American Petroleum Institute

Compilation of Field Analytical Methods for Assessing Petroleum Product Releases

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Compilation of Field Analytical Methods for Assessing Petroleum Product Releases

Health and Environmental Sciences Department

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ABSTRACT

A variety of improved field-based methods are available to perform on-site analyses of organic compounds in soil and groundwater samples. The appropriate use of these field analytical methods can increase spatial site information in less time and with fewer assessment phases than conventional sampling methodologies using offsite laboratories. This report presents a compilation of the most widely used field analytical methods, including total organic vapor analyzers, field gas chromatograph, immunoassay, infrared analyzers, and dissolved oxygen/oxidation-reduction potential electrodes. Practical applications and limitations of each method are discussed and an objective-oriented Data Quality Classification scheme is presented to assist in selecting the appropriate method for the task. There is a chapter surveying other field analytical techniques not as widely used but showing promise for future application.

This publication is the first of two documents, designed to fill the gaps that now appear to exist in the application of certain field technologies for the analysis of petroleum hydrocarbon contamination. The second report will address technology selection, QA/QC protocols, and recommendations for training and recordkeeping.

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EXECUTIVE SUMMARY

Over the last decade the variety and capability of field-based analytical methods used to analyze organic compounds have significantly increased. In the past 3 to 4 years, tremendous advances in portable and transportable instrumentation have been made that enable cost-effective on-site analysis of soil and groundwater samples. The analytical results from these improved methods can be an integral part of the site characterization where on-site decision-making is used to direct the investigation. Appropriate use of these methods in this approach can result in increased spatial definition of contaminant distribution and subsurface characteristics. At many sites, this information is usually obtained in less time and with fewer phases of assessment than typical of conventional sampling with off-site or fixed base laboratories. If off-site laboratory analyses are needed, field analytical results can be used to minimize the number of samples shipped off site to the laboratory. Consequently, the use of field analytical methods can, for many investigations, lower the costs of the site characterization to less than those incurred in the conventional approach using off-site laboratories.

Some site owners and investigators realize the cost- and time-effectiveness of field analytical methods but are reluctant to use them for a variety of reasons, including the following:

- Lack of regulatory acceptance and clear guidance.
- Lack of information on type and quality of data provided by each method.
- Uncertainty regarding the capabilities, limitations, and practical considerations for each method.
- Lack of supporting field information and performance data for specific methods.
- Perception that field analytical methods do not provide data of adequate quality for decision making.
- Perception that field analytical methods do not necessarily result in cost savings.
- Absence of willingness and mechanisms for making on-site decisions while the investigation is ongoing.

Optimal use of these field analytical methods requires that quantitative methods be distinguished from qualitative field screening. Several field analytical methods that are currently used only for "screening" activities can also provide reliable quantitative information that does not necessarily require a high degree of validation at off-site laboratories. This validation/confirmation process often impedes the site characterization process and relegates field analytical methods that may provide higher quality data to a secondary screening role.

The key to the effective use of field analytical methods, whether for screening or for interpretative purposes, is to optimize their reliability through informed and consistent test selection, field protocols, and quality control. The primary goal of this compilation document is to provide information that can assist and enable effective use of these field analytical methods.

In this document, technical and practical information is compiled on five field analytical methods used for evaluating petroleum release sites. The methods presented are most frequently used at underground storage (UST) sites and are considered to be relatively mature techniques (compared with emerging field analytical methods). Packaged equipment is available through several vendors for use in these methods. The following field analytical methods are discussed in detail in the compilation document:

- Total organic vapor (TOV) detectors and headspace analysis
- Field gas chromatographs
- Immunoassay field test kits
- Portable infrared detectors
- Dissolved oxygen and oxidation reduction potential (DO/REDOX) electrodes

Much of the information compiled on the different field analytical methods focuses on principles of operation and application. Each manufacturer and investigator may have developed a specific variation on the instrumentation and procedures for a particular method; therefore, use of the compilation document in combination with the manufacturers' literature will provide the best basis for an overall evaluation of the effective use of a particular field analytical method. A brief summary of each method is presented which (1) describes the method; (2) identifies the appropriate application and limitations for evaluating hydrocarbon contaminants/constituents of concern; and (3) specifies quality control checks that should be included in the field analysis quality assurance program.

A general scheme is presented in the compilation document for field analytical methods of different data quality. The quality of the data generated by a particular method is referred to as the data quality level (DQL). DQLs are based on data quality classifications for site investigations that were developed by the New Jersey Department of Environmental Protection and were modified for use in this compilation document based on a review of method operation and reported use.

TOTAL ORGANIC VAPOR (TOV) DETECTORS

TOV detectors and headspace analysis are discussed in Section 3. TOV headspace analysis is widely used to provide relatively low-cost screening of soil and groundwater for volatile hydrocarbons. The primary applications for which this method is best suited include:

- Qualitative "hot spot" or source area screening of volatile hydrocarbons in soil;
- Selecting soil boring, soil vapor monitoring, and soil vapor extraction locations; and
- Identifying potential vapor pathways and infiltration in underground structures.

TOV headspace analysis is less suited for screening of groundwater and less volatile contaminants found in heavier fuels such as diesel fuel and weathered gasoline. The total volatile organic concentrations measured are indicative of the total fraction of the vapor entering the detection instrument. The TOV concentrations are therefore general, qualitative measurements and TOV instruments are not suitable for analysis of specific constituents or samples containing low (e.g., <1 ppm) volatile organic concentrations.

TOV analyzers are direct reading instruments equipped with a flame-ionization detector (FID) or a photoionization detector (PID).

In general, volatile hydrocarbons (aromatics, alkanes, alkenes, and alkynes) and the natural gas constituents (e.g., methane) plus the C_4 to C_8 fuel constituents, depending on the detector, are measured. Headspace analysis is best suited for relatively fresh or slightly weathered gasoline.

There are two general types of headspace analysis: static and agitated. For static headspace analysis, the sample is kept stationary for a period of time to allow volatilization of hydrocarbon constituents with high vapor pressures prior to analysis. The agitated headspace procedure consists of agitating the sample in the container for a standard period of time prior to analysis. In some cases, the sample is heated to promote volatilization. The sample volume, size and type of containers used, headspace volume, sample preparation techniques, quality assurance/quality control and detection limits depend on the particular headspace technique and TOV detector used.

The estimated cost for performing the TOV headspace analysis ranges from $1 to $5 per sample for the static and agitated jar headspace analysis and $10 per sample for the agitated headspace analysis using the polyethylene system. The estimated analytical time is 10 minutes per sample for the jar methods and the polyethylene bag system.

GAS CHROMATOGRAPHS

Section 4 discusses the use of field gas chromatographs (GCs) to support investigations of petroleum product releases. GCs are the most widely used analytical instruments for constituent-specific analysis of groundwater, soil, and soil vapor samples for volatile and semivolatile hydrocarbons.

Analysis of soil and groundwater samples using field GCs involves preparation of the soil or groundwater sample, injection of an aliquot of sample headspace or extract, separation in the GC column, and measurement by the selected detector (e.g., FID, PID). Soil or groundwater samples are commonly prepared by headspace development, purge and trap, or solvent extraction. The key component for proper selection of GCs is the detector. FIDs will measure a general range of hydrocarbons, including aliphatic and aromatic hydrocarbons. PIDs are generally best suited for measuring aromatics (e.g., BTEX) at a higher sensitivity.

Field GCs are available in two general types: portable GCs and transportable GCs. Portable GCs generally involve less capital cost than transportable GCs and are compact in size, operate isothermally, and contain internal batteries and operating gas supplies. Transportable GCs are laboratory-grade instruments which require external power and gas supplies. Sample preparation for portable GCs is often done by headspace development. Sample preparation for transportable GCs can be done by either headspace development or solvent extraction used in conjunction with purge and trap. In general, transportable GCs can provide higher resolution of individual constituents than portable GCs primarily because of the longer column length and step heating of the sample. Although portable GCs may have less resolution, they can provide constituent-specific information that can be useful for risk evaluation and on-site decision making.

Field GCs can provide high quality data that can be used to meet a wide range of assessment objectives. The primary applications for which field GCs are best suited include:

- Quantitative analysis of contaminant indicators such as Gasoline Range Organics (GRO) and Diesel Range Organics (DRO);
- Quantitative constituent analysis to parts per billion (ppb) in groundwater; and
- Contaminant delineation in soil and groundwater plume mapping.

Field GCs are least suited for quantitative analysis of fuels heavier than gasoline and light distillates, highly contaminated media (e.g., >100 ppm), and open air environments with high background concentrations. Samples with high concentrations may need to be diluted and reanalyzed in order to bring concentrations into the calibration range of the instrument and to discriminate the individual peaks on a chromatogram. If many peaks are present, the separation of peaks may not be adequate to resolve specific constituents. In this case, integration of the total chromatogram can be used to determine total volatiles or contaminant indicators, depending on whether a headspace sample was taken (for volatiles only) or a solvent extraction was performed (for contaminant indicators).

Field GCs can discriminate and quantify specific constituents and generate a high level of data. Often, the regulatory agency overseeing an investigation requires the analysis and reporting of individual constituents of concern to determine the potential risk of exposure. This is especially the case for benzene or BTEX constituents. By resolving specific constituents, the location of the source areas and delineation of the magnitude and extent of contamination in soil and groundwater can be evaluated.

The approximate cost of analysis ranges from $50 to $70 per sample. Analytical time per sample is 10 to 40 minutes.

IMMUNOASSAYS

Section 5 discusses the application of Immunoassay test kits for on-site measurement of petroleum product releases. Immunoassay field tests measure a target constituent or analyte using antibody-antigen reactions where an antibody is developed to have a high degree of selectivity and sensitivity to that target constituent. Immunoassay testing has been successfully used in the medical industry for years, and is currently being used as a field analytical method for hydrocarbons, pesticides, and PCBs. Contaminants are extracted from soil samples using a solvent (e.g., methanol); water samples are analyzed directly. The extract or water is placed in a reaction vessel (e.g., test tube) that contains the antibodies. Reagents which behave as tracers (e.g., enzyme conjugates) are added in a series of steps with appropriate incubation periods. The target analyte "competes" with an enzyme conjugate for a limited number of antibody binding sites. A substrate solution is then added and reacts with the enzyme conjugate to produce a color. The intensity of the color is inversely proportional to the contaminant concentration of the target analyte in the sample. The absence/presence or relative concentration is made by comparing the color developed from the unknown sample with a reference standard, or measured directly on a small portable colorimeter.

Depending on the biochemical design, a particular test kit will measure a specific constituent (e.g., benzene), a set of constituents (e.g., BTEX), or a general assay range (total petroleum hydrocarbons). Depending on the manufacturer, immunoassay test kits are designed for either semiquantitative or quantitative analyses. For semiquantitative analyses, an action level is set and the assay will indicate if the sample concentrations are above or below that level. Alternatively, multiple action levels can be set to place the sample in a discrete range (e.g., above 100 ppm but below 1000 ppm). For quantitative analyses, multipoint calibration curves are used that are usually internal to the colorimetric detector. The selection of the most appropriate kit is related to (1) the design of the kit (i.e., action level, concentration range, or specific concentration); (2) what parameter needs to be measured; and (3) the objective of the assessment.

Immunoassay test kits can provide high quality data that can be used to meet a wide range of assessment objectives. The primary applications for which immunoassays are best suited include:

- Detection of a wide range of fuels;
- BTEX/benzene or TPH in soil; and
- Source area/zone of contamination mapping in soil.

Immunoassay test kits are least suited for BTEX or TPH analysis at low concentrations (e.g., <1 ppm) in groundwater, analysis of clay-rich soils, and analysis of highly weathered/biodegraded hydrocarbons. Extraction recoveries of contaminants is difficult from clay-rich soil. Certain test kits can overestimate weathered gasoline concentrations in soil when compared to laboratory methods (both GC and IR).

When choosing which kit to use, the selectivity of the test needs to be closely examined to assure that the appropriate parameters are not biased. For example, certain BTEX kits use antibodies that are designed to bind preferentially to toluene and xylenes, and to some extent, to naphthalene. They have little affinity (cross-reactivity) for benzene. A benzene-specific immunoassay test, however, is currently available and may be used for an evaluation of groundwater quality. The detection limit and accuracy of a particular immunoassay kit depends largely on how close the mixture of contaminants on-site is to the mix of antibody target constituents.

The estimated cost of analysis ranges from $20 to $60 per sample. Five to eight tests can be completed per hour by an experienced operator analyzing samples in batches.

INFRARED DETECTORS

Section 6 discusses the field application of portable infrared (IR) detectors. Portable infrared detectors can be used to perform total recoverable petroleum hydrocarbon (TRPH) analyses of soil and water relatively quickly. The comparable laboratory methodology is EPA Method 418.1. The reference method includes fluorocarbon-113 extraction of petroleum hydrocarbons from soil, followed by IR analysis. The field IR extraction procedure uses different extraction apparatus than the laboratory method. The extract is passed through a small column of silica gel to remove naturally occurring polar hydrocarbons.

Field IR methods are best suited for the following applications:

- Detection of a wide range of heavier hydrocarbons such as diesel and motor oil (C_6 to C_{26} range, hydrocarbons with boiling points >70°C);
- Detection of relatively higher hydrocarbon concentrations; and
- Source area/zone of contamination mapping in soil.

Portable IR detectors are least suited for evaluating "fresh" unweathered volatile gasoline and hydrocarbons in clay or organic-rich soil. Although the method is applicable to the measurement of light fuels, approximately half of any gasoline present may be lost during the extraction process. The extraction process itself is potentially a significant limitation for using this method. The solvent currently being used for extraction (fluorocarbon-113) will likely be phased out in the near future. Other solvents are being examined; however, there is no equivalent solvent for this method at this time, and continued use of this method will likely require that a new solvent be found. In addition, volatile constituents may be lost by evaporation during the extraction process. No simple method exists for directly comparing the portable IR results for different fuel types which have different volatile constituent compositions.

The estimated cost of analysis ranges from $5 to $31 per sample and the estimated analytical time per sample varies from 5 to 20 minutes.

