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FUGITIVE EMISSIONS FROM EQUIPMENT LEAKS II: CALCULATION PROCEDURES FOR PETROLEUM INDUSTRY FACILITIES

Health and Environmental Affairs Department
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American Petroleum Institute Environmental, Health, and Safety Mission and Guiding Principles

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Fugitive Emissions From Equipment Leaks II: Calculation Procedures for Petroleum Industry Facilities

Health and Environmental Affairs Department

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ABSTRACT

The American Petroleum Institute (API) commissioned two manuals to be prepared, providing options and recommendations on procedures for obtaining inspection and maintenance (I/M) data from certain process equipment with the potential to leak "fugitive emissions." These manuals are designed to provide assistance to those who collect fugitive data, ensure regulatory compliance, and calculate emissions associated with these fugitive emissions. The manuals are focused on the recommended fugitive emission practices in the petroleum industry, specifically for refineries, petroleum marketing terminals, and the oil and gas production industries.

This second volume is entitled *Fugitive Emissions from Equipment Leaks II: Calculation Procedures for Petroleum Industry Facilities*. This manual is designed primarily for those who perform the emission calculations associated with fugitive emissions. This manual also discusses equipment categories, provides an overview of available emission estimation approaches, provides sample calculations for different calculation methods, discusses issues that affect the determination of fugitive emissions, and addresses data management.

The first volume, *Fugitive Emissions from Equipment Leaks I: Monitoring Manual* (API Publ. 342), is designed primarily for those who manage or apply fugitive emission I/M programs at a facility. It discusses the compilation of a component inventory, describes monitoring equipment that meet specifications identified in the United States Environmental Protection Agency's (U.S. EPA) Method 21, describes quality control practices, explains the screening procedures, and addresses alternative measurement methods.

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LIST OF ACRONYMS

AC - actual concentration
API - American Petroleum Institute
ASTM - American Society for Testing and Materials
FID - flame ionization detector
HAP - hazardous air pollutant
I/M - inspection and maintenance
ID - identification
LDAR - leak detection and repair
MTBE - methyl tert-butyl ether
NDIR - nondispersive infrared
NSPS - New Source Performance Standards
OEL - open-ended line
OVA - organic vapor analyzer
PID - photo ionization detector
ppmv - parts per million by volume
PRV - pressure relief valve
RF - response factor
SOCMI - Synthetic Organic Chemical Manufacturing Industry
SV - screening valve
TLV - threshold limit valve
TOC - total organic compounds
TVA - total vapor analyzer
U.S. EPA - United States Environmental Protection Agency
VOC - volatile organic compound

SECTION 1.0
INTRODUCTION

The American Petroleum Institute (API) initiated the development of this document to provide member companies guidance with up-to-date information on the methods to estimate equipment leak emissions (fugitive emissions) from valves, pump seals, flanges, etc., for the petroleum industry.

The objective of this document is to present in a readily available format the latest recommendations for calculating fugitive emissions from refineries, petroleum marketing terminals, and the oil and gas production industries. This volume is a companion document to Volume I, which provides guidance on monitoring fugitive emissions from process equipment leaks.

Several different emission factors and correlation equations have been developed over nearly twenty years for each sector of the petroleum industry. This document will not list all of these emission factors and emission correlation equations, although many of the studies that produced these factors and equations will be referenced. Generally, only one set of emission correlation equations, pegged component emission factors, and zero component emission factors applicable to refineries, petroleum marketing terminals, and the oil and gas production industries will be presented in this document. The selected factors and equations are the most recent ones that have received United States Environmental Protection Agency (USEPA) approval or are expected to receive U.S. EPA approval. Two sets of average emission factors for refinery components in heavy liquid service are provided. The first set has received prior U.S. EPA approval. The second set was developed by API and will be reviewed by the U.S. EPA.

Section 2.0 contains a general description of the equipment categories. Section 3.0 provides an overview of available emission estimation approaches for equipment leaks and also includes sample calculations for the different methods. Section 4.0 discusses several issues that affect the determination of emissions. Section 5.0 discusses data management. Finally, Section 6.0 contains the references.

The appendices to this document provide tabulations of relevant information that might be useful in calculating emissions from a wide variety of facilities. These include:

- U.S. EPA guidance on component count estimation methods for refinery units (Appendix A);
- U.S. EPA guidance on methods to account for benefits of an inspection/maintenance program (Appendix B);
- Fugitive emission factors and equations for the Synthetic Organic Chemical Manufacturing Industry (SOCMI) (Appendix C);
- U.S. EPA tabulation of response factors (Appendix D); and
- A calculation example demonstrating the use of published response factors (Appendix E).

SECTION 2.0
EQUIPMENT DESCRIPTION

In order to calculate emissions from process equipment components, it is first necessary to understand the types of equipment that potentially have fugitive emissions. This equipment is described in this section. Control techniques or inspection and maintenance practices that can affect emission calculations are also discussed. In addition, procedures for counting these components for equipment inventories are presented.

Please note that most of the material in this section is essentially the same as that provided in Volume I of this series. It is repeated here for completeness and because these considerations are important both for monitoring and for calculations.

2.1 EQUIPMENT TYPES

The primary equipment types (or component types) that are fugitive emission sources are:

- Agitators;
- Compressors;
- Connectors;
- Open-ended lines;
- Pressure relief devices;
- Pumps;
- Sampling connections;
- Valves; and
- Others.

Graphical depictions of these types of components are shown in Section 5.0 of Volume I.

Note that the terminology in this document for leaks from "pumps," "agitators" and "compressors" is used interchangeably with the words "pump seals," "agitator seals" and "compressor seals." Other terminology is also often used interchangeably to describe equipment leaks. For example, "connectors" can also be referred to as "fittings."

Subsequent sections of this report give a description of these component types and information related to how these components leak.

2.1.1 Agitators

Agitators are used to stir or blend chemicals. Four seal arrangements are commonly used with agitators: packed seals, mechanical seals, hydraulic seals, and lip seals.

A packed seal consists of a cavity, called a *stuffing box*, in the agitator casing filled with a packing gland to form a seal around the shaft. There are several types of single mechanical seals, with many variations to their basic design and arrangement, but all have a lapped seal face between a stationary element and a rotating seal ring. There are also many variations of dual and tandem mechanical seals. Dual mechanical seals with the following characteristics are considered to be leak free (and therefore typically do not require monitoring):

- Barrier fluids pressurized higher than the agitator cavity;
- A barrier fluid reservoir vented to a control device; and
- A pressure tight barrier fluid with a pressure alarm indicator.

In a hydraulic seal, an annular cup attached to the process vessel contains a liquid that contacts an inverted cup attached to the rotating agitator shaft. Although it is the simplest agitator shaft seal, the hydraulic seal is limited to low temperature/low pressure applications and can handle only very small pressure changes. A lip seal consists of a spring-loaded, non-lubricated elastomer element, and is limited in application to low-pressure, top-entering agitators.

Agitator seals can leak because of poor installation, aging, and deterioration of the seals themselves, thermal stress, and vibration.

2.1.2 Compressors

Compressors provide the force to transport gases through a process unit in much the same way that pumps transport liquids. There are centrifugal, reciprocating, and rotary compressors in use by industries affected by equipment leak regulations. The sealing mechanisms for compressors are similar to the packed and mechanical seals for agitators.

2.1.3 Connectors

Connectors are used to join sections of piping and equipment. Connectors can be flanges, screwed or threaded connectors, union connectors, tubing connectors, caps, plugs, etc. For the recent petroleum industry studies, flanges were analyzed separately from the other connectors.

Flanges are bolted, gasket-sealed connectors. Flanges are normally used for pipes with diameters of 2.0 inches or greater. The primary causes of flange leakage are poor installation, aging and deterioration of the gasket, thermal stress, and vibration. Flanges can also leak if improper gasket material is used.

The non-flange connectors (screwed, union, tubing, plugs) typically are used to connect piping and equipment having diameters of 2.0 inches or less. Emissions can occur as the sealant ages and eventually cracks. Leakage can also occur as the result of poor assembly or sealant application, or from thermal stress or vibration on the piping and fittings.

2.1.4 Open-ended Lines

Some valves are installed in a system so that they function with the downstream line open to the atmosphere. A faulty valve seat or incompletely closed valve on such an open-ended line would result in leakage through the open end.

The primary control technology is installing a cap, plug or blind flange. However, even the cap, plug or blind flange can leak from improper installation and aging and deterioration of the gasket or threads. These leaks are similar to those found in connectors, and when an open-ended line is controlled in this way, it should be considered a connector for emission calculation purposes.

2.1.5 Pressure Relief Devices

Pressure relief devices are safety devices commonly used in petroleum and chemical facilities to prevent operating pressures from exceeding the maximum allowable working pressures of the process equipment. Note that when a pressure relief device functions as designed during an over-pressure incident and allows pressure to be reduced, it is not considered an equipment leak. Equipment leaks from pressure relief devices occur when material escapes from the pressure relief device when it is in the closed position. These leaks can occur from the aging and deterioration of packing or sealing materials.

The most common pressure relief device is a spring-loaded pressure relief valve (PRV). The PRV is designed to open when the operating pressure exceeds a set pressure and to reseat after the operating pressure has decreased to below the set pressure.

Another pressure relief device used in the petroleum industry is a rupture disk. These disks rupture when a set pressure is exceeded, thereby allowing the system to depressurize. When the rupture disk pressure is exceeded, the rupture disk must be replaced. Rupture disks do not permit emissions during normal operations and PRV emission factors should not be applied. During normal operation it should be assumed that rupture disks do not have any fugitive emissions. It should also be noted, as a pre-caution, that rupture disks are generally not advisable for small diameters due to restriction of flow.

2.1.6 Pumps

Pumps are used extensively in the petroleum industry for the movement of liquids. The centrifugal pump is the most widely used pump type in the petroleum industry; however, other types, such as the positive displacement (reciprocating) pump, are also used. Liquids transferred by pump can leak at the point of contact between the moving shaft and the stationary casing. Consequently, all pumps except the sealless, such as canned-motor, magnetic drive, and diaphragm pumps, require a seal at the point where the shaft penetrates the housing in order to isolate the pumped fluid from the environment. Pumps without seals do not have fugitive emissions.

Packed and mechanical seals for pumps are similar in design and application to packed and mechanical seals for agitators. Packed seals can be used on both reciprocating and centrifugal pumps. Mechanical seals are limited in application to pumps with rotating shafts.

2.1.7 Sampling Connections

Sampling connections are fittings where samples are routinely taken to characterize the process and to control quality. A sampling connection can leak from a faulty valve seat or incompletely closed valve that is upstream of the sampling connection. A sampling connection can also emit from the flushing of the line during the sampling process.

The sampling connection emission factor takes into account the emissions during flushing of the line and filling of the sample container, as opposed to an open-ended line emission factor which estimates the leakage through the open-end when the valve is closed and no flow is intended. Emissions from sampling connections can be reduced by using a closed-loop sampling system or by collecting the purged process fluid and transferring it to a control device or back to the process.

2.1.8 Valves

Except for connectors, valves are the most common process equipment type found in the petroleum industry. Valves are available in many designs, and most contain a valve stem that operates to restrict or allow fluid flow. Typically, the stem is sealed by a packing gland or O-ring to prevent leakage of process fluid to the atmosphere. Emissions from valves occur at the stem or gland area of the valve body when the packing or O-ring in the valve deteriorates. Some emissions could also occur from the valve housing, generally at the bonnet flange.

Bellows valves and rubber diaphragm valves have negligible emissions as long as there is not a break in the bellows or the diaphragm. As long as there is no break in the bellows or the diaphragm, no fugitive emissions should be assigned to these valves. If a break does occur, the screening value associated with these valves should be used to calculate emissions.

2.1.9 Others

Other component types can also be a source of fugitive emissions. These other types are usually small in number at a facility, and they might be unique to one sector of the petroleum industry. Other equipment types that are not listed above that may be considered as sources of fugitive emissions are: instruments, loading arms, stuffing boxes, site glasses, vents, dump lever arms, diaphragms, drains, hatches, meters, and polished rods. These component types can leak for a variety of reasons including improper installation, aging and deterioration, thermal stress, and vibration.

2.2 COUNTING COMPONENTS

An accurate inventory of components is essential for a precise determination of fugitive emissions as well as to ensure that all appropriate components are monitored. The first step in developing this inventory is to define the process unit boundaries. A process unit is the smallest set of process equipment that can operate independently and includes all operations necessary to achieve its process objective. All of the components, by component type, need to be specified within that process unit.

Components can, in some cases, be identified from process flow diagrams. However, process flow diagrams may not include all of the components that emit fugitive emissions, because all changes in the number of valves or connectors may not have been included on the flow diagrams. Therefore, it is usually necessary to systematically follow process streams while counting, categorizing, and labeling components as you go. Even after this systematic approach, it is recommended to divide the process unit into a grid to search for components (usually connectors) that were missed on the initial survey.

Some components may be monitored at a reduced frequency or may not be monitored at all, but still need to be included in component counts for emission calculation purposes. Examples of these components are ones defined as "inaccessible," "difficult to reach," unsafe-to-monitor" or in "heavy liquid" service. This often necessitates counting more components for emission estimation purposes than need to be monitored as part of a leak detection and repair program.

Other components may not need to be monitored or included in emission estimations. For example, leakless components (such as welded connectors), components not in VOC or HAP service, or components under a vacuum should be excluded from inventories used for monitoring or emission calculation purposes.

Some facilities may only need estimates of component counts in order to estimate emissions. Detailed component count estimation methods for refineries are found in Appendix A (Wetherold, 1984). Other estimation techniques can be found in *Improving Air Quality: Guidance for Estimating Fugitive Emissions from Equipment* (Chemical Manufacturers Association, 1989).

The components need to be counted in accordance with the governing regulation. If emission calculations are being performed for submittal to a regulatory agency, it should be noted that each agency may define differently what constitutes a component. Therefore, it is critical to understand the regulations that govern the inspection and maintenance activities for each facility.

2.2.1 Agitators

Each agitator seal is associated with a single agitator housing penetration. Therefore, an agitator may have a single housing penetration equipped with either a single or double mechanical seal that is counted as one agitator seal. Some agitators, however, have a shaft that penetrates both sides of the agitator housing with a separate seal on both the inboard and outboard sides. This type of arrangement is counted as two agitator seals.

2.2.2 Compressors

Compressors can have housing penetrations and seals that are similar to agitators and are counted in the same fashion. A compressor may have a single housing penetration equipped with either a single or double mechanical seal that is counted as one compressor seal. However, if the compressor has a shaft that penetrates both sides of the compressor housing with a separate seal on both the inboard and outboard sides, it should be counted as two compressor seals.

Large compressors often include several other component types that are needed for the compressor to function. For instance, a compressor could also include valves on cylinders and multiple connectors on the compressor housing or piping. These other component types, although attached to the compressor, should be counted separately as components themselves and not included as a part of the compressor.

2.2.3 Connectors

A connector is typically defined for equipment leak purposes as any fitting used to join two pieces of pipe and/or components together, with the exception of welded connectors which are assumed to be leak free. This definition includes flanges, threaded connectors, unions, tubing fittings, caps, plugs, etc.

The definition of what is a connector may, however, vary by regulation. In some cases, connectors have been identified as only including flanges. In other cases, all types of connectors, including screwed (threaded), union, tubing, etc. are included. These other types of connectors have occasionally been found to leak. Therefore, if it is desired to develop the most accurate estimate of fugitive emissions, these other types of connectors should be included in component inventories.

There has been some confusion over how to count the many varieties of connectors. Much of this confusion arises from the use of aggregate component names that include multiple connectors. For instance, an elbow fitting is a common fitting in petroleum facilities that would have a connector on each end of a 90 degree bend of pipe. (See Figure 2-1). Although many people think of an elbow as one fitting, there are actually two connectors, either of which can leak independently of the other. Similarly, a "Tee" fitting would be counted as three connectors. A spool piece or swage piece would be counted as two connectors. The most difficult fitting to explain is the union connector, which has two potential leak sites (one at the threads and one at the back of the collar nut) but is counted as a single connector.

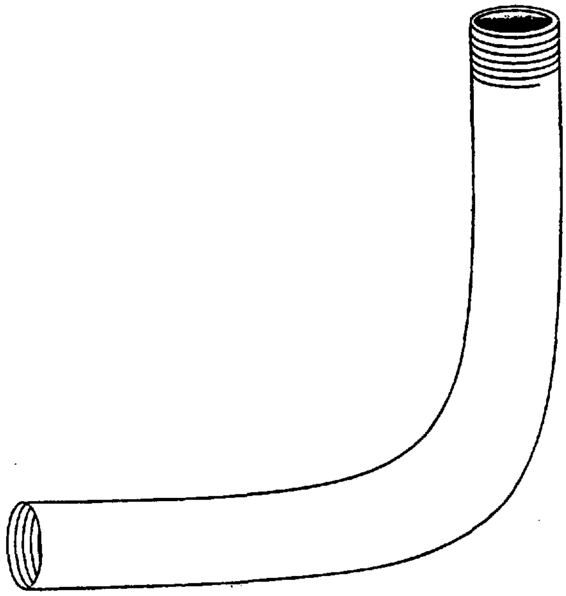

Figure 2-1. Threaded Connector Elbow

Heat exchangers have flanged ends and often have several screwed connectors. Some facilities and regulators count these components in inventories and others do not. Again, regulatory direction and facility operating practice for maintenance of these components should be followed. However, note that these flanged ends and screwed connectors have also been found to leak on occasion.

2.2.4 Open-ended Lines

Open-ended lines are generally easy to count. Some confusion does occur when a potentially open-ended line is controlled with a cap, plug, or blind flange. Such a controlled potentially open-ended line is counted as a connector, because that is the effective leak sealing mechanism.

2.2.5 Pressure Relief Devices

The most common pressure relief device is a spring-loaded pressure relief valve (PRV). Another pressure relief device is a rupture disk. Both pressure relief valves and rupture disks should be counted in the same fashion as valves. It is recommended that the flange on the upstream side of pressure relief devices be counted as a separate component from the pressure relief device. The downstream flange should also be counted as a separate component if the downstream line is not exposed to the atmosphere (such as a line connected to a different process vessel).

2.2.6 Pump Seals

Like agitators, each pump seal is associated with a single pump housing penetration. Therefore, a pump may have a single housing penetration equipped with either a single or double mechanical seal that is counted as one pump seal. Some pumps, however, have a shaft that penetrates both sides of the pump housing with a separate seal on both the inboard and outboard sides. This type of arrangement is counted as two pump seals.

2.2.7 Sampling Connections

Each uncontrolled sampling connection should be counted uniquely. Sampling connections can have emissions reduced by using a closed-loop system or collecting purged process fluid and transferring it to a control device or back to the process.

