion (H^+) concentration in an aqueous solution. It is used widely as a measure of the degree of acidity or alkalinity of a solution. Typical refinery applications for pH measurement include:

a) refinery wastewater;

b) cooling tower water;

c) boiler feedwater;

d) crude tower overhead systems;

e) corrosion control in processing facilities;

f) chemical reaction systems.

Application and process requirements usually dictate the type of equipment required for each installation. The majority of pH measuring systems use sensing elements located in:

a) a piped sample stream at atmospheric pressure (see Figure 30-4);

b) a piped main process stream or piped sample stream at positive pressure (see Figure 30-5);

c) a tank, trough, or stream at constant level (see Figure 30-6);

d) a tank, trough, or stream at variable level (see Figure 30-7).

e) a sampling system for heavily contaminated oily samples containing light oil and heavy sludge (see Figure 30-8).

Electrode flow chambers are used in install pH sensor assemblies directly installed into piped process streams or into bypass sample streams.

Immersion assemblies are used in a tank, trough, or open stream at constant level. The tips of the electrodes are immersed in the process fluid. If immersion assemblies are used where the level is variable, the assembly is submerged to a point where the electrodes are still immersed when the level drops to its lowest point.

Electrode flow chambers are used to admit pH sensitive electrode assemblies directly into piped process streams or into bypass sample streams. In some instances, individual glands may be used to advantage instead of a flow chamber. These glands permit mounting the electrodes directly into a large process line. A more convenient method is to provide a flow chamber in a bypass. The bypass can easily be shut off when the electrode system needs to be serviced.

A flow-type system can be utilized as long as its discharge point is below the lowest level experienced.

It is important to remember, particularly when pH control of a process is being considered, that the pH number itself is an exponential number; that is, a change of just one pH unit means a tenfold change in hydrogen ion concentration.

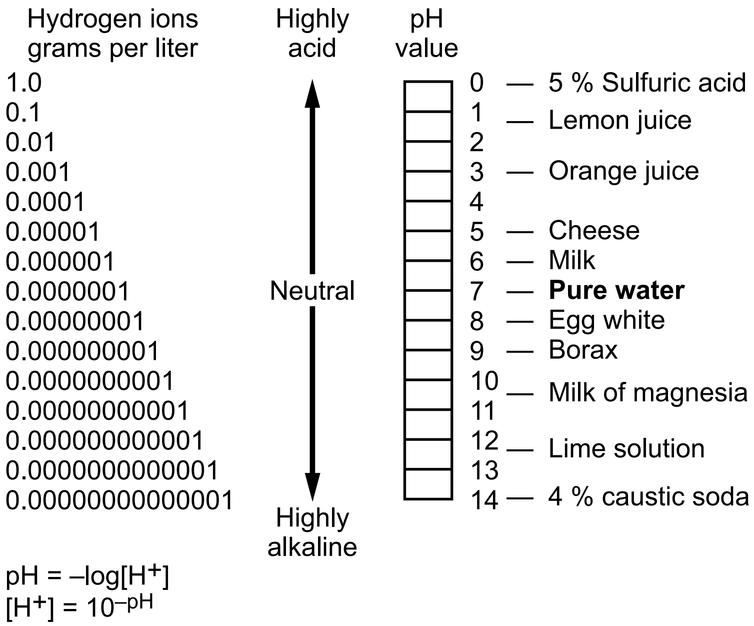
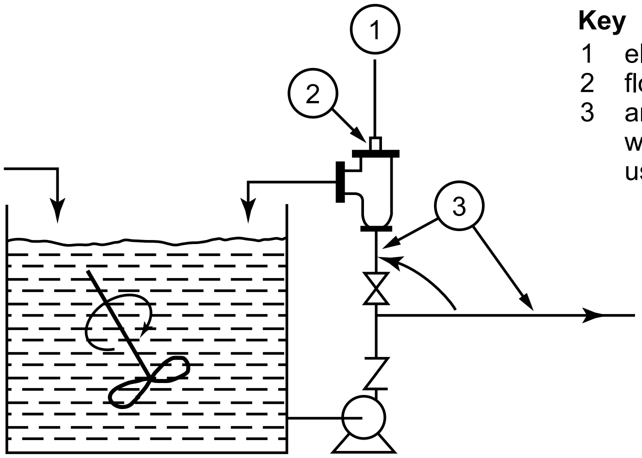


Figure 30-3—Typical pH Scale



Key

1 electrode cable to measuring element
2 flow chamber
3 arrange piping to assure that electrode will not run dry. As an alternative, some users install an S-trap under flow chamber.

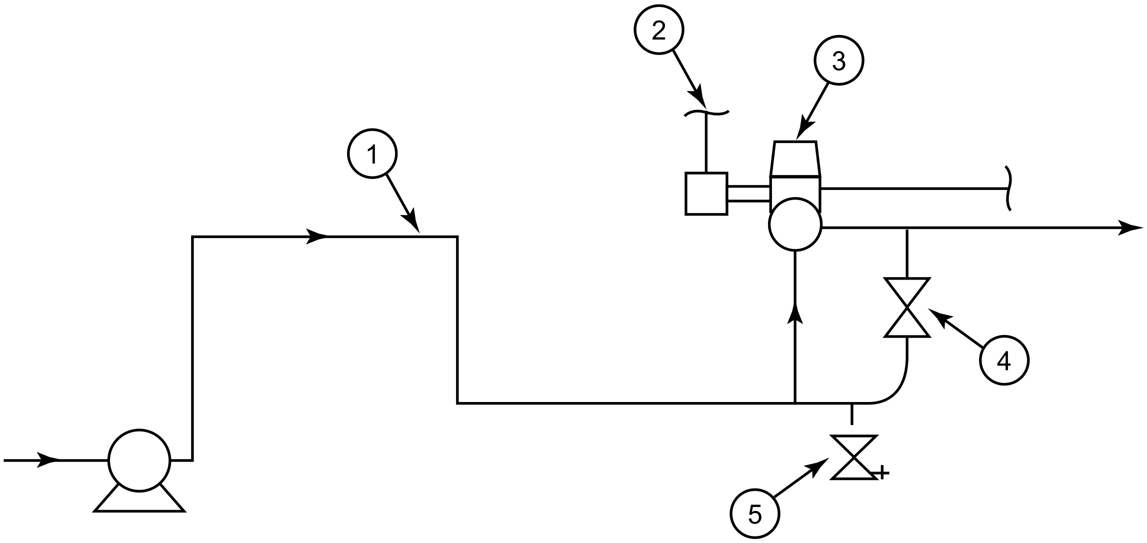
Figure 30-4—Piped Sample Stream at Atmospheric Pressure

As a result of the large change in acidity or alkalinity per pH unit, the need for sensitive, precise pH measurement and control equipment cannot be overemphasized.

Additionally, the pH of a solution usually varies with the solution temperature. pH meters read the pH of the solution in contact with the electrodes at the temperature existing when the measurement is made.

30.3 Typical pH Application Specifications

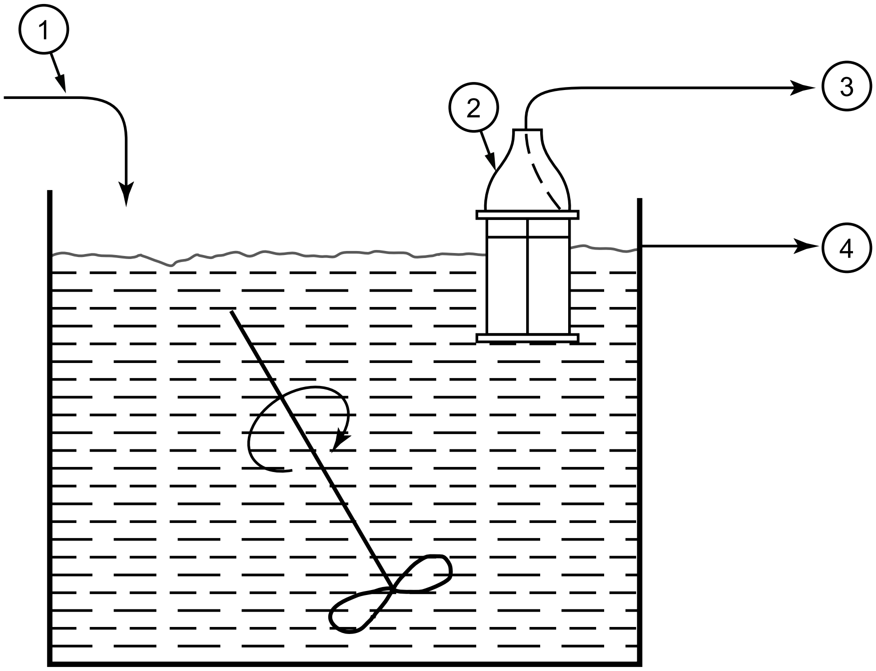
Sample system complexity:	simple to average (depends on application)
Typical analysis ranges:	0 through 1 pH to 0 through 14 pH
Typical analyzer outputs:	alarms, local meter, recorder, 4 mA to 20 mA



Key

1	loop to maintain level on loss of flow	4	bypass
2	cable to measuring instrument	5	drain valve
3	flow chamber		