DISSOLVED OXYGEN AND OXIDATION POTENTIAL DETECTORS

Section 7 discusses the use of dissolved oxygen and oxidation/reduction potential (DO/REDOX) electrodes for field use. Field measurements of dissolved oxygen (DO) and oxidation/reduction potential (REDOX) can be performed using a number of available methods. Many DO probes consist

of a membrane covering a sensing electrode that measures reduction of oxygen dissolved in groundwater. REDOX electrodes measure the electron affinity of the oxidizing and reducing species in groundwater. These probes can be used either "down hole" or on site once a water sample has been removed as either a discrete sample or by flow-through sampling. DO meters may perform and operate differently. For example, DO is actually consumed by most meters during measurements. These meters characteristically exhibit a decreasing trend in DO levels within a few minutes of when the sensor probe is placed in water. Other DO meters do not consume oxygen and therefore will provide more stable readings over time.

DO/REDOX measurements are best suited for use in groundwater with low organic content and a reducing environment. The primary use for DO/REDOX is to evaluate and monitor *in situ* remediation. Dual DO/REDOX measurements can be complementary. For example, if REDOX measurements are negative, indicating a reducing environment, the corresponding DO measurement should also be low (e.g., <1 mg/L). DO can also be used during well purging to determine when the well has been sufficiently purged prior to sampling.

In addition to the sensors and probes used to make DO measurements, the sample collection procedure can also influence the results. Some practitioners will perform in-well measurements with down-hole probes. General experience indicates that this approach produces highly variable results (by 1 to 2 mg/L or more). Many practitioners raise and lower the sensor probe to circulate the water within the well in an attempt to avoid errors caused by oxygen consumption. Another approach is to set up a flow-through cell above the ground in which the sensors are placed. Water is slowly pumped (e.g., 100 mL/min) and passed through the cell. A continuous source of water is provided, and thereby minimizes concerns about the influence of oxygen consumption.

REDOX measurements cannot be assigned to a specific oxidizing or reducing species in the field unless the sample composition is known. Active fouling by high concentrations of sediment and other insoluble materials, oils, and biological growths that react, coat, or clog the surface of the membrane in the DO and the REDOX probes will affect the instrument readings.

The acquisition cost for DO meters is high while maintenance and operating costs are quite low. Acquisition cost of REDOX electrodes for portable pH meters is low. The cost of submersible REDOX sensors, however, is high. Maintenance and operating costs for REDOX electrodes and sensors are low.

EMERGING TECHNOLOGIES

A variety of emerging field analytical methods are being developed, tested, and used for evaluating petroleum releases. The emerging methods identified in this document are those that are commercially available and have been tested and used to a limited extent for evaluating petroleum releases. The methods described include: fiber optic chemical (FOC) sensors, visible ultraviolet (UV) fluorescence UV fluorescence spectroscopy, UV absorption spectroscopy, and gas chromatography/mass spectrometry (GC/MS). The number of manufacturers, instrument models, application at petroleum release sites, and available performance information is limited for all of these methods except for GC/MS. To date, GC/MS typically has been employed primarily in mobile laboratories and generally has not been used as a field analytical method at petroleum release sites.

Section 1
INTRODUCTION

BACKGROUND

In the last decade, and especially in the last 3 to 4 years, there has been a dramatic increase in the variety and capability of field-based analytical methods that can be used to analyze organic compounds. Tremendous advances in portable and transportable instrumentation and improvements in the methodologies have been made that enable the rapid and cost effective on-site analysis of soil and groundwater samples. The use of these improved field analytical methods can result in an effective site characterization that is conducted in a more streamlined fashion than conventional assessments.

Currently, it is not clearly defined how these technologies can be integrated into the present site characterization process and whether there is significant difference in the quality of the conclusions drawn about the site contamination or the resultant decisions that are made. One thing is certain about the current cost consciousness and regulatory climate: current laboratory-based testing methodologies cannot support all of the needs of environmental decision-making in a cost effective manner at underground storage tank (UST) sites.

Conclusions of a U.S. Environmental Protection Agency (EPA) -sponsored symposium on measuring and interpreting volatile organic compound (VOC) data in soils (EPA, 1993) called for a greater emphasis to be placed on the use of field analytical methods for decision-making purposes. As part of these conclusions, it was indicated that laboratory analytical results were not inherently superior to field analytical results for decision-making. A key requirement for optimal use of field methods, however, is that quantitative field analytical methods must be distinguished from qualitative field screening. In fact, field analyses when used in appropriate circumstances may provide more reliable results. Consequently, part of the objective of this project is to differentiate qualitative versus quantitative methods, which may be better defined in terms of "reliability."

Many field analytical methods are being evaluated for use in Resource Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response Compensation and Liability Act (CERCLA) as well as UST-expedited characterizations [e.g., proposed 4000 series methods, EPA's Monitoring and Measurements Testing Program as part of the Superfund Innovative Technologies Evaluation (SITE) Program, and development of improved field methods by EPA's Environmental Monitoring Systems

Laboratory]. Select state regulatory programs are also in the process of examining existing field methods to determine their appropriate use (e.g., New Jersey Department of Environmental Protection and Energy Field Analysis Manual). In addition, the Department of Defense (Wynne, 1991) and Department of Energy (Frank *et al.*, 1991) are developing and evaluating a variety of field analytical methods.

Although the evaluation and use of field analytical methods for conducting on-site analysis of hydrocarbon-contaminated soil and groundwater is commanding increased acceptance and notoriety, such methods are still not currently in wide use, probably for the following reasons: (1) the lack of clear regulatory acceptance (some regulatory programs allow the use of field methods but have not clearly defined their use); (2) the perception that field analytical methods do not provide data of adequate quality for making regulatory or remedial decisions; and (3) the perception that field analytical methods do not necessarily result in cost savings. Further, more explicit reasons are primarily related to actual use of these methods in the field, such as:

- Lack of information on the type and quality of data provided by each method;
- Uncertainty regarding the capabilities, limitations, and practical considerations of each method;
- Lack of information on the appropriate selection and use of each method in an effective site characterization and corrective action strategy or process [i.e., the best method(s) and application of these methods for measuring the type of contaminant(s) present at a specific site];
- Lack of a framework or guidelines in which to conduct field analyses and interpret resulting data;
- Concerns with operator training and quality assurance/quality control (QA/QC) issues;
- Inability to recognize the advantages of using field analytical methods; and
- Reluctance of the site owners and the consulting community to take the time to inform State regulators of the benefits of field-generated data and to encourage acceptance where appropriate.

Because of the potential misapplication of these field analytical methods, site owners may consider the use of these methods to be a cost that is incurred in addition to "standard" laboratory analytical costs (i.e., another layer of cost). In most investigations, however, the appropriate use of these methods could result in an effective characterization with increased spatial and temporal information in less time and with fewer phases of assessment than typical of conventional sampling with off-site or fixed-

base laboratories. If laboratory analyses are needed, field analyses can be used to minimize the number of samples shipped off-site to the laboratory. Consequently, the initial site characterization costs would probably be lower than those incurred in the conventional approach using off-site laboratory analyses. Some site owners and investigators realize the cost and time effectiveness of field analytical methods but are reluctant to use them because of the lack of supporting field information on each method and lack of regulatory acceptance/guidance.

PURPOSE AND SCOPE

API intends to publish a series of documents to fill the gaps that now appear to exist in the application of certain field technologies for the analysis of petroleum hydrocarbon contamination, with specific emphasis on petroleum fuels, but with some potential application to heavier products and fractions of crude oil. Since fuels are best suited to field analyses, UST site assessments are the most appropriate. CERCLA (Superfund) and RCRA Corrective Action regulations, however, also allow for streamlined site assessments based on on-site analysis. The documents to be published, therefore, have applicability for all of the above and are intended to evolve as follows:

> Phase I - A compilation of technical information and resources on various techniques, with summarized performance specifications and data quality classification.
>
> Phase II - A decision tree on technology selection, QA/QC protocols for the field, a manual on how to optimize use in the field, and recommendations for training and record keeping.
>
> Phase III - A field demonstration of data gathering, interpretation, and decision-making of a selected mix of technologies.

The purpose of this report is to compile technical and practical information on five selected field analytical methods for characterizing petroleum release sites (Phase I). The technologies selected are most frequently used in UST situations and are considered to be examples of mature techniques. These techniques have packaged equipment or kits that are available through several vendors on the market. In addition, another five were reviewed as emerging technologies that are developing but are not in widespread use or uniquely suited for petroleum fuel situations. This report is intended to summarize information on each of the five mature methods, which includes (1) data quality classification; (2) the compound(s) or indicator measured; (3) the achievable and practical detection or quantitation limit; (4) general QA/QC practices; and (5) interferences, limitations, and other practical considerations. The following field analytical methods are included in this report:

- Total Organic Vapor (TOV) Detectors and Headspace Analysis
- Field Gas Chromatographs

- Immunoassay (IA) Field Test Kits
- Portable Infrared Detectors, and
- Dissolved Oxygen/Oxidation-Reduction Potential (DO/REDOX) Electrodes

This report provides a summary of these five field analytical methods currently being used by investigators. An overview of data quality classifications for these methods is presented in Section 2. This overview is intended to provide a general context for using the methods described in Sections 3 through 7. Section 8 provides an overview of new and emerging field analytical methods, without performance summaries.

Much of the information compiled on the different field analytical methods focuses on principles of operation and application. Each manufacturer and investigator may have developed his own specific variation on the instrumentation and procedure for a particular method. Therefore, this document, in combination with the manufacturer's literature, will provide the best overall picture for potential users. This is reflected in the literature, which reports variable information for different procedures and instruments used for a particular method. Variations and performance information for different procedures, media, and instrumentation are reported where available.

Section 2
DATA QUALITY CLASSIFICATIONS

The quality of the data that can be generated using a particular field analytical method is referred to in this report as the data quality level (DQL). DQLs are based on data quality classifications developed by the New Jersey Department of Environmental Protection (NJDEP, 1994) and were modified for use in this report. These NJDEP data quality classifications are based on those developed by the EPA and are used by the NJDEP as a guide to define the minimum data quality standards for contaminant investigation plans. Table 2-1 presents a summary of the DQLs along with the modifications.

Two significant modifications have been incorporated into the quality level scheme that should present a more definitive description for selecting the quality of testing that may be preferred at a site. First, the Field Applications column was made more "job" or objective oriented. This was because, in many cases, selecting the test procedure and the associated quality of data is driven by the job at hand. For example, the following objectives would normally require somewhat different levels of data quality: well placement, mass identification or removal, plume configuration with or without isopleth delineation, monitoring, and clean fringe detection.

The second modification was the designation of Levels 1A and 1B as screening levels, either qualitative or semiquantitative, which normally require confirmatory laboratory analyses. Levels 2, 3, and 4 are considered basically quantitative, with Level 2 being less reliably quantitative than Level 4. These levels could produce data of sufficient quality that they would not necessarily need routine laboratory confirmation. They generate interpretive rather than screening results.

It is important to define the measurement "quality" of methods as it relates to the data quality classification levels noted in Table 2-1. Qualitative techniques, as described in this document, identify a substance or mixture of constituents and, as such, have formats that do not produce specific values or data points. A positive/negative result or a pass/fail are examples of formats that basically identify the presence or absence of a substance of concern.

Semiquantitative techniques measure constituents in a sample and produce results that are within ranges of concentrations, such as 10X, 100X, and 1000X. Therefore, they can identify and grossly estimate concentrations of constituents.

Table 2-1. Data Quality Levels (DQL) for Field Analytical Methods

Data Quality Level[1]	Field Applications	Methodologies[2,3]
1A Screening: Qualitative	- Health and safety monitoring - Qualitative contaminant screening	- FID and PID portable meters - Jar headspace analysis
1B Screening: Semiquantitative	- Contaminant mass location	- TOV bag headspace analysis with QA/QC
2 Delineation: Quantitative	- Contaminant plume delineation - Well placement - Remediation (process) monitoring	- Immunoassay - Portable Infrared analyzers - Field (portable) Gas Chromatographs - DO/REDOX meters (SW-846 field methods, as above) - Mobile laboratories (noncertified methods)
3 Clean Zone: Quantitative	- Clean zone delineation - Regulatory monitoring - Site closure	- Standard laboratory analyses with SW-846 QA/QC - Mobile laboratories with certified methods
4 Nonstandard Quantitative	- Constituent surveys of unknown contamination - Specialty analyses	- Survey instrumentation, e.g., gas chromatography/mass spectrometry (GC/MS) - Modified laboratory methods, with full QA/QC

[1] Data Quality Classifications are modified from NJDEP classifications, noted in Field Analysis Manual, July 1994.

[2] Methodologies noted would be suitable for all data quality levels above the category in which it is placed. For example, a portable GC (Level 2) can be used for Level 2, 1B, or 1A field applications, but not for higher Levels 3 and 4.

[3] Only those field methodologies reviewed in this report are noted.

Finally, quantitative techniques are defined as having test formats that express results in a specific quantity or amount, such as percent or parts per million (ppm). Some techniques obviously have greater accuracy and precision than others, with most field methods falling into Data Quality Level 2 - moderate accuracy and precision. In addition, measurements may be by individual compound (e.g., benzene) or by groups of compounds [e.g., benzene, toluene, ethylbenzene, xylenes (BTEX); polynuclear aromatic hydrocarbons (PNAs); and total petroleum hydrocarbons (TPHs)]. The results, however, all have numerical values associated with them that can potentially be used for statistical evaluation and interpretation.

This section provides an overview of the DQLs and classification of various analytical methods. It is intended to provide a general context for using the various field analytical methods presented in later sections of this report. State regulatory programs may develop their own definitions for data quality for these methods, and may have specific reporting requirements when using these methods. Details on DQLs, use of field analytical methods, and specific reporting requirements can be obtained by contacting the appropriate state environmental regulatory agency or other local jurisdictions.

DATA QUALITY LEVEL 1A

Level 1A field analytical methods can be used for health and safety evaluations of ambient air and initial contaminant screening of soil and groundwater. The data from flame-ionization detector (FID) and photoionization detector (PID) portable meters and jar headspace analyses are qualitative and only provide an indication of the presence of contamination above a specified value (i.e., pass/fail, positive/negative, or low/medium/high). Because the measurements made with these methods may not always be consistent, the data should be used only as an initial screening for evaluating sample locations for analysis using higher level methods.

Clean samples cannot be determined solely from methods at this DQL. QC is limited primarily to instrument calibration, consistency in the method procedure, and background level checks. Data quality is very much a function of sample handling techniques, the instrument, and the skill of the investigator.