The distinction between sampling connections and other open-ended lines is dependent on both the configuration and use. An open-ended line that is used for routine sampling would be counted as both an open-ended line and a sampling connection. If equipped with a cap or plug, the same system would be counted as a connector (threads of the cap or plug) and a sampling connection. On the other hand, an open-ended line that is used as a drain or a high point vent would not be counted as a sampling connection.

2.2.8 Valves

Valves are most commonly defined for counting purposes as including the stem seal, the packing gland, and the connection between the parts of a multi-part valve body (like the bonnet flange). This definition should provide the most accuracy in calculating emissions, because it is the same definition that was used in the bagging studies from which the average factors and the emission correlation equations were developed (Ricks, 1993; Ricks, 1994; Webb, 1993). Most regulatory agencies also use this definition for valves.

Although not supported by methods used to develop emission factors and emission correlation equations, some regulatory agencies may define a valve for inspection and maintenance purposes as including the flanges on either side of the valve. Figure 2-2 shows the locations of these flanges on some valves. Regulations may provide conflicting definitions of a valve, or may not provide a definition at all. The result is that facilities across the nation may differ in their counting practices. Some include the flanges on either side as part of the valve, and some facilities count these flanges as separate components. Therefore, one needs to refer to regulations for the appropriate action.

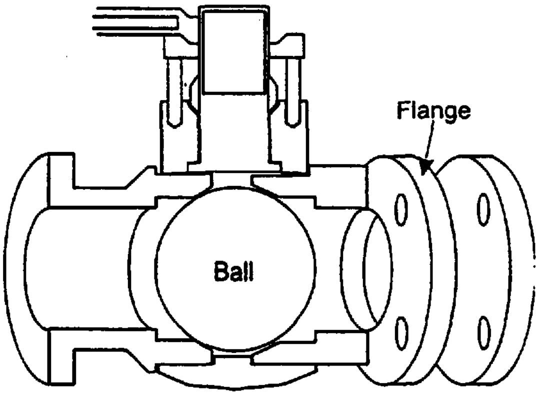

Figure 2-2. Ball Valve with Side Flanges

2.2.9 Others

Other component types such as: instruments, loading arms, stuffing boxes, site glasses, vents, diaphragms, drains, hatches, meters, and polished rods may also need to be counted to develop a complete inventory of potential fugitive emission sources. Again, one needs to refer to regulations for appropriate counting of these other types of components.

SECTION 3.0
EMISSION ESTIMATION METHODS

Over the years, a variety of methods to calculate fugitive emissions from components have been developed for use in the petroleum industry. The approaches for each industry type are listed as follows:

- Average emission factor method;
- Screening ranges method;
- U.S. EPA emission correlation equation method; and
- Unit-specific correlation equation method.

The methods are listed in increasing complexity and in the amount of data collection and analysis required. A discussion of these methods is found in the *Protocol for Equipment Leak Emission Estimates* (Epperson, 1995), also referred to in this document as the U.S. EPA Protocols Document. Generally, a method lower on the above list provides more accurate information (i.e., the screening ranges method provides more accurate information than the average emission factor method). The last method requires bagging of individual components to develop unit-specific correlation equations. Because of the limited use of this method due to costs of bagging, it is not addressed here. For more information on this method refer to the U.S. EPA Protocols Document.

The type of estimating method used depends on the amount of information available to a facility and the intended use of the data. Measured hydrocarbon concentrations in parts per million by volume (ppmv), called screening values, for each component can be determined by a portable hydrocarbon analyzer. More details on the use of hydrocarbon analyzers to generate screening values can be found in Volume I of this series: Monitoring Manual. Facilities that do not have individual screening values for components should use the average emission factor method.

The screening ranges method divides screening values into distinct categories by ppmv ranges. The screening values have been divided into two ranges, 0 to 9,999 ppmv and ≥10,000 ppmv. The screening ranges method has been used to reduce the amount of data that must be recorded and the number of required calculations compared with using the emission correlation equation method. The trade-off is that generally the emission correlation equation method provides more accurate results.

The emission correlation equation method equates a specific mass emission rate for each screening value for each component screened. Emission correlation equations provide a more exact determination of emissions from a facility than do average emission factors or factors based on the screening ranges method. With more and more availability of data management programs that can manipulate the large amounts of data in a fugitive emission monitoring program, it is becoming increasingly easier to use the emission correlation equation method.

If emission correlation equations are used, separate factors need to be used for components that are screened at background hydrocarbon concentrations (zero components) and also for components that are screened beyond the range of the screening instrument (pegged components). The recommended zero component emission rates and pegged component emission rates for refineries, petroleum marketing terminals, and the oil and gas industry are included in this section.

Note that the emissions estimate for an entire facility might include a combination of emission estimating methods.

Also discussed in this section are recommendations on fugitive emission estimation methods for petrochemical facilities and the recommended method to estimate equipment leak emissions of inorganic compounds.

3.1 AVERAGE EMISSION FACTOR METHOD

Average emission factors do not require individual screening values for each component. Usually, the only necessary information is the number of components in each component (e.g., valves, connectors, etc.) and service type (gas, light liquid, heavy liquid) categories. The number of components in each category is multiplied by the appropriate average emission factor. The resulting mass emissions for each category can then be added together to determine the total hourly emissions from the facility. Annual emissions are obtained by multiplying hourly emissions by the number of hours during the year that the line was in service (i.e., contained product):

$$\text{Number of comp.} \times \text{emission factor } (kg/hr/comp) \times \frac{hr}{yr} \text{ in service} = \text{annual emissions } \left(\frac{kg}{yr}\right) \quad \text{(Eq. 3-1)}$$

Average emission factors are typically used in facilities that do not have leak detection and repair programs. They can also be used to estimate emissions when new equipment is being added to a facility (i.e., a new process unit) and no screening values have yet been gathered from the new equipment. They are also used to estimate emissions from components that are not routinely monitored as part of leak detection and repair programs (such as "unsafe-to-monitor," or those in heavy liquid service).

Average refinery emission factors recommended by the U.S. EPA are shown in Table 3-1 (Epperson, 1995). The U.S. EPA 1980 refinery average emission factors are based on data collected in the late 1970s. Note that this table has different emission factors for different component types and different service types. Light liquids are defined, for the average factors shown, as a liquid having a vapor pressure greater than 0.1 psia at 100°F or 689 Pa at 38°C. However, individual regulations may have different definitions for light liquids, heavy liquids, and gas. For instance, the regulation NSPS Subpart GGG defines a light liquid as having a vapor pressure greater than 0.3 k PA at 20°C for one or more constituents, or a 10% evaporation point at 150°C using ASTM Method

Table 3-1. Refinery Average Emission Factors[a] (kg/hr/component)

Equipment Type	Service	Emission Factor[b]
Valves	Gas	0.0268
	Light Liquid	0.0109
	Heavy Liquid	0.00023
Pump Seals[c]	Light Liquid	0.114
	Heavy Liquid	0.021
Compressor Seals	Gas	0.636
Pressure Relief Valves	Gas	0.16
Connectors	All	0.00025
Open-ended Lines	All	0.0023
Sampling Connections[d]	All	0.0150

[a] Source: Radian, 1980; Epperson, 1995.

[b] These factors are for non-methane organic compound emission rates. These factors are for uncontrolled components.

[c] The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

[d] Emission factors for sampling connections are related to the amount of fluid "flushed" from the sampling connection lines when these lines are purged.

D-86. The definition for applicable regulations should be followed.

Table 3-2 contains new average refinery emission factors for components in heavy liquid service. These factors are from a recent API study (Hal Taback Company, 1996). Note that these new average emission factors have not yet received U.S. EPA endorsement.

3.1.1 Reduction Factors

The original refinery average emission factors were developed using data from facilities that did not have any inspection and maintenance (I/M) program. An I/M program is the leak detection and repair activity related to components that potentially emit fugitives. These factors were developed as uncontrolled average emission factors.

The U.S. EPA allows for reductions in the refinery average emission factors based on having an I/M program. The U.S. EPA Protocols Document (Epperson, 1995) includes reduction factors for a number of different component types, for monthly and quarterly monitoring frequencies. This information is shown on Table 3-3. We recommend using the factors from Table 3-3 if they are applicable to the I/M program that a facility intends to use. However, if none of the factors are applicable, then the U.S. EPA previously released another estimation method to calculate reduction factors (Radian, 1982).

A detailed explanation of alternative reduction factors is found in Appendix B. This explanation is a reprint of a portion of *VOC Fugitive Emissions in Petroleum Refining Industry - Background Information for Proposed Standards, Draft EIS*, (Radian, 1982). The reduction efficiency from this document is based on four factors, referred to as "A," "B," "C," and "D." The A factor is from Table 4-2 in Appendix B. The B, C, and D factors are from Table 4-3 in Appendix B. These factors are defined as follows:

- A factor: percent of total mass emissions affected at various leak definitions (theoretical maximum control efficiency);
- B factor: leak occurrence and recurrence factor (function of inspection interval);
- C factor: non-instantaneous repair correction factor (function of allowable repair time); and
- D factor: imperfect repair correction factor (accounts for fact that some components which are repaired are not reduced to zero ppmv leaks).

The above factors were developed for leak definitions of 1,000 ppmv or greater. Unless additional factors are developed, the 1,000 ppmv factors should be used for lower leak definitions.

An example of using this alternative method to estimate a reduction factor would be a valve in gas service with a 10,000 ppmv leak definition, quarterly inspections, and a 15 day allowable repair time. Given this information

Table 3-2. Refinery Average Emission Factors for Components in Heavy Liquid Service[a,b] (kg/hr/component)

Equipment Type	Emission Factor
Valves	8.12 E-05
Pump Seals	3.76 E-03
Connectors (flanged and unflanged)	3.63 E-05
Flanges	3.70 E-05
Open-ended Lines	1.79 E-05
Other	2.82 E-05

[a] From Hal Taback Company, 1996. Factors are from combined southern California and Washington State data. Factors are for uncontrolled emissions.

[b] Not yet endorsed by the U.S. EPA.

Table 3-3. Reduction Factors for an I/M Program at a Refinery Process Unit

[illegible]	[illegible] 10,000 ppmv Leak Definition	[illegible] 10,000 ppmv Leak Definition
Valves - gas	88	70
Valves - light liquid	76	61
Pumps - light liquid	68	45
Connectors - all	a	a

[a] Data are not available to estimate control effectiveness.

Source: Epperson, 1995.

and utilizing Tables 4-2 and 4-3 in Appendix B, the above factors would be as follows:

- A = 0.98 (Appendix B, Table 4-2);
- B = 0.90 (Appendix B, Table 4-3);
- C = 0.979 (Appendix B, Table 4-3); and
- D = 0.996 (Appendix B, Table 4-3).

The combined reduction factor would be:

$$\mathit{Reduction\ Efficiency} = A \times B \times C \times D \qquad \text{(Eq. 3-2)}$$

0.98 x 0.90 x 0.979 x 0.996 = 0.860.

This means that the average refinery emission factor shown in Table 3-1 for valves in gas service (0.0268 kg/hr) could be reduced 86.0% by having the I/M program discussed, resulting in a revised emission factor of (1-0.86) x 0.0268 = 0.00375 kg/hr. If the factors from Table 3-3 had been used, the reduction factor would have been 70% for a quarterly monitoring program with a 10,000 ppmv leak definition. Note that the U.S. EPA methodology also allows a facility to estimate the benefits of having different levels of I/M programs.

The recommended average emission factors for marketing terminal and oil and gas production operations, based on recently conducted studies (1990s), are shown in Tables 3-4 and 3-5, respectively (Epperson, 1995; Webb, 1993).

The same reduction factors used for refineries may also be appropriate for the oil and gas industry. Nearly all of the oil and gas industry data collected for the recent fugitive emission studies were from uncontrolled facilities.

The marketing terminal data collected for the recent fugitive emission studies were from a mixture of controlled and uncontrolled facilities. At this time, no reduction factors have been developed for marketing terminals. Even though the benefits of an I/M program are not being fully accounted for, the use of the marketing terminal average emission factors without any reduction factors is recommended at this time.

Light liquids are defined for the marketing terminals average factors as a liquid having a vapor pressure greater than 0.1 psia at 100°F or 689 Pa at 38°C (Ricks, 1993). Light liquids (oils) are defined as being those with an API gravity ≥20 for the oil and gas production operations (Webb, 1993).

Note that no heavy liquid average factors were developed for marketing terminals. Light liquid factors would be expected to be higher than heavy liquid factors if heavy liquid factors were developed. Until heavy liquid average factors are developed, we recommend use of the light liquid factors shown in Table 3-4.

3.1.2 Adjustment for Inorganics

The U.S. EPA (Epperson, 1995) provides an option for the average emission factor method that does not apply to the other emission

Table 3-4. Average Emission Factors for Petroleum Marketing Terminals[a] (kg/hr/component)

Equipment Type	Service[c]	Average Emission Factor
Fittings (connectors and flanges)[b]	Gas	4.2E-05
	Light Liquid	8.0E-06
Other[d] (compressor seals and others)	Gas	1.2E-04
	Light Liquid	1.3E-04
Pump Seals	Gas	6.5E-05
	Light Liquid	5.4E-04
Valves	Gas	1.3E-05
	Light Liquid	4.3E-05

[a] These factors are for total organic compound emission rates (including non-VOCs such as methane and ethane). These factors apply to uncontrolled and controlled operations.

[b] "Fittings" were not identified as flanges or connectors; therefore, the fitting emissions were estimated by averaging the estimates from the connector and the flange equations.

[c] For components in heavy liquid service, use the light liquid factors from this table. Average light liquid factors are expected to be higher than average heavy liquid factors.

[d] The "other" equipment type should be applied for any equipment type other than fittings, pumps, or valves.

Source: Epperson, 1995.

Table 3-5. Average Emission Factors for Oil and Gas Production Operations[a] (kg/hr/component)

Equipment Type	Equipment Type/Service			
	Gas	Heavy Oil (<20 API Gravity)	Light Oil (≥20 API Gravity)	Water/Oil[b]
Connectors	2.0E-04	7.5E-06	2.1E-04	1.1E-04
Flanges	3.9E-04	3.9E-07	1.1E-04	2.9E-06
Open-ended Lines	2.0E-03	1.4E-04	1.4E-03	2.5E-04
Other[c]	8.8E-03	3.2E-05	7.5E-03	1.4E-02
Pump Seals	2.4E-03	NA	1.3E-02	2.4E-05
Valves	4.5E-03	8.4E-06	2.5E-03	9.8E-05

[a] These factors are for total organic compound emission rates, including non-VOCs such as methane and ethane, and apply to light crude, heavy crude, gas plant, gas production, and off-shore facilities. These factors apply to uncontrolled components.

[b] Water/Oil emission factors apply to water streams in light oil service with a water content greater than 50%, from the point of origin to the point where the water content reaches 99%. For water streams with a water content greater than 99%, the emission rate is considered negligible.

[c] The "other" equipment type includes compressors, diaphragms, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, and vents. This "other" equipment type should be applied for any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

Source: Webb, 1993; Epperson, 1995.

estimation methods. The inorganic concentration in the process lines can be removed from the emission estimates when using the average emission factor method. (Removal of the inorganics is not appropriate for the other methods because each of the other methods is based on actual screening values that measure hydrocarbon concentrations only). For example, if a stream contained 90 weight percent VOC and 10 weight percent water vapor, the emissions calculated by the average emission factor method could be multiplied by 0.90 to determine the VOC portion of the emissions. If a refinery gas valve (0.0268 kg/hr) were part of this example process stream, the estimated emissions would be calculated as follows:

$$VOC = 0.0268\frac{kg}{hr} \cdot 0.90 = 0.0241\frac{kg}{hr}.$$

3.1.3 Adjustment for Non-VOC Organic Compounds

It should be noted that not all organic compounds detected by a screening instrument are VOCs. These instruments instead often measure Total Organic Compounds (TOCs). In particular, methane and ethane are detected by many screening instruments but are not classified as VOCs. Other organic compounds not classified as VOCs include methylene chloride, 1,1-1-trichloroethane, and several chlorofluorocarbons. The U.S. EPA allows an adjustment to the VOC estimate for the non-VOCs detected by a screening instrument. The VOCs can be determined as follows:

$$VOC = TOC \times \frac{Weight\ Percent\ (VOC)}{Weight\ Percent\ (TOC)}$$

(Eq. 3-3)

The above equation can be used to convert TOC emissions, or a TOC emission factor, to VOC emissions or a VOC emission factor.

As an example, if a stream contained 90 weight percent TOC, of which 10 weight percent was ethane, the weight percent VOC would be:

90 (weight percent TOC) - 10 (weight percent ethane) = 80 (weight percent VOC).

The VOCs for this example would be:

$$VOC = \frac{80}{90}\ TOC = 0.889\ TOC.$$

Note that the average refinery emission factors shown in Table 3-1 are based on non-methane organic emissions.

3.1.4 Adjustment for Methane at Refineries for Total Organic Compounds

For refineries only, the U.S. EPA has recommended an additional correction to the average emission factor if a Total Organic Compound (TOC) factor is desired. The refinery average emission factors were based on data that excluded methane. Therefore, if process streams contain methane, the methane percentages need to be added to the non-methane organic compound totals to develop a TOC total. However, only a maximum of 10 percent by weight methane is permitted by the U.S. EPA (even if the streams contain fluid greater than 10 percent methane) because components used to develop these factors typically were part of streams that contained 10 percent or less methane. The adjustment for methane is calculated as follows:

$$\frac{\textit{Weight Fraction TOC}}{\textit{Weight Fraction TOC} - \textit{Weight Fraction Methane}} \qquad \text{(Eq. 3-4)}$$

Following is an example of the correction for methane. Given that a refinery gas valve (0.0268 kg/hr) is part of a stream that contains 75 weight percent VOC, 20 weight percent methane (will show as 10 weight percent in the calculation), and 5 weight percent water vapor, what are the emissions? The TOC weight fraction for this example is 75 for VOC plus 20 for methane equals 95. Calculating emissions while adjusting for methane gives:

$$TOC = 0.0268\frac{kg}{hr} \cdot \frac{95}{95-10} = 0.0300\frac{kg}{hr}.$$

Note that, unlike refineries, the marketing terminal and oil and gas industry average emission factors already represent TOC emissions and do not require any adjustment for methane.

3.1.5 Sample Calculation Using Average Emission Factor Method

Emission calculations for a marketing terminal with gas and light liquid streams and that does not have recorded screening values would be calculated using:

$$\textit{Emissions} = \textit{avg emission factor} \times \textit{\# comp.} \qquad \text{(Eq. 3-5)}$$

as shown in Table 3-6.

3.2 SCREENING RANGES METHOD

The recommended factors to use for the screening ranges method for refineries, marketing terminals, and oil and gas production are shown on Tables 3-7 to 3-9 (Epperson, 1995).

To calculate emissions, first select the most applicable of the three tables, depending on your type of facility. Next, multiply the number of components of each component type, service type and screening range by the appropriate emission factor from one of the three tables. The resulting mass emissions for each component type and service type can then be added together to determine the total emissions from the facility. An example follows in Section 3.2.1.