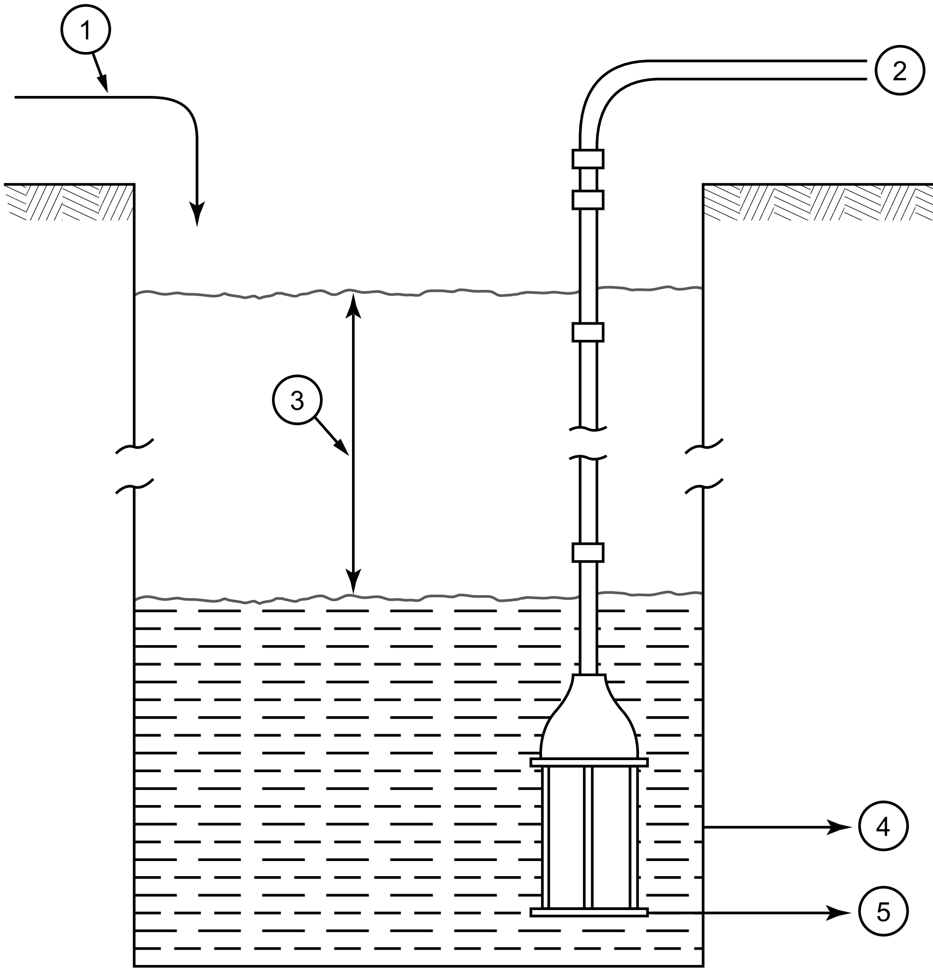
Figure 30-5—Piped Main Process (or Sample) Stream



Key

1	flow in	3	to measuring instrument
2	immersion assembly	4	flow out

Figure 30-6—Tank at Constant Level



Key

1 flow in
2 cable to measuring instrument
3 variable level
4 flow out
5 submersion assembly

Figure 30-7—Tank at Variable Level, Submersion Assembly

Manufacturer's listed accuracy:	± 0.02 pH units
Typical analysis precision:	± 0.02 pH units
Typical analysis time:	continuous
Typical on-stream time:	low (< 95 % stream factor, usually 85 % to 95 %)
Relative installed price:	low (< $15 K)
Relative maintenance frequency:	low (< 1 man-hour/day)
Average startup:	< 2 man-days

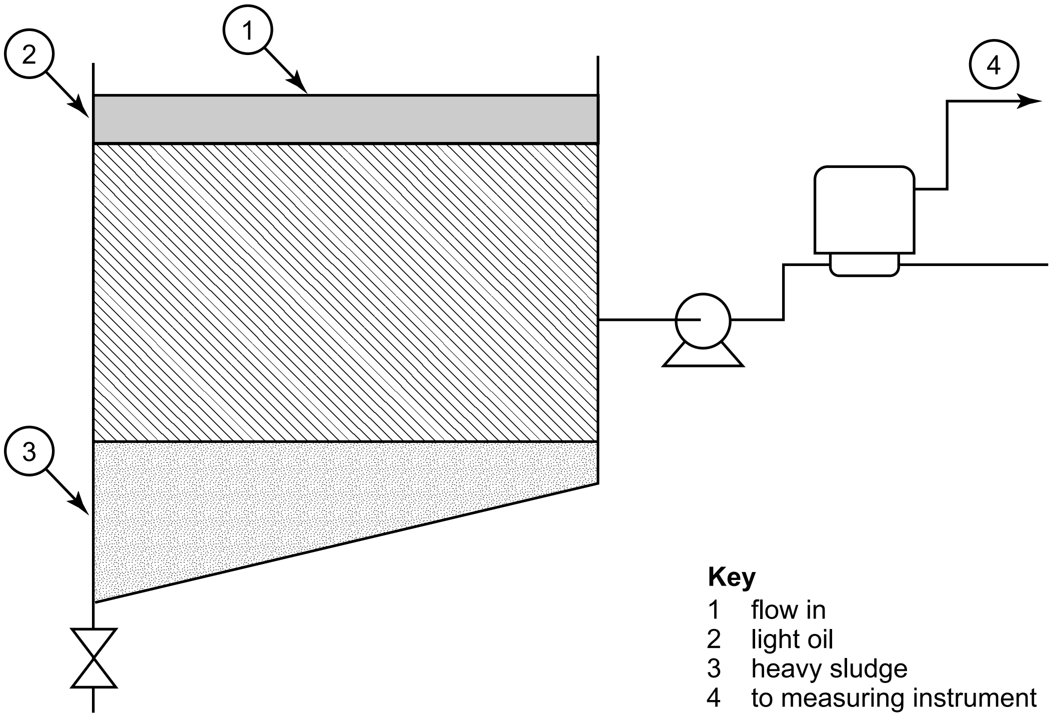


Figure 30-8—Sampling Technique for Heavily Contaminated Oily Systems

30.4 Electrode Measuring System

The electrode measuring system is comprised of three elements: the glass measuring electrode, the reference electrode, and the sensing element for automatic temperature compensation. A schematic arrangement of these elements is shown in Figure 30-9.

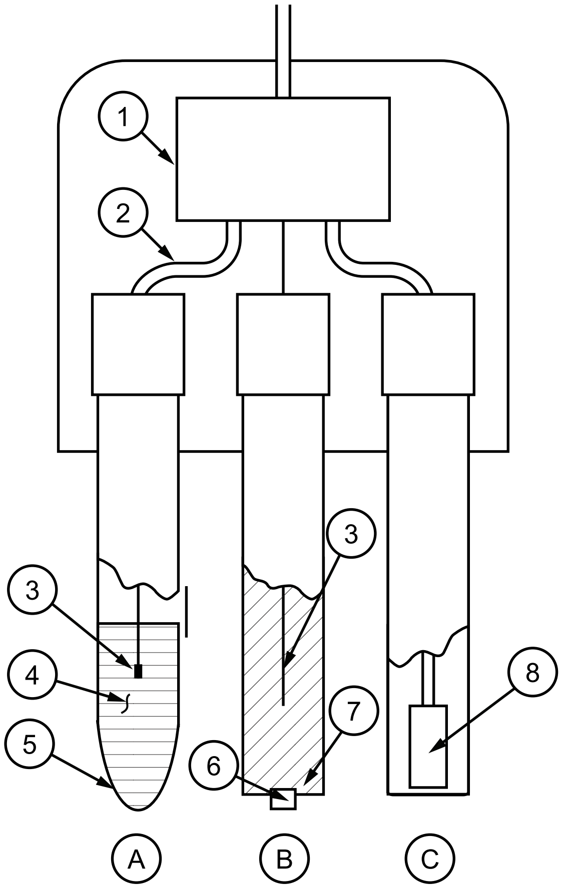
30.4.1 The Measuring Electrode

The primary function of the glass measuring electrode is to develop a potential voltage proportional to the hydrogen ion concentration (the pH value) of the process stream. For practical purposes, the pH value is determined by measuring the voltage potential developed between the process stream and the standard solution contained within the glass measuring electrode. This potential is developed because of the difference in hydrogen ion concentration of the two solutions.

If the hydrogen ion concentration in the process stream is higher than that inside the glass measuring electrode, there will be a positive potential. If the process stream is lower in hydrogen ion concentration, there will be a negative potential. The potential generated is amplified and fed to the measuring instrument where it is translated into a direct reading in pH.

30.4.2 The Reference Electrode

The reference electrode is designed to produce a constant potential regardless of the solution in which it is immersed. This constant potential is used as a base or reference point from which the variable potential produced by the glass electrode can be measured. It is essential to maintain a conductive path between the electrodes in the process stream. There are two types of reference electrodes: diffusion and flowing. Care should be taken to ensure compatibility between the electrolyte and the process stream.



Key

1 transmitter
2 shielded cable and cap
3 silver-silver chloride element
4 internal buffer and electrolyte
5 pH sensitive glass membrane
6 liquid junction (porous plug)
7 potassium chloride salt or gel slurry
8 tempurature sensitive resistor

NOTE 1 Arrangement A shows a glass electrode.
NOTE 2 Arrangement B shows a reference electrode.
NOTE 3 Arrangement C shows a temperature compensator.