DATA QUALITY LEVEL 1B

Level 1B field analytical methods can be used for qualitative and semiquantitative screening and defining the location of known types of contamination (i.e., orders of magnitude or ranges). Level 1B data can be generated when Level 1A TOV instruments are used with a more controlled sample preparation (e.g., agitation, heating, etc.) and analysis procedures that include additional QA/QC requirements such as TOV polyethylene bag headspace. QA requirements include multipoint calibration curves generated using matrix-spiked standards, a calibration check using matrix spike duplicates at least twice during a day (or 1 per 20 samples), and a field blank/background sample. Depending on the state or local regulatory agency, laboratory confirmation analyses may be needed for establishing laboratory-field correlation over the concentration ranges measured and for confirming the achievable lower detection limit.

DATA QUALITY LEVEL 2

Level 2 field analytical methods can be used for delineation of contamination, in addition to the work activities noted in Levels 1A and 1B. Level 2 methods are typically laboratory methods that have been adapted for field use or are EPA-derived, such as SW-846 field methods. Level 2 methods may not be as rigorous (e.g., field extractions are typically not directly comparable with the laboratory extraction methods) as the corresponding laboratory methods.

QA requirements include initial multipoint calibration curves, continuing calibration checks, matrix spike duplicates, background/blank samples, and laboratory confirmation of clean or contaminated samples. In addition, a matrix spike recovery should be performed on a site-specific basis.

Level 2 methods are quantitative in that they provide a direct numerical value for the contaminant indicator [e.g., total recoverable petroleum hydrocarbon (TRPH) or BTEX] measured. Depending on the state or local regulatory agency, laboratory confirmation analyses may be needed for establishing laboratory-field correlation over the concentration ranges measured and for confirming the achievable lower detection limit. Level 2 methods also include EPA field screening and laboratory methods from SW-846. The laboratory methods considered to be Level 2 have limited documented QA information. The quality of the data generated using Level 2 laboratory methods depends on the sample handling, storage, and preservation procedures, and the analytical procedures and QC used.

DATA QUALITY LEVEL 3

Level 3 analytical methods are approved laboratory methods with complete QA/QC (e.g., EPA SW-846 Laboratory Methods, 3rd or more recent edition) that may be used to confirm "clean" samples and for regulatory monitoring, as opposed to site assessment for Level 2. Level 3 analyses can be performed at off-site laboratories or on-site mobile laboratories that perform EPA methodologies (not modified methods). Certain regulatory agencies may require these laboratories to be certified.

DATA QUALITY LEVEL 4

Level 4 methods are laboratory methods specifically developed for a particular site or contaminant and are used when standard laboratory methods are not practical or appropriate. Generation of Level 4 data may require the use of a laboratory that specializes in methods development, with subsequent use of those methods at an on-site field laboratory.

Section 3
TOTAL ORGANIC VAPOR DETECTORS AND HEADSPACE ANALYSIS

SUMMARY

TOV instruments or analyzers are widely used in the investigation of volatile hydrocarbons for initial qualitative screening of soil and groundwater samples. When different headspace analysis techniques are used, TOV instruments can also provide semiquantitative screening information. These instruments are relatively inexpensive, easy to operate, versatile in application, durable under field conditions, and can provide rapid results. Consequently, TOV analyzers allow the quick generation of a large number of screening analyses of volatile hydrocarbons at relatively low cost.

General TOV screening is typically performed by taking direct readings on the TOV instruments (PIDs and FIDs) in the ambient air immediately above soil or groundwater samples. TOV headspace analysis involves collecting a soil or groundwater sample, placing it in an airtight container (usually a glass jar or a polyethylene or tedlar bag), allowing the volatile hydrocarbons to partition into the headspace, and withdrawing a vapor sample for analysis by a TOV instrument. (The volume between the sample and the container is referred to as the headspace where vapors originating from the sample collect.)

Although TOV headspace analysis is relatively rapid and inexpensive, it only measures total volatile hydrocarbon concentrations in the vapor, not directly in the soil or groundwater. The total volatile concentrations are indicative of the total ionizable fraction of the vapor entering the detection instrument. These concentrations can be correlated with a sample of known contaminant concentration. Because preparation of the headspace is critical but highly variable, and the use of spiked field standards is limited, TOV headspace analysis is used primarily as a general, qualitative measurement and is not suitable for analysis of specific constituents or samples containing low (e.g., <1 ppm) concentrations of volatiles. In addition, false positives and negatives are a potential problem with TOV headspace analysis. Samples used for comparison with regulatory limits are usually verified by a higher quality analytical method except where the regulatory limits are based on a TOV headspace method.

METHOD OVERVIEW

Applications and Advantages

TOV headspace analysis can be used in the field to rapidly provide indications of contamination in soil or groundwater samples. TOV headspace screening of soil samples during sample collection activities is best suited for performing qualitative "hot-spot" or source area screening of volatile hydrocarbons in soil, selecting soil boring and soil vapor monitoring locations, identifying potential vapor migration pathways and the need for additional sampling, and selecting samples for laboratory analysis. (The UST section of the New Mexico Environmental Improvement Division allows the use of TOV headspace analysis to propose site closure. The Florida Department of Environmental Protection can provide guidance on the use of TOV headspace analysis to establish contamination levels for determining site categories for contaminated soils.) The capabilities and practical considerations for use of TOV headspace analysis are summarized in Table 3-1.

TOV headspace screening of groundwater can be used to determine if groundwater is impacted above a specified value and to make a preliminary determination of the extent of highly impacted groundwater. Because TOV detectors with static headspace analysis cannot detect low (<1 ppm) concentrations of specific constituents, they are not often used for this application.

INTERFERENCES AND LIMITATIONS

Headspace techniques that use TOV instruments do not distinguish specific constituents in hydrocarbon vapor samples and, therefore, represent an integrated response to the hydrocarbon mixture. When an unknown mixture of multiple constituents is analyzed, nonlinear responses can result from concentration variations of different constituents in the mixture. The selectivity and sensitivity of each TOV instrument to different hydrocarbon constituents can lead to bias in results. A multipoint calibration curve using spiked standards can be used as a reference for correlating the response from different instruments for the same headspace technique.

FID instruments are less sensitive than PID instruments to environmental effects such as temperature and humidity; however, high winds and excess carbon dioxide could extinguish the ionization flame. FIDs detect methane and background, or naturally occurring, volatile hydrocarbons that can potentially give anomalously high readings. FIDs require a relatively high sample flow rate for reliable readings. Restricting airflow can cause erratic readings and may deplete the oxygen present in the vapor sample below the level necessary (15 percent) to support the hydrogen flame.

Table 3-1. TOV Headspace Analysis Capabilities and Practical Considerations

	Capabilities	
Compounds detected:	Volatile hydrocarbons (aromatics, alkanes, alkenes, and alkynes), depending on the detector. Typically, natural gas constituents (e.g., methane) plus C_4 to C_8 fuel constituents. Specific constituents are not measured.	
Matrix:	Soils - Qualitative screening Water - Screening	
Achievable lower detection limits:	Variable depending on fuel or contaminant type measured, sample matrix, and the headspace method or detector used. Controlled procedures using a polyethylene bag can provide lower detection limits with greater precision than jar headspace methods and in some cases show correlation with laboratory water analyses. Variable ranges for the lower detection limits are provided below.[1,2]	
	Static and agitated jar headspace analysis:	Agitated headspace analysis using a polyethylene bag system:
Gasoline in water	10's to 100's mg/L range	0.1 to 1 mg/L range
Gasoline in soil	10's to 100's mg/kg range	1 to 10 mg/kg range
Diesel in soil	100's mg/kg range	10's to 100's mg/kg range
	Practical Considerations	
Soil type:	Clayey soils or soils with high organic content may result in incomplete soil desorption and yield erratic results when jar headspace techniques are used. Agitated headspace analysis of soils using the polyethylene bag method disaggregates the sample, thereby reducing the effects of these variables.	
Hydrocarbon type:	Headspace analysis is best for relatively fresh or slightly weathered gasoline. These techniques have been used for analysis of diesel fuels, but with much higher detection limits. Natural gas and petroleum-derived solvents are also measured.	
Estimated cost per sample:	Static and agitated jar headspace analysis:	$<1-5
	Agitated headspace using a polyethylene bag system:	$10
Estimated analytical time per sample:	Static and agitated jar headspace analysis:	10 minutes
	Agitated headspace using a polyethylene bag system:	10 minutes
Quality of data:	Static and agitated jar headspace analysis:	Level 1A
	Agitated headspace using a polyethylene bag system:	Level 1B
Difficulty of procedure:	Static and agitated jar headspace analysis:	Low
	Agitated headspace using a polyethylene bag system:	Medium
Laboratory method equivalent:	None approved.	

[1] Range refers to concentrations in soil or water as determined by laboratory analyses.

[2] Measured concentrations are a function of the range of sensitivity of the TOV instrument, the headspace method employed, contaminant type, and sample matrix.

PID instruments are affected by relative humidity and may become unusable under humid conditions when condensation occurs, which is indicated when the needle on the meter drops below zero on the scale. Jar headspace and bag headspace analyses measure vapors that are at nearly 100 percent humidity. PIDs do not respond to certain low-molecular-weight hydrocarbons such as methane and ethane, and do not detect constituents if the ultraviolet (UV) lamp selected has a lower energy than the ionization potential. In addition, nearby electrical sources, such as power lines and transformers, can cause interferences. PID readings should not be considered representative for hydrocarbon mixtures and for high concentrations. PID readings can be correlated with samples with known concentrations of aromatic hydrocarbons. Depending on the instrument, PIDs have a nonlinear response above 150 to 300 ppmv. In addition, sampling from a fixed or limited volume sample container may restrict the airflow and provide low readings. For headspace analysis, liquids should be prevented from inadvertently being drawn into the probe.

Correlations of TOV jar headspace analysis with laboratory analyses are poor. TOV jar headspace analysis using portable FIDs has been reported to grossly overestimate gasoline concentrations present in soil samples (Klopp, *et al.*). It is not clear why this is so, since many of the errors in sampling would appear to result in lower values for the field methods. Soil type (clay vs. sandy soils) may be a factor in poor correlation between TOV headspace and laboratory analytical results. The disparities between headspace analysis using the polyethylene bag sampling system and laboratory analyses depend on ensuring that a representative sample is taken for both methods and that the laboratory analyses are completed within the appropriate hold time. Consistent procedures should be followed, especially in preparing field standards (accurate injection of standards), to ensure complete volatilization of the standard and to establish instrument responses.

Sources of significant degrees of error in field measurements using TOV headspace techniques may be due to (1) vapor dilution by drawing air into the headspace while sampling; (2) inducing a vacuum in leak-tight and rigid sample containers that curtails detector response; and (3) not controlling concentration-dependent factors such as temperature, volume of headspace to sample, agitation time, and encapsulation time.

It is important to ensure that the headspace volume is sufficient compared with the sampling rate of the portable TOV analyzer to prevent outside air from accidentally being drawn in, thus diluting the analysis. When using PID analyzers, it is possible to use a recirculating loop so that the headspace

vapor passes through the PID and returns to the jar or bag. This is not possible with an FID, which is a destructive detector.

Comparison of field TOV data with laboratory total hydrocarbon analyses is complicated by the fact that the laboratory GC, with its FID having separate oxygen and hydrogen jets, has a very efficient response for carbon atoms. For hydrocarbons the response is generally proportional to the number of carbon atoms in the molecule: 1 ppm of octane will have a signal about four times that of 1 ppm of ethane. This is not true for the field instruments that use the ambient air carrier vapors as a source of oxygen for the FID. As a result, the combustion is inefficient and the response factors for individual hydrocarbons are variable and not directly comparable to that of a laboratory GC/FID. Response factors for different compounds should be provided by the manufacturer and checked periodically by the user.

Most readings from TOV instruments are provided in units above background or ppm relative to a gas standard. Unless these readings are reported and referenced to calibration curves generated from spiked field standards, they represent the relative response of the TOV instrument and the headspace used. Therefore, it is recommended that the instrument readings be reported along with all QC information (e.g., calibration curves). TOV headspace analysis does not measure nonvolatile hydrocarbons and is not suited for sites where the contamination is unknown or contains fuels with low volatility (e.g., diesel, fuel oil).

OPERATING PRINCIPLES/INSTRUMENTATION

The two types of TOV instruments commonly used with headspace analysis are PIDs and FIDs. Portable GCs are also employed for ambient headspace analysis with volatile organic analysis (VOA) vial methods (see EPA Method 3810) or with bag headspace methods, and will be discussed in Section 4.

Flame Ionization Detectors (FIDs)

Portable FIDs use a hydrogen flame to ionize most organic constituents that contain carbon and hydrogen in the vapor sample. The vapor sample is drawn through the instrument probe into the detection chamber, and into the hydrogen flame, which ionizes the sample. The resulting ionized molecules produce a current that is proportional to the ionized vapor sample. The FID will detect the presence of volatile hydrocarbon vapors, including methane, that may yield high natural background readings in areas where methane is higher than normal (e.g., wetlands, sewers).

Volatile constituents usually detected at petroleum release sites include lower-molecular-weight aliphatic hydrocarbons and the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes. Weathered gasoline and heavier fuels such as diesel fuel and fuel oils are not as readily detected using FIDs because of the low volatile content.

An example of the relative response of an FID for different hydrocarbon constituents is shown in Table 3-2 A direct-reading colorimetric detector tube can be used in conjunction with an FID to evaluate methane concentrations. A summary of different FID instruments is shown in Table 3-3.

Table 3-2. Relative Response of One Type of FID Calibrated to Methane[1]

Compound	Response (%)
Benzene	150
Toluene	120
Methane	100 (reference)
Pentane	100
Ethane	90
Hexane	70
Propane	64
Butane	61
Ethanol	25

[1] Relative response will differ depending on the instrument.

FIDs are less sensitive than PIDs to environmental conditions such as relative humidity and temperature; however, winds, excess carbon dioxide, and depleted oxygen (<15 percent) can extinguish the flame in the instrument. These instruments are more sensitive than PIDs to alkanes such as hexane and butane, which make up a higher fraction of gasoline than do the aromatics.