Note that the adjustment for inorganics to calculate VOCs is not allowed for by the screening ranges method. However, the adjustment for non-VOC organic compounds is still allowed for the screening ranges method as explained in Section 3.1.3. Furthermore, the adjustment for methane at refineries is still recommended by the U.S. EPA for the screening ranges method as was explained in Section 3.1.4. Examples follow in Section 3.2.2.

Also note that the U.S. EPA is no longer supporting the use of "stratified emission factors" which divide the screening ranges into three screening divisions rather than two screening divisions. The stratified emission factors were released in earlier versions of the U.S. EPA Protocols Document.

Table 3-6. Sample Calculation for a Petroleum Marketing Terminal Using the Average Emission Factor Method

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Connectors	Gas	4.2E-05	1,000	0.042
	Light Liquid	8.0E-06	3,000	0.024
Valves	Gas	1.3E-05	200	0.0026
	Light Liquid	4.3E-05	600	0.026
Pump Seals	Light Liquid	5.4E-04	20	0.011
Other	Gas	1.2E-04	10	0.0012
	Light Liquid	1.3E-04	10	0.0013
Total			4,840	0.108

[a] Arbitrary number of components for purpose of example.

Table 3-7. Screening Ranges Emission Factors for Refineries[a] (kg/hr/component)

Equipment Type	Service	≥10,000 ppmv Emission Factor[b]	<10,000 ppmv Emission Factor[b]
Valves	Gas	0.2626	0.0006
	Light Liquid	0.0852	0.0017
	Heavy Liquid	0.00023	0.00023
Pump Seals[c]	Light Liquid	0.437	0.0120
	Heavy Liquid	0.3885	0.0135
Compressor Seals	Gas	1.608	0.0894
Pressure Relief Valves	Gas	1.691	0.0447
Connectors	All	0.0375	0.00006
Open-ended Lines	All	0.01195	0.00150

[a] Source: Epperson, 1995.

[b] These factors are for non-methane organic compound emission rates.

[c] The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

Table 3-8. Screening Ranges Emission Factors for Petroleum Marketing Terminals[a] (kg/hr/component)

[illegible]	[illegible]	≥10,000 ppmv Emission [illegible]	<10,000 ppmv Emission Factor
Valves	Gas Light Liquid	NA 2.3E-02	1.3E-05 1.5E-05
Pump seals	Light Liquid	7.7E-02	2.4E-04
Other (compressors and others)[b]	Gas Light Liquid	NA 3.4E-02	1.2E-04 2.4E-05
Fittings (connectors and flanges)[c]	Gas Light Liquid	3.4E-02 6.5E-03	5.9E-06 7.2E-06

[a] These factors are for total organic compound emission rates (including non-VOC's such as methane and ethane).

[b] The "other" equipment type should be applied for any equipment type other than fittings, pump seals, or valves.

[c] "Fittings" were not identified as flanges or connectors; therefore, the fitting emissions were estimated by averaging the estimates from the connector and the flange correlation equations.

NA = indicates that not enough data were available to develop the indicated emission factor.

Source: Epperson, 1995.

Table 3-9. Screening Ranges Emission Factors for Oil and Gas Production Operations[b] (kg/hr/component)

Equipment type	Service[a]	≥10,000 ppmv Emission Factor	<10,000 ppmv Emission Factor
Valves	Gas	9.8E-02	2.5E-05
	Heavy Oil	NA	8.4E-06
	Light Oil	8.7E-02	1.9E-05
	Water/Oil	6.4E-02	9.7E-06
Pump seals	Gas	7.4E-02	3.5E-04
	Heavy Oil	NA	NA
	Light Oil	1.0E-01	5.1E-04
	Water/Oil	NA	2.4E-05
Others[c]	Gas	8.9E-02	1.2E-04
	Heavy Oil	NA	3.2E-05
	Light Oil	8.3E-02	1.1E-04
	Water/Oil	6.9E-02	5.9E-05
Connectors	Gas	2.6E-02	1.0E-05
	Heavy Oil	NA	7.5E-06
	Light Oil	2.6E-02	9.7E-06
	Water/Oil	2.8E-02	1.0E-05
Flanges	Gas	8.2E-02	5.7E-06
	Heavy Oil	NA	3.9E-07
	Light Oil	7.3E-02	2.4E-06
	Water/Oil	NA	2.9E-06
Open-ended lines	Gas	5.5E-02	1.5E-05
	Heavy Oil	3.0E-02	7.2E-06
	Light Oil	4.4E-02	1.4E-05
	Water/Oil	3.0E-02	3.5E-06

[a] Water/Oil emission factors apply to water streams in oil service with a water content greater than 50%, from the point of origin to the point where the water content reaches 99%. For water streams with a water content greater than 99%, the emission rate is considered negligible.

[b] These factors are for total organic compound emission rates, including non-VOC's such as methane and ethane, and apply to light crude, heavy crude, gas plant, gas production, and offshore facilities. "NA" indicates that not enough data were available to develop the indicated emission factor.

[c] The "other" equipment type was derived from compressors, diaphragms, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents. This "other" equipment type should be applied for any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

Key:

Heavy Oil = <20° API gravity
Light Oil = ≥20° API gravity

Source: Epperson, 1995.

3.2.1 Sample Calculation Using Screening Ranges Method

Emission calculations for a refinery unit that has light liquid streams and that uses the screening ranges method are shown in Table 3-10.

3.2.2 Sample Calculations Applying Non-VOC Organic Compounds and Methane Adjustment to Screening Ranges Method

The adjustment for non-VOC organic compounds to the emission calculation for the screening ranges method uses the same methodology as explained in Section 3.1.3. Using the example in Section 3.1.3 where: VOC = 0.889 TOC, and the results from the example on Table 3-10 where:

$$TOC = 1.567 \ \frac{kg}{hr} \text{ gives}$$

$$VOC = 0.889 \times 1.567 \ \frac{kg}{hr} = 1.393 \ kg/hr.$$

The following example explains how to adjust refinery emission for methane when using the screening ranges method. For the example discussed in Section 3.1.4, supplying Equation 3-4 for stream content information (95/95-10), and using the emission results from the example on Table 3-10 (without a non-VOC organic compound adjustment) gives:

$$TOC = 1.567 \ \frac{kg}{hr} \times \frac{95}{95-10} = 1.751 \ \frac{kg}{hr}.$$

3.3 EMISSION CORRELATION EQUATION METHOD

The recommended emission correlation equations are shown on Table 3-11. Use of the emission correlation equations requires obtaining exact screening values for components. Note that the recommended emission correlation equations, pegged component emission rates, and zero component emission rates for refineries, marketing terminals, and oil and gas production operations have been combined. The U.S. EPA combined the data from these three parts of the petroleum industry and developed combined emission correlation equations, zero component emission factors, and pegged component emission factors (Epperson, 1995).

The emission correlation equations were developed from bagging test data. The emission correlation equations show the empirically derived relationship between screening values and the mass of hydrocarbons emitted.

Pegged components are those components that have screening values that exceed the limit of the hydrocarbon analyzer. For example, the Organic Vapor Analyzer (OVA) 108 analyzer, without a dilution probe, can read up to 10,000 ppmv. With a dilution probe, the organic vapor analyzer (OVA) 108 can typically read up to 100,000 ppmv. The emission correlation equations are not valid for pegged components. That is why separate pegged component emission rates were developed. It is important to use the pegged component emission rate that most closely matches how the data are collected. Table

Table 3-10. Sample Calculation for a Refinery Unit Using the Screening Ranges Method

Component Type	Service Type	>10,000 pmv Factor (kg/hr/component)	Number of Components >10,000 ppmv	Emissions from Components >10,000 ppmv (kg/hr)	<10,000 ppmv Factor (kg/hr/component)	Number of Components <10,000 ppmv	Emissions from Components <10,000 ppmv (kg/hr)	Emissions (kg/hr)
Valves	Light Liquid	0.0852	5	0.426	0.0017	100	0.17	0.596
Pump Seals	Light Liquid	0.437	1	0.437	0.0120	10	0.12	0.557
Connectors	Light Liquid	0.0375	10	0.375	0.00006	200	0.012	0.387
OELs	Light Liquid	0.01195	1	0.01195	0.00150	10	0.0150	0.027
Total								1.567

Table 3-11. Recommended Emission Correlation Equations, Zero Component and Pegged Component Emission Rates for Refineries, Marketing Terminals, and Oil and Gas Production Operations[a] (kg/hr/component)

Component Type	Service Type	Emission Correlation Equation	Zero Component Emission Rate	Pegged Component Emission Rate	
				10,000 ppmv	100,000 ppmv
Connectors (non-flange)	All	$1.53 \times 10^{-6} \times SV^{0.735}$	7.5×10^{-6}	0.028	0.030
Flanges	All	$4.61 \times 10^{-6} \times SV^{0.703}$	3.1×10^{-7}	0.085	0.084
Open-ended Lines	All	$2.20 \times 10^{-6} \times SV^{0.704}$	2.0×10^{-6}	0.030	0.079
Pump Seals	All	$5.03 \times 10^{-5} \times SV^{0.610}$	2.4×10^{-5}	0.074	0.160
Valves	All	$2.29 \times 10^{-6} \times SV^{0.746}$	7.8×10^{-6}	0.064	0.140
Other[b]	All	$1.36 \times 10^{-5} \times SV^{0.589}$	4.0×10^{-6}	0.073	0.110

[a] From data in U.S. EPA Protocols Document (Epperson, 1995). These correlations and emission rates predict total organic compound emission rates (including non-VOCs such as ethane and methane).

[b] Includes instruments, loading arms, pressure relief valves, vents, and stuffing boxes. This "other" equipment type should be applied to any equipment type other than connectors, flanges, open-ended lines, pump seals or valves.

SV = Screening value in ppmv.
All = Gas, light liquid, and heavy liquid.

3-11 lists pegged component emission rates that are to be used if the limit of the analyzer is 10,000 ppmv, and separate pegged component emission rates if the limit of the analyzer is 100,000 ppmv.

The emission correlation equations were developed by excluding components that were found to be leaking drops of liquid, and instead counting them as pegged components. For components leaking liquids with low volatility, sometimes the screening values for the components did not peg the analyzer. However, these components were still considered as pegged components. To be consistent with how the emission correlation equations were developed, all components leaking liquids in VOC service should be considered pegged components (possibly excluding components with very low volatility if the liquid is not allowed to evaporate).

The great majority of components at a facility will typically be found to screen at the background reading on the analyzer. Typically, the background reading at a facility is less than 10 ppmv. When components screen at background, the exact screening value of the component cannot be determined by the analyzer. Bagging tests have shown that some of these components do leak at low levels (Radian, 1980; Ricks, 1993; Ricks, 1994). The average leak level for components that screen at background readings are referred to as zero component emission rates (also referred to as "default zeros"). Table 3-11 also lists the zero component emission rates at refineries, marketing terminals, and oil and gas production facilities.

The total fugitive emissions from a facility would be calculated by determining the mass emissions for each screened component individually and then summing up the emissions from each of the components. Because the mass can be determined for each component screened, the use of emission correlation equations should be the most accurate method of determining the emissions.

Note that the adjustment for inorganics to calculate VOCs is not allowed for the emission correlation equation method. Furthermore, the adjustment for methane at refineries is not needed because the refinery emission correlation equations were developed from data that did not exclude methane (different data than used for the average emission factor method and the screening ranges method). However, the adjustment for non-VOC organic compounds (Section 3.1.4) is still allowed by the U.S. EPA for the emission correlation equation method.

3.3.1 Sample Calculation Using Emission Correlation Equation Method

Emission calculations for five valves from a petroleum facility that uses the emission correlation equation method are shown in Table 3-12.

3.4 EMISSION ESTIMATION METHODS FOR PETROCHEMICAL FACILITIES

The previously listed average emission factors, screening ranges emission factors, emission correlation equations, pegged component emission factors and zero component emission factors were developed specifically for

Table 3-12. Sample Calculation for Five Valves from a Petroleum Facility Using the Emission Correlation Equation Method

[illegible] Component [illegible]	[illegible] Screening Value (ppmv)	Emission Correlation Equation/Emissions Factor (kg/hr/component)	[illegible] Calculation	Emissions (kg/hr)
A001	0	("Zero") 7.8×10^{-6}	7.8×10^{-6}	0.000008
A008	8	$2.29 \times 10^{-6}\ sv^{0.746}$	$2.29 \times 10^{-6}\ (8)^{0.746}$	0.000011
A011	995	$2.29 \times 10^{-6}\ sv^{0.746}$	$2.29 \times 10^{-6}\ (995)^{0.746}$	0.000395
A044	9,950	$2.29 \times 10^{-6}\ sv^{0.746}$	$2.29 \times 10^{-6}\ (9{,}950)^{0.746}$	0.00220
A048	>10,000	("Pegged") 0.064	0.064	0.064
Total				0.067

SV = Screening value in ppmv.

refineries, marketing terminals, and the oil and gas production industry. Separate factors apply for the chemical industry. These separate factors are specifically for the synthetic organic chemical manufacturing industry (SOCMI). Occasionally, some refineries also have SOCMI units (e.g., MTBE, aromatics) and need to apply the SOCMI emission factors and equations. To assist these refineries, the comparable SOCMI emission factors and equations, from the U.S. EPA Protocols Document (Epperson, 1995), are reprinted in Appendix C.

3.5 ESTIMATING EQUIPMENT LEAK EMISSIONS OF INORGANIC COMPOUNDS

The majority of data collected and explained in the previous sections is for estimating equipment leak emissions for VOCs and not for inorganic compounds. Accordingly, the previously discussed emission factors and correlations are generally not intended to be applied for the use of estimating emissions of inorganic compounds. However, in some cases, there may be a need to estimate equipment leak emissions of inorganic compounds, particularly for those that exist as a gas/vapor or for those that are volatile. Some examples of these inorganic compounds include sulfur dioxide, ammonia, hydrochloric acid, hydrogen sulfide, and hydrogen fluoride.

The best way to estimate equipment leak emissions of inorganic compounds would be to develop unit-specific correlations, described in the U.S. EPA Protocols Document (Epperson, 1995). To do this, it would be necessary to obtain a portable monitoring instrument that could detect the inorganic compounds. Another method is also supported by guidance in the U.S. EPA Protocols Document. If it is not possible to develop a unit-specific correlation, or if developing unit-specific correlations is prohibitively expensive, but a portable monitoring instrument (or some other approach) can be used to indicate the actual concentration of the inorganic compound at the equipment leak interface, then the "screening values" obtained with this instrument can be entered into the emission correlation equations (Table 3-11) to estimate emissions. Alternatively, the equal to or greater than 10,000 ppmv, or the less than 10,000 ppmv emission factors could be applied. In the event that there is no approach that can be used to estimate the concentration of the inorganic compound at the leak interface, then in the absence of other data, the EPA Protocols Document allows the use of the average emission factors presented in Table 3-1.

Another option to estimate the inorganic emissions that may be possible in certain circumstances (i.e., mixed organic and inorganic streams) is to:

- Calculate the VOC emissions using a VOC analyzer and applying the appropriate emission factor or emission correlation equation;
- Determine the ratio of inorganic to organic materials in the stream; and
- Apply the ratio of inorganic to organic materials to the calculated VOC estimated.

Other than developing unit-specific correlations, none of these methods is likely to be particularly accurate, but each provides an estimate of inorganic emissions.

SECTION 4.0
ISSUES AFFECTING DETERMINATION OF EMISSIONS

The previous section identified the recommended equations and factors to use in determining fugitive emissions. Use of the equations and factors is generally straightforward. However, additional issues that affect the determination of emissions frequently come up. This section addresses several of these issues including:

- Size of a component;
- Measurement and use of background hydrocarbon levels;
- Use of response factors;
- Analyzer correction factors;
- Length of time to consider a component leaking;
- Emission factors for new emission sources;
- Stream speciation;
- Calculating emissions from inaccessible and difficult to monitor components; and
- Impact of temperature and pressure on emissions.

4.1 SIZE OF A COMPONENT

During the recent development of emission correlation equations for refineries (Ricks, 1994), one of the surprising results was that no significant correlation could be made to relate the size of a component with the screening value to mass emission relationship. Smaller components may develop fewer leaks (Ricks, 1992). However, once a leak is found, it has not yet been shown to make a difference whether that leak comes from a small or large component. For example, a 10,000 ppmv leak from a 0.5" valve should be considered equivalent to a 10,000 ppmv leak from a 4" valve.

4.2 USE OF BACKGROUND HYDROCARBON LEVELS

All petroleum facilities have some background hydrocarbon readings. Background readings should be subtracted from the screening values used for the screening ranges method or the emission correlation equation method to estimate emissions. However, background readings should not be subtracted from pegged component screening values because this could lead to errors in calculating emissions. For example, if the instrument pegs at 10,000 ppmv and the background reading is 10 ppmv, it could cause errors to report a leak as 9,990 ppmv. The >10,000 ppmv pegged component emission factors should be applied to these components. Reporting this leak as 9990 ppmv could cause an erroneous emissions calculation.

4.3 USE OF RESPONSE FACTORS

Not every compound screened will respond with the same intensity to all detectors. Response factors (RFs), which correct for the sensitivity of an analyzer to certain compounds, must be determined for each compound to be measured by any type of analyzer. Some discussion of response factors is found in Section 4.0 of Volume I.

The U.S. EPA recommends that if a compound (or mixture) has a RF greater than three, then the RF should be used to adjust the screening value before it is used in estimating emissions. When a compound has a RF greater than three for an instrument, the emissions estimated using the unadjusted screening value will underestimate the actual emissions.

Because of the difficulty in using RFs and the fact that few petroleum process streams actually have RFs greater than three or significantly less than one, RFs have seen little use in the petroleum industry to date. There are a few exceptions to this, such as freon streams, MTBE streams, and other non-petroleum streams. Perhaps as more data become available and with more sophisticated data management software being developed, RFs will see greater use in the future. It should be noted that including RFs has the potential (if RF <1) to reduce the effective screening values and resulting emission estimates.

A RF is a correction factor that can be applied to a screening value to relate the actual concentration to the measured concentration of a given compound. The RF is calculated using the equation:

$$RF = AC/SV \qquad \text{(Eq. 4-1)}$$

where:

RF = Response factor;

AC = Actual concentration of the organic compound (ppmv); and

SV = Screening value (ppmv).

The value of the RF is a function of several parameters. These parameters include the monitoring instrument, the calibration gas used to calibrate the instrument, the compound(s) being screened, and the screening value.

A detailed listing of published RFs is presented in Appendix D. These RFs, developed for pure compounds, can be used to estimate the RF for a mixture by using the equation:

$$RF_m = \frac{1}{\sum_{i=1}^{n} (x_i/RF_i)} \qquad \text{(Eq. 4-2)}$$

where:

RF_m = Response factor of the mixture;

n = Number of components in the mixture;

x_i = Mole fraction of constituent i in the mixture; and

RF_i = Response factor of constituent i in the mixture.