Figure 30-9—Schematic Diagram of a Typical Electrode System

In the diffusion-type reference electrode, the electrolyte diffuses through a large porous area to contact the process. These electrodes contain a salt slurry or a gel that resists contamination and drying. The electrode consists of a sealed system that permits diffusion without the need for external pressure. Diffusion-type electrodes are recommended for nearly all applications. In processes where a high dissolved-solids concentration exists (sugars, for example), precipitation of the solids around the porous area of the electrode may cause it to become plugged, resulting in very high resistance and poor measurement.

In flowing-type electrodes, a small amount of the electrolyte constantly flows out of the reference electrode creating a conductive path between the electrode and the process stream. To measure the pH of a process under pressure, a positive pressure of the electrolyte solution must be maintained.

30.4.3 Automatic Temperature Compensator

Due to the fact that the electromotive force developed by the glass electrode will be affected by the temperature of the electrode itself, a temperature compensator is usually necessary. The compensator consists of a resistance thermometer built into the probe, which is immersed in the process stream. The thermometer automatically alters circuit constants so that a given electromotive force will indicate the correct pH at the process stream temperature. The pH meter is not compensated to read to a base temperature. The temperature compensator corrects for the temperature coefficients of the electrodes, but it does not compensate for changes in solution pH caused by temperature variations. Automatic temperature compensation is usually unique to a specific measuring-instrument. Consult the manufacturers' specifications for details.

Many manufacturers supply a probe configuration that includes the measuring and reference cell, and the temperature compensator element built into a single housing (see Figure 30-10). Specialty probes for sterile and sanitary applications (Figure 30-11) and field-repairable sensors (Figure 30-12) are also available.

Three common probe configurations include: in-line (Figure 30-13), retractable (Figure 30-14) and flow-through (Figure 30-15).

30.5 Installation

30.5.1 Electrode Location

The electrode assembly should be located to permit quick and easy standardization, cleaning, and replacement; however, the most important decision concerning electrodes is the selection of the most desirable measurement point in the stream. The assembly and its associated piping should be arranged so that the reference electrode will remain immersed in the process solution at all times. In some instances, it may be necessary to "pocket" the piping near the flow assembly or to draw a slipstream through a pocketed flow assembly.

Reference electrodes should not be allowed to become dry. Some companies have installed a separate source of water adjacent to the flow assembly so that when the sample is shut off, water may be substituted keeping the electrodes wet.

If the reference electrode (flowing type) in a flow chamber is not pressurized, the sample stream must be at atmospheric pressure. For this reason, the discharge flow from the assembly must not be:

a) located at a higher elevation than the flow assembly itself.

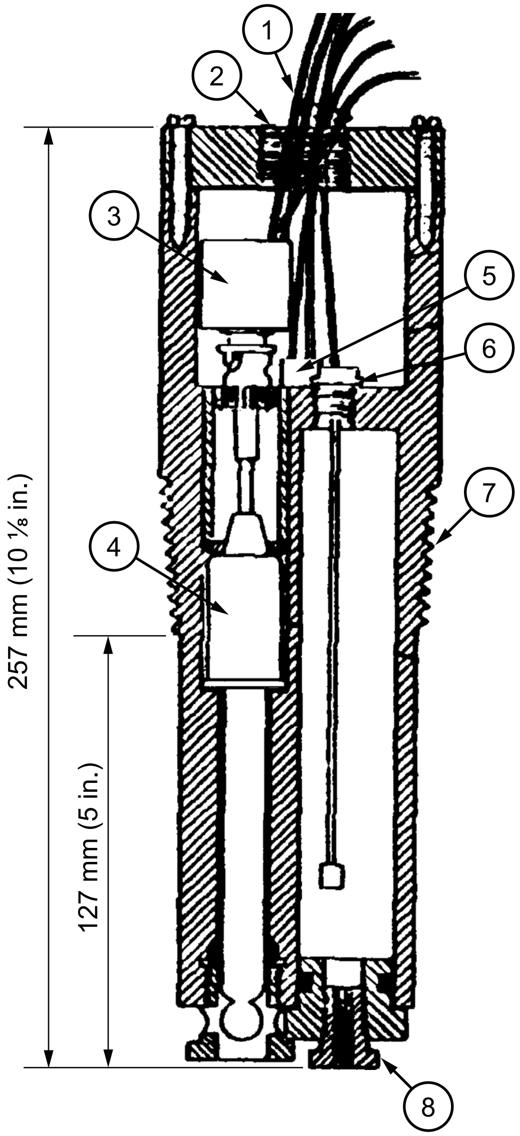
b) piped through pipe or tubing of such small diameter that a positive pressure will be created within the discharge from the flow chamber.

c) discharged into a pressurized system.

In neutralization systems, the electrodes must be located far enough downstream of the point of injection of the neutralizing material to ensure proper mixing and reaction.

In recording applications, where lag is a minor factor, locating the electrode assembly far enough downstream for complete mixing is permissible. In control applications, where lag must be minimized, better mixing by use of an agitator, or an in-line static mixer, will reduce the process lag and make control easier. Control of the pH of a process stream flowing in small pipes can only be maintained if the pH change of the material to be treated is small and changes slowly. If there are large or rapid fluctuations, a retention tank is necessary.

Because the electrode measures the pH of only the thin layer of solution in contact with the electrode, it is essential that this layer be representative of the bulk of the solution being measured. The correct flow rate around the electrode must be obtained to minimize stagnation and to ensure a representative measurement.



Key

1 pigtails to instrument (10 in. LG.)
2 ¾ in. FNPT conduit entrance
3 pre-amp
4 glass electrode
5 temp-comp
6 reference element
7 2 ½ in. MNPT
8 liquid junction

Figure 30-10—Combination pH Probe Schematic

When oil-contaminated water must be measured, the assembly may be submerged (as in Figure 30-5) or a tank may be used (as in Figure 30-6) to allow the oil to float up and out of the sample stream or to allow the heavy sludge to settle to the bottom. A flow chamber with high sample velocity is desirable. The washing action of the process may minimize buildup of oil or sludge clinging to the electrodes. In this case, the mixer should be omitted. Such an installation may introduce an undesirable time lag; however, oil cannot be tolerated on the electrode surfaces.

30.5.2 Electrode Cleaning

pH electrodes are vulnerable to coating and subsequent signal degradation in installations where precipitates, oils, and fine suspended matter adhere to electrode surfaces. Large junction reference electrodes minimize coating problems by offering a relatively large surface area to complete the electrode measuring circuit.

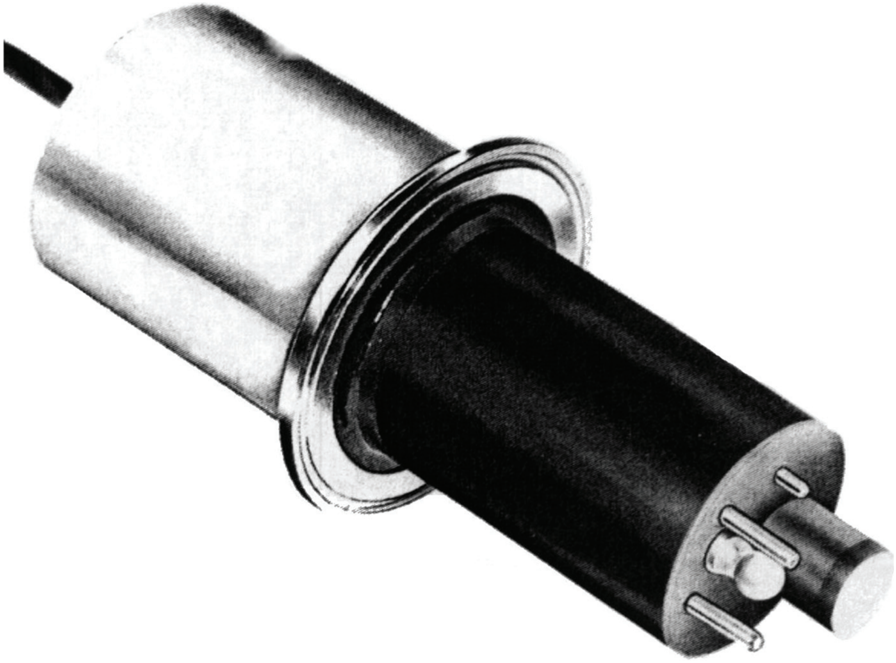


Figure 30-11—Sanitary pH Probe

Figure 30-12—Field Repairable Probes

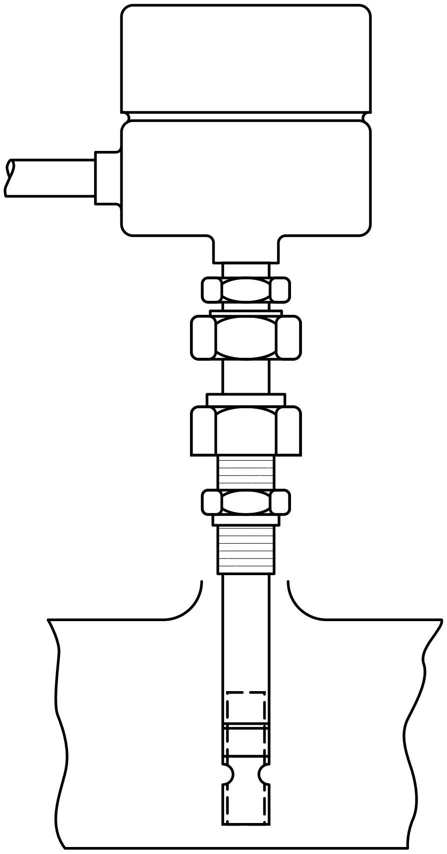


Figure 30-13—In-line pH Probe

Manual cleaning usually consists of routinely dipping or scrubbing the electrodes in acid, detergent, or solvent, depending on the nature of the coating. In flow-type electrode mountings, this can be partially automated by periodically flushing with a cleaning agent. Cleaning can be facilitated by installing a three-way valve that selects either the process sample or the cleaning agent.