Photoionization Detectors (PIDs)

Portable PIDs are relatively easy to use in the field and sensitive to aromatic hydrocarbons for which they are primarily used. A UV light in the instrument is used to ionize organic constituents present in the vapor sample. An internal pump draws the vapor sample through the instrument probe and past the lamp. If the UV light can excite the hydrocarbons in the vapor sample and cause them to ionize, a signal registers on the instrument meter or digital display. The strength of the signal is a relative measure of the concentration.

Table 3-3. Summary of TOV Instrument Characteristics

Manufacturer	Model	Detector Type	Moisture Compensation[1]	Sample Flow Rate (L/min.)	Maximum Range (ppm)	Linear Range[2] (ppm)	Detection Limit (ppm)	Intrinsically Safe
1	A	FID	NA	2.0	0.5-10,000	Not reported	0.5 Methane	Yes
	B	FID	NA	2.0	0.2-1,000	Not reported	0.2 Methane	Yes
	C	FID/ PID	NA No	1.0	1-50,000 0.5-2,000	1-10,000 0.5-500	0.3 Hexane 0.1 Benzene	Yes
2	A	FID	NA	0.25	0.1-10,000	0.1-10,000	0.1 Methane	No
	B	PID	Yes[3]	0.2	0.1-2,000	0.1-200	0.1 Isobutylene	Yes
	C	PID	No	0.25	0.1-2,000	0.1-200	0.1 Isobutylene	No
3	A	PID	No	0.175	0.1-2,000	Not reported	0.1 Benzene	Yes
	B	PID	Yes[4]	0.25	0.1-2,000	Not reported	0.1 Benzene	No
	C	PID	Yes[4]	0.25	0.1-2,000	Not reported	0.1 Benzene	No
4	A	PID	Yes[5]	>0.5	0.1-2,000	Not reported	0.1 Isobutlyene	IS-3,000
5	A	FID	NA	1.0	0.05-10,000	Not reported	0.05 Methane	2.028
6	A	PID	NA	0.4	0.1-2,000	Not reported	0.1 Benzene	No
7	A	PID	Yes[6]	0.4	0.1-2,000	Not reported	0.1 Benzene	No
	B	FID	NA	0.8	0.1-20,000	Not reported	0.5 Methane	Yes

[1] NA = Not applicable.

[2] Linear range of instrument based on calibration gas only.

[3] Patented sensor to compensate for moisture.

[4] Vacuum in the detector chamber to minimize condensation.

[5] Dilution probe and new detector added to electrode to minimize moisture effects.

[6] Electrode used for moisture adsorption and grounding.

Most PIDs have interchangeable UV lamps that are sensitive to different ranges of hydrocarbon constituents. All PIDs have a specific sensitivity to BTEX. A variety of lamps of different energies are available [e.g., 9.5, 10.0, 10.2, 10.6, and 11.7 electron volts (eV)]. All five detect many aromatic and large-molecule hydrocarbons. The 10.2- and 11.7-eV lamps also detect smaller organic molecules. Lamps in the 10.0- to 10.5-eV range are the most useful because they are responsive to more constituents than the lower-energy lamps (9.5 eV) and are more durable than the higher energy lamps (11.7 eV). An example of PID response to different hydrocarbon groups is shown in Table 3-4.

Table 3-4. PID Response to Different Hydrocarbon Groups

	Photoionization Response		
Chemical Group	9.5-eV	10.2-eV	11.7-eV
Aromatics (e.g., benzene, toluene)	H	H	H
Paraffins (C_5-C_7) (e.g., pentane, hexane, heptane)		L	H
Paraffins (C_1-C_4) (e.g., methane, ethane)	NR	NR	NR

H = High
L = Low
NR = No response

PID accuracy varies with the concentration level being measured, the type of constituent present in the sample, and the amount of moisture drawn into the instrument. The responsiveness of PIDs decreases in moist conditions when the relative humidity of the sample or the ambient air is high (above 90 percent). PIDs tend to have a nonlinear response to spiked hydrocarbon samples above 150 to 300 ppmv. Some instruments compensate for moisture effects using different methods. A summary of the characteristics of different PID instruments is shown in Table 3-3.

METHOD REQUIREMENTS

Initial Setup

The TOV instrument is calibrated to a calibration gas standard that is provided by the manufacturer (typically isobutylene for PIDs, and methane for FIDs). Other C_4 to C_6 gas hydrocarbon standards are available and are generally preferred over pure methane when calibrations are made for volatile gasoline constituents. In addition to instrument calibration, a multipoint calibration curve should be generated by use of the on-site materials (e.g., released product or fuel from the pump dispensers and actual site background soils or water) as standards for spiking background soil and water samples if

the polyethylene bag system is used (see QA/QC requirements). A leak test of the bag seal should also be performed. The valve and tubing associated with the bag should be checked to determine if purging has removed the remaining hydrocarbons. If contaminant concentrations remain, the tubing should be replaced, purged, and rechecked.

Sampling and Analysis Procedures

The proper sample volume, size and type of containers, headspace volume, sample preparation techniques, QA, and TOV instrument are determined by the technique used. For general field screening, static and dynamic jar headspace techniques are commonly performed. A glass jar, typically with a capacity of 8 to 32 ounces (250 to 1000 mL), is filled one-half to two-thirds with a soil or water sample. Then the jar is typically covered and sealed with one or more sheets of aluminum foil or Teflon™ sheeting and an airtight screw-on lid. For static headspace screening, the sample is allowed to equilibrate to a constant temperature to minimize temperature variation effects on hydrocarbon volatility. Constant temperature can be achieved by placing the sample in a controlled-temperature environment for a period of time. Controlled-temperature environments include water baths, constant-temperature ovens, and buildings with adequate temperature control. Temperature equilibration can be achieved in as little as 5 minutes if a water bath is used. When air is used, equilibration can take 2 hours or more. After the sample has reached the desired temperature, the lid is removed and the aluminum foil or Teflon™ sheet is pierced with a TOV instrument probe that is inserted to a point at about one-half of the headspace depth. The maximum TOV instrument response to the volatile organic vapors is then recorded. If outside air is inadvertently drawn into the sample container, vapors in the headspace will be diluted and instrument readings will not represent the contaminant concentration in the headspace. If a leak-tight and rigid sample container is used, a vacuum induced by the instrument pump can curtail instrument response.

When the agitated headspace procedure is used for headspace screening, the sample is usually agitated for a standard period of time (reported agitation times range from 15 to 20 seconds to several minutes). The lid is then removed, the aluminum foil or Teflon™ sheet is pierced with a TOV instrument probe, and measurements are taken during the TOV instrument response to the volatile organic vapors.

Agitated headspace analysis of soil and water by use of a polyethylene freezer bag system is an improvement over the commonly used agitated jar headspace analysis. This technique involves

collecting a 25-g soil or 100- to 300-mL water sample, placing it in a reclosable freezer bag, and for soil samples, adding 100 mL of water, inflating the bag with a fixed volume of air, and then agitating the sample (<4 minutes) to release vapors in the bag (see Figure 3-1). Following agitation, the TOV instrument is connected to a valve system on the bag, the valve is then opened to the bag, and the vapor concentration in the bag headspace is measured by a TOV instrument. Unlike most jar headspace methods, multipoint calibration curves using spiked standards are developed prior to performing analyses with this technique. These curves are used to evaluate the instrument response over time and to interpret the readings from the TOV detector relative to a standard.

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENT

QA/QC requirements for static and dynamic jar headspace analysis are typically minimal and in many applications there are no specific QC requirements used to check technique performance. For any jar headspace technique, the TOV instrument should be calibrated to the standard gas appropriate for that instrument at least once a day prior to beginning analysis. The procedures and equipment used in jar headspace techniques should be consistent for all analyses performed. For example the sample size/volume or mass, container type and volume, headspace to sample volume, equilibration or agitation time, TOV instrument used, etc., should all be consistent for the headspace technique being performed.

Agitated headspace analysis using the polyethylene bag system provides a more controlled system and has more stringent QA/QC requirements that allow lower detection and more consistent results than the typical jar headspace analysis. A summary of suggested calibration and QC requirements is presented in Table 3-5. The TOV instrument is calibrated before analyses are performed using the manufacturer's standard gas (see Instrumentation, presented earlier in this section). Single- and multiple-constituent standards are used to develop multipoint calibration curves over the linear range of the instrument. Soil or water samples are spiked with a standard at zero plus three higher concentrations. The concentration of the standard must be below the solubility of the standard. For multiple-constituent contaminants, the following approaches can be used to generate calibration curves:

- A single-constituent calibration is used and multiconstituent results can be reported as concentration equivalents;
- A multiple-constituent standard with the same constituents in proportion similar to those of the contaminated water is used; or
- A groundwater sample may be serially diluted to develop a relative concentration curve that can later be semiquantified by a laboratory analysis of the sample.

A calibration check is performed at least twice during the day. Matrix spike and matrix spike duplicates are used to determine analytical precision. Field blanks are used to measure cumulative interferences. A range of acceptable variance can be established for the specific TOV instrument being used.

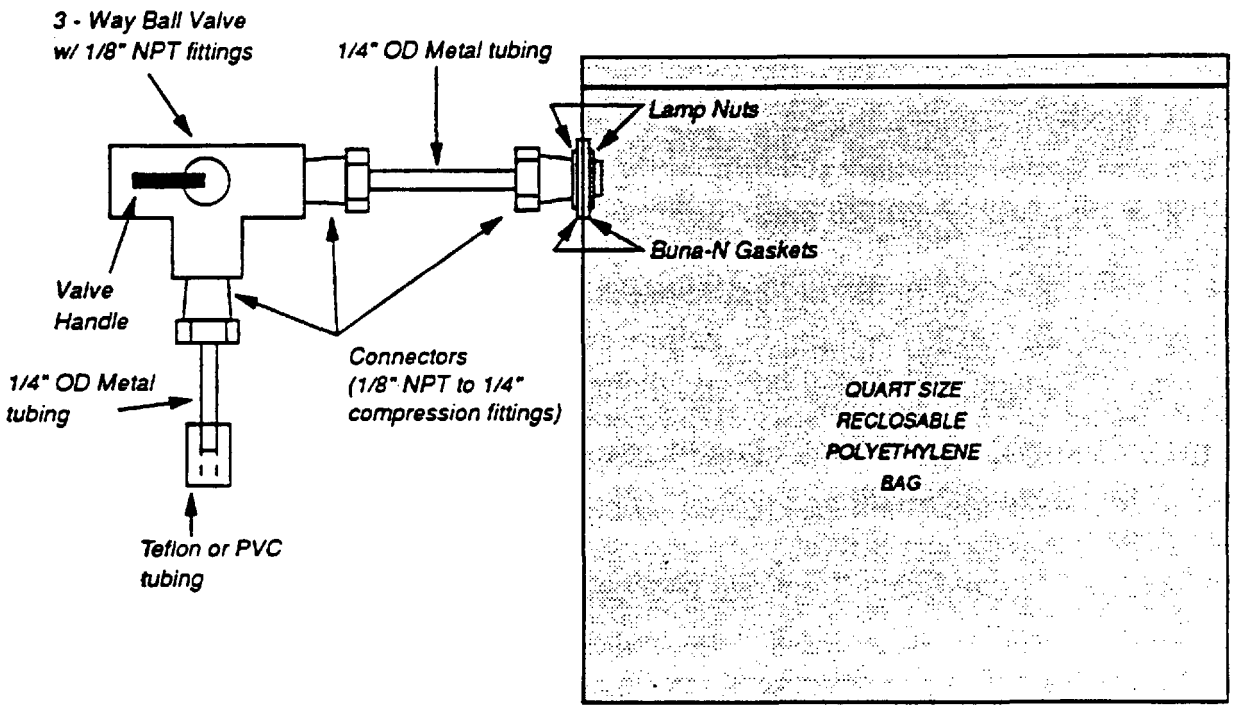


Figure 3-1. Apparatus Setup for the Polyethylene Bag Sampling System

Table 3-5. Summary of Suggested Calibration and Quality Control Requirements for Analytical Systems

Type of Instrument	Detector Type	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action
TOV Instrument	FID	(1) Multipoint calibration (zero plus three upscale concentrations)	At start of program	Aliphatic hydrocarbons from the site	Correlation coefficient ≥ 0.995	Repeat multipoint calibration after checking calibration dilution system
		(2) Zero/span calibration	Daily	UHP Air or N_2/ Methane	Response factor agreement within ± 20% of mean RF for multipoint calibration	(1) Repeat zero/span calibration (2) If still unacceptable, repeat multipoint calibration
		(3) Control sample analysis	Daily, prior to testing	Methane	Measured concentration within ± 10% of certified concentration	(1) Repeat zero/span calibration (2) Repeat control sample analysis
		(4) Drift check	Daily, at conclusion of testing	Methane	Drift value ≤ 20% of the input value	(1) Flag day's data as questionable (2) Repair or discontinue use of analyzer
	PID	(1) Multipoint calibration (zero plust three upscale concentrations)	At start of program	Aromatic hydrocarbons from the site	Correlation coefficient ≥ 0.995	Repeat multipoint calibration after checking calibration dilution system
		(2) Zero/span calibration	Several times throughout the day	UHP Air or N_2/ aromatic hydrocarbons from the site	Response factor agreement within ± 20% of mean RF for multipoint calibration	(1) Repeat zero/span calibration (2) If still unacceptable, repeat multipoint calibration
		(3) Control sample analysis	Daily, prior to testing	Aromatic hydrocarbons from the site	Measured concentration within ± 10% of certified concentration	(1) Repeat zero/span calibration (2) Repeat control sample analysis
		(4) Drift check	Daily, at conclusion of testing	Aromatic hydrocarbons from the site	Drift ≤ 20% of the input value	(1) Flag day's data as questionable (2) Repair or discontinue

Section 4
FIELD GAS CHROMATOGRAPHS

SUMMARY

Field GCs are used in the investigation of petroleum hydrocarbon contamination to identify and quantify specific constituents in either a liquid or vapor phase. These instruments provide rapid, high quality data, allowing personnel to make decisions in the field. They provide a higher level of sensitivity and discrimination of compounds than do TOV detectors. They are moderately expensive and require a higher level of operator expertise and more frequent maintenance. Field GCs are available in two types: portable and transportable. Portable GCs are generally very compact in size, operate isothermally, and contain internal batteries and operating gas supplies. Transportable GCs are laboratory-grade instruments that require external power and gas supplies. This section describes the most common field GCs available and their standard operating procedures.