For an example of the use of this equation, please refer to Appendix E.

In general, response factors can be used to correct all screening values, if so desired. The following steps can be carried out to evaluate whether a RF correction to a screening value should be made (please refer to Appendix E for the details of these steps).

i) For the combination of monitoring instrument and calibration gas used, determine the RFs of a given material at an actual concentration of 500 ppmv and 10,000 ppmv. When it may not be possible to achieve an actual concentration of 10,000 for a given material, the RF at the highest concentration that can be safely achieved should be determined.

ii) If the RFs at both actual concentrations are below three, it is not necessary to adjust the screening values.

iii) If either of the RFs are greater than three, then the U.S. EPA recommends a RF be applied for those screening values for which the RF exceeds three.

One of the following approaches (see Appendix E) can be applied to correct screening values:

i) Use the higher of either the 500 ppmv RF or the 10,000 ppmv RF to adjust all screening values.

ii) Generate a response factor curve to adjust the screening values (refer to Appendix E, page E-13).

iii) Use the response factor closest to the leak definition.

When it is necessary to apply RFs, site personnel should use engineering judgment to group process equipment into streams containing similar compounds. All components associated with a given stream can then be assigned the same RF, as opposed to calculating a RF for each individual equipment piece.

For most petroleum facilities it will not be necessary to routinely calculate RFs for process streams. Most streams in petroleum facilities will have a RF less than three. Furthermore, it is often very difficult to determine accurate RFs at petroleum facilities for the following reasons:

- Accurate process stream speciation is often unknown or changes frequently;
- RFs are not yet available for all chemicals; and
- RFs require significantly more data management effort to develop emission estimates.

If RFs are going to be used, process stream speciation will be required. As mentioned, this process stream information is frequently unknown. No specific U.S. EPA guidance is provided that suggests that estimates can be made of the RF for materials not speciated. However, as a rough means of determining if a process stream has a RF greater than three, it could be assumed that unspeciated portions of a process stream have a RF of one. This estimate is likely to prove sufficiently accurate if the unspeciated portions of a process stream make up a small percentage of the process stream. Clearly, this estimate could be very inaccurate if the unspeciated portion of the process stream is a large percentage of the total. Otherwise, engineering judgment will need to be used to approximate the composition of the unspeciated portion, based on process knowledge and other similar streams in the facility or at other facilities.

4.4 ANALYZER CORRECTION FACTORS

Each type of analyzer responds differently to different chemicals. The recently developed petroleum industry emission correlation equations were based on measurements with an Organic Vapor Analyzer (OVA) 108. To be most accurate, if an instrument other than an OVA is used, the values from the alternate instrument should be compared to the OVA values. Correlations between OVA (calibrated with methane) measurements and TLV Sniffer® (calibrated with hexane) measurements (Eq. 4-3), and TVA 1000 (using the Flame Ionization Detector calibrated with methane) measurements (Eq. 4-4), have been developed (Ricks, 1995), as follows:

$$\text{OVA} = 0.609 \times \text{TLV}^{1.216} \qquad \text{(Eq. 4-3)}$$

$$\text{OVA} = 1.54 \times \text{TVA}^{0.935}. \qquad \text{(Eq. 4-4)}$$

A screening value taken by a TLV Sniffer® or TVA 1000 could be used in one of the above equations to determine the comparable OVA screening value. For example, a TLV Sniffer® reading of 10,000 ppmv, used in Equation 4-3, would be comparable to an OVA reading of 44,526 ppmv.

Note that in the same study (Ricks, 1995), correlations with two photoionization detector (PID) instruments (HNU® and TVA PID) could not be made. PIDs have very different response characteristics from FIDs. They have a particular limitation related to petroleum facilities in that PIDs do not respond well in general to alkanes, and almost not at all to the light alkanes (methane, ethane, propane, etc.). In the API study, components were selected from all areas of refineries, and there was no attempt made to restrict PID use to only those areas where its use is appropriate. This wide application identified the fact that PIDs should not be selected for general use in petroleum facilities. PIDs should be used (as specified in U.S. EPA Method 21) only in those process areas where process knowledge indicates that materials with good response characteristics (i.e., streams rich in aromatics, olefins, and substituted hydrocarbons) are present. It is not known whether an acceptable correlation could have been obtained on a set of components restricted to process areas appropriate for PIDs. The U.S. EPA guidance does not warn against the use of PID screening values directly in the emission correlation equation or screening value range emission factors. It may be advisable to develop your own analyzer correction factors when using PID screening values to estimate emissions where the highest degree of accuracy is required.

An analyzer correction factor is not required by any regulation. These correction factors, however, could improve emission calculation accuracy.

4.5 LENGTH OF TIME TO CONSIDER A COMPONENT LEAKING

The exact moment a component leak begins is usually unknown. However, some start time of a leak must be assumed to estimate emissions over a period of time.

There are basically three options for estimating the length of time a component has been leaking between measurements:

- Leaks begin immediately after the last monitoring;
- Leaks begin immediately before the most recent monitoring; and
- Leaks occur at some average time between monitorings.

Figure 4-1 graphically depicts these three options. These options are also discussed in the following subsections. In addition, some estimate of a leak rate prior to any screening measurements often is required and is discussed in this section.

Use of an option may depend on applicable regulatory requirements.

4.5.1 Immediately After Last Monitoring

The method that usually results in the highest potential mass emitted over the time period is to assume that a leak began immediately following the last measurement. In other words, if a component screened at 10 ppmv on July 1 and at 10,000 ppmv on October 1, this method would assume that the component began leaking at 10,000 ppmv on July 1 immediately after the previous measurement.

4.5.2 Immediately Prior to Most Recent Monitoring

The method that usually results in the lowest potential mass emitted over the time period is to assume that a leak does not begin until the instant before a screening measurement is made at the higher leak rates. In other words, if a component screened at 10 ppmv on July 1 and at 10,000 ppmv on October 1, this method would assume that the component began leaking at 10,000 on October 1.

4.5.3 Average Between Monitorings

Because leaks could occur at any point of time between measurements, an intermediate method may be most suitable. One intermediate method assumes that the mass emitted between screening measurements is the average mass emitted between measurements. For example, on July 1 a component was screened and found to have a mass emission of 1.3×10^{-5} kg/hr. On October 1 the component was screened and found to have a mass emission of 2.2×10^{-3} kg/hr. The average mass for the period from July 1 to October 1 would be:

$$\frac{1.3 \times 10^{-5} + 2.2 \times 10^{-3}}{2} = 1.1 \times 10^{-3}\ kg/hr.$$

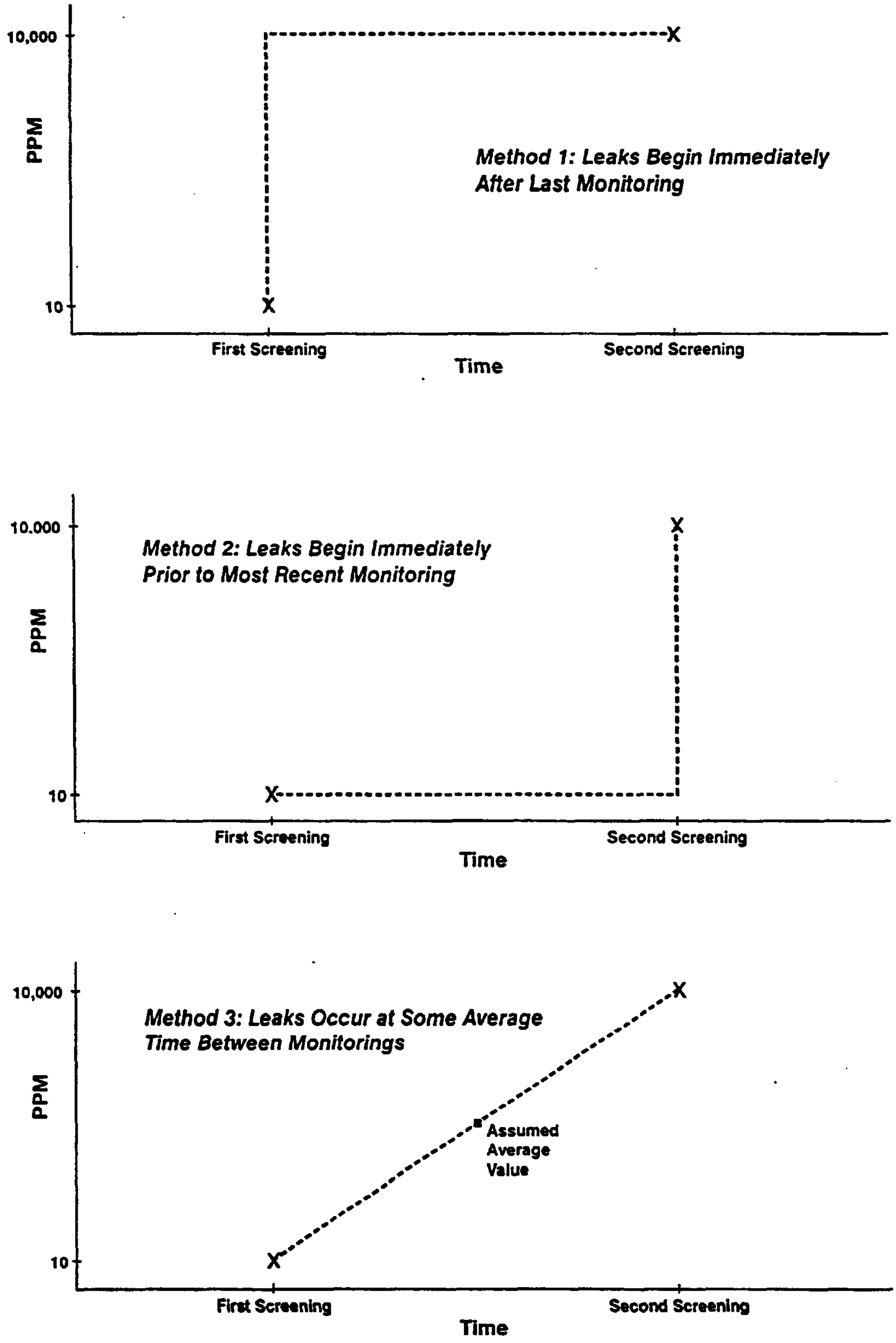

Figure 4-1. Example of Options for Length of Time to Consider a Component Leaking

Another intermediate approach assumes that the average screening value between screening measurements is the average of the first and second screening measurements. As an example, if a component screened at 10 ppmv on July 1 and at 10,000 ppmv on October 1, the average screening value would be:

$$\frac{10 + 10{,}000}{2} = 5005\ ppmv.$$

This average screening value could represent the screening value throughout the time period from July 1 to October 1. Note that this second method will result in somewhat higher mass emission estimates than the other intermediate method because of the shape of the emission correlation equations. However, given the uncertainties in screening value measurements and the timing of the leak, both methods should be considered acceptable and generally much more accurate than either of the first two methods discussed in this section.

Note that once a repair has been made and a post repair inspection has been conducted, this post repair inspection screening value will become the screening value that will be averaged with the next inspection value.

4.5.4 Prior to Any Monitoring

If no prior measurements had been made for a component, it could be assumed that the first measurement represents the leak prior to the measurement. As an alternative, the average emission factor for that type of component could be used for the time period prior to any screening measurements. Either approach should be acceptable for emission estimates.

4.6 EMISSION FACTORS FOR NEW EMISSION SOURCES

Facilities that add, or plan to add, new fugitive emission sources often need to estimate fugitive emissions prior to having any monitoring information. If no I/M program is planned for the new sources, then the average emission factors presented in Section 3.1 should be used to estimate emissions. If an I/M program is planned, at least two alternatives to estimate emissions are possible.

For refineries, the first alternative to estimate emissions for these new sources is to apply the I/M reduction factors, or control effectiveness factors, discussed in Section 3.1 and, in part, in Appendix B. The reduction factors shown in Table 3-3, or those that can be calculated using the methodology described in Appendix B, account for the implementation of an I/M program. For marketing terminals, no reduction factors have been developed and are therefore not recommended for this facility type at this time.

Another alternative, which should be reviewed in advance with the appropriate regulatory agencies, is to use existing data from a facility to develop a unit- or facility-specific average emission factor. The most representative portion of a facility should be used to determine a unit- or facility-specific average emission factor. For smaller facilities, the entire facility data may need to be used. For larger facilities, a representative portion, perhaps a single unit, should be used. If new components are being added to a unit that currently has an I/M program, then an average emission factor can be developed for that unit that accounts for the typical screening values found in that unit. If an entirely new unit is being added, then an average emission factor can be developed from an existing unit that is expected to be most like the new unit from a fugitive emission standpoint.

To develop a unit- or facility-specific average emission factor, first determine the fugitive emissions for a representative time period, typically a one year period, or possibly a quarterly period. Screening values from all components in that unit during the representative time period are applied to the emission correlation equations and related factors. All components in the representative portion of the facility should be included in these calculations, including pegged components and zero components. After emissions are calculated for the unit or facility, the resulting number is divided by the total number of components used to calculate the applicable average emission factor.

The above determination of a unit- or facility-specific average emission factor may not account for the fact that new components, especially those components specifically designed for low emissions, may leak less than the existing components. The specific average emission factor may, therefore, overestimate emissions. This potential to overestimate the fugitive emissions is more likely to convince regulatory agencies to allow this type of calculation procedure. Even with this potential overestimation, the development and use of unit- or facility-specific average emission factors may be more accurate than the use of the average emission factors discussed in Section 3.1, with or without the use of I/M reduction factors.

4.7 STREAM SPECIATION

Different field studies in the petroleum industry have attempted to compare the relative concentration of selected chemical species in the vapor leaking from components as fugitive emissions to the concentration of those same chemical species in the product flowing through the components as a process stream (Ricks, 1993; Ricks, 1994). Because of data scatter, no statistically significant correlations could be made. Future studies under a more controlled setting may later prove able to develop these correlations.

Traditionally, it has been assumed that the composition of the vapor leak was the same as the liquid stream. It is assumed that the liquid in the line makes its way through the seal and vaporizes after it reaches the ambient air. Unless future studies demonstrate otherwise, the assumption that mass fractions in emitted VOCs are the same as the mass fractions in the process streams is still recommended.

An API study of fugitive emissions from the oil and gas production industry (Webb, 1996) did develop weight fractions of benzene, toluene, ethyl-benzene, and xylenes that can be applied to emission correlation equations and emission factors from this segment of this industry. This information, along with the weight fraction of compounds with specific numbers of carbons, is shown in Table 4-1.

It is necessary to have stream speciation to accurately describe specific fugitive emission compounds. A number of methods to determine the speciated emissions from components in streams throughout a facility are being used by industry. If speciation data exist for each process stream, the following methods could be applied:

- Applying the screening ranges emission factors or the emission correlation equations to calculate the total VOCs from individual components in each stream, then using stream specific speciation data (in weight percent) to calculate the emissions of individual constituents of those streams;
- Applying the average emission factors shown in Section 3.1 to calculate the VOCs from all components in each stream, then using stream specific speciation data to calculate the emissions of individual constituents of those streams; and
- Developing unit- or facility- specific emission factors (see Section 4.6) to calculate the VOCs from all components in each stream, then using stream specific speciation data to calculate the emissions of individual constituents of those streams.

The above methods are not an all-inclusive list of methods to speciate emissions. Other methods can also yield acceptable results.

Often specific stream speciation data for each stream in a facility are not available, or the information is very difficult to obtain. The best available data or estimates of what is in each stream may need to be used. The following estimates or assumptions are sometimes used:

- Determining a small number of streams that are representative of streams throughout a facility, obtaining speciated information for each of these representative streams, then applying these representative speciations throughout the facility where appropriate;
- Obtaining speciation information from comparable facilities or units and using this speciation information to speciate streams; or
- Using one representative stream speciation for each process unit.

The above calculation methods and speciation methods involve varying degrees of effort and accuracy. More specific information will lead to more accurate results but will require more effort to obtain. A trade-off between accuracy and effort must be made. The most accurate and most difficult method is to speciate each individual process stream and apply the individual screening values to each component that is associated with those process streams. The least accurate and also the easiest method is to develop one representative stream speciation for each process unit, then apply the published average emission factors to all of the components in that process unit.

Table 4-1[a]. Speciation Fractions for Total Hydrocarbon (THC) Emissions Calculated Using U.S. EPA Average Emission Factors

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Methane	0.687	0.942	0.612	0.612
Non-methane	0.313	0.058	0.388	0.388
VOC	0.171	0.030	0.296	0.296
C_{6+}[b]	0.00693	0.00752	0.02300	0.02300
Benzene	0.00069	0.00935	0.00121	0.00121
Toluene	0.00038	0.00344	0.00105	0.00105
Ethyl-Benzene	0.00003	0.00051	0.00016	0.00016
Xylenes	0.00009	0.00372	0.00033	0.00033

[a] Source: API Publication 4638 (Webb, 1996).

[b] The C_{6+} fraction can be used to calculate an upper limit for n-hexane.

4.8 CALCULATING EMISSIONS FROM INACCESSIBLE AND DIFFICULT- TO-MONITOR COMPONENTS

Emissions from difficult to monitor (or reach) components should be calculated in the same way as "normal" components. In other words, if the average emission factor method is used to calculate emissions for other components at a facility, then the average emission factor method should be used to calculate emissions from difficult to monitor components. Likewise, if the screening ranges method or the emission correlation equation method are being used with the other components, then these methods should be used.

If a component cannot be monitored, an average emission factor must be used to calculate emissions from this component. Average emission factors from Section 3.1 can be used to estimate emissions from inaccessible components.

4.9 IMPACT OF TEMPERATURE AND PRESSURE ON EMISSIONS

Several research studies, including the *Assessment of Atmospheric Emissions from Petroleum Refining* (Radian, 1980), have attempted to find evidence of a correlation between the temperature and pressure in process lines and the fugitive emissions from components that are part of these lines. To date, there is no significant evidence of a correlation to the line temperatures or pressures.

SECTION 5.0
DATA MANAGEMENT

As tens of thousands of screening measurements are often made each year, managing these data can be a tremendous undertaking. Volume I, Section 2.3, addresses several of these data management issues. This management includes:

- The collection of data in the field;
- The entry of the data into a database;
- The use of the data to calculate emissions or statistics; and
- Printing the data/reports.

A variety of options are available to a facility to collect data and enter the data into a database. Hand-held (or wearable) data loggers are becoming increasingly common. These data loggers allow data to be entered into a data file in the field when the measurements are made. The data files are then uploaded, usually daily, directly to a database in the facility. If data loggers are not used, then the hardcopy sheets with the data are key-punched into the facility's database.