Some self-cleaning can be achieved by electrode mountings that develop a high flow velocity past the electrode surfaces. This technique is especially effective for water/oil mixtures.

Ultrasonic cleaning accessories are available from pH sensor manufacturers and prevent solid particles from adhering to electrodes, eliminating or reducing the need for manual cleaning. Some care is required in adjusting the power output for an ultrasonic cleaner since too much power can crack measuring electrode glass membranes.

Another automatic method of cleaning electrodes is accomplished mechanically using moving wipers. Some manufacturers offer brushes to scrub the surface of the electrodes; others use flow agitated balls which impinge on the electrode surfaces limiting the build-up of coatings.

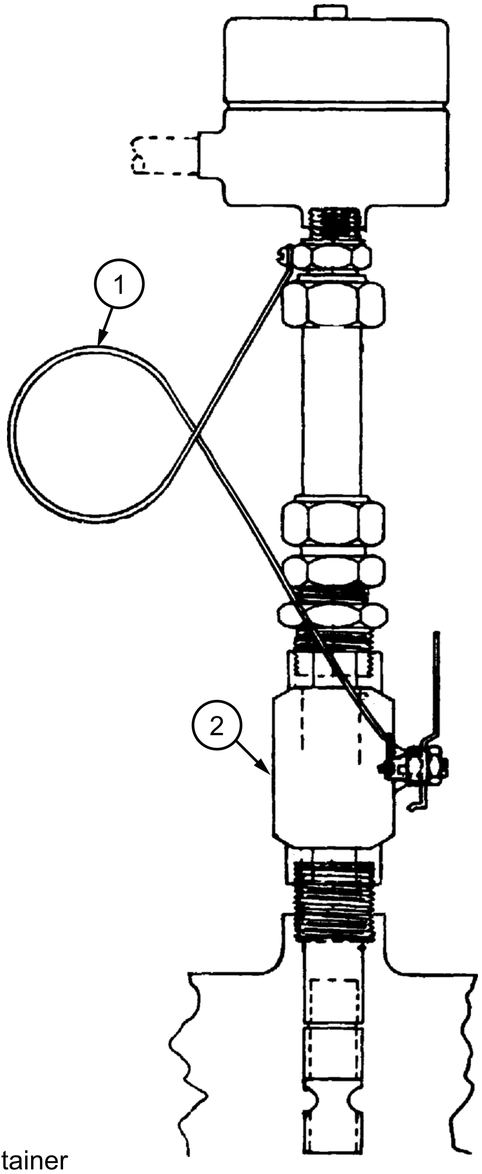
Where frequent cleaning is necessary, some users install twin flow chambers in control applications thus switching the stream from one chamber to the other on a regular schedule. The idle assembly should be cleaned promptly and kept wet until returned to service.

30.5.3 Analyzer Location

The pH meter (or preamplifier converter) should be located as close as is practical to the electrode assembly to facilitate calibration and standardization and to minimize electrode lead lengths. Most manufacturers provide transmitters located in or near the electrode mounting head. These transmitters convert the high-impedance signal to a low impedance millivolt or a current signal that can be transmitted over long distances. Refer to manufacturers' specifications for details. When the readout device is remotely mounted, a local indicating meter is desirable.

30.5.4 Cable and Conduit

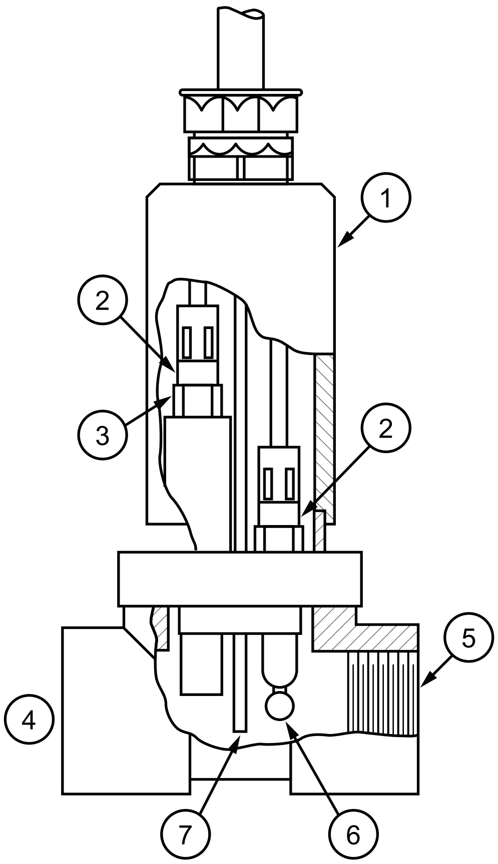
If a local transmitter is not used, the electrode cables between the assembly and the meter should be installed in a rigid steel conduit that contains no other wiring. This will help to avoid any flexing of the coaxial cable and keep out stray electromotive force as well. The leads should be pulled in one continuous length. Where this is impossible and splices are necessary, they should be made by qualified personnel. Only connections and junction boxes specifically designed for coaxial cable should be used; thus the entrance of moisture into the coaxial cable is minimized, and the high impedance required for glass measuring electrode assemblies is maintained.



Key

1 probe retainer
2 1 in. steel ball valve

Figure 30-14—Retractable pH Probe



Key

1 cover-threaded PVC
2 electrodes quick-disconnect
3 replaceable standard cell electrode
4 standard electrode
5 1 ½ in. NPT (PVC)
6 replaceable pH glass electrode
7 solution ground electrode
titanium palladium

Figure 30-15—Flow-through pH Probe

Care must be taken in the installation of coaxial cable not to contaminate the surface of any of the insulating materials. Even the salts present on the fingertips, if transferred to the insulator surface, can cause the formation of a bridging condensate film.

The special cable precautions apply specifically to the shielded cable for the glass measuring electrode. Normal wiring methods and precautions apply to the reference electrode lead and the temperature compensator. Every precaution should be followed to keep junction boxes and conduits dry.

30.5.5 Grounding

Proper grounding of the components of the pH measuring system is essential. One of the major sources of startup difficulties is improper grounding. Manufacturers' instructions should be carefully followed.

Process origin and discharge points must be at the same potential. Otherwise, an extraneous voltage will be impressed between the electrodes and indicated on the readout. Locating a section of metal pipe before and after the assembly and grounding both ends to a common ground will reduce this effect.

For additional information on grounding see Chapter 7.

30.6 Weather Protection

All flow assemblies must be designed to withstand and seal out moisture at the electrode caps and cable connections. The electrode assembly should be located in a clean, dry housing to protect it from atmospheric conditions. In humid locations, the assembly should be housed and heated to avoid condensation on the electrodes and connecting leads. If possible, routine maintenance work should be scheduled only during clear, dry weather if cable junction boxes or the electrode housing are to be opened. In some areas, protection against freezing may be necessary.

Conduit connections should be watertight. All leads should be scaled. Special care must be taken to prevent capillary action in the coaxial cable. Desiccant should be installed in accordance with the manufacturer's recommendations.

30.7 Safety

A discussion of safety factors, which may require consideration, is presented in Chapter 7.

30.8 Calibration

The instrument should be calibrated by immersing the electrode in at least two different buffering solutions bracketing the range of intended use. A buffered solution is a standard solution of a known hydrogen ion concentration. This standard solution has been buffered with salts so that it resists changes in its pH from dilution or from the addition of either acids or alkalis. There are three National Bureau of Standards buffering solutions: 4.01, 6.86, and 9.18 pH. Many more are available from manufacturers.

The buffering solutions used for calibration should be a minimum of 3 pH units apart and at, or near, operating temperature. If the pH system reading does not agree with buffer values within 0.1 pH units, trouble exists in the electrodes, wiring, or recorder. Temporarily, electrodes may be connected directly at the recorder to isolate wiring problems.

Electrodes may be separately tested and buffered on a laboratory instrument. A color comparator (for example, litmus paper) is inadequate for calibration purposes and should not be used. When checking against a laboratory pH meter, it is sometimes advisable to draw the samples in preheated thermos jugs to permit laboratory pH checks at operating temperatures, minimizing temperature errors.

30.9 Startup

The manufacturer's operating manual should be used as a reference for starting up a continuous process stream pH analyzer.

In general, the following steps apply.

1) Check the electrode assembly for proper installation and cleanliness of the electrodes. If the electrodes are to be used immediately, soak the lower half of the glass measuring electrode in approximately 0.1 Normal HCl at 122 °F (50 °C) for half an hour, then wash thoroughly with distilled water. If time is available, this soaking period should be extended overnight at room temperature and followed by washing the electrode thoroughly with distilled water. This procedure should be used with all new glass electrodes and with electrodes that have become dry between periods of use. It is also very important to use the glass measuring electrode within the strict design limits set by the manufacturer. Glass measuring electrodes designed specifically for high-temperature service are generally unusable at temperatures lower than those indicated by the manufacturer. Their resistance may be so high that low recorder sensitivity and erratic readout occur.