METHOD OVERVIEW

Applications and Advantages

Gas chromatography is the most widely used analytical technique for constituent-specific analysis of groundwater, soil, and soil vapor samples for volatile and semivolatile hydrocarbons. In a traditional site assessment, samples collected from one or more of these matrices are sealed in labeled containers, preserved, and transported to a laboratory remote from the actual sampling location. Analysis for trace volatile organic content is generally performed in the laboratory by purge-and-trap techniques such as EPA Method 8020 using GC or EPA Method 8240 using GC/MS (EPA SW-846, 3rd Edition).

On-site analysis of groundwater, soil, and soil vapor for selective VOCs via GC has emerged in recent years as a practical, reliable, and cost effective means of gathering high quality data in the course of a subsurface investigation. The use of a field procedure capable of specific constituent analysis with a practical quantification limit of a few parts per billion (ppb) should reduce the time needed for the assessment of any site and facilitate appropriate siting of monitoring wells. Field GC analysis for VOCs helps reduce problems associated with inadequate or improper preservation of samples, which result in loss of targeted analytes due to volatilization and/or bacterial degradation. Presently, equipment and GC methods are available that utilize an on-site mobile laboratory as a climate-controlled environment for a research-quality transportable GC, with one or more detectors, linked to a multichannel data-acquisition system. Sampling results are reported in ppb or ppm, depending on the range of calibration utilized.

Because field GCs provide quantitative analyte-specific results, they provide a higher level of interpretive capability than TOV analyzers. By resolving individual analytes, the location of the source of a release and the relative direction of contaminant migration can be inferred. Often, the regulatory agency overseeing an investigation requires the analysis and reporting of individual analytes because of their potential exposure risk; this is especially true for benzene or BTEX constituents.

INTERFERENCES AND LIMITATIONS

Field GCs operate most effectively when located in a stable, climate-controlled environment. For field use, the instrument must be located in an area where temperature variations can be minimized. Highly contaminated samples may require dilution to prevent them from exceeding the detector's maximum calibration range. Contaminants in the ambient air and in syringes could interfere with analysis, especially at the method detection limit.

Individual compounds are tentatively identified by matching the retention time of the sample peak to the retention time of the known analyte peak. If a nontarget compound has the retention time, it can be misidentified as the target compound. If two compounds have similar retention times (coelute), they may cause an additive effect on the calculation of concentrations. In fact, if many interfering peaks are present, the separation may not be adequate to determine concentrations. In this case, total chromatogram integration can be used to determine total volatile petroleum hydrocarbons (TVPH). Table 4-1 presents capabilities and practical considerations of field GCs.

Table 4-1. Capabilities and Practical Considerations of Field GCs

Capabilities	
Compounds detected:	Most organic volatiles
Matrix:	Water, soil, and gas
Achievable Quantitation Limit:	1 ppb in water samples 5 ppb in soil samples 20 ppb in vapor samples
Practical Considerations	
Cost per sample (approx.):	$50 to $70
Analytical time per sample:	10 to 40 minutes
Quality of Data (level):	Excellent (2 to 3)
Difficulty of procedure:	Moderate to difficult
Laboratory method equivalent:	GC with similar detector

OPERATING PRINCIPLES/INSTRUMENTATION

GCs utilize a column and a detector to isolate and analyze specific constituents in either a liquid or vapor phase. The basic components of a GC are a sample injection system, a column, a detector, and a data collection system. Samples composed of a mixture of compounds are introduced onto the separation column through the sample injection port, which vaporizes any liquids present, and the vapor mixture is transported through the column by an inert carrier gas (i.e., helium, hydrogen, or nitrogen). The column acts to separate the individual components of the sample mixture so that each reaches the detector(s) at different elution or retention times through reproducible rates. The low molecular weight or highly volatile constituents elute or come through the column first, followed by those which have higher molecular weights or are less volatile. Characteristics of different GCs are listed in Table 4-2.

Table 4-2. Summary of Field Gas Chromatograph Characteristics

Model	Detector Type(s)	Instrument Detection Limit (ppb)	Linear Detection Range[1] (orders of magnitude)	Temperature Control	Analysis Time, BTEX (min)
Portable[2]					
1	PID	0.1	N/R[3]	Isothermal	<10
2	PID	100 (benzene)	10E3	Isothermal	10
3	PID	N/R	10E5	Isothermal	5-10
4	PID	N/R	N/R	Isothermal	N/R
5	PID	<1	10E4	Isothermal/ programmable	<20
6	FID	200 (methane)	10E3	Isothermal	10
7	FID	Low to mid ppb	10E6	Programmable	3-5
8	PID	ppt to low ppb	10E6	Programmable	3-5
Transportable[4]					
1	FID	100 (toluene)	10E6	Programmable	5-10
2	PID	1-10 (toluene)	10E3	Programmable	5-10
3	FID	100 (toluene)	10E6	Programmable	5-10
4	PID	1-10 (toluene)	10E3	Programmable	5-10
5	FID	10-100 (benzene)	10E5	Programmable	10-15
6	PID	1-10 (benzene)	10E4	Programmable	10-15
7	FID	10-100 (benzene)	10E5	Programmable	10-15
8	PID	1-10 (benzene)	10E4	Programmable	10-15
9	FID	0.1 (BTEX)	10E6	Programmable	6-20
10	PID	0.1 (BTEX)	10E6	Programmable	6-20
11	FID	N/R	>10E6	Programmable	8-12
12	PID	N/R	>10E6	Programmable	8-12
13	FID	N/R	10E7	Programmable	10
14	PID	N/R	10E7	Programmable	10
15	FID	<1000	10E6	Isothermal	10
16	FID	<1000	10E6	Programmable	10

1 Using a response factor within 15%.
2 Portable GCs can operate on internal battery power (or converted line power) and have internal operating gas supplies.
3 N/R = Not reported.
4 Transportable GCs rely on on-line power and require separate operating gas supplies.

The most common detectors used in GCs for petroleum investigations are the PID and the FID. The range of detectable compounds and the inherent sensitivity of each detector must be considered in the selection of an appropriate detector for particular site conditions. The responses from the detector are displayed as a chart record, or chromatogram, showing detector response versus retention time for each component. The integrated area under each detector response (peak) is proportional to the concentration of that constituent (components response factor). Constituents present in the original sample can be tentatively identified by comparing peak retention times with reference standards.

Detectors

A PID consists of a UV lamp mounted on a low-volume flow-through cell. The light energy emitted will ionize molecules with ionization potentials that are lower than the energy of the lamp. A 10.2-eV lamp is sufficient to ionize most aromatic molecules such as benzene, toluene, and xylene and many aliphatic molecules such as alkenes, cycloalkanes, and higher molecular weight alkanes. The detection limits for a PID are in the 1- to 10-ppb range for aromatics. The biggest advantages of the PID are its high sensitivity and its nondestructive nature. The biggest disadvantage of any PID is the tendency of the lamp window to become dirty from contaminated samples and column bleed.

An FID consists of a stainless steel jet constructed so that carrier gas exiting the column flows through the jet, mixes with hydrogen and air, and burns at the tip of the jet. Hydrocarbons and other molecules that ionize in the flame are attracted to a metal collector electrode located at the side of the flame. The resulting electric current is converted to a millivolt level signal that is sent to the data system. The FID is the most commonly used GC detector because it detects the full range of petroleum fuel constituents, including aliphatic, olefinic, and aromatic hydrocarbons with detection limits in the 10- to 100-ppb range, and responds linearly over a large concentration range.

Field Gas Chromatographs

Although portable GCs are limited in temperature-programming capabilities and carrier gas controls, they are available with selective detectors [FID, PID, electron capture detector (ECD)] and can be very effective in analyzing the volatile organic species encountered in headspace analysis. When equipped with megabore columns (3 to 30 meters), they can resolve all but the most complex mixtures. Calibration standards can be run in the laboratory and entered into a reference library. These instruments are either equipped with their own personal computer PC or can be run using a small laptop computer to store data and perform QA in the field.

For more complex samples, it may be necessary to use a transportable research-quality instrument that can be equipped with longer capillary columns to ensure better separation and analysis.

METHOD REQUIREMENTS

Comparative Sample Preparation and Analysis Procedures

Static (equilibrium) headspace, purge-and-trap (dynamic headspace), and solvent extraction are sample preparation/extraction methods that have all been widely used in the determination of VOCs in soil, wastewater, and drinking water. All three methods work satisfactorily for one or more of these matrices.

Solvent Extraction

EPA Methods 8020 and 8240 recommend the extraction of soils with methanol for high- and medium-level contaminated samples. A known mass of soil is dispersed (ultrasonic mixing is recommended) in methanol to dissolve the volatile organic constituents. An aliquot of the methanolic solution is then combined with analyte-free water. The aqueous sample solution is then prepared for introduction on the GC column using the purge-and-trap method.

Manual solvent extraction is a slow, labor intensive procedure requiring very high purity solvents (even minor impurities can have serious impact on chromatographic analysis). Losses of target analytes due to volatilization during extraction/dispersion are both high and variable.

Solvent extraction in the field is not recommended for volatile analyses, which are best handled by purge-and-trap or headspace GC techniques.

Purge-and-Trap Method

Purge-and-trap (dynamic headspace) is used extensively in some parts of the world, principally in North America, for waste and drinking water analysis. This method of sample preparation/extraction requires that a low-level-contaminated aqueous sample or soil/analyte-free water mixture be sparged with an inert gas (usually helium) in a specially designed vessel (purge chamber) at ambient temperature for a specified period of time. This causes a transfer of volatile components from the aqueous phase to the vapor phase. The vapor is continuously swept through an adsorbent trap that strongly retains selective organic compounds. Following the purge step, the sorbent column is quickly heated to release or desorb the organics and a precise volume of the column effluent is transferred

directly onto the GC column for analysis. The purge-and-trap technique is especially suited for determining sub-parts-per-billion levels of target analytes in water. However, this technique is primarily a manual procedure. Automatic sample handling is unreliable if there is the possibility of an occasional highly contaminated sample being present among a batch of relatively clean samples. In this case, carryover from the highly contaminated sample may affect subsequent analyses. Similar cross-contamination problems occur with samples that undergo excessive foaming in the purge chamber. The manual procedure has similar drawbacks, except that cross-contamination problems can be identified prior to the next analytical run and cleanup steps can be initiated. This can result in extensive equipment downtime. Some form of preanalysis sample screening is therefore often required prior to purge-and-trap analysis of aqueous samples, necessitating significant sample dilution, whereas solvent extraction is recommended for contaminated soils. These sample dilutions result in high method detection limits. It is generally recommended that samples containing more than 200 ppb of a particular analyte be diluted in order not to exceed the detector's maximum calibration range. These factors slow down sample throughput and add significantly to the cost of analysis.

The purge-and-trap method has limited application to soil samples having significant organic content because of the inability to overcome the soil's strong affinity for VOCs. In addition, the analytical precision of the purge-and-trap method is on the order of 30 to 40 percent, with extraction efficiencies below 50 percent in some cases (Voice and Kolb, 1993).

Static Headspace Method

The static headspace procedure of sample preparation/extraction requires that an aqueous sample be placed directly into a septum-top vial, sealed, and incubated at a constant temperature. Volatile organics from the sample partition between the aqueous phase and the headspace gas, eventually reaching equilibrium. Once the equilibrium is established, the concentration of VOCs in the headspace is proportional to the concentration of dissolved VOCs in the aqueous phase at a given temperature. Soil sample preparation requires that a known mass of soil be transferred into a known volume of analyte-free water, sealed in a septum-top vial, and incubated at constant temperature. Agitation of the vial is recommended to facilitate headspace gas/aqueous phase equilibration and increase recovery of extractable organics from the soil matrix.

Once the headspace gas/aqueous phase equilibrium is established, a precise volume of the headspace gas is injected directly onto the GC column and the chromatographic run is initiated. Samples with

analyte concentration range from a few ppb to several thousand ppb and can be analyzed without sample dilution. Static headspace analysis overcomes the limitations of solvent extraction (soils) and purge-and-trap (soil/water) and provides a highly productive and cost effective technique for the analysis of VOCs in soil and water. There is little risk of cross-contamination between samples, thus facilitating reliable automated operation without prescreening. The detection limits offered by static headspace/GC methods are more than adequate for most standard soil, wastewater, and drinking water methodologies. This variation of the analysis procedure is described in U.S. EPA SW-846 Method 3810.

Research indicates that the static headspace/GC method can be effectively utilized to determine VOCs in soil and water samples and to provide results that are not significantly different from slower, more expensive purge-and-trap methods (Hewitt, *et al.*, 1992A, 1992B, 1993; Voice and Kolb, 1993; Dietz and Singley, 1979; Cincotta, 1994; Roe, *et al.*, 1989; Stuart, *et al.*, 1991; Wylie, 1988; Chiang, Loos, and Klopp, 1992).

Headspace/GC and Soils

The inadequacy of the current methods of soil preservation for subsequent volatile constituent analysis has been widely recognized (EPA, 1993). Loss of up to 95 percent of volatiles from soil samples stored for acceptable hold times has been claimed (Hewitt, 1994). On-site constituent-specific analysis of soil by the static headspace/GC method is a far more accurate approach for delineating contamination in soils and is a valuable tool in planning an effective remediation strategy.

Total Petroleum Hydrocarbon Analysis Using Field GCs

Within the last few years, laboratories have modified EPA methods (i.e., Methods 8010, 8015) to address the analysis and monitoring of contaminated sites for gasoline range organics (GRO) and diesel-range organics (DRO). These fuel ranges are analyzed separately via GC analysis. Regulatory agencies such as the Wisconsin Department of Natural Resources and the California State Water Resources Board have aggressively adopted LUST methods to standardize these analytical results within their jurisdiction.

A field static headspace/GC method for GRO and DRO in groundwater samples was recently claimed (Cincotta, 1994). This method yields a tentative fuel identification relative to available standards, quantitative BTEX analysis, and semiquantitative analysis of GRO and DRO fractions from a single

chromatographic run. This field GC method provides valuable information for on-site decision-making when tracking multiple fuel plumes in groundwater to method detection limits of 2 ppb for BTEX components and 20 to 200 ppb for each petroleum fraction.