It is recommended that a data validation check be applied to the data, either as it is entered into the data logger, or as it is entered into the facility's database. Data validation could be made to check for data that have obviously been entered incorrectly, such as:

- Screening values less than background readings;
- Negative screening values;
- Screening values greater than pegged component levels;
- Component type service anomalies (i.e., liquid compressors);
- Tag numbers that do not exist; or
- Component types that do not exist.

Catching these errors in advance will aid in regulatory compliance and will assist in more accurate emission calculations.

Some data validation checks could aid in fugitive inspection and maintenance (I/M) program management. For example, if the data loggers record the times of inspection, the I/M team's performance can be examined and optimized. A validation check could be made to see if the length of time to perform an inspection is too fast (or too slow) against known averages.

Data can be analyzed using a variety of methods. Again, please refer to Volume I for more information in this area. If average emission factors are used, then very minimal data records need to be maintained. However, if individual screening values are taken, then data manipulation almost always requires some form of electronic data management. This electronic data management can be spreadsheets, word processing files, or a simple database. Several facilities are using sophisticated relational databases to assist in the data analysis tasks.

SECTION 6.0
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Appendix A

COMPONENT COUNT ESTIMATION METHODS FOR REFINERY UNITS

Copied from *A Model for Evaluation of Refinery and Synfuels VOC Emission Data,*
(Wetherold, 1984)

DCN 84-234-004-15

A MODEL FOR EVALUATION OF REFINERY AND SYNFUELS VOC EMISSION DATA

FINAL REPORT

Volume I - Report
- Detailed Case Results

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September, 1984

Component Count Estimation Methods for Refinery Units
(U.S. EPA, 1984)

Process Unit	Pump Seals	Compressor Seals	Valves	Connections	Relief Valves	Open-ended Lines	Process Drains	Sampling Systems
Atmospheric Crude Distillation	if unknown use 12 LL and 19 HL	if unknown assume no compressor seals	41X#Pump 10% G 35% LL 55% HL	3.5X#Valve	if unknown use 16 G and 2 Liq.	3.1X#Pump	1.8X#Pump	1.3X#Pump
Vacuum Crude Distillation	if unknown use 1 LL and 21 HL	if unknown assume no compressors	39X#Pump 10% G 4% LL 86% HL	3.4XValve	if unknown use 8 G and 4 Liq.	3.0X#Pump	2.0X#Pump	1.0X#Pump
Naphtha Hydrotreating	if unknown use 14 LL and 0 HL	if unknown use 4 compressor seals	66X#Pump 30% G 70% LL	3.5X#Valve	if unknown use 13 G and 1 Liq.	3.5X#Pump	1.8X#Pump	1.7X#Pump
Middle Distillate Hydrotreating	if unknown use 4 LL and 13 HL	if unknown use 6 compressor seals	62X#Pump 52% G 11% LL 37% HL	3.5X#Valve	if unknown use 14 G and 2 Liq.	3.1X#Pump	1.4X#Pump	1.7X#Pump
Vacuum Resid Hydro-desulfurization	if unknown use 0 LL and 11 HL	if unknown use 4 compressor seals	71X#Pump 35% G 0% LL 65% HL	3.3X#Valve	if unknown use 12 G and 1 Liq.	3.8X#Pump	2.2X#Pump	1.6X#Pump
Catalytic Reforming	if unknown use 15 LL and 1 HL	if unknown use 6 compressor seals	59X#Pump 23% G 72% LL 5% HL	3.5X#Valve	if unknown use 11 G and 1 Liq.	3.5X#Pump	2.0X#Pump	1.5X#Pump
Aromatics Extraction	if unknown use 22 LL and 5 HL	if unknown use 0 compressor seals	49X#Pump 10% G 73% LL 17% HL	3.4X#Valve	if unknown use 18 G and 2 Liq.	3.2X#Pump	1.9X#Pump	1.3X#Pump

Component Count Estimation Methods for Refinery Units
(U.S. EPA, 1984)
(Continued)

Process Unit	Pump Seals	Compressor Seals	Valves	Connections	Relief Valves	Open-ended Lines	Process Drains	Sampling Systems
Catalytic Cracking	if unknown use 20 LL and 26 HL	if unknown use 8 compressor seals	46X#Pump 29% G 31% LL 40% HL	3.3X#Valve	if unknown use 11 G and 1 Liq.	2.1X#Pump	1.0X#Pump	1.1X#Pump
Hydrocracking	if unknown use 17 LL and 24 HL	if unknown use 6 compressor seals	30X#Pump 19% G 44% LL 37% HL	4.0X#Valve	if unknown use 6 G and 0 Liq.	3.6X#Pump	1.9X#Pump	1.7X#Pump
Thermal Cracking & Visbreaking	if unknown use 2 LL and 12 HL	if unknown use 0 compressor seals	25X#Pump 10% G 13% LL 77% HL	3.6X#Valve	if unknown use 6 G and 0 Liq.	3.6X#Pump	1.9X#Pump	1.7X#Pump
Delayed Coking	if unknown use 6 LL and 11 HL	if unknown use 1 compressor seals	61X#Pump 10% G 32% LL 58% HL	3.3X#Valve	if unknown use 16 G and 2 Liq.	2.5X#Pump	1.4X#Pump	1.5X#Pump
Fluid Coking	if unknown use 3 LL and 10 HL	if unknown use 4 compressor seals	23X#Pump 10% G 35% LL 55% HL	3.4X#Valve	if unknown use 6 G and 0 Liq.	3.9X#Pump	2.2X#Pump	1.7X#Pump
Light Ends Recovery & Fract.	if unknown use 27 LL and 0 HL	if unknown use 6 compressor seals	56X#Pump 49% G 51% LL	3.3X#Valve	if unknown use 24 G and 2 Liq.	3.0X#Pump	1.9X#Pump	1.1X#Pump
Miscellaneous Fractionation	if unknown use 19 LL and 3 HL	if unknown use 2 compressor seals	52X#Pump 10% G 78% LL 12% HL	3.3X#Valve	if unknown use 15 G and 2 Liq.	3.0X#Pump	1.9X#Pump	1.1X#Pump

Component Count Estimation Methods for Refinery Units (U.S. EPA, 1984) (Continued)

Process Unit	Pump Seals	Compressor Seals	Valves	Connections	Relief Valves	Open-ended Lines	Process Drains	Sampling Systems
Alkylation	if unknown use 24 LL and 0 HL	if unknown use 2 compressor seals	49X#Pump 13% G 87% LL	3.4X#Valve	if unknown use 12 G and 1 Liq.	3.1X#Pump	1.9X#Pump	1.2X#Pump
Polymerization	if unknown use 17 LL and 0 HL	if unknown use 0 compressor seals	50X#Pump 35% G 65% LL	3.3X#Valve	if unknown use 11 G and 1 Liq.	3.0X#Pump	1.9X#Pump	1.1X#Pump
Isomerization	if unknown use 14 LL and 0 HL	if unknown use 4 compressor seals	46X#Pump 53% G 47% LL	3.6X#Valve	if unknown use 6 G and 0 Liq.	3.6X#Pump	1.9X#Pump	1.7X#Pump
Lubes Processing - Volatile Organic Solvents	if unknown use 8 LL and 12 HL	if unknown use 2 compressor seals	36X#Pump 10% G 36% LL 54% HL	3.6X#Valve	if unknown use 9 G and 1 Liq.	1.7X#Pump	1.9X#Pump	1.7X#Pump
Lubes Processing - Other	if unknown use 0 LL and 12 HL	if unknown use 0 compressor seals	59X#Pump 0% G 0% LL 100% HL	3.1X#Valve	if unknown use 6 G and 6 Liq.	3.2X#Pump	1.9X#Pump	1.3X#Pump
Asphalt Production	if unknown use 0 LL and 6 HL	if unknown use 0 compressor seals	50X#Pump 0% G 0% LL 100% HL	3.6X#Valve	if unknown use 3 G and 3 Liq.	3.6X#Pump	1.9X#Pump	1.7X#Pump
Hydrogen Production	if unknown use 2 LL and 2 HL	if unknown use 6 compressor seals	251XPump 15% G 43% LL 42% HL	3.3X#Valve	if unknown use 15 G and 2 Liq.	10.4XPump	4.3X#Pump	6.1X#Pump

Component Count Estimation Methods for Refinery Units (U.S. EPA, 1984) (Continued)

Process Unit	Pump Seals	Compressor Seals	Valves	Connections	Relief Valves	Open-ended Lines	Process Drains	Sampling Systems
Gasoline Treating	if unknown use 6 LL and 5 HL	if unknown use 0 compressor seals	71X#Pump 5% G 52% LL 43% HL	3.3X#Valve	if unknown use 4 G and 4 Liq.	3.1X#Pump	1.9X#Pump	1.2X#Pump
Other Product Treating	if unknown use 0 LL and 8 HL	if unknown use 0 compressor seals	55X#Pump 2% G 0% LL 98% HL	3.4X#Valve	if unknown use 1 G and 1 Liq.	3.4X#Pump	1.9X#Pump	1.5X#Pump
Olefins Production	if unknown use 17 LL and 5 HL	if unknown use 4 compressor seals	103XPump 54% G 36% LL 10% HL	3.6X#Valve	if unknown use 30 G and 5 Liq.	5.2X#Pump	3.3X#Pump	1.9X#Pump
Other Volatile Petrochemicals	if unknown use 25 LL and 6 HL	if unknown use 2 compressor seals	21X#Pump 28% G 58% LL 14% HL	3.4X#Valve	if unknown use 9 G and 2 Liq.	4.7X#Pump	2.2X#Pump	2.4X#Pump
Low Volatility Petrochemicals	if unknown use 4 LL and 8 HL	if unknown use 2 compressor seals	43X#Pump 13% G 29% LL 58% HL	3.5X#Valve	if unknown use 8 G and 6 Liq.	3.4X#Pump	1.9X#Pump	1.5X#Pump

Appendix B

METHOD TO ACCOUNT FOR BENEFITS OF AN INSPECTION/MAINTENANCE PROGRAM FOR FUGITIVE EMISSIONS

(Radian, 1982)

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450 3-81-015a
November 1982

Air

EPA

VOC Fugitive Emissions in Petroleum Refining Industry — Background Information for Proposed Standards

Draf
EIS

NSPS

from leaking valves until a shutdown is scheduled. Leaks that cannot be repaired on-line can be repaired by drilling into the valve housing and injecting a sealing compound. This practice is growing in acceptance, especially for safety concerns.[11]

4.2.2.3 Flanges. One refinery field study noted that most flange leaks could be sealed effectively on-line by simply tightening the flange bolts.[5] For a flange leak that requires off-line gasket seal replacement, a total or partial shutdown of the unit would probably be required because most flanges cannot be isolated.

For many of these cases, there are temporary flange repair methods that can be used. Unless a leak is major and cannot be temporarily corrected, the temporary emission from shutting down a unit would probably be larger than the continuous emissions that would result from not shutting down the unit until time for a shutdown for other reasons.

4.2.2.4 Compressors. Leaks from compressor seals may be reduced by the same repair procedure that was described for pumps (i.e., tightening the packing). Other types of seals, however, require that the compressor be taken out of service for repair. Since most compressors do not have spares, seal replacement necessitates a partial or complete unit shutdown. The shutdown for repair and the subsequent start-up can result in greater emissions than the emissions from the seal if it were allowed to leak until the next scheduled shutdown.

4.2.3 Emission Control Effectiveness of Leak Detection and Repair

The control efficiency achieved by a leak detection and repair program is dependent on several factors, including the leak definition, inspection interval, and the allowable repair time.

4.2.3.1 Definition of a Leak. The first step in developing a monitoring plan for fugitive VOC emissions is to define an instrument meter reading that is indicative of an equipment leak. The choice of the meter reading for defining a leak is influenced by several considerations. The percent of total mass emissions that can potentially be controlled by the leak detection and repair program can be affected by varying the leak definition. Table 4-2 gives the percent of total mass emissions predicted to be affected at various leak definitions

Table 4-2. PERCENT OF TOTAL MASS EMISSIONS AFFECTED AT VARIOUS LEAK DEFINITIONS[1]

	Percent of Mass Emissions Affected at This Leak Definition[a]			
Source Type	100,000 ppmv	50,000 ppmv	10,000 ppmv	1,000 ppmv
Pump Seals				
Light Liquid[b]	62	73	92	98
Heavy Liquid[c]	0	0	37	85
Valves				
Gas[d]	89	95	98	99
Light Liquid[b]	53	65	86	98
Heavy Liquid[c]	0	0	0	35
Safety/Relief Valves (Gas)[d]	30	47	74	95
Compressor Seals	48	66	91	98
Flanges	0	0	0	57

[a] These figures relate the leak definition to the percentage of total mass emissions that can be expected from sources with concentrations at the source greater than the leak definition. If these sources were instantaneously repaired to a zero leak rate and no new leaks occurred, then emissions could be expected to be reduced by this maximum theoretical efficiency.

[b] Light liquid is defined as a petroleum liquid with a vapor pressure greater than the vapor pressure of kerosene.

[c] Heavy liquid is defined as a petroleum liquid with a vapor pressure equal to or less than that of kerosene.

[d] Equipment in gas service contain process fluid in the gaseous state.

for a number of equipment types. From the table, it can be seen that, in general, a low meter reading leak definition results in larger potential emission reductions. The monitoring instruments presently in use for fugitive emission surveys have a maximum meter reading of 10,000 ppm. Add-on dilution devices are available to extend the range of the meter beyond 10,000 ppm, but these dilution probes are inaccurate and impractical for fugitive emissions monitoring surveys. Other considerations are more source specific.

For valves, the selection of an action level for defining a leak is a tradeoff between the desire to locate all significant leaks and to ensure that emission reductions are possible through maintenance. Although test data show that some few valves with meter readings less than 10,000 ppm have significant emission rates, most of the major emitters have meter readings greater than 10,000 ppm. Information obtained through EPA in-house testing and industry testing[12,13] indicates that in actual fugitive emission surveys, most sources of VOC have meter readings which are very low or very high. Maintenance programs on valves have shown that emission reductions are possible through on-line repair for essentially all valves with non-zero meter readings. There are, however, cases where on-line repair attempts result in an increased emission rate. The increased emissions from such a source could be greater than the emission reduction if maintenance is attempted on low leak valves. These valves should, however, be able to achieve essentially 100 percent emission reduction through off-line repair because the leaking valves can either be repacked or replaced. The emission rates from valves with meter readings greater than or equal to 10,000 ppm are significant enough so that an overall emission reduction will occur for a leak detection and repair program with a 10,000 ppm leak definition.

For pump and compressor seals, selection of an action level is different because the cause of leakage is different. As opposed to valves which generally have zero leakage, most seals leak to a certain extent while operating normally. The routine leakage is generally low, so these seals would tend to have low instrument meter readings. With time, however, as the seal begins to wear, the concentration and emission rate are likely to increase. At any time, catastrophic seal failure can occur with a large increase in the instrument meter reading and emission rate. As shown in Table 4-2, slightly over 90 percent of the emissions from pump and compressor seals are from sources with instrument meter readings greater than or equal to 10,000 ppm. Properly designed, installed, and operated seals have low instrument meter readings, and the bulk of the pump and compressor seal emissions are from seals that have worn out or failed such that they have a concentration equal to or greater than 10,000 ppm.

4.2.3.2 Inspection Interval. The length of time between inspections should depend on the expected occurrence and recurrence of leaks after a piece of equipment has been checked and/or repaired. This interval can be related to the type of equipment and service conditions, and different intervals can be specified for different pieces of equipment. Monitoring may be scheduled on an annual, quarterly, monthly, or weekly basis. Monitoring may also be scheduled for a "skip period" approach.

A skip-period schedule would allow less frequent monitoring for units that achieve a specified level of performance over a number of consecutive periods. For example, a unit that achieves less than 2 percent of its valves leaking for five consecutive quarterly monitoring periods might use an annual monitoring schedule as long as the percentage of its valves leaking does not exceed 2 percent. The skip-period approach allows flexibility for units that do not require regular monitoring to maintain good performance.

In the refinery VOC leak Control Technique Guideline (CTG) document,[4] the recommended leak detection intervals are as follows: annual -- pump seals and pipeline valves in liquid service; quarterly -- compressor seals, pipeline valves in gas service, and safety/relief valves in gas service; weekly -- visual inspection of pump seals; and no individual monitoring -- pipeline flanges and other connections, and safety/relief valves in liquid service. The choice of the interval affects the emission reduction achievable, since more frequent inspection will result in earlier detection and repair of leaking sources.

4.2.3.3 Allowable Repair Time. If a leak is detected, the equipment should be repaired within a certain time period. The allowable repair time should reflect an interest in reducing emissions, but it should also allow the plant operator sufficient time to obtain necessary repair parts and maintain some degree of flexibility in overall plant maintenance scheduling. The determination of this allowable repair time will affect emission reductions by influencing the length of time that leaking sources are allowed to continue to emit VOCs.

4.2.3.4 Estimation of Reduction Efficiency. Data are presented in Table 4-2 that show the expected fraction of total emissions from each type of source contributed by those sources with VOC concentrations greater than given leak definitions. If a leak detection and repair program resulted in repair of all such sources to 0 ppmv, elimination of all sources over the leak definition between inspections, and instantaneous repair of those sources found at each inspection, then emissions could be expected to be reduced by the amount reported in Table 4-2. However, since these conditions are not met in practice, the fraction of emissions from sources with VOC concentrations over the leak definition represents the theoretical maximum reduction efficiency. The approach to estimation of emission reduction presented here is to reduce this theoretical maximum control efficiency by accounting quantitatively for those factors outlined above.

This approach can be expressed mathematically by the following equation:[14]

$$\text{Reduction efficiency} = A \times B \times C \times D$$

Where:

A = Theoretical Maximum Control Efficiency = fraction of total mass emissions from sources with VOC concentrations greater than the leak definition (from Table 4-2).

B = Leak Occurrence and Recurrence Correction Factor = correction factor to account for sources which start to leak between inspections (occurrence), for sources which are found to be leaking, are repaired and start to leak again before the next inspection (recurrence), and for known leaks that could not be repaired.

C = Non-Instantaneous Repair Correction Factor = correction factor to account for emissions which occur between detection of a leak and subsequent repair, since repair is not instantaneous.

D = Imperfect Repair Correction Factor = correction factor to account for the fact that some sources which are repaired are not reduced to zero. For computational purposes, all sources which are repaired are assumed to be reduced to an emission level equivalent to a concentration of 1,000 ppmv.

As an example of this technique, Table 4-3 gives values for the "B," "C" and "D" correction factors for various possible inspection intervals, allowable repair times, and leak definitions.

An alternative to the ABCD correction factor model that may be used to determine leak detection and repair program effectiveness is an empirical approach which utilizes recently available data on leak occurrence, leak recurrence, and effectiveness of simple in-line repair (LDAR model). Estimates of leak detection and repair program effectiveness based on LDAR model results are presented in Appendix F.