2) Check electrical wiring and connections and ensure that all gaskets and seals have been carefully made up in accordance with the manufacturer's instructions.

3) Check that the reference electrode contains electrolyte.

4) Start sample flow using the manufacturer's recommended rate.

5) Turn instrument power on.

6) Calibrate chemically as described in 30.8, as well as electrically.

31 Oxidation-Reduction Potential (ORP) Measurement

31.1 General

Ionized solutions contain dissolved compounds that convey electrons. The development of an oxidation-reduction potential involves the transfer of electrons in a solution. The measurement of oxidation-reduction potential (redox) is widely used in waste treatment and chemical processing.

Figure 31-1 illustrates an electrolysis cell in which a battery is used to put energy into an electrochemical system. When a voltage is applied to electrodes immersed in the solution, ions in the solution migrate. Positive ions migrate to the cathode and negative ions to the anode. In this cell, the positive particle (M^+) approaches the cathode and picks up an electron, reducing its positive charge. This is called reduction. On the left hand side of the cell at the anode, the negative particle (X^-) loses an electron to the anode and becomes more positive. This is called oxidation. The electrons accepted by the anode cause an electron discharge at the cathode. It is essential to the continued operation of this cell that the reduction at the cathode and the oxidation at the anode continue simultaneously under the driving force of the battery. These reactions are called oxidation-reduction or redox reactions. The material that loses electrons is said to be oxidized. The material that gains electrons is reduced. The oxidized material will act as a reducing agent in the solution. The material that is reduced will act as an oxidizing agent.

Chemical reactions can also produce electrical potentials. Figure 31-2, a diagram of a galvanic cell, illustrates this point. The zinc anode on the left and the copper cathode on the right both participate in the reaction with the electrolytes copper and zinc sulfate.

31.2 Typical ORP Application Specifications

Sample system complexity:	simple
Typical analysis ranges:	0 mV through 200 mV to 0 mV through 1000 mV
Typical analyzer outputs:	local meter, 4 mA to 20 mA, 0 V to 5 V
Manufacturer's listed accuracy:	depends on scale
Typical analysis precision:	± 0.1 % of scale
Typical analysis time:	continuous
Typical on-stream time:	low (< 95 % stream factor, usually 85 % to 95 %)
Relative installed price:	average ($15 K to $30 K)
Relative maintenance frequency:	low (< 1 man-hour/day)
Average startup:	< 2 man-days
Applications:	wastewater, biotreaters, cooling towers

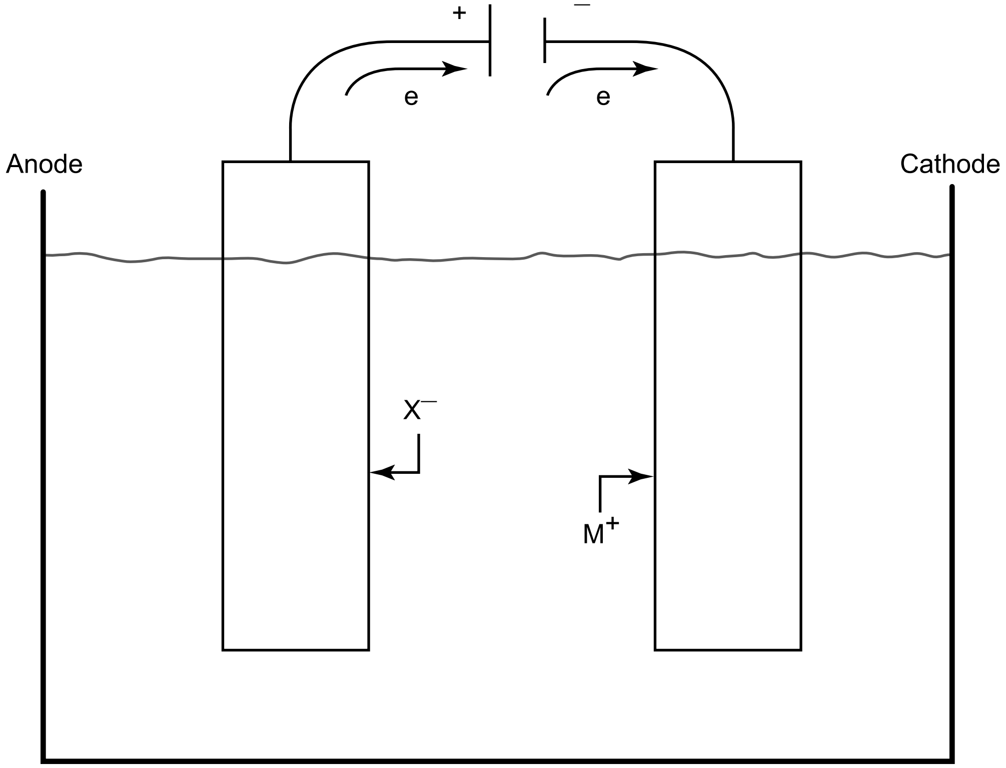


Figure 31-1—Electrolysis Cell

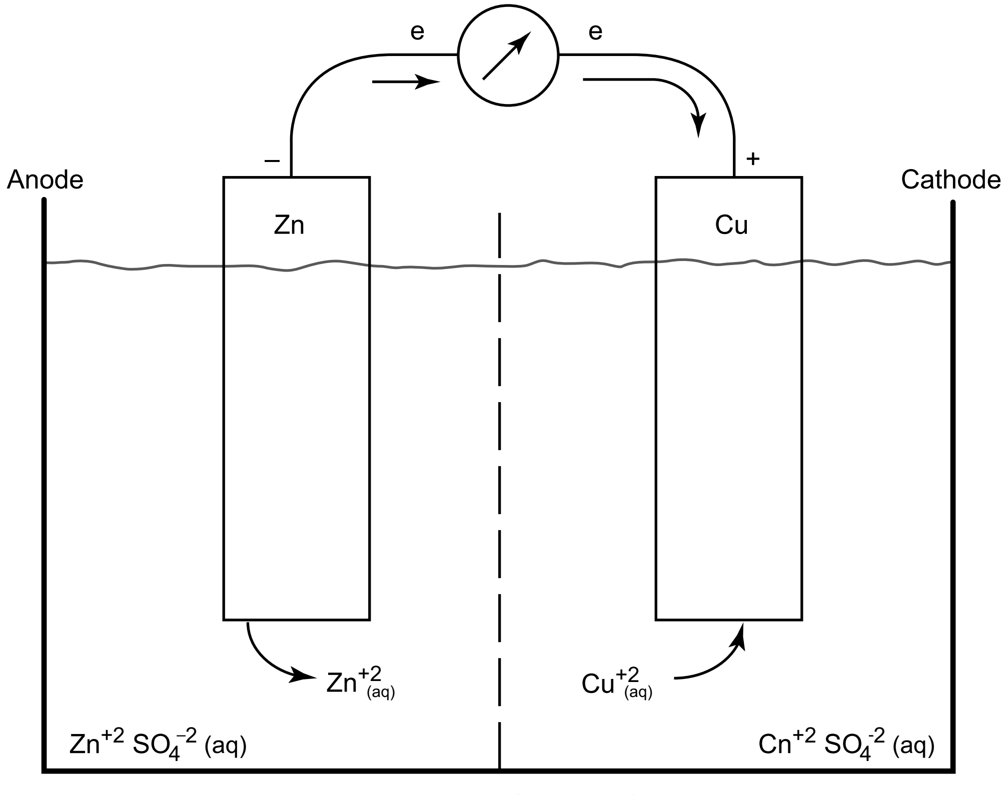


Figure 31-2—Galvanic Cell

31.3 Factors Affecting Oxidation/Reduction Measurements

Theoretically, a host of chemical processes involving oxidation-reduction reactions can readily be monitored. However, under plant conditions, many factors may affect oxidation-reduction potentials and thus the accuracy and reliability of their measurement.

Most waste and process streams are quite complex. The presence of several oxidizing and reducing agents may generate conflicting potentials. Calculated and actual potentials may not agree under these conditions.

The measurement of oxidation-reduction potential is a function of the ionic concentrations of reacting species. Numerous oxidation-reduction reactions involve hydrogen ions and are therefore pH dependent. When the reactions involve the hydrogen ion, measured potentials may vary 30 to 90 millivolts per pH unit from predicted values. pH should be controlled to achieve a constant hydrogen ion content.

Solution temperature has only a slight effect on oxidation-reduction potential measurements, usually about 1 millivolt per degree C. Temperature compensation is not required. (It would be almost impossible to develop a temperature compensator with characteristics suitable for all types of reactions.) The most significant effect of temperature variation is to change the reaction rate.

Both oxidants and reductants must be present so that a stable reaction rate can be achieved. This is an important consideration! Systems that contain an oxidant or reductant alone usually exhibit a random potential drift. In the absence of both oxidized and reduced species, the electrode will respond to pH or the presence of oxygen in the solution.

Complexes of cyanide and chromium, particularly in waste treatment systems where silver and gold are present, may affect the oxidation-reduction potential measurement.

For this reason. it is often necessary to actually perform an oxidation-reduction titration to determine the effects of solution environment.

31.4 Oxidation-Reduction Voltages

Substantial voltages are generated from oxidation/reduction potential reactions. The electromotive force level may reach up to 3 volts. Standard ranges of oxidation/reduction measuring instruments are usually under 1000 millivolts. Positive, negative, or zero centered electromotive force levels are used. Polarity reversals are obtained by reversing electrode leads. The range will depend upon the anticipated variations in electromotive force resulting from the actual reaction.