QUALITY ASSURANCE/QUALITY CONTROL

Field analysis should meet the same calibration and QA/QC requirements that apply in fixed environmental testing laboratories. This will ensure the precision and accuracy of the field-generated data and maintain the confidence of regulators.

Prior to project startup, a trained analyst must develop a GC method for the target analytes on a column that ensures that they are adequately resolved from each other. The oven temperature should be set at the maximum temperature appropriate for the column and a GC trace run to verify that the column is clean. Once a satisfactory method is developed and analyte retention times have been noted, a calibration curve (peak area versus analyte concentration) should be generated for each target analyte using a minimum of four different concentrations. These concentrations should span the expected range of sample concentrations.

At the start of each analysis day, the GC and detector(s) should be turned on and allowed to stabilize to operating conditions. Instrument blank and method blank runs must be conducted to check equipment and materials. A calibration check at mid-range concentration and one near but above the method detection limit should be analyzed to verify each of the working calibration curves. Sample analysis may proceed if the results of the calibration check are within the range of acceptable variance. In the course of the day, a calibration standard, a duplicate sample analysis, and at least one matrix spike should be run. Field splits (5 to 10 percent) for confirmatory laboratory analysis may be necessary in some investigations, especially where possible coelution problems are suspected.

Section 5
IMMUNOASSAY FIELD TEST KITS

SUMMARY

Immunoassay (IA) field tests measure a target constituent or analyte using antibody-antigen reactions, where a natural antibody protein is developed in animals to have a high degree of selectivity and sensitivity to the target constituent (compound). IAs have been successfully developed and used in the medical industry for years, and are currently being used as a field analytical method for hydrocarbons, pesticides, polychlorinated biphenyls (PCBs), and explosives.

In the testing process, contaminants are extracted from soil samples using a solvent such as methanol, and water samples are analyzed directly. The methanol extract or the water sample is placed in a small reaction test tube or detector that is coated with the sensitized antibodies. Reagents that act as tracers (called enzyme conjugates) are added in a series of steps with appropriate incubation periods of a minute or two. The contaminants in the sample extract compete with the enzyme conjugate for a limited number of antibody binding sites. A substrate solution which reacts with the bound conjugate to produce a color (yellow or blue, depending on kit manufacturer) is added last. The intensity of the color is inversely proportional to the contaminant concentration. The contaminant concentration is determined by comparing the color developed from the sample with a reference standard, or it is measured directly on a small portable spectrophotometer or optical density meter.

Depending on the biochemical design, a particular test kit will measure a specific constituent (benzene), a set of constituents (e.g., BTEX), or a general assay range (TPH). Depending on the manufacturer, IA kits are designed (formatted) for either semiquantitative or quantitative analyses. For semiquantitative analyses, an action level is set and the assay will indicate if the sample concentration is above or below that level. Multiple action levels can be set to place the sample in a discrete range (e.g., above 100 ppm but below 500 or 1000 ppm). For quantitative analyses, multipoint calibration curves are used that are usually internal to the detector. Because the kit format is a key criterion in its selection, it is important to review the following considerations: (1) the kit design, including concentration range measured or action level, and the specificity (e.g., BTEX or TPH); (2) the regulatory parameter that needs to be measured; (3) the type of hydrocarbon (fuel) contamination at the site; and (4) the engineering objective of the analytical assessment.

IA field screening methods will be included in the Third Update to the Third Edition of Test Methods for Evaluating Solid Waste, SW-846.

METHOD OVERVIEW

Applications and Advantages

IAs are highly selective, sensitive, portable, and provide rapid turnaround time measured in minutes. Individual kits can be calibrated to specific fuels or mixtures of fuels, or an internal calibration, set by the manufacturer, can be used. As a result of their selectivity, IA is an excellent screening technique when the site contaminant is known, or it can be a quantitative tool for delineation of the contamination at the Level 2 stage.

IA tests are best suited for delineating BTEX or TPH concentrations, determining if BTEX levels are above a prescribed level of concern (e.g., Tier 1 Risk Assessment), and monitoring the effectiveness of cleanup activities.

Overall, light fuels IA can quickly measure the key regulatory parameters at low concentrations (low ppm) that encompass most state cleanup action levels, except for benzene at the ppb level. In addition, the test has specificity toward aromatic gasoline and distillate fuels, based on a good false-positive/false-negative performance. Another distinct advantage is the immediate extraction of a soil sample with methanol. This provides the best sample preparation, under most cases, and is consistent with modern methodology for preservation of soil for volatile organic constituents (i.e., GRO and DRO) by GC. In fact, it is easier to perform confirmatory laboratory analyses by GRO/DRO methods because the field sampling and preservation techniques are the same for these GC methods and IA analyses.

As with all the field technologies discussed in this compilation, a chief advantage from a quality control standpoint is the ability of the operator to receive constant feedback of data. Consequently, decisions can be made regarding obvious outliers, when to reanalyze, which samples to duplicate, the number of duplicates needed, and the selection of "blank" areas. This interactive on-site activity adds to the overall control and quality of the data being generated, which is not afforded through off-site lab analyses.

IAs can be used at sites contaminated with fuels and solvents. These include gasoline, aromatic solvents, kerosene, jet fuels, diesel fuel, and fuel oils. Sites with unknown fuel contamination can be analyzed for BTEX using a BTEX kit and a BTEX calibration mixture. PNAs, including the 16 listed as hazardous compounds by EPA (Table 5-1), can also be detected with the PNA kits. The PNA kit may also be used to detect light crude oils and mid-boiling-range semi-refined streams such as light oils.

Table 5-1. Hazardous PNA Compounds

Acenaphthene	Phenanthrene
Acenaphthylene	Benzo[a]anthracene
Anthracene	Benzo[b]fluoranthene
Benzo[a]pyrene	Benzo[k]fluoranthene
Benzo[g,h,i]perylene	Dibenzo[a,h]anthracene
Chrysene	Fluorene
Fluoranthene	Naphthalene
Indeno[1,2,3-cd]pyrene	Pyrene

Field-portable IA kits require minimal space and are easily transported. The spectrophotometers are single-wavelength, battery-operated devices, and the sample chamber is specifically designed to accommodate the cells supplied with the kit. Data output options include printers and computer interfaces (from some suppliers). The capabilities and practical considerations for use of IA kits are summarized in Table 5-2.

INTERFERENCES AND LIMITATIONS

Each kit is analyte specific and subject to little interference from other compounds in the sample. However, petroleum contaminants not targeted by the antibody may cross-react to some degree. For example, an assay designed to detect PNAs may give a positive result in the presence of a high concentration of lighter aromatic compounds such as BTEX or nontarget polynuclear aromatics (PNAs). Conversely, heavier aromatics such as those in fuel oil may create false-positive results with BTEX kits if they are present at high concentrations.

Clay and other cohesive soils present an extraction problem. Emulsions may be formed that will not allow the extraction solvent to separate into a clear layer. Adding more solvent facilitates separation with a proportional increase in detection limits.

Table 5-2. Immunoassay Capabilities and Practical Considerations

	Capabilities	
Compounds detected:	Benzene, BTEX, TPH, total PNA	
Matrix:	Soils Water	
Achievable quantitation limit:	BTEX - 2 ppm soils, 200 ppb in water TPH - 10 to 500 ppm in soil, 200 to 500 ppb in water PNA - Approximately 1 ppm in soil, approximately 10 ppb in water	
	Practical Considerations	
Estimated cost per sample:	$20 to $60. Capital cost for the colorimeter and other hardware is approximately $1500. Expendable costs are high and the $20 to $60 covers the disposable items needed to complete one assay.	
Estimated analytical time per samples:	Five to eight tests per hour for an experienced operator running samples in batches.	
Quality of data:	1A (yes/no semiquantitative results) 2 (quantitative readout)	
Difficulty of procedure:	Moderate. 1 to 2 days of training required. The number of steps and manipulations of small reagent volumes make field IAs technique-dependent. Operator skill has a direct correlation with the quality of results.	
Equivalent laboratory methods:[1]	Benzene/BTEX TPH PNA	SW-846 8020 (FID), 8240 (GC/MS) SW-846 8015 (modified) SW-846 8270 (GC/MS), 8100 (GC/FID), 8310 (HPLC)

[1] Laboratory reference methods are used to confirm field results and must be used to meet closure requirements.

The extraction of gasoline and BTEX from soils with methanol gives recoveries similar to those obtained by using the GC reference method which uses the same extraction procedure. The field extraction procedure for PNAs with methanol or isopropanol, however, is not as rigorous as the laboratory extraction, and the recoveries will be significantly less. The correlation of PNA results to the equivalent laboratory method will reflect this bias.

Recovery of PNAs from soils depends on the type of PNAs in the soil, the soil type, and the residence time of the contaminant in the soil. Recovery from cohesive soils is more difficult than from sandy soils, and the longer the residence time in the soil, the more difficult they may be to extract. If very low recovery is indicated by laboratory confirmation samples, action levels may have to be reevaluated.

Most of the IA kits currently on the market have a low selectivity for benzene as part of the BTEX, but are designed for selectivity around xylene with varying sensitivity for other aromatics. It should be noted that a benzene-specific assay of water samples is available on the market. Heavier refined petroleum products such as residual oils, greases, and waxes will not be detected at all. (They have very little affinity for TPH antibodies.)

In addition, some IA demonstrations in the field have shown IA to slightly overestimate the concentration of highly weathered gasoline, primarily because of the increase in the heavier, substituted aromatic constituents. However, this potential drawback is typically used to provide a safety margin in the test, which can be taken into account because of the generally good repeatability of the system.

False Positives/False Negatives

The false positive/false negative rates for a particular IA kit are very important (see definitions in the Glossary). Very low false negative rates are important to minimize liability from contaminated areas that would be left untreated if cleanup decisions are based on the IA. Higher false positive rates can be tolerated from a liability standpoint, but will limit the cost effectiveness of the test if the rate is too high. High false positive rates require an excessive number of laboratory confirmations and additional cleanup activities. The frequency of false negatives/false positives that can be tolerated should be specified in the work plan prior to commencement of field analytical investigations. Laboratory confirmation of negative as well as positive samples must be performed to document the frequency of false positives/false negatives for each sample matrix encountered at the site. Each kit recommended for use with the SW-846 IA methods has undergone extensive validation and Agency review. For this reason, only kits approved by EPA for use with SW-846 should be used in the field.

Temperature Ranges for Storage and Operation

Because the kits must be used within the temperature limits specified by the manufacturer, their outdoor use on very cold or hot, sunny days may be limited. Standards must be analyzed with each batch of samples. Some IA reagents and antibodies should be refrigerated when not in use. Although storage at ambient temperature on the day of use is acceptable, the kits should be protected from freezing and from prolonged exposure to temperatures above room temperature. Use on hot days may require transportation and storage on-site in a styrofoam cooler.

Calibration Standards

The antibodies developed for the detection of petroleum hydrocarbons are sensitive to a broad range of petroleum products. They do not measure every constituent present in the fuel as part of a TPH result. The antibodies are engineered to respond to a selected subset of the chemical components in the sample. These usually include the lighter aromatic compounds (e.g., BTEX and naphthalenes) and possibly some aliphatic compounds. The exact specificity of the antibodies in a chosen kit will depend on the manufacturer and the lot number. Therefore, it is best to calibrate with a known site contaminant or closely related fuel. A sample of the weathered product recovered from the site would be ideal. A number of kits have direct-readout colorimeters that are internally calibrated. The calibration is stable and provides a good alternative to preparing spiked standards in the field.

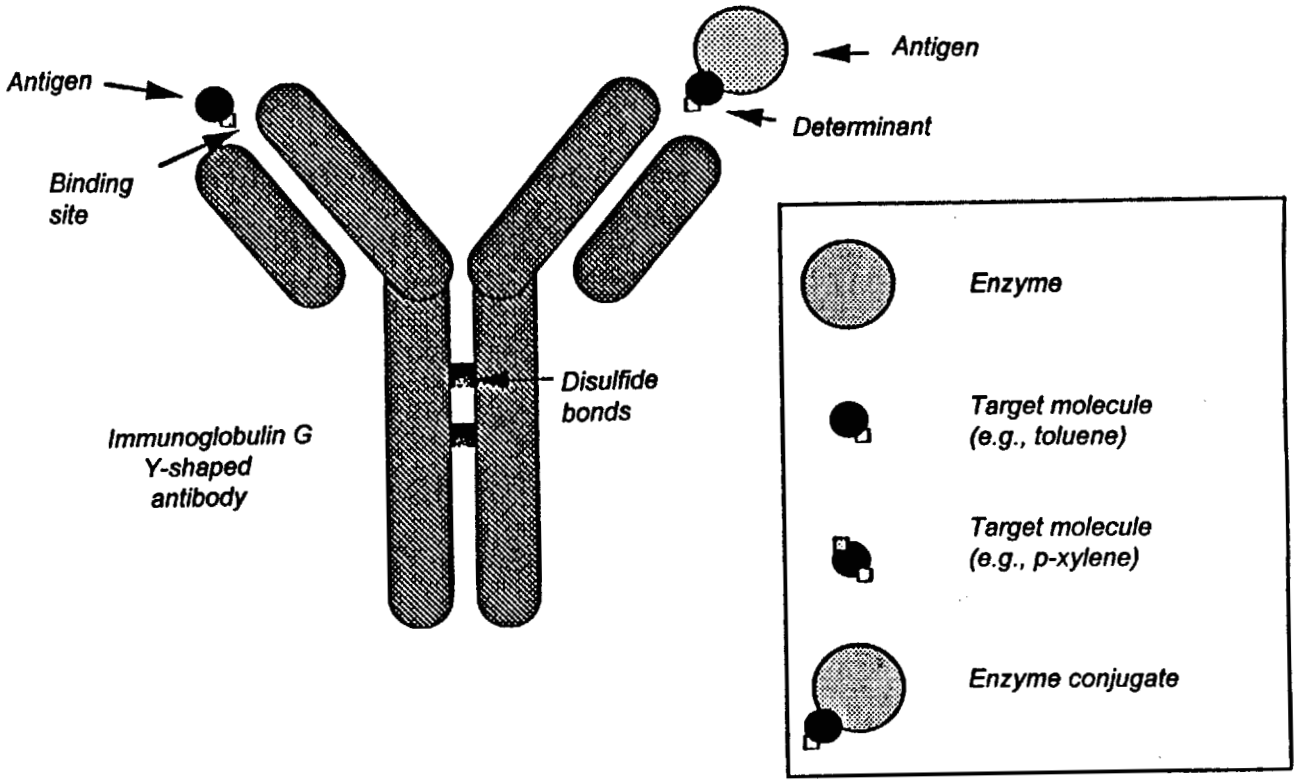
OPERATING PRINCIPLES

The antibody is the heart of any IA, and the important characteristics of the assay depend on how the antibody was produced. These characteristics are its selectivity and sensitivity for the targets of interest—in this case BTEX, TPH, and PNAs.