4.3 PREVENTIVE PROGRAMS

An alternative approach to controlling fugitive VOC emissions from refinery operations is to replace components with leakless equipment. This approach is referred to as a preventive program. This section will discuss the kinds of equipment that could be applied in such a program and the advantages and disadvantages of this equipment.

4.3.1 Pumps

As discussed in Chapter 3, pumps can be potential fugitive VOC emission sources because of leakage through the drive-shaft sealing mechanism. This kind of leakage can be reduced to a negligible level through the installation of improved shaft sealing mechanisms, such as dual mechanical seals, or it can be eliminated entirely by installing sealless pumps.

4.3.1.1 Dual Mechanical Seals. As discussed in Chapter 3, dual mechanical seals consist of two mechanical sealing elements usually arranged in either a back-to-back or a tandem configuration. In both configurations a (nonpolluting) barrier fluid circulates between the seals. The barrier fluid system may be a circulating system, or it may rely on

Table 4-3. EMISSION CORRECTION FACTORS FOR VARIOUS INSPECTION INTERVALS, ALLOWABLE REPAIR TIMES, AND LEAK DEFINITIONS[a] (Reference 14)

	Leak Occurrence and Recurrence Correction Factor[b]			Non-Instantaneous Repair Correction Factor[c]			Imperfect Repair Correction Factor[d]			
	Inspection Interval			Allowable Repair Time (Days)			Leak Definition (ppmv)			
Source	Yearly	Quarterly	Monthly	15	5	1	100,000	50,000	10,000	1,000
Pump Seals										
Light Liquid[e]	0.800	0.900	0.950	0.979	0.993	0.999	0.974	0.972	0.941	0.886
Valves										
Gas[f]	0.800	0.900	0.950	0.979	0.993	0.999	0.998	0.998	0.996	0.992
Light Liquid[e]	0.800	0.900	0.950	0.979	0.993	0.999	0.988	0.980	0.958	0.916
Safety/Relief Valves[g]	0.800	0.900	0.950	0.979	0.993	0.999	0.995	0.993	0.985	0.968
Compressor Seals	0.800	0.900	0.950	0.979	0.993	0.999	0.994	0.992	0.984	0.972

[a] Note that these correction factors taken individually do not correspond exactly to the overall emission reduction obtainable by a monitoring and maintenance program. The overall effectiveness of the program is determined by the product of all correction factors.

[b] Values are assumed and account for sources that start to leak between inspections (occurrence), for sources that are found to be leaking, are repaired, and start to leak again before the next inspection (recurrence), and for leaking sources that could not be repaired.

[c] Accounts for emissions that occur between detection of a leak and subsequent repair.

[d] Accounts for the fact that some sources that are repaired are not reduced to zero. The average repair factors at 1,000 ppmv are assumed.

[e] Light liquid is defined as a petroleum liquid with a vapor pressure greater than that of kerosene.

[f] Valves in gas service carry process fluids in the gaseous state.

[g] Gas service only.

Appendix C

SOCMI FUGITIVE EMISSION FACTORS AND EQUATIONS

(From U.S. EPA 1995 Protocol for Equipment Leak Emission Estimates)
(Epperson, 1995)

TABLE 2-1. SOCMI AVERAGE EMISSION FACTORS

Equipment type	Service	Emission factor[a] (kg/hr/source)
Valves	Gas	0.00597
	Light liquid	0.00403
	Heavy liquid	0.00023
Pump seals[b]	Light liquid	0.0199
	Heavy liquid	0.00862
Compressor seals	Gas	0.228
Pressure relief valves	Gas	0.104
Connectors	All	0.00183
Open-ended lines	All	0.0017
Sampling connections	All	0.0150

[a] These factors are for total organic compound emission rates.

[b] The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

TABLE 2-5. SOCMI SCREENING RANGES EMISSION FACTORS

Equipment type	Service	≥10,000 ppmv Emission factor (kg/hr/source)[a]	<10,000 ppmv Emission factor (kg/hr/source)[a]
Valves	Gas	0.0782	0.000131
	Light liquid	0.0892	0.000165
	Heavy liquid	0.00023	0.00023
Pump seals[b]	Light liquid	0.243	0.00187
	Heavy liquid	0.216	0.00210
Compressor seals	Gas	1.608	0.0894
Pressure relief valves	Gas	1.691	0.0447
Connectors	All	0.113	0.0000810
Open-ended lines	All	0.01195	0.00150

[a] These factors are for total organic compound emission rates.

[b] The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

TABLE 2-9. SOCMI LEAK RATE/SCREENING VALUE CORRELATIONS

Equipment type	Correlation[a,b]
Gas valves	Leak rate (kg/hr) = 1.87E-06 × $(SV)^{0.873}$
Light liquid valves	Leak rate (kg/hr) = 6.41E-06 × $(SV)^{0.797}$
Light liquid pumps[c]	Leak rate (kg/hr) = 1.90E-05 × $(SV)^{0.824}$
Connectors	Leak rate (kg/hr) = 3.05E-06 × $(SV)^{0.885}$

[a] SV = Screening value in ppmv.

[b] These correlations predict total organic compound emission rates.

[c] The correlation for light liquid pumps can be applied to compressor seals, pressure relief valves, agitator seals, and heavy liquid pumps.

TABLE 2-11. DEFAULT-ZERO VALUES: SOCMI PROCESS UNITS

Equipment type	Default-zero TOC emission rates (kg/hr/source)[a]
Gas valve	6.6E-07
Light liquid valve	4.9E-07
Light liquid pump[b]	7.5E-06
Connectors	6.1E-07

[a] The default zero emission rates are for total organic compounds (including non-VOC's such as methane and ethane).

[b] The light liquid pump default zero value can be applied to compressors, pressure relief valves, agitators, and heavy liquid pumps.

TABLE 2-13. 10,000 PPMV AND 100,000 PPMV SCREENING VALUE PEGGED EMISSION RATES FOR SOCMI PROCESS UNITS

Equipment type	10,000 ppmv pegged emission rate (kg/hr/source)[a,b]	100,000 ppmv pegged emission rate (kg/hr/source)[a]
Gas valves	0.024	0.11
Light liquid valves	0.036	0.15
Light liquid pump seals[b]	0.14	0.62
Connectors	0.044	0.22

[a] The SOCMI pegged emission rates are for total organic compounds.

[b] The 10,000 ppmv pegged emission rate applies only when a dilution probe cannot be used or in the case of previously-collected data that contained screening values reported pegged at 10,000 ppmv.

[c] The light liquid pump seal pegged emission rates can be applied to compressors, pressure relief valves, and agitators.

TABLE 5-2. CONTROL EFFECTIVENESS FOR AN LDAR PROGRAM AT A SOCMI PROCESS UNIT

Equipment type and service	Control effectiveness (%)		
	Monthly monitoring 10,000 ppmv leak definition	Quarterly monitoring 10,000 ppmv leak definition	HON reg neg[a]
Valves - gas	87	67	92
Valves - light liquid	84	61	88
Pumps - light liquid	69	45	75
Connectors - all	b	b	93

[a] Control effectiveness attributable to the requirements of the proposed hazardous organic NESHAP equipment leak negotiated regulation are estimated based on equipment-specific leak definitions and performance levels.

[b] Data are not available to estimate control effectiveness.

Appendix D

RESPONSE FACTORS

Source: (Epperson, 1995, Appendix D)

APPENDIX D

RESPONSE FACTORS

The response factors presented in table D-1 were taken from two separate sources. The response factors at an actual concentration of 10,000 ppmv are from the EPA document entitled, "Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Chemicals," EPA-600/2-81-002 (September 1980). The document presents results of analytical tests performed to determine the response factors at 10,000 ppmv of two portable monitoring instruments--the Foxboro OVA-108 and the Bacharach TLV-108. Both instruments were calibrated with methane.

The response factors at a concentration of 500 ppmv are from the document entitled "Method 21 Evaluation for the HON, "90-ME-07)" (March 1991) prepared for the Emission Measurement Branch of the U.S. Environmental Protection Agency. This document presents the results of analytical tests performed to determine the response factors at an actual concentration of 500 ppmv of several emission monitors including the Foxboro OVA-108, two of Foxboro OVA-128 units, the Heath Detecto-PAK III, and the HNU Systems HW-101. The two Foxboro OVA-128 instrument response factors are presented in the table to indicate the variability of individual instruments. To determine the response factor for the OVA-128, the average of the two instrument response factors should be used. All of the instruments except the HNU HW-101 were calibrated with methane. The HNU HW-101 was calibrated with benzene.

A dashed line in table D-1 indicates that the study did not test that particular chemical. If the emission monitor did not respond to a chemical, N/R was recorded to indicate no response.

Operators of portable leak detection devices should be thoroughly familiar with their instrumentation. Even under the best of circumstances, no two analyzers will perform exactly the same and the effect of changes in instrument parameters upon accuracy can be significant. Other external quality controls, such as a checklist for periodically noting battery condition, fuel pressure, post-survey calibration checks, etc., will support the validity of the data. An audit program testing both the operator and the analyzer should be a requirement whenever a situation warranting an exacting determination of a fugitive emission is encountered.

In general, the response factors follow the pattern which would be predicted for increasing flame ionization detector response with increasing hydrocarbon character for the molecule. The sequence of compounds methyl chloride, methylene chloride, chloroform, and carbon tetrachloride exhibits progressively decreasing response on the OVA detectors (response factors ranging from 2 to 12) as the substitution on the methyl carbon atom increases (i.e., decreasing hydrocarbon character for the molecule). In general, increasing electronegativity of the substituent decreases the system response: methyl chloride, response factor approximately 2; methyl bromide, response factor approximately 5; iodomethane, response factor approximately 8. Carbon tetrachloride exhibits a response factor of 12 or more, but tetrachloroethylene has a response factor of 2 or less. The lack of carbon-hydrogen bonds in tetrachloroethylene is apparently compensated by the presence of a site of unsaturation in the molecule (chlorobenzene, response factor 0.60 vs. trichlorobenzene, response factor of 12 or greater). The difficulty of obtaining a reproducible and useful response factor for compounds of insufficient volatility such as nitrobenzene, m-cresol, and oxygenated compounds such as acrylic acid demonstrates that there is a point dictated by vapor pressure or possibly boiling point where an accurate measurement cannot be made using the portable field analyzers. With compounds which are not very volatile, the portable field analyzers can be usedonly qualitatively, at best; if a large amount of the compound is present in the air, the compound will be observed but not with a proportionate quantitative response.

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108[a]	Bacharach TLV[a]	Foxboro OVA - 108[a]	Foxboro OVA - 128[a]	Foxboro OVA - 128[a]	Heath DP 111[a]	HNU HW - 101[b]
75-07-0	Acetaldehyde	LL	--	--	8.41	9.96	7.95	5.36	6.07
64-19-7	Acetic Acid	LL	1.83	5.70	--	--	--	--	--
108-24-7	Acetic anhydride	LL	1.36	2.89	--	--	--	--	--
67-64-1	Acetone	LL	0.79	1.22	--	--	--	--	--
75-86-5	Acetone cyanohydrin	HL	3.42	7.84	--	--	--	--	--
75-05-08	Acetonitrile	LL	0.94	1.17	1.20	1.24	1.27	1.27	N/R
98-86-2	Acetophenone	HL	10.98	54.86	2.71	2.62	2.43	2.92	3.07
75-36-5	Acetyl chloride	LL	1.99	2.59	--	--	--	--	--
74-86-2	Acetylene	G	0.37	11.95	--	--	--	--	--
107-02-8	Acrolein	LL	--	--	6.25	6.69	5.64	3.71	2.73
79-10-7	Acrylic acid	LL	4.65	36.95	10.51[c]	10.81[c]	9.63[c]	8.61[c]	8.91[c]
107-13-1	Acrylonitrile	LL	0.96	2.70	1.55	1.58	1.56	1.47	3.04
	Allene	G	0.55	5.78	--	--	--	--	--
107-18-6	Allyl alcohol	LL	0.94		--	--	--	--	--
107-5-1	Allyl chloride	LL	--	--	2.77	2.73	2.51	1.56	1.46
71-41-0c	Amyl alcohol, N-	HL	0.69	1.78	--	--	--	--	--
	Amylene	LL	0.31	1.03	--	--	--	--	--

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108[a]	Bacharach TLV[a]	Foxboro OVA - 108[a]	Foxboro OVA - 128[a]	Foxboro OVA - 128[a]	Heath DP III[a]	HNU HW - 101[b]
62-53-3	Aniline	HL	--	--	14.44[c]	20.45[c]	22.68[c]	14.71[c]	15.23[c]
100-66-3	Anisole	LL	0.92	2.69	--	--	--	--	--
100-52-7	Benzaldehyde	HL	2.36	6.30	--	--	--	--	--
71-43-2	Benzene	LL	0.21	1.07	0.56	0.54	0.50	0.38	1.00
100-47-0	Benzonitrile	HL	2.24	9.13	--	--	--	--	--
98-88-4	Benzoyl Chloride	HL	6.40	6.60	--	--	--	--	--
100-44-7	Benzyl Chloride	HL	4.20	4.87	1.43	1.42	1.21	0.95	1.34
10-86-0	Bromobenzene	LL	0.36	1.16	--	--	--	--	--
75-25-2	Bromoform	LL	--	--	5.90	6.71	5.68	5.12	0.62
106-99-0	Butadiene, 1,3-	G	0.37	6.00	2.41	2.69	2.37	1.68	2.15
106-97-8	Butane, N-	G	0.38	0.68	--	--	--	--	--
71-36-3	Butanol, N-	LL	1.43	2.80	--	--	--	--	--
78-92-2	Butanol, Sec-	LL	0.70	1.26	--	--	--	--	--
75-65-0	Butanol, Tert-	S	0.44	2.19	--	--	--	--	--
106-98-9	Butene, 1-	G	0.51	2.97	--	--	--	--	--
111-76-2	Butoxyethanol, 2-[c]		--	--	19.37[c]	26.11[c]	24.69[c]	13.93[c]	9.23[c]
123-86-4	Butyl acetate	LL	0.60	1.30	--	--	--	--	--
141-32-2	Butyl acrylate, N-	LL	0.64	1.98	--	--	--	--	--

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108[a]	Bacharach TLV[a]	Foxboro OVA - 108[a]	Foxboro OVA - 128[a]	Foxboro OVA - 128[a]	Heath DP III[a]	HNU HW - 101[b]
142-96-1	Butyl ether, N-	LL	2.70	2.66	--	--	--	--	--
	Butyl ether, Sec-	LL	0.26	1.13	--	--	--	--	--
109-73-9	Butylamine, N-	LL	0.63	1.91	--	--	--	--	--
13952-84-6	Butylamine, Sec-	LL	0.67	1.50	--	--	--	--	--
75-64-9	Butylamine, Tert-	LL	0.58	1.80	--	--	--	--	--
98-06-6	Butylbenzene, Tert-	HL	1.27	6.42	--	--	--	--	--
123-72-8	Butyraldehyde, N-	LL	1.39	1.89	--	--	--	--	--
107-92-6	Butyric acid	HL	0.74	4.58	--	--	--	--	--
109-74-0	Butyronitrile	LL	0.46	1.33	--	--	--	--	--
75-1-50	Carbon disulfide	LL	--	2.96	33.87	53.06	N/R	57.06	0.71
56-23-5	Carbon tetrachloride	LL	--	--	12.07	15.99	13.72	11.11	3.06
463-58-1	Carbonyl Sulfide	G	--	--	103.95	N/R	N/R	N/R	3.14
107-20-0	Chloroacetaldehyde	LL	13.40	5.07	--	--	--	--	--
79-04-9	Chloroacetyl chloride	LL	--	--	1.86	1.93	1.66	1.28	3.21
108-90-7	Chlorobenzene	LL	0.36	0.88	0.62	0.60	0.54	0.38	1.06
75-00-3	Chloroethane	G	0.67	2.16	--	--	--	--	--
67-66-3	Chloroform	L	4.48	8.77	2.06	2.38	1.91	1.38	3.35
	Chloromethyl methyl ether		--	--	7.77	9.76	7.52	4.28	1.65

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108^{a}	Bacharach TLV^{a}	Foxboro OVA - 108^{a}	Foxboro OVA - 128^{a}	Foxboro OVA - 128^{a}	Heath DP 111^{a}	HNU HW - 101^{b}
25167-80-0	Chlorophenol, O-	HL	3.33	5.87	--	--	--	--	--
	50% Chloroprene/xylene		--	--	1.46	1.47	1.27	0.77	1.37
	Chloropropene, 1-	LL	0.59	0.86	--	--	--	--	--
	Chloropropene, 3-	LL	0.75	1.24	--	--	--	--	--
108-41-8	Chlorotoluene, M-	LL	0.43	0.92	--	--	--	--	--
95-49-9	Chlorotoluene, O-	LL	0.45	1.05	--	--	--	--	--
106-43-4	Chlorotoluene, P-	LL	0.52	1.15	--	--	--	--	--
95-48-7	Cresol, O-	S	0.95	3.98	--	--	--	--	--
108-39-4	Cresol, M-	LL	--	--	75.60^{c}	115.20^{c}	N/R	N/R	N/R
106-44-5	Cresol, P-	S	--	--	N/R	N/R	N/R	N/R	N/R
4170-30-0	Crotonaldehyde	LL	1.32	8.54	--	--	--	--	--
98-82-8	Cumene	LL	1.92	12.49	2.05	1.82	1.55	0.79	1.87
110-82-7	Cyclohexane	LL	0.36	0.72	--	--	--	--	--
108-93-0	Cyclohexanol	HL	0.82	4.92	--	--	--	--	--
108-94-1	Cyclohexanone	LL	1.50	3.99	--	--	--	--	--
110-83-8	Cyclohexene	LL	0.40	1.84	--	--	--	--	--
108-91-8	Cyclohexylamine	LL	0.47	1.38	--	--	--	--	--
124-18-5	Decane	HL	0.00	0.20	--	--	--	--	--

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108^a	Bacharach TLV^a	Foxboro OVA - 108^a	Foxboro OVA - 128^a	Foxboro OVA - 128^a	Heath DP III^a	HNU HW - 101^b
123-42-2	Diacetone alcohol	HL	1.53	0.98	--	--	--	--	--
431-03-8	Diacetyl	LL	1.61	2.81	--	--	--	--	--
	Dichloro-1-propene, 2,3-	LL	61.51	34.34	--	--	--	--	--
541-73-1	Dichlorobenzene, M-	HL	0.66	1.89	--	--	--	--	--
95-50-1	Dichlorobenzene, O-	HL	0.70	1.22	--	--	--	--	--
75-34-3	Dichloroethane, 1,1-	LL	0.77	1.80	--	--	--	--	--
107-06-2	Dichloroethane, 1,2-	LL	0.95	2.08	--	--	--	--	--
540-59-0	Dichloroethylene, 2-	LL	1.31	1.93	--	--	--	--	--
540-59-0	Dichloroethylene, TRANS, 1,2	LL	1.13	1.86	--	--	--	--	--
111-44-4	Dichloroethyl ether^c		--	--	22.12^c	25.10^c	24.48^c	16.88^c	8.79^c
	Dichloromethane	LL	2.26	3.63	--	--	--	--	--
	Dichloropropane, 1,2-	LL	1.03	1.80	--	--	--	--	--
542-75-6	Dichloropropene, 1,3-		--	--	2.03	2.08	1.93	1.23	1.18
25167-70-8	Diisobutylene	LL	0.24	1.39	--	--	--	--	--
	Dimethoxy ethane, 1,2-	LL	1.28	1.43	--	--	--	--	--
68-12-2	Dimethylformamide, N,N-	LL	3.89	2.95	6.42	6.38	7.20	7.09	5.73
57-14-7	Dimethylhydrazine, 1,1-	LL	1.04	2.74	2.68	2.84	3.00	2.89	2.29