31.5 Electrode Measuring System

A two electrode system is required for the measurement of oxidation-reduction potential. One electrode is a measuring electrode, which is always an inert (noble metal) electrode of platinum, gold, or silver. The second is the reference electrode.

31.5.1 Measuring Electrode

The metal selected for the measuring electrode depends upon the type of solution to be measured. If a solution is oxidized (a deficiency in electrons), it has a tendency to acquire electrons from the metal electrode immersed in the solution. This will cause the electrode to become positively charged. If the solution is in a reduced state, there are quantities of electrons available. The metal electrode will acquire these electrons, producing a negative potential at the surface. The electrode acquires the potential of the solution and does not react with the solution at all. The metal electrode potential indicates the ratio of oxidized to reduced ions around the electrode. Characteristic curves are available for standard oxidation-reduction reactions.

Platinum tends to be the most commonly used measuring electrode and can be used on all applications except cyanide destruction applications, which will poison the platinum. Gold electrodes can be used on any oxidation/ reduction application. Silver electrodes are not commonly recommended because they tend to be sensitive to specific ions such as the bromide ion.

31.5.2 Reference Electrode

The measuring electrode potential is continuously compared with a reference electrode, which has a stable potential unaffected by the solution. The most common reference electrodes are calomel or silver-silver chloride. These are identical in construction and performance to the reference electrodes used for pH measurement.

31.5.3 Electrode Holder Assemblies

Assemblies are similar to those used for pH measurement. Refer to Section 30.2.

31.6 Installation

The installation of oxidation-reduction equipment is similar to the practices used for pH measurement equipment except for minor circuitry differences and indicator scales. Refer to Chapter 30 Section 5.1.

31.7 Standardization

The actual control point of an oxidation-reduction reaction is often determined empirically. As a result, routine standardization procedures are seldom applicable. Nonetheless, a solution having a known potential may be used for establishing whether an electrode or oxidation-reduction potential amplifier is malfunctioning. Before standardizing, the following steps must be taken.

1) Chemically clean the metal electrode surface by immersing it in an acid solution as recommended by the manufacturer.

2) Scrub the metal surface, if necessary, with a mild abrasive detergent, rinse with water, and blot dry.

3) Place the electrodes in a standardizing solution (for example. quinhydrone).

Table 31-1 lists standard potentials of saturated quinhydrone solutions relative to a reference electrode.

31.8 Calibration

There are two techniques available to calibrate or troubleshoot oxidation-reduction potential analyzers.

Table 31-1—Oxidation-reduction Potentials of Saturated Quinhydrone Solutions

All measurements in millivolts.

	pH 4.0 Temperature °C				pH 7.09 Temperature °C		
Electrode	20	25	30		20	25	30
Silver-silver chloride	268	263	258		92	86	79
Calomel	223	218	213		47	41	34

First, the measuring loop, excluding the electrode system, may be checked for zero and total millivolt span by using an external source of electromotive force, such as a portable potentiometer to develop a signal in place of the electrodes. The reference electrode terminal is positive and increasingly positive oxidation-reduction levels will move the pointer from left to right.

Second, the complete system may be checked by immersing the electrodes in a solution that will generate a known oxidation-reduction potential, such as the saturated quinhydrone solutions discussed in 31.5.

32 Electrolytic Conductivity Measurement

32.1 General

Electrolytic conductivity is the ability of a solution to conduct electric current. It is referred to as specific conductance or simply conductivity. Specific conductance is defined as the mho (siemen), which is the reciprocal of the resistance in ohms of 1 cubic centimeter of the liquid at a specified temperature. The common unit of measurement in conductivity is the micromho (microsiemen), which is one millionth of a mho (siemen).

The mechanism of electrolytic conduction in solutions differs from that of metals. In metals, current is carried by free electrons. In solutions, current is carried by ions only. Electrolytic conductivity is nonspecific and all ions present in a solution contribute. This is in contrast to the general lack of influence of other ions in pH measurement, which, over most of its useful range, is responsive to the H^+ ion concentration alone.

Figure 32-1 is a continuum of the conductivity of common solutions and illustrates the very wide range encountered in aqueous systems. High quality condensed steam and distilled or demineralized water have specific conductances at room temperature as low as, or lower than, 1 micromho per centimeter. Absolutely pure water has a conductivity of 0.055 micromhos per centimeter at 25 °C.

Aqueous solutions of acids, bases, or salts are good conductors of electricity. The degree of electrical conductivity of such solutions is affected by the nature of the electrolyte, solution concentration, and temperature. A measurement of the conductivity at a fixed temperature can be a measurement of the solution's concentration and can be expressed in percent by weight if the solution is binary. If the conductivity value of various concentrations of an electrolyte are known, it is then possible to measure the concentration by passing current through a solution of known dimensions and measuring its electrical resistivity or conductivity. Figure 32-2 illustrates this relationship for some common electrolytes.

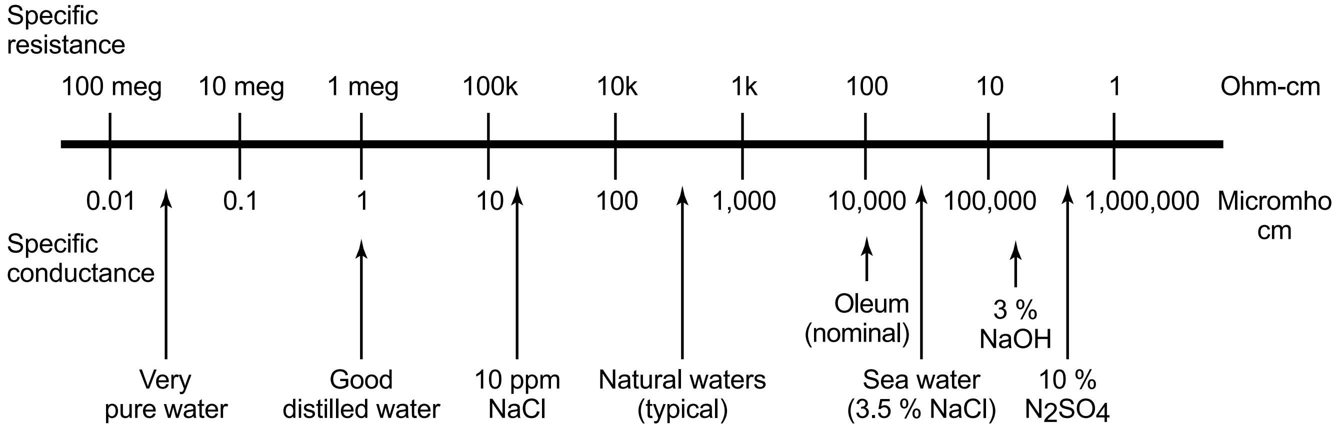
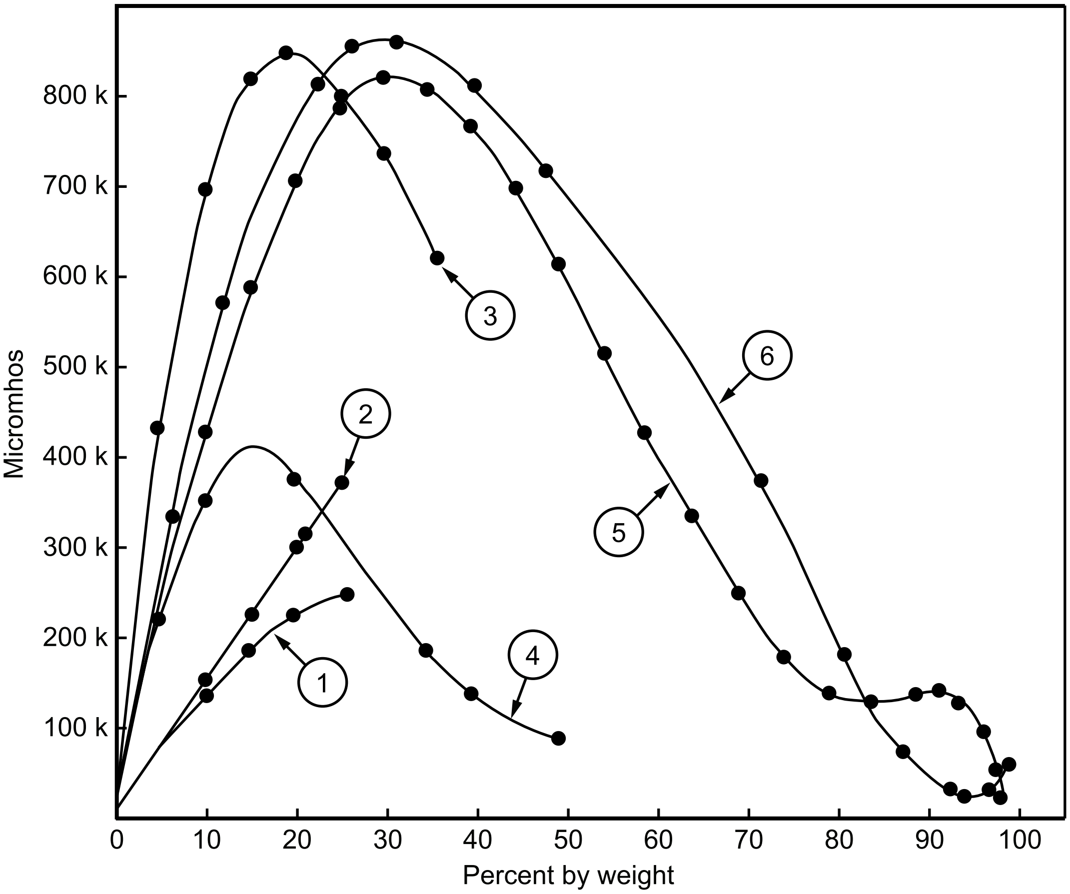