The antibodies synthesized by animals will have specific binding sites that will preferentially bond to its corresponding antigen. More specifically, it recognizes a constant structural feature of the antigen. These features are called determinants (see Figure 5-1). For example, antibodies designed to detect BTEX and TPH bind preferentially to aromatic compounds such as toluene and xylene, and to some extent, naphthalene.

It is the specific binding reaction in an IA test that results in its very high degree of selectivity for target compounds. Cross-reactivity is a measure of this selectivity. Benzene has very low cross-reactivity for the BTEX assay, implying that the antibody has very little affinity for benzene. Naturally, the BTEX antibody has little affinity for aliphatic hydrocarbons and nonhydrocarbon species as well. This low cross-reactivity is because benzene, aliphatic hydrocarbons, and nonhydrocarbons do not have appropriate determinants for the BTEX antibody. For this reason, a benzene-specific assay is being developed by one manufacturer.

The cross-reactivity has been documented for many hydrocarbon species and mixtures, and is available from the manufacturers of IA kits. This information is important for planning site investigations and interpretation of field data. For example, an antibody designed and calibrated for BTEX will provide a



An antibody will bind to a target molecule, to an enzyme conjugate containing the target molecule, and to compounds with similar structure to the determinant for which the antibody was designed (cross reactivity).

Figure 5-1. Antibody Terminology

total BTEX result regardless of whether the BTEX was present as a result of a gasoline release or a jet fuel release. In order to quantify gasoline or jet fuel, the investigator must obtain a correction factor from the supplier based on the cross-reactivity of gasoline to the BTEX antibody. Alternatively, the assay could be calibrated with the type of gasoline known to be present at the site. Similar considerations apply to IAs for PNAs. The antibodies will bind preferentially to PNAs, but the cross-reactivity for each individual PNA varies, and there is even a small but measurable cross-reactivity to single-ring aromatics.

A typical IA can be described in five basic steps (See Figure 5-2):

Step 1. A cell is supplied with the antibodies attached to the walls. The antibodies are thus immobile, and the cell walls act as an adsorbent for target molecules.

Step 2. The sample or soil extract is added along with a known amount of enzyme conjugate. The analyte in the sample competes for a limited number of sites on the walls with the enzyme conjugate. An equilibrium is established that is proportional to the relative concentrations of target analyte versus enzyme conjugate (referred to in Figure 5-2 as "labeled antigen"). This process can be illustrated by considering two extremes: a blank BTEX sample and a highly concentrated BTEX sample. In a blank, the sample contributes no BTEX molecules and all of the sites will be taken up by the enzyme conjugate. Conversely, in a highly concentrated sample, most of the sites will be taken up by sample BTEX molecules, not by the enzyme conjugate.

Step 3. A wash step is initiated to remove any unreacted analyte and enzyme conjugate from the cell and to prepare the cell for color development. Since the antibodies are affixed to the cell walls, this separation step is easily accomplished.

Step 4. The color development reagents are added. These reagents are a substrate solution and a chromogen. The sample is allowed to incubate for a specified time period. During this period, the enzyme will catalyze the transformation of the substrate into a product, which then reacts with the chromogen to color the solution in the cell.

Step 5. A stop solution is added to halt the reaction, and the optical density (OD) is measured with the detector or spectrophotometer.

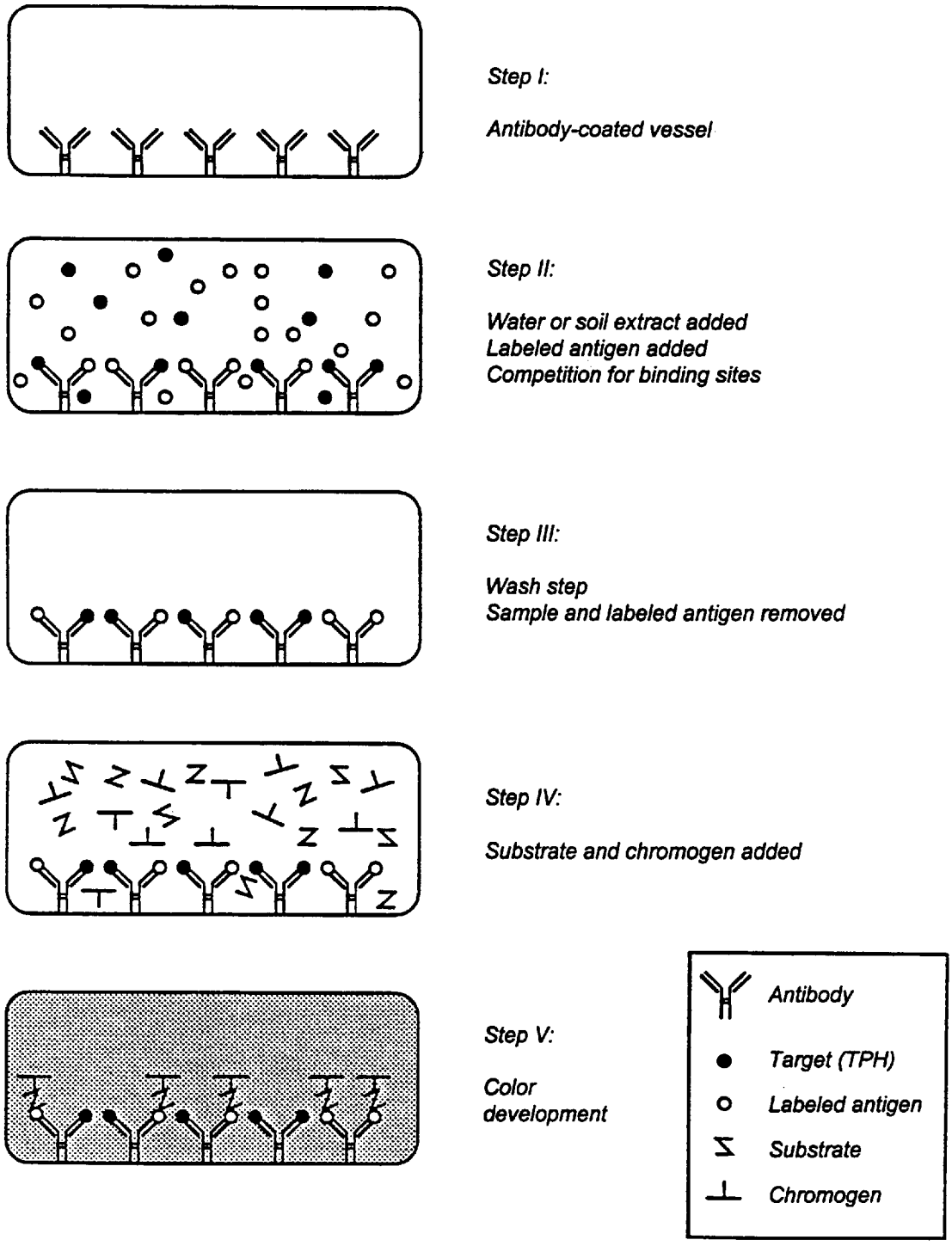


Figure 5-2. Competitive Binding Immunoassay

It is important to note that color development is inversely proportional to the concentration of analyte present. For the example above, the blank would produce a very dark solution (high OD) and the concentrated sample a nearly colorless solution (low OD).

IA kits consist of all the reagents, reaction vessels, and detectors necessary to perform multiple assays in the field. Kits include some means to measure the proper soil or water aliquot. Soils may be sampled by volume or by weight. Detectors are small, and in some cases integrated in a suitable style laboratory station capable of holding all of the reagents and hardware needed for a typical batch of assays. Table 5-3 summarizes the features of several IA kits.

A typical batch of assays includes standards, blanks, and samples. The number and type of standards and blanks differ with each kit. Although the basic theory of operation is the same among the five suppliers, the calibration and detection techniques differ considerably. Reagents are available in bulk form or in single-use ampules. The number of tests that can be run in a single batch depends on the format of the kit.

Detectors available to measure the color intensity of the final solution vary considerably among manufacturers of IA kits, and each manufacturer offers various options. All the detectors are similar in that they measure the optical density or absorbance of the final developed solution in the reaction vessel. They differ in the physical configuration of the cell or cuvette in which the OD is measured and in the presentation of the results. One displays a yes or a no to indicate a level above or below the action level. Most display absorbance, which can be compared with the absorbance of standards at one or more action levels to place the result in a discrete range. Some provide continuous readings over the concentration range, with the option to read directly in reportable units.

METHOD REQUIREMENTS

Samples are collected from soil borings and/or monitoring wells and prepared for analysis by measuring an aliquot of soil using a small top-loading balance or alternately by measuring a specified soil aliquot by volume. Water samples are aliquoted and filtered. All of the necessary equipment for measuring sample aliquots is provided in the kits.

Although all of the IA test kits are basically the same, the number of steps and procedures required varies for the different kits and, in particular, the method of detection and conversion to concentration

Table 5-3. Summary of Specifications for Immunoassay Test Kits

Kit	Target Matrix	Detection Limit	Range (ppm)	% False Negative	% False Positive	Storage Temperature (Shelf Life)	Quantitation	Time (Assays/Batch)	Cost/Test
1	TPH-Water (customized to user-selected fuel)	0.16 ppm (as gasoline)	Customized	<5% at chosen action level)	High near action level, decreases rapidly with higher conc.)	25°C (12 Months)	Yes/No at 1 to 2 levels (semi-quant.)	5 samp/45 min. (12 assays/batch)	$35/test
	TPH-Soil (customized fuel)	10 ppm (as gasoline)	Customized					(10 samp/batch at single detection level; 5 samp/batch at 2 levels)	
	PNA-Soil	1 ppm	Customized	(<5% at chosen action level)					$56/test
2	BTEX-Soil (TPH, calibrators avail.)	2 ppm	2-300 ppm	(5% in calibration range)	95% confidence in calibration range	4°C (1 year) 25°C (short periods)	Discrete ranges (semi-quant.)	18 assays/hour (18 assays/batch)	$20/test
	BTEX-Water (TPH calibrators avail.)	0.1 ppm	0.1-25 ppm						
	PNA-Soil	1 ppm	1-10,000 ppm (with dilution)	(>5% in calibration range)					$20/test
3	BTEX-Water (TPH calibrators avail.)	0.02 ppm	0.02-3 ppm	<5% at .09 ppm	N/A	4°C (3-6 Mo.)	Quantitative	51 samp/batch (up to 60 assays/ batch)	$20/test
	BTEX-Soil (TPH calibrators avail.)	0.2 ppm	0.2 to 30 ppm	<5% at 0.9 ppm	N/A				$20/test
	PNA-Soil	0.07 ppm	0.07-5 ppm	<5% at DL	<10% near DL				$40/test
	PNA-Water	0.007 ppm	0.007 ppm on up						$11/test
4	BTEX-Water	0.25 ppm	0.25-60 ppm	<5%		4°C (3-6 Mo.)	Quantitative	10-20 Samp/Hr. (30 samp/batch)	$40/test
	BTEX-Soil	3.5 ppm	3.5-950 ppm						$40/test
	PNA-Water	0.05 ppm	0.05-0.82 ppm	<5%					$50/test
	PNA-Soil	0.7 ppm	0.7-140 ppm						$50/test
5	BTEX-Water	0.6 ppm	0.6-10 ppm	<0.1% vs. 8020	<3% vs. 8020	25°C (9 months)	Discrete ranges (semi-quant.)	4 samp./20 min (4 tests/kit)	$30/soil $25/water
	BTEX-Soil	2.5 ppm	2.5-35 ppm			4°C (1 year)			
	PNA-Soil	0.6 ppm	0.6-25 ppm						
	PNA-Water	0.008 ppm	0.008-0.25 ppm						

units differs among kits. Each kit contains specific instructions for sample, blank, and standard preparation. Generally, a 5- to 10-gram soil sample is extracted and 200 μL of water is aliquoted for analysis. All reagents are allowed to reach room temperature, and the spectrophotometer is allowed to warm up in accordance with kit instructions. Assays are run in batches that include the appropriate standards, blanks, QC checks, and the actual samples. The number of assays that can be analyzed in a single batch depends on the kit as well as the skill and training of the field technician. About 30 minutes is required to complete all of the steps in a typical assay. Five to eight assays per hour is a realistic goal in the field, but larger numbers are possible.

Calibration procedures range from a 3-point standard curve analyzed in the field to one or two standards analyzed at the action level. Some analytical kits have preprogrammed standard curves and claim to require no calibration in the field.

QUALITY ASSURANCE/QUALITY CONTROL

Generally an important feature of field QC is the interactive approach of obtaining results, then adjusting the QC analyses to suit the actual conditions at the site. Ideally, the process of adjusting the amount of QC sampling along with optimizing locations for taking the samples produces the best possible overall data. Optimization of sampling locations and collection of QC samples will be addressed more fully in Phase 2 of this project.

In order to achieve Level 2 data quality objectives, the following basic QA/QC elements should be included in the sampling plan.

Calibration

A multipoint calibration with the target species or calibration at one or two action levels should be performed with each batch of samples. The manufacturer's recommendations should be followed exactly to ensure good results. (Calibration with a known site contaminant is recommended.) If standard curves are preprogrammed, a check standard should be analyzed with each batch of samples to verify the calibration.

Method Blank

Extraction solvent should be analyzed with each batch. The blank will develop the darkest color and provide an indication that the assay was properly executed. If the blank does not develop color, the

entire batch is invalid and should be repeated. If the results are used, they should be qualified by non-conformance.

Duplicate Field Analyses

Between 10 and 20 percent of all field samples should be analyzed in duplicate.

Confirmation by Reference Method

Confirmation of both negative and positive samples (above and below the action level) should be provided using an EPA-approved laboratory method. The exact number of samples subject to confirmation depends on the data quality objectives specified in the project plan.