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108[a]	Bacharach TLV[a]	Foxboro OVA - 108[a]	Foxboro OVA - 128[a]	Foxboro OVA - 128[a]	Heath DP III[a]	HNU HW - 101[b]
67-68-5	Dimethylsulfoxide	HL	0.00	4.88	--	--	--	--	--
123-91-1	Dioxane, 1,4-	LL	1.58	1.23	3.74	4.27	3.60	3.21	1.66
106-89-8	Epichlorohydrin	LL	1.72	2.02	2.30	2.41	2.07	1.27	1.95
106-88-7	Epoxybutane, 1,2-		--	--	2.67	2.54	2.16	1.89	2.68
74-84-0	Ethane	G	0.57	0.73	--	--	--	--	--
64-17-5	Ethanol	LL	2.04	--	--	--	--	--	--
110-80-5	Ethoxy ethanol, 2-	LL	1.68	1.61	3.55	4.09	3.50	2.02	1.70
141078-6	Ethyl acetate	LL	0.84	3.13	--	--	--	--	--
141-97-9	Ethyl acetoacetate	HL	3.02	3.13	--	--	--	--	--
140-88-5	Ethyl acrylate	LL	0.72	--	2.49	2.64	2.18	1.16	1.09
75-00-3	Ethyl chloride	G	--	--	1.68	1.84	1.65	1.10	2.38
105-39-5	Ethyl chloroacetate	LL	1.97	1.47	--	--	--	--	--
60-29-7	Ethyl Ether	LL	0.97	1.11	--	--	--	--	--
100-41-4	Ethylbenzene	LL	0.70	3.14	0.77	0.76	0.66	0.51	1.08
74-85-1	Ethylene	G	0.52	4.49	--	--	--	--	--
106-93-4	Ethylene dibromide		--	--	2.03	2.22	2.03	1.36	0.98
107-06-2	Ethylene dichloride	LL	--	--	1.37	1.59	1.41	1.19	1.42
107-21-1	Ethylene glycol[c]		--	--	24.81	39.39	N/R	33.13	10.91

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108[a]	Bacharach TLV[a]	Foxboro OVA - 108[a]	Foxboro OVA - 128[a]	Foxboro OVA - 128[a]	Heath DP III[a]	HNU HW - 101[b]
75-21-8	Ethylene oxide	G	2.72	2.43	2.40	2.77	2.40	1.81	6.61
107-15-3	Ethylenediamine	LL	1.78	2.46	--	--	--	--	--
64-18-6	Formic Acid	LL	34.87	33.21	--	--	--	--	--
	Formalin (37% formaldehyde/H_2O)		--	--	18.83	31.39	27.66	16.50	4.04
556-52-5	Glycidol	LL	8.42	5.23	--	--	--	--	--
142-82-5	Heptane	LL	0.30	0.75	--	--	--	--	--
87-68-3	Hexachlorobutadiene[c]		--	--	16.28[c]	22.99[c]	18.06[c]	14.56[c]	19.34[c]
100-54-3	Hexane, N-	LL	0.31	0.72	1.42	1.49	1.33	0.93	1.49
592-41-6	Hexene, 1-	LL	0.39	2.92	--	--	--	--	--
	Hydroxyacetone	LL	8.70	9.34	--	--	--	--	--
74-88-4	Iodomethane		--	--	8.06	8.76	7.35	4.59	0.72
75-28-5	Isobutane	G	0.30	0.61	--	--	--	--	--
115-11-7	Isobutylene	G	2.42	6.33	--	--	--	--	--
540-84-1	Isooctane	LL	--	--	1.05	1.05	0.89	0.56	0.98
78-79-5	Isoprene	LL	0.38	--	--	--	--	--	--
78-59-1	Isophorone[c]		--	--	28.80	40.71	N/R	29.69	17.76
67-63-0	Isopropanol	LL	0.90	1.35	--	--	--	--	--
108-21-4	Isopropyl acetate	LL	0.68	1.25	--	--	--	--	--

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108[a]	Bacharach TLV[a]	Foxboro OVA - 108[a]	Foxboro OVA - 128[a]	Foxboro OVA - 128[a]	Heath DP III[a]	HNU HW - 101[b]
75-29-6	Isopropyl chloride	LL	0.62	0.99	--	--	--	--	--
590-86-3	Isovaleraldehyde	LL	0.55	2.04	--	--	--	--	--
141-79-7	Mesityl oxide	LL	1.12	3.12	--	--	--	--	--
78-85-3	Methacrolein	LL	1.27	3.10	--	--	--	--	--
79-41-4	Methacrylic acid	HL	0.71	6.61	--	--	--	--	--
67-56-1	Methanol	LL	5.69	1.88	13.24	17.34	N/R	21.73	4.59
111-90-0	Methoxy-ethanol, 2-	LL	2.70	2.19	9.61[c]	9.87[c]	N/R	7.91[c]	2.80[c]
79-20-9	Methyl acetate	LL	1.80	1.76	--	--	--	--	--
74-99-7	Methyl acetylene	G	0.53	3.92	--	--	--	--	--
74-83-9	Methyl bromide	G	--	--	3.71	3.83	3.46	2.43	1.47
74-87-3	Methyl chloride	G	1.75	2.45	1.97	2.38	1.97	1.27	1.77
78-93-3	Methyl ethyl ketone	LL	0.57	1.12	1.78	1.84	1.59	1.19	2.92
107-31-3	Methyl formate	LL	3.47	1.93	--	--	--	--	--
60-34-4	Methyl hydrazine	LL	--	--	5.47	5.50	5.74	5.44	3.93
108-10-1	Methyl isobutyl ketone	LL	--	--	1.65	1.69	1.40	0.98	1.46
80-62-6	Methyl methacrylate	LL	0.99	2.36	2.02	2.16	1.81	0.92	1.84
	Methyl tert-butyl ketone		--	--	1.23	1.25	1.03	0.72	1.69
108-11-2	Methyl-2-pentanol, 4-	LL	1.70	1.94	--	--	--	--	--

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108[a]	Bacharach TLV[a]	Foxboro OVA - 108[a]	Foxboro OVA - 128[a]	Foxboro OVA - 128[a]	Heath DP III[a]	HNU HW - 101[b]
	Methyl-2-pentanone, 4-	LL	0.49	1.54	--	--	--	--	--
	Methyl-3-butyn-2-OL, 2-	LL	0.51	--	--	--	--	--	--
109-87-5	Methylal	LL	1.46	1.41	--	--	--	--	--
100-61-8	Methylaniline, N-	HL	4.13	5.25	--	--	--	--	--
108-87-2	Methylcyclohexane	LL	0.38	0.85	--	--	--	--	--
	Methylcyclohexene, 1-	LL	0.33	2.22	--	--	--	--	--
75-09-2	Methylene chloride	LL	2.26	3.63	1.67	1.72	1.41	0.84	2.06
77-75-8	Methylpentynol	LL	1.17	2.82	--	--	--	--	--
98-83-9	Methylstyrene, A-	LL	10.24	31.46	--	--	--	--	--
110-91-8	Morpholine	LL	0.92	1.93	--	--	--	--	--
98-95-3	Nitrobenzene	HL	29.77	40.61	16.41[c]	16.52[c]	N/R	26.01[c]	19.98[c]
79-24-3	Nitroethane	LL	1.40	2.54	--	--	--	--	--
75-52-5	Nitromethane	LL	3.32	5.25	--	--	--	--	--
24332-01-4	Nitropropane, 2-	LL	1.06	1.77	1.86	1.91	1.60	1.06	3.29
111-84-2	Nonane-N	LL	1.62	5.54	--	--	--	--	--
111-65-9	Octane	LL	1.04	2.06	--	--	--	--	--
	Phenol (90% carboxylic acid)	LL	--	--	16.38	44.89	47.01	N/R	71.06
109-66-0	Pentane	LL	0.42	0.62	--	--	--	--	--

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108^{a}	Bacharach TLV^{a}	Foxboro OVA - 108^{a}	Foxboro OVA - 128^{a}	Foxboro OVA - 128^{a}	Heath DP III^{a}	HNU HW - 101^{b}
109-06-8	Picoline, 2-	LL	0.34	1.17	--	--	--	--	--
74-98-6	Propane	G	0.88	0.63	--	--	--	--	--
123-38-6	Propionaldehyde	LL	1.19	1.65	4.01	4.27	3.95	2.53	4.79
79-09-4	Propionic acid	LL	1.34	3.51	--	--	--	--	--
71-23-8	Propyl alcohol	LL	0.91	1.55	--	--	--	--	--
103-65-1	Propylbenzene, N-	LL	0.44	5.97	--	--	--	--	--
115-07-1	Propylene	G	0.79	2.80	--	--	--	--	--
78-87-5	Propylene dichloride	LL	--	--	1.49	1.48	1.26	0.84	1.37
75-56-0	Propylene oxide	LL	0.80	1.15	2.02	2.14	1.78	1.26	3.09
75-55-8	Propyleneimine, 1,2-		--	--	1.75	1.52	1.53	1.33	2.31
110-86-1	Pyridine	LL	0.41	1.17	--	--	--	--	--
100-42-5	Styrene	LL	4.16	36.83	1.10	1.08	0.93	0.57	1.36
96-09-3	Styrene Oxide	L	--	--	2.61	2.49	2.06	2.61	3.03
79-34-5C	Tetrachloroethane, 1,1,1,2-	LL	3.00	6.52	--	--	--	--	--
	Tetrachloroethane, 1,1,2,2-	LL	6.06	14.14	1.64	1.69	1.66	1.14	1.52
127-18-4	Tetrachloroethylene	LL	3.16	11.46	1.77	2.09	1.72	1.20	0.74
108-88-3	Toluene	LL	0.33	2.32	0.87	0.87	0.76	0.57	1.25

TABLE D-1. RESPONSE FACTORS AT ACTUAL CONCENTRATIONS OF 10,000 PPMV AND 500 PPMV (Cont.)

			Actual Concentration: 10,000 ppmV		Actual Concentration: 500 ppmV				
CAS No.#	Compound Name	Volatility Class	Foxboro OVA - 108[a]	Bacharach TLV[a]	Foxboro OVA - 108[a]	Foxboro OVA - 128[a]	Foxboro OVA - 128[a]	Heath DP 111[a]	HNU HW - 101[b]
120-82-1	Trichlorobenzene, 1,2,4		1.35	0.39	12.55	16.71	N/R	18.66	16.58
71-55-6	Trichloroethane, 1,1,1-	LL	0.79	2.41	1.09	1.16	1.03	0.70	1.85
79-00-5	Trichloroethane, 1,1,2-	LL	1.26	3.68	1.19	1.27	1.11	0.79	1.33
79-01-6	Trichloroethylene	LL	0.94	3.35	2.26	2.60	2.14	1.25	1.09
96-18-4	Trichloropropane, 1,2,3-	LL	0.95	2.23	--	--	--	--	--
121-44-8	Triethylamine	LL	0.46	1.41	0.47	0.49	0.48	0.35	0.73
108-05-4	Vinyl acetate	LL	1.31	3.99	3.63	3.36	2.80	1.48	2.07
593-60-2	Vinyl bromide	G	--	--	2.14	2.41	2.33	1.68	1.37
75-01-4	Vinyl chloride	G	0.65	1.10	2.03	2.11	2.11	1.76	2.18
	Vinyl propionate	LL	0.94	0.70	--	--	--	--	--
75-35-4	Vinylidene chloride	LL	1.15	2.38	2.73	2.97	2.61	1.79	1.70
106-42-3	Xylene, P-	LL	2.27	5.35	0.89	0.88	0.74	0.54	0.93
108-38-3	Xylene, M-	LL	0.30	3.56	0.89	0.89	0.75	0.54	0.96
95-47-6	Xylene, O-	LL	0.36	1.40	0.95	0.95	0.80	0.60	1.09

N/R = No response
[a] = Calibrated with methane in air.
[b] = Calibrated with benzene in air.
[c] = Volatility problem with compound.

Appendix E

RESPONSE FACTOR CALCULATION EXAMPLE

Source: (Epperson, 1995, Appendix A)

A-5. UNIT-SPECIFIC CORRELATION APPROACH

Correlation equations may be developed for specific units rather than using the more general EPA Correlation Equations. Appendix B presents details on developing unit-specific correlations. Once correlations are developed using the approach outlined in appendix B, they are applied in the same manner as described for the EPA correlations.

A-6. SPECIATING EMISSIONS

The emission rate of specific compounds in a mixture can be calculated if the concentration of the compound in the stream is known. The equation for speciating emissions is

$$E_X = E_{TOC} \times (WP_X/WP_{TOC})$$

where:

E_X = The mass emissions of organic chemical "x" from the equipment piece (mass/time);

E_{TOC} = The TOC mass emissions from the individual equipment piece (mass/time) calculated from either the Average Emission Factor, Screening Ranges, Correlation, or Unit-Specific Correlation approaches;

WP_X = The concentration of organic chemical "x" in the equipment piece (weight percent);

WP_{TOC} = The total TOC concentration in the equipment piece (weight percent).

See table A-5 for a demonstration of speciating emissions of Stream B. Because all of the equipment in Stream B contains the same composition, the emissions can be speciated on a stream-wide basis.

A-7. RESPONSE FACTORS

Response factors are used to correct screening values to compensate for variations in a monitor's response to different compounds. Determination of whether an adjustment to the screening value will provide more valid emission estimates can be made by reviewing RF's at actual concentrations of 500 ppmv and 10,000 ppmv for the material in the equipment being screened.

TABLE A-5. SPECIATING EMISSIONS OF STREAM B[a]

Method of calculation	Total TOC emission (kg/yr)	Ethyl acrylate emissions[b] (kg/yr)	Styrene emissions[b] (kg/yr)
Avg. emission factor	1,050[c]	105	945
Screening ranges	1,230[d]	123	1,110
Correlation equation	740[e]	74	666

[a] Equipment type: Light liquid pumps
Total TOC wt. fraction 1.0
Ethyl acrylate wt. fraction 0.1
Styrene wt. fraction 0.9

[b] Emissions for species = (total TOC emissions) × (wt. fraction of individual chemical)/(total TOC wt. fraction).

[c] From Table A-2.

[d] From Table A-3.

[e] From Table A-4.

The RF's can be taken from table D-1 in appendix D, or may be calculated based on analytical measurement performed in a laboratory. For materials with RF's below three at both actual concentrations, the screening value does not need to be corrected. If the RF at either concentration is above three, the screening value obtained from the monitoring device should be adjusted.

If it is necessary to adjust the screening value, one of two approaches can be applied:

(1) Use the higher of either the 500 ppmv or 10,000 ppmv RF to adjust all screening values, or

(2) Plot the RF versus screening value and determine the applicable RF for each screening value.

Table D-1 in appendix D presents the RF's for chemical compounds at actual concentrations of 500 ppmv and 10,000 ppmv for several different monitoring devices. For the example calculations presented here, data for the Foxboro OVA-108 is utilized. Table A-6 presents the RF's for ethyl acrylate and styrene. From table A-6, it can be seen that at both concentrations, the RF for ethyl acrylate is below three. Therefore, it is not necessary to adjust any of the screening values taken from the equipment in Stream A. (The only TOC constituent in Stream A is ethyl acrylate.) Stream B contains 10 percent ethyl acrylate and 90 percent styrene. The RF's at both concentration values for Stream B are calculated using the following equation:

$$RF_m = \frac{1}{\sum_{i=1}^{n} (X_i/RF_i)}$$

where:

RF_m = Response factor of the mixture;

n = Number of constituents in the mixture;

X_i = Mole fraction of constituent i in the mixture; and

TABLE A-6. APPLICATION OF RESPONSE FACTORS[a]

Chemical	Molecular weight	Mole fraction for stream B[b]	Response factor at actual conc. of 500 ppmv	Response factor at actual conc. of 10,000 ppmv
Ethyl Acrylate (0.10 wt. frac.)	100.1	0.1036	2.49	0.72
Styrene (0.90 wt. frac.)	104.2	0.8964	1.10	6.06

[a] Response factors are taken from Table D-1 in Appendix D and are based on a Foxboro OVA-108 calibrated with methane.

[b] Mole fraction calculated as:

$$= \frac{\dfrac{\text{Weight fraction compound } i}{\text{MW of compound } i}}{\displaystyle\sum_{i=1}^{n} \dfrac{\text{Weight fraction compound } i}{\text{MW of compound } i}}$$

RF_i = Response factor of constituent i in the mixture;

The derivation of the above equation is presented in table A-7. Using the RF's and mole fraction information from table A-6, the RF for the mixture in Stream B is calculated as follows:

$$RF_m(@\ 500\ \text{ppmv}) = (0.1036/2.49 + 0.8963/1.10)^{-1} = 1.17$$

and

$$RF_m(@\ 10{,}000\ \text{ppmv}) = (0.1036/0.72 + 0.8964/6.06)^{-1} = 3.43$$

From the above calculations, it can be seen that at an actual concentration of 10,000 ppmv the RF is above three, which means the screening values need to be adjusted. Table A-8 demonstrates the simplest approach for adjusting the screening values. This approach involves multiplying all of the screening values by whichever RF is higher.

Correcting the screening values by the approach described above may be inaccurate in some cases. For example, if all or most of the equipment have low screening values, using the RF based on an actual concentration of 10,000 ppmv may cause an over estimate in the calculated emission rate. A more precise application of RF's is to plot the RF versus the screening value. This can be done by fitting a straight line between the RF and the corresponding screening values associated with the 500 and 10,000 ppmv actual concentrations. For the example case, this is done as follows.