Figure 32-1—Conductivity Scale



Key

1 sodium chloride
2 potassium chloride
3 hydrochloric aid
4 sodium hydroxide
5 sulfuric acid
6 nitric acid

Figure 32-2—Conductivity of Common Electrolytes vs. Weight

32.2 Typical Conductivity Application Specifications

Sample system complexity:	average
Typical analysis ranges:	0 through 0.2 µs/cm^3 to 0 through 20,000 µs/cm^3
Typical analyzer outputs:	4 mA to 20 mA, local meter
Manufacturer's listed accuracy:	±1 % of span
Typical analysis precision:	depends on application
Typical analysis time:	continuous
Typical on-stream time:	low (< 95 % stream factor, usually 85 % to 95 %)
Relative installed price:	average ($15 K to $30 K)

Relative maintenance frequency:	low (< 1 man-hour/day)
Average startup:	< 2 man-days
Typical applications:	boiler feedwater, cooling towers, wastewater

32.3 Conductivity Cells

The conductivity cell typically consists of two metal plates or other electrodes firmly spaced within an insulating chamber that serves to isolate a portion of the liquid. This arrangement makes the measured resistance independent of both sample volume and proximity to surfaces, like tank walls and metal piping. The electrodes are almost always coated with a deposit of spongy black platinum that, by increasing the effective surface, reduces the polarizing effect of the passage of current between the electrodes. This coating is easily deposited during original manufacture, as well as user maintenance, and is quite resistant to mechanical removal.

32.3.1 Cell Constants

The conductance between two electrodes varies as follows:

$$C \propto A/L \tag{1}$$

where

C is the conductance, in mhos (siemens);

A is the area of electrodes, in square centimeters;

L is the distance between electrodes, in centimeters.

To establish a common basis when comparing conductivity of different solutions, a standard conductivity cell is considered where A = 1 square centimeter. L = 1 centimeter. and the volume of solution is completely insulated from its surrounding. The conductance of a solution in this standard cell is called specific conductivity (K) and has units of mhos per centimeter (siemens per centimeter).

As the physical dimensions of the cell are changed, the conductance relationship is as follows.

$$C = K/F \tag{2}$$

where

F is the cell factors, centimeter^{-1} (or cell constant);

K is the specific conductivity.

It is common practice to omit the dimension unit when referring to the cell factor, so that a cell factor of 10 centimeter^{-1} is said to have a cell constant of 10. Referring back to Equation 1, F is a function of L/A or the physical dimensions of the cell.

By selecting a low cell constant for low-conductivity (high-resistivity) solutions and a high cell constant for high-conductivity (low-resistivity) solutions, the cell factor serves as a multiplying factor to increase or decrease conductance of the cell to a desirable value.

Table 32-1 may be used as a guide in selecting the proper cell constant for a particular conductivity range.

Table 32-1—Typical Ranges for Conductivity Cells

Cell Constant	Ohms		Micromhos	
	Specific	Measured	Specific	Measured
50.0	1,000 to 1.0	50,000 to 50	1,000 to 1,000,000	20 to 20,000
25.0	2,000 to 50	50,000 to 50	400 to 400,000	20 to 20,000
1.0	50,000 to 50	50,000 to 50	20 to 20,000	20 to 20,000
0.1	Infinity to 500	Infinity to 50	0 to 2,000	0 to 20,000
0.01	Infinity to 5,000	Infinity to 50	0 to 200	0 to 20,000

32.3.2 Cell Construction

Conductivity cells are constructed in a variety of configurations, depending on the application requirements. Electrode material may be nickel, platinized nickel, titanium, graphite, or other materials. The cell body is constructed from various materials, including stainless steel and corrosion-resistant plastics. The manufacturer should be consulted to determine the appropriate construction for the specific application.

32.4 Electrodeless Conductivity

In the electrodeless conductivity system, two toroid coils are encapsulated in close proximity within the sensor, which is immersed in the solution (see Figure 32-3). The sensor is designed so that the conductive solution couples the two toroids. An alternating current signal produced by an oscillator in the monitor is applied to one coil. A current is then generated in the solution and varies directly with the conductance of the solution. This induces a current in the second coil, which is detected in the monitor. The resulting output signal is directly proportional to solution conductance.

Electrodeless conductivity sensors are available in a variety of configurations and materials. The sensors generally incorporate short passages and large bores to minimize clogging.

Electrodeless conductivity is well suited for high conductivity applications where fouling by oil, algae, or metallic corrosion may present maintenance problems with conventional conductivity cells. Electrodeless conductivity is generally not suited for low conductivity applications, such as high purity water.

32.5 Conductivity Monitors and Transmitters

32.5.1 The Measuring Circuit

The determination of conductivity consists of measuring the resistance of a volume of solution. Alternating current is used to avoid polarization effects. Although other measuring systems are in use, the alternating current Wheatstone Bridge is the most widely used circuit and is very sensitive, stable, and accurate.

Another successful technique uses a square wave generator that provides a linear, stable, and accurate measurement over a wide range of conductivities and eliminates the quadrature error caused by the capacitance of the sensor. Sensors used with this type of system do not require platinization.

The bridge voltage varies from several millivolts to as much as 50 volts. The frequency of the bridge current is commonly 60 or 100 hertz. For measurements on high resistance electrolytes, such as demineralized water and steam condensate, the lower bridge source frequency is preferred. For measurements in highly conductive solutions, higher bridge frequencies are advantageous.

Electrodeless conductivity monitors determine solution conductivity by measuring the current in a loop of solution coupling the pair of toroidal transformer coils.

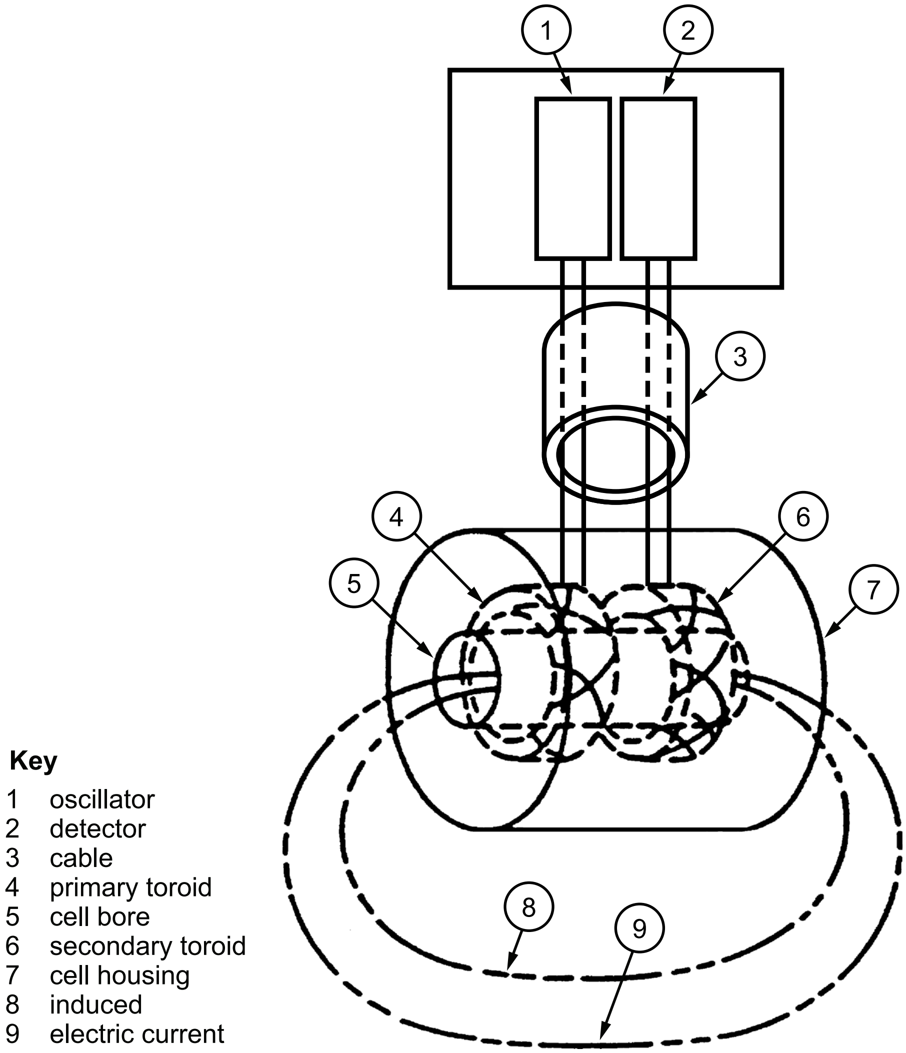


Figure 32-3—Electrodeless Conductivity System

32.5.2 Temperature Compensation

The solution conductivity varies with temperature as well as with electrolyte concentration. It is desirable to relate conductivity measurements to a reference temperature, usually 25 °C. The function of temperature compensation is to correct the conductivity measured at the temperature prevailing at the cell to the reference temperature. The instrument, properly temperature compensated, will read conductivity at 25 °C, regardless of the sample temperature.