Screening value associated with actual concentration of 500 ppmv:

= (500 ppmv)/(RF at actual concentration of 500 ppmv)

= 500 ppmv/1.17

= 427 ppmv

Screening value associated with actual concentration of 10,000 ppmv:

= (10,000 ppmv)/(RF at actual concentration of 10,000 ppmv)

TABLE A-8. APPLYING RESPONSE FACTORS FROM TABLE C-1a

Equipment ID	Unadjusted screening value (ppmv)	Response factor of mixture	Adjusted screening value[b] (ppmv)	VOC Emission rate[c] (kg/yr)
B-1	0	--	Default zero	0.033
B-2	0	--	Default zero	0.033
B-3	0	--	Default zero	0.033
B-4	10	3.43	34	1.5
B-5	30	3.43	103	3.8
B-6	250	3.43	858	22
B-7	500	3.43	1,715	39
B-8	2,000	3.43	6,860	120
B-9	5,000	3.43	17,150	260
B-10	8,000	3.43	27,440	380
B-11	25,000	3.43	85,750	970
B-12	Not Screened	--	--	87[d]
Total Emissions of Stream B				1,880

[a] Equipment type: Light liquid pumps
Correlation equation: Leak rate (kg/hr) = 1.90×10^{-5} $(SV)^{0.824}$
Default-zero mass emission rate: 7.49×10^{-6} kg/hr
Hours of operation: Stream B = 4,380

[b] Adjusted SV = (unadjusted SV) × (RF of mixture)

[c] VOC Emission = (correlation equation or default-zero emission rate) × (WP_{VOC}/WP_{TOC}) × (hours of operation)

[d] VOC Emission = (average emission factor) × (wt. fraction of VOC) × (WP_{VOC}/WP_{TOC}) × (hours of operation)

TABLE A-7. DERIVATION OF EQUATION USED TO ESTIMATE RESPONSE FACTOR FOR A MIXTURE

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(1) **Response Factor (RF) Equation:**

$$RF = \frac{\text{Actual Concentration (ppmv)}}{\text{Screening Value (ppmv)}} = \frac{A}{SV}$$

(2) For a mixture, each compound will contribute to the actual concentration and to the screening value, thus:

$$A = A_1 + A_2 + A_3 \ldots = A_{TOT}$$

$$SV = SV_1 + SV_2 + SV_3 \ldots$$

Thus, the above equation converts to:

$$RF = \frac{A_{TOT}}{SV_1 + SV_2 + SV_3 \ldots}$$

(3) The value for the screening value of each individual compound (SV_i) is calculated as:

$$SV_i = \frac{A_i}{RF_i}; \text{ substituting gives:}$$

$$RF = \frac{A_{TOT}}{\frac{A_1}{RF_1} + \frac{A_2}{RF_2} + \frac{A_3}{RF_3} \ldots}$$

(4) The mole fraction of each individual compound (X_i) is calculated as:

$$X_i = \frac{A_i}{A_{TOT}};$$

Thus, the actual concentration of compound i is calculated as:

$A_i = X_i\, A_{TOT}$; substituting gives:

$$RF = \frac{A_{TOT}}{\frac{X_1 A_{TOT}}{RF_1} + \frac{X_2 A_{TOT}}{RF_2} + \frac{X_3 A_{TOT}}{RF_3} \ldots} = \frac{1}{\frac{X_1}{RF_1} + \frac{X_2}{RF_2} + \frac{X_3}{RF_3} \ldots}$$

(5) Thus, the response factor of a mixture is calculated as:

$$RF = \frac{1}{\sum_{i=1}^{n} X_i/RF_i}$$

= 10,000/3.43

= 2,915 ppmv

Figure A-1 plots this screening value/RF relationship. Table A-9 uses this plot to calculate emissions. Note that in table A-9, all of the screening values are adjusted. An alternative would be to adjust only those screening values having an associated RF greater than three. Note that for all screening values less than 427 ppmv, the RF calculated at 427 ppmv is applied, and, similarly, for all screening values above 2,915 ppmv, the RF at 2,915 ppmv is applied.

An alternative to using the RF's in appendix D is to use the analytical technique described in chapter 3.0 to determine RF's at several different actual concentrations. These RF's are then related to the screening value. Once the RF's and associated screening values are determined, a first-order or second-order (if the relationship appears nonlinear) equation can be fitted to the RF data. Table A-10 demonstrates how the collected data of RF's at actual concentrations is converted to RF's for the associated screening values. A hypothetical plot of the RF/screening value relationship is shown in figure A-2. Table A-11 demonstrates how emissions can then be calculated by applying the plot. Note that the line is not extrapolated beyond the highest screening value for which data were obtained.

A-8. ANNUALIZING EMISSIONS

If more than one screening value is obtained from an equipment piece, all of the screening values can be used to estimate emissions, as long as the elapsed time between each screening value obtained is known. This is demonstrated for pump A-15 in Stream A. Table A-12 shows how emissions are calculated for each period between the collection of screening values. Notice that each screening value is used to estimate emissions since the last screening value was obtained.

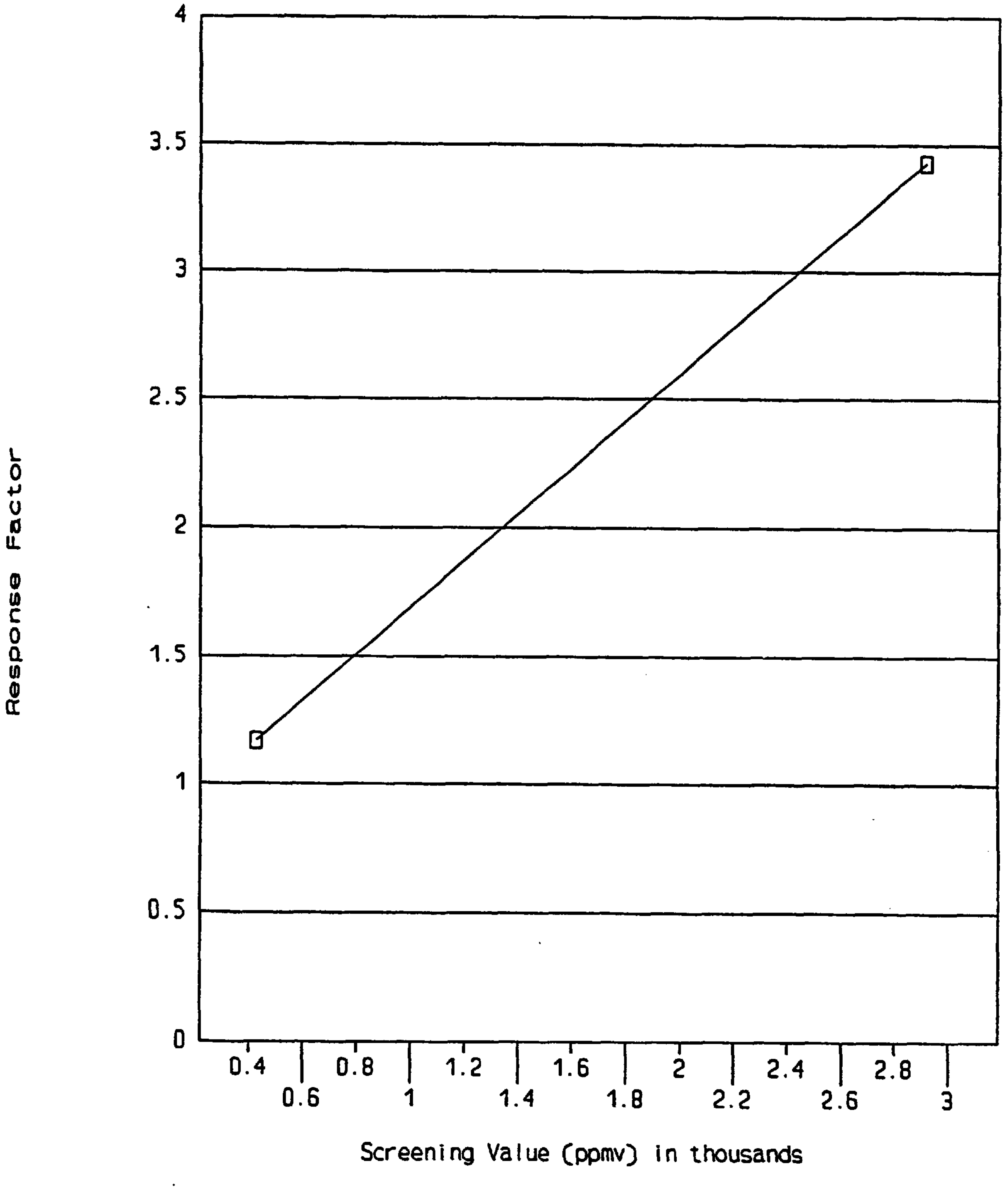

Figure A-1. **Response Factor Curve Generated From Response Factor Data in Table C-1**

TABLE A-9. ESTIMATING EMISSIONS USING RESPONSE FACTORS GENERATED FROM FIGURE A-1[a]

Equipment ID	Unadjusted screening value (ppmv)	Response factor of mixture	Adjusted screening value[b] (ppmv)	VOC Emission rate[c] (kg/yr)
B-1	0	--	Default zero	0.033
B-2	0	--	Default zero	0.033
B-3	0	--	Default zero	0.033
B-4	10	1.17	12	0.63
B-5	30	1.17	35	1.6
B-6	250	1.17	293	9.0
B-7	500	1.24	620	17
B-8	2000	2.62	5,240	97
B-9	5000	3.43	17,150	260
B-10	8000	3.43	27,440	380
B-11	25000	3.43	85,750	970
B-12	Not screened	--	--	87[d]
Total Emissions of Stream B				1,820

[a] Equipment type: Light liquid pumps
Correlation equation: Leak rate (kg/hr) = 1.90×10^{-5} $(SV)^{0.824}$
Default-zero mass emission rate: 7.49×10^{-6} kg/hr
Hours of operation: Stream B = 4,380

[b] Adjusted SV = (unadjusted SV) × (RF of mixture taken from Figure A-1)

[c] VOC Emission = (correlation equation or default-zero emission rate) × (WP_{VOC}/WP_{TOC}) × (hours of operation)

[d] VOC Emission = (no. of components) × (average emission factor) × (wt. fraction of VOC) × (WP_{VOC}/WP_{TOC}) × (hours of operation)

TABLE A-10. GENERATION OF HYPOTHETICAL RESPONSE FACTOR DATA FOR STREAM B[a]

Actual standard gas concentration (ppmv)	Sample number	Measured screening value (ppmv)	Response factor
500	1	375	1.33
500	2	390	1.28
500	3	390	1.28
		Avg = 385	Avg = 1.30
2,000	1	1,219	1.64
2,000	2	1,205	1.66
2,000	3	1,258	1.59
		Avg = 1,227	Avg = 1.63
5,000	1	1,865	2.68
5,000	2	1,930	2.59
5,000	3	1,872	2.67
		Avg = 1,889	Avg = 2.65
10,000	1	2,976	3.36
10,000	2	3,040	3.29
10,000	3	2,994	3.34
		Avg = 3,003	Avg = 3.33
25,000	1	6,361	3.93
25,000	2	6,394	3.91
25,000	3	6,476	3.86
		Avg = 6,410	Avg = 3.90

[a] This table is a demonstration of how analytical determination of response factors can be used to generate a response factor/screening value relationship.

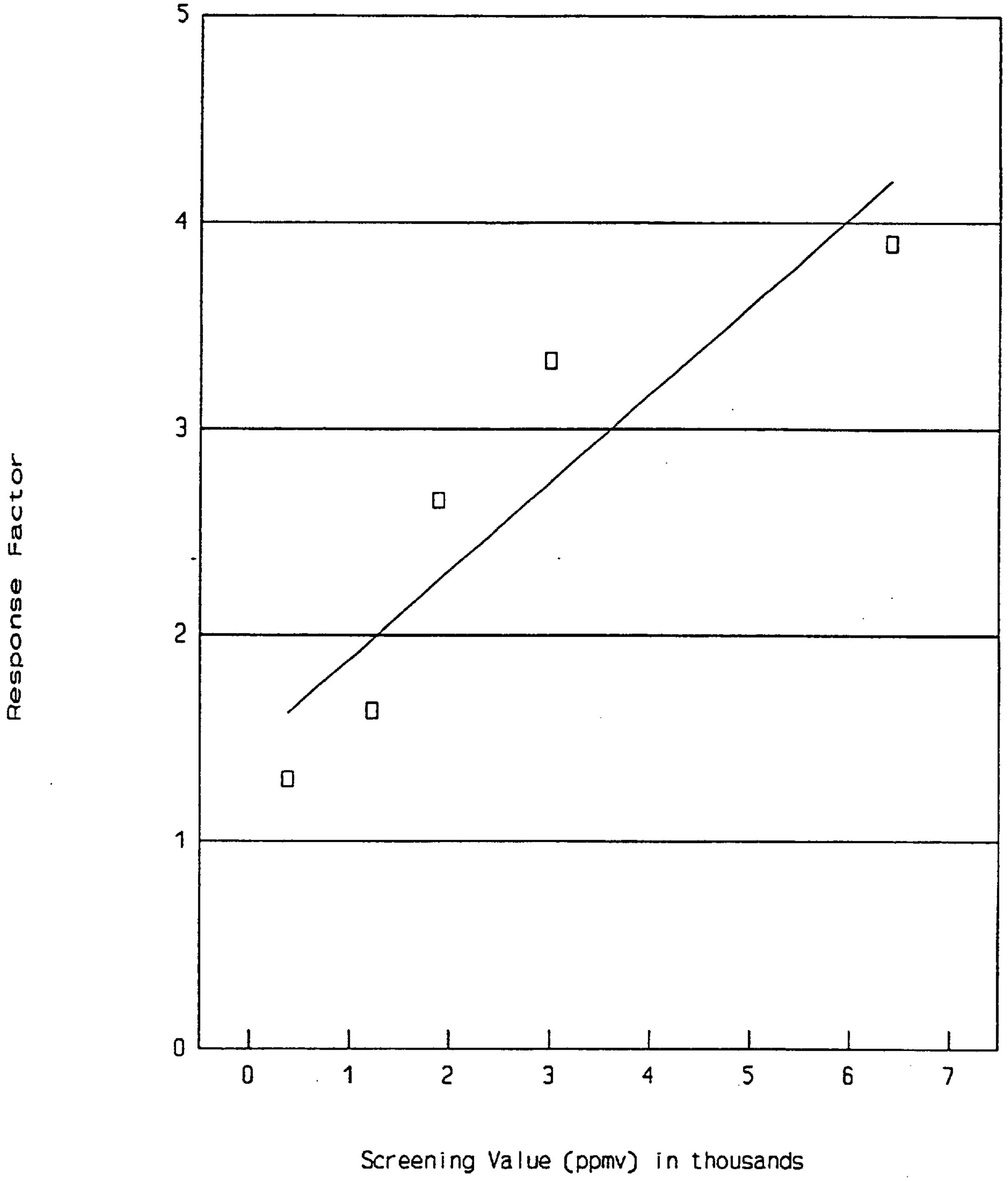

Figure A-2. Response Factor Curve Generated by Analytical Determination of Response Factors

TABLE A-11. RESPONSE FACTORS GENERATED FROM FIGURE A-2[a]

Equipment ID	Unadjusted screening value (ppmv)	Response factor of mixture	Adjusted screening value[b] (ppmv)	VOC Emission rate[c] (kg/yr)
B-1	0	--	Default zero	0.033
B-2	0	--	Default zero	0.033
B-3	0	--	Default zero	0.033
B-4	10	1.46	15	0.76
B-5	30	1.47	44	1.9
B-6	250	1.56	390	11
B-7	500	1.69	845	21
B-8	2,000	2.31	4,620	87
B-9	5,000	3.60	18,000	270
B-10	8,000	4.20	33,600	450
B-11	25,000	4.20	105,000	1,140
B-12	Not screened	--	--	87[d]
Total Emissions of Stream B				2,070

[a] Equipment type: Light liquid pumps
Correlation equation: Leak rate (kg/hr) = 1.90×10^{-5} $(SV)^{0.824}$
Default-zero mass emission rate: 7.49×10^{-6} kg/hr
Hours of operation: Stream B = 4,380

[b] Adjusted SV = (unadjusted SV) × (RF of mixture taken from Figure A-2).

[c] VOC Emissions = (correlation equation or default-zero emission rate) × (WP_{VOC}/WP_{TOC}) × (hours of operation).

[d] VOC Emission = (no. of components) × (average emission factor) × (wt. fraction of VOC) × (WP_{VOC}/WP_{TOC}) × (hours of operation).

TABLE A-12. ANNUALIZING EMISSIONS FOR LIGHT LIQUID PUMP A-15a

Hypothetical date	Screening value (ppmv)	Hours elapsed since last screening value[b]	VOC emissions since last screening value[c] (kg)
January 1	5,000	--	--
February 1	0	744	0.006
March 1	0	672	0.005
April 1	8,000	744	23.3
May 1	100	720	0.6
June 1	1,000	744	4.2
July 1	0	720	0.005
August 1	0	744	0.006
September 1	0	744	0.006
October 1	10,000	720	27.0
November 1	0	744	0.006
December 1	0	720	0.005
January 1	0	744	0.006
	TOTALS:	8,760	55.1

[a] Equipment type: Light liquid pumps
Correlation equation: Leak rate (kg/hr) = 1.90×10^{-5} $(SV)^{0.824}$
Default-zero mass emission rate: 7.49×10^{-6} kg/hr

[b] Hours elapsed since the last screening value was obtained. For example, the hours elapsed since the screening value obtained on March 1 are the hours from February 1 to March 1, which equal 24 hr/day × 28 days, or 672 hours.

[c] VOC Emissions = (correlation equation or default-zero emission rate) × (WP_{VOC}/WP_{TOC}) × (hours elapsed).

A-9. ESTIMATING VOC EMISSIONS FROM EQUIPMENT CONTAINING ORGANIC COMPOUNDS NOT CLASSIFIED AS VOC's.

Stream C contains ethane, which is an organic compound, but is not classified as a VOC. When a monitoring instrument is used to screen equipment in Stream C, the resulting screening value will include measurement of the ethane. However, the ethane should not be included in the estimated VOC emission rate. The following equation is applied to subtract out the ethane contribution:

$$E_{VOC} = E_{TOC} \times (WP_{VOC}/WP_{TOC})$$

where:

E_{VOC} = The VOC mass emissions from the equipment (kg/hr);

E_{TOC} = The TOC mass emissions from the equipment (kg/hr); calculated from either the Average Emission Factor, Screening Ranges, Correlation, or Unit-Specific Correlation approaches;

WP_{VOC} = The concentration of VOC in the equipment in weight percent;

WP_{TOC} = The TOC concentration in the equipment in weight percent.

The above calculation is demonstrated below by assuming that screening values have been obtained from equipment in Stream C as either greater than or equal to 10,000 ppmv or less than 10,000 ppmv. Assume 2 of the 40 gas valves in Stream C screened above 10,000 ppmv, and the remainder screened below 10,000 ppmv. Uncorrected VOC emissions are calculated using the Screening Ranges Approach:

$$E_{TOC} = (F_G \times N_G) + (F_L \times N_L)$$

where:

E_{TOC} = TOC emission rate for an equipment type (kg/hr);

F_G = Applicable emission factor for sources with screening values greater than or equal to 10,000 ppmv (kg/hr/source);

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