A practical means of providing temperature compensation is to introduce into the measuring circuit a resistive element that will change resistance with temperature at the same rate as the solution under test. Temperature compensation can be provided by either a manual adjustment in the analyzer or a resistive temperature element provided with the conductivity cell for automatic compensation.

32.6 Installation

Conductivity electrode assemblies are available with a wide variety of mounting assemblies, including insertion, removable, and flow through types.

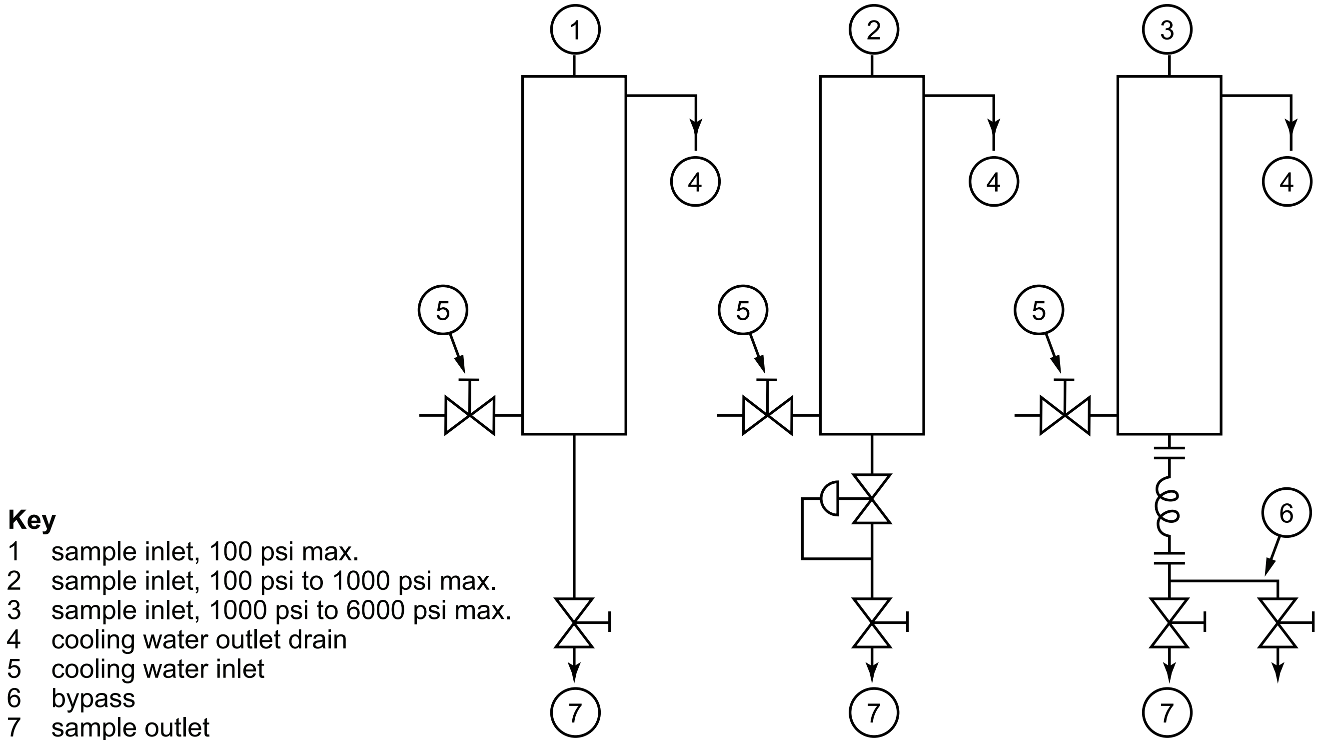
Significant factors in choosing the measurement point include pressure, temperature, flow velocity, pipe size, and the presence of solids.

Where the temperature and the pressure in the system are higher than the maximum rating of available conductivity cells, it is common practice to draw a continuous small sample through a cooling coil of adequate rating, through a throttling valve to reduce the pressure, and only then to bring the sample into contact with a conductivity cell (see Figure 32-4). Alternatively, by running the sample through a proper length of suitable capillary tubing, its temperature and pressure can be reduced without the use of the throttling valve.

To ensure accuracy, efforts should be made to hold temperature as constant as is practical. Uncontrolled or uncompensated temperature severely limits the overall accuracy of the measurement.

While solution conductivity is influenced by pressure, the magnitude of the effect is negligible at ordinary pressures. High velocities of flow do not affect conductivity measurements. When flow velocity is extremely low, the conductivity cell should be selected and installed to ensure circulation of liquid between the electrodes. For example, the screw-in type of cells should be introduced at a bend in the piping and mounted with the open end facing the flow.

The presence of undissolved solids in the system should influence the choice and especially the location of the conductivity cell. Where velocities are high, entrained solids will increase the scouring effect. To avoid stripping the platinum-black coating from the electrodes, the cell should be placed to avoid direct impingement of flow on the electrodes. but in no case should the mounting be such that solids may settle and eventually plug the cell chamber. Where velocities are low and suspended solids present, the cell is best located facing the flow with the open end pointing downstream to avoid accumulation of solids. In solutions with undissolved solids it is good practice to install an electrodeless conductivity analyzer.



Key
1 sample inlet, 100 psi max.
2 sample inlet, 100 psi to 1000 psi max.
3 sample inlet, 1000 psi to 6000 psi max.
4 cooling water outlet drain
5 cooling water inlet
6 bypass
7 sample outlet

Figure 32-4—Sample Cooler and Accessories

32.7 Maintenance and Calibration

The cell will require cleaning if sludge, slime, or other material accumulates in the flow channels. Since the materials of construction are chemically inert, chemical agents may be used and are recommended for cleaning the cells. The particular cleaning agent used should be selected according to the type of contamination to which the cell is exposed. In general, a detergent cleaning solution is effective. Refer to manufacturers' instructions.

The electrodes must be platinized if the velvety black deposit has been rubbed off the electrodes in service or in cleaning or if platinized electrodes are recommended and this black deposit is not present when the new cell is received. Always re-platinize if a brush was used in cleaning the electrodes. Loss of sensitivity (slow response of measuring instrument), erratic behavior of the measuring instrument, or difficulty in balancing indicates that re-platinization of the electrodes is required.

33 Water Quality General Information

33.1 Sample Systems

33.1.1 In-situ Sampling

Electrode-type instruments, measuring pH, dissolved oxygen, conductivity, and specific ions, should be located so that the electrode is directly in the flowing stream, thereby eliminating a fabricated sampling system. Important considerations for in-situ wastewater analysis are as follows.

a) Cleaning of electrodes by ultrasonic or other means should be provided.

b) Access must be provided to electrodes for servicing.

c) Variations in stream flows must be recognized.

d) Solids or debris may damage or destroy electrodes.

e) Design of sample point should allow probe removal with minimum exposure of the process to maintenance personnel.

33.1.2 Remote Sampling

The sample point should be located as close to the analyzer as possible to avoid excessive lag time. Fast sample loops may be used to reduce lag time with excess sample being returned downstream of the sample point or to a sewer. Sample loop pumping can be an advantage as in the case of turbidity measurement, to keep undissolved particles suspended in the carried liquid or may be a disadvantage, as in the case of hydrocarbons in water, where pumping tends to dissolve the hydrocarbons, or in the case of dissolved oxygen where O_2 is liberated by sub-atmospheric suction pressures. Peristaltic pumps disturb the sample less than centrifugal or reciprocating pumps.

Sample probe location and type are important depending upon the type of analysis. Surface wastewater should be included for hydrocarbons-in-water measurement but should not be included for electrode-type analysis where oil could coat the electrodes.

Filters should be avoided (with the possible exception of pump screens or coarse wire strainers near the sample point) to prevent loss of critical components. which may be agglomerated or absorbed on particulate matter in the stream.

Sample conditioning is normally not required for water quality instruments except to protect the analyzer and water lines from freezing. Sample systems should be constructed of polyvinyl chloride or other suitable plastic for corrosion resistance where possible.

For additional sample system information, refer to Chapter 4.

33.2 Installation and Maintenance

For installation and maintenance of the analyzers and sample systems, refer to Chapter 6.

33.3 Calibration and Startup

Before calibration or startup, check to confirm that all utilities such as air, water, steam, and electricity, conform to specifications and are available. Confirm that consumables such as carrier gas, dilution and distilled water, zero and span fluids, standard samples, and reagents, are on hand.

Perform all safety checks, such as inspecting electrical, mechanical, piping, and pneumatic systems for compliance with manufacturers and engineering contractors specifications and drawings. Initiate all safety purges and start ventilating fans. Review the manufacturer's installation, operating, and maintenance manuals.

Start sample system pumps and check for tightness, flow rates, pressures temperatures and, if applicable, stream switching.

Energize electrical control circuits and allow for warm-up and stabilization. Proceed with electronic, mechanical, and optical calibration in accordance with manufacturers' step-by-step instructions. Run a standard sample and compare the results with laboratory analysis.

For additional information refer to Chapter 6.

33.4 Training

Operating and maintenance personnel should be familiar with the proper use of and troubleshooting procedures for each type of analyzer. Manufacturers can usually provide training courses and start-up assistance. Most water quality analyzers are fairly simple so that well written and detailed manufacturer's manuals should be adequate for routine operation calibration and maintenance.

Annex F—References

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