Matrix Blanks

Uncontaminated soil from the site should be collected and analyzed to document matrix effects on the assay. Significant differences from the solvent blank indicate an increased possibility of false positives.

Section 6
PORTABLE INFRARED DETECTORS

SUMMARY

Portable infrared (IR) analyzers can be used to perform TRPH field analyses of soil and water samples relatively quickly. The comparable laboratory methodology is EPA Method 418.1. The scope of the reference method includes the fluorocarbon-113 extraction of a liquid sample followed by IR analysis at about 2950 cm^{-1} (wavelength of 3.4 to 3.5 microns). The parameter TRPH is defined as the fluorocarbon-113 extractable hydrocarbons that remain after the addition of silica gel to the extract to remove polar nonpetroleum hydrocarbons. Although the method is applicable to the measurement of light fuels, about half of any gasoline present may be lost during the extraction process. The method is most effective for detecting petroleum hydrocarbons in heavier fuels such as diesel and motor oil in the C_6 to C_{26} range (i.e., hydrocarbons having boiling points >70°C).

Sample preparation by the reference method for water samples consists of extracting a 1-liter sample using the separatory funnel procedure included in the method. The preparation procedure for soil and sludge samples is presented in EPA Method 9071. It consists of chemical drying and soxhlet extraction of a 20-gram sample using fluorocarbon-113.

The portable IR analyzers differ from the laboratory models in that they are relatively small and rugged, generally built on a sturdy platform, equipped with a carrying case, and designed to operate on DC current. The field IR procedure involves a modification of EPA Method 418.1. The modification involves the sample preparation phase of the analysis. Sample extraction for soil samples is conducted in the sample containers or special containers designed for field extraction, as opposed to the conventional extraction apparatus used in the laboratory. The accuracy of the field IR test depends on the efficiency of the field extraction procedure and the soil type. A strong correlation between soil type and precision of the analyses was reported in the literature; the analytical precision of granular soil samples was notably higher than that of cohesive soil samples.

METHOD OVERVIEW

Application and Advantages

The IR field methodology test provides immediate on-site TRPH results that can be used to make field decisions regarding contaminant location. This method provides semiquantitative results because it

measures a range of hydrocarbons rather than specific constituents (see Interferences and Limitations in the following section). A portable IR instrument can be used for screening soil and water samples that are contaminated with weathered gasoline or heavy fuels such as diesel fuel and motor oil. The method is simple and inexpensive to perform and can result in significant time and analytical cost savings. Table 6-1 summarizes the capabilities and practical considerations for the IR field methodology.

Table 6-1. Field IR Capabilities and Practical Considerations

	Capabilities
Compounds detected:	Fluorocarbon-recoverable petroleum hydrocarbons
Matrix:	Soils/sludge, water
Achievable detection limit:	0.08 ppm - Water 2 ppm - Soil
	Practical Considerations
Soil type:	Extraction efficiency is generally poor for more cohesive or silt- and clay-rich soils and better for looser more sandy soils.
Hydrocarbon type:	Distillate materials (e.g., fuel oils, diesel fuel, and jet fuels) and lubricating oils are effectively extracted and measured, whereas aromatic hydrocarbons tend to have a low bias.
Estimated cost per sample:	$5 to $31
Estimated analytical time per sample:	5 to 20 minutes
Quality of data:	Level 2
Difficulty of procedure:	Moderate
Laboratory equivalent method:	EPA Method 9071/418.1

INTERFERENCES AND LIMITATIONS

A significant limitation for using portable IR detectors is the extraction process. The solvent currently being used for extraction (fluorocarbon-113) will likely be phased out in the near future. EPA is currently evaluating other solvents that can be used with EPA Method 418.1 (EPA, 1993a and b) such as n-hexane or perchloroethane. Initial results indicate that currently no solvent is equivalent for use with this method (n-hexane interferes with the analysis; perchloroethane, like other IR solvents traditionally used such as carbon tetrachloride, is no longer acceptable from a health and safety standpoint). Continued use of this method requires that a new solvent be found.

Two accessories recently introduced for IR analysis show promise in minimizing the interference caused by n-hexane. Disposable IR cards, although optimized for use with Fourier Transformer Infrared Spectrometers, have been used with dispersive IR spectrometers. The sample preparation procedures for the cards include a solvent evaporation step that may eliminate interference caused by the solvent during analysis. Solid phase extraction disks are used in the proposed EPA Method 1664, "N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons)." This n-hexane extraction method was developed to replace the gravimetric procedure (413.1) that employs fluorocarbon-113 as the extraction solvent. The proposed method minimizes solvent usage and disposal and results in a more concentrated eluate/lower solvent volume.

For both the field extraction and the extraction procedure specified for soil/sludge extraction (EPA Method 9071), light hydrocarbons or constituents may volatilize during the procedure. Up to 50 percent of the volatile constituents in gasoline may be lost using the fluorocarbon-113 extraction procedure specified for sludge/soil extraction (EPA Method 9071) prior to IR analysis. Evaporation of light hydrocarbons (C_4 to C_6) can occur for soil samples during the addition of sodium sulfate to dry the sample. The field extraction procedure using the available extraction kits for soil samples does not produce as rigorous an extraction as is produced by the EPA Method 9071 procedure and may not be directly comparable because of the differences between extraction procedures. Insufficient data are available, however, to define the recovery rate for the field extraction procedures. In addition, a high bias caused by nonpetroleum hydrocarbons will result if the silica gel step is omitted or not properly performed during sample preparation and extraction. As indicated, the method may not perform well with compacted cohesive soils such as clays and silts.

This method measures a range of hydrocarbons that could be recovered from the sample rather than specific constituents (thus the title of the method, TRPH). The accuracy has not been fully determined for measuring petroleum-based fuels in soil. As mentioned previously, lighter constituents (e.g., BTEX) are not accurately measured.

These problems are compounded when attempts are made to interpret the results for different types of petroleum hydrocarbons. No simple method exists for directly comparing the analytical results of gasoline-contaminated soils with those of diesel-fuel-contaminated soils. These inherent problems

make it difficult to determine the relationship of potential health or environmental risks to concentrations of TRPH.

OPERATING PRINCIPLES/INSTRUMENTATION

In this method, petroleum hydrocarbons are extracted from contaminated soil, water, and sludges using 1,1,2-trichloro-1,2,2-trifluoroethane, also known as fluorocarbon-113, and are directly measured by IR spectroscopy. Fluorocarbon-113 was chosen as the extraction solvent primarily because it will not interfere with IR energy in the 3.4- to 3.5-μm range where absorption is nearly 100 percent for most petroleum hydrocarbons. Because of the effects of fluorocarbon on the atmosphere, however, efforts are being made to replace fluorocarbon as a solvent (see Interferences and Limitations, page 6-2). Hydrocarbons that are recoverable using fluorocarbon are typically those that have a boiling point greater than 70°C. Many of the more volatile constituents are lost during sample extraction.

To quantify the amount of hydrocarbons present in an extract, the IR detector measures IR absorption at 3.4 μm. This wavelength corresponds to the hydrogen-carbon bond of alkanes. The intensity of the IR energy at this wavelength is converted to the TRPH concentration in ppm.

The user has a choice of several portable IR instruments (Table 6-2). These instruments are completely portable, rugged, and can be used at the contaminated site or in the laboratory. The analyzers are available with single- or multiple-wavelength photometers and use a conventional

Table 6-2. Summary of Field IR Instruments[a]

Instrument	Measurement Method	Analyte	Output	Ease of Use	Matrix	Sample Size[b]	Detection Limit	Analysis Time	Comparable Reference Method
1	Synchronous 2- or 3-wavelength infrared	TRPH[c] aliphatic aromatic	mg/L	Moderate	Soil water	Soil 20 g Water 1 L	2 ppm 0.08 ppm	15 min	EPA Method 418.1
2	Single beam infrared	TRPH	AU or %T[d]	Moderate	Soil water	Soil 20 g Water 1 L	2 ppm 0.08 ppm	15 min	EPA Method 418.1
3	Nondispersive infrared	TRPH	ppm	Moderate	Soil water	Soil 10 g Water 20 mL	2 ppm 0.08 ppm	15 min	EPA Method 418.1

[a] Adequate documentation of IR instrument method precision and accuracy was not available.
[b] Required for analysis.
[c] TRPH = Total recoverable petroleum hydrocarbon.
[d] AU = absorbance units; %T = percent transmission.

IR source. Single-wavelength instruments measure at 3.4 μm as specified in the reference method. This wavelength produces a low response to aromatic compounds, and the analysis generally relies on the calibration standard to contain about the same aromatic content as the sample. Dual-wavelength analyzers measure at the conventional 3.4 μm and also at 3.3 μm. The two-wavelength methodology measures absorbance due to aliphatic hydrocarbons at 3.4 μm as well as absorbance due to aromatic hydrocarbons at 3.3 μm, providing a better quantitative measurement of the contamination.

Several portable single- and dual-wavelength instruments are also equipped with the capability to measure absorbance at a reference wavelength. These scanning or interference filter-based analyzers have the advantage of providing greater stability by canceling short-term source and electronic fluctuations as well as long-term IR source and optical component changes.

Several on-site extraction/sample preparation kits available from the manufacturers contain instruments and apparatus to simplify soil sample preparation in the field. The field extraction procedure generally consists of a single extraction step performed by adding fluorocarbon-113 to the chemically dried soil sample and manually shaking for a specified time period. Water samples are also typically prepared using a single extraction in a separatory funnel. In contrast, the typical laboratory extraction procedure results in the sample being extracted at least three times. One nondispersive infrared (NDIR) instrument is equipped with an internal extraction vessel with a 20-mL capacity for water samples. Soil sample analysis is conducted using this instrument by extracting the soil sample externally and adding the extract to the internal extraction vessel. The small sample size results from the increased sensitivity of the NDIR methodology.

METHOD REQUIREMENTS

Initial Setup

TRPH field analysis is conducted by use of a portable IR spectrophotometer calibrated with standards comprised of the petroleum hydrocarbons of interest or the reference oil standard specified in EPA Method 418.1. The reference oil standard has a composition of 37.5 percent isooctane, 37.5 percent hexadecane, and 25 percent chlorobenzene by weight. The aromatic compound (chlorobenzene), however, produces a poor response at the 3.4-μm analytical wavelength and results in a disproportionate contribution to the absorbance of the standard. This standard is best suited for the measurement of aliphatic hydrocarbons. Calibration standards can also be made using the actual contaminant present at the site. These standards may be made using gasoline, diesel fuel, jet fuel,

kerosene, lubricating oils, etc., based on the type of contamination present at the site. Care should be taken, however, to prepare a standard that is representative of the contamination at the site at the time of measurement. For example, a standard prepared with fresh gasoline may not be appropriate at a site where only the weathered components of gasoline remain. Dual-channel analyzers can be calibrated on the 3.4-μm channel using an aliphatic (hexadecane) standard and on the 3.3-μm channel using an aromatic (benzene) standard.

An estimated 2 to 3 hours will be required for startup at the site, including instrument setup and standards preparation. After the instrument has warmed up (approximately 30 minutes), it is zeroed and the calibration range is set. A multipoint calibration curve is developed using calibration standards, and a calibration check is performed.

Sampling and Analysis Procedures

Soil and water samples are prepared for analysis by extracting standard aliquots with fluorocarbon-113 or equivalent to remove petroleum hydrocarbons. The extraction procedure for soil samples consists of extracting 15 to 20 g of soil with fluorocarbon-113. The soil samples are mixed with anhydrous sodium sulfate to remove water prior to extraction.

Care should be taken during the mixing step because some of the volatile compounds can be lost when the sodium sulfate is added to the sample. This may be insignificant at a site where weathered gasoline and heavier petroleum products are the contaminants of interest. The field extraction procedure for soils has not been standardized, and most of the literature case studies describe a slightly different extraction methodology. The procedures, however, generally consist of a single-stage extraction using a manual shaking technique. Performance of the field extraction is directly related to soil type. Extraction efficiency by matrix decreases in the order: sand, organic soil, clay.

The extraction procedure for water samples consists of adding approximately 30 mL of fluorocarbon-113 to 1 liter of water and performing the extraction by shaking in a separatory funnel.

Silica gel is added to the soil and water fluorocarbon extracts to remove polar nonpetroleum hydrocarbon materials such as fatty acids. A portion of the extract is then placed in the spectrophotometer for analysis.

Samples should be collected and placed in appropriate containers with minimum exposure. Samples that cannot be analyzed within 4 hours should be properly preserved. Water samples should be preserved using hydrogen chloride (HCl) and cooled to 4°C. Soil samples should be preserved by cooling to 4°C.

QUALITY ASSURANCE/QUALITY CONTROL

The specific QC check and frequency should be determined based on the data quality level selected for the project and the intended use of the data. The QC checks that are appropriate for this method include: (1) generating a multipoint calibration curve over the linear range of the instrument using either field calibration standards or a standard synthetic mixture; (2) performing calibration checks; (3) using matrix spikes, matrix spike duplicates, and sample preparation blanks to determine the relative percent difference in recoveries for analytical accuracy and precision; and (4) using sample analysis blanks to measure cumulative interferences. Ideally, calibration standards should be developed from hydrocarbons from the site if they are available. Alternatively, the synthetic mixture specified in EPA Method 418.1 can be used.

Section 7
DO/REDOX ELECTRODES

SUMMARY

Field portable meters capable of measuring DO concentrations are available from a variety of manufacturers. These instruments can record DO levels in fresh water or saltwater and most are equipped to make temperature and salinity corrections. Oxidation/reduction potential (ORP, Eh or REDOX) can be difficult to measure even with the best available instrumentation. The sensing device (most often a platinum electrode in a circuit with a standard reference electrode) may be unstable in fresh waters with low ionic strength. The time required to obtain a stable reading may be quite long in some cases. Although it is possible to measure REDOX in the field, considerable operator skill and experience are necessary to obtain accurate results.

Two types of field measurements for DO and REDOX are possible with the current generation of water quality instrumentation: on-site and *in situ*. On-site refers to measurements in which the water samples are removed from the aquifer or body of water and the sensor is immediately placed in the water sample for measurement. Great care is taken to isolate the sample from the atmosphere. *In situ* or "down-hole" sensors refer to measurements made by lowering the probe directly into the well or surface water at the desired depth. After a suitable equilibration time, continuous monitoring of water quality can be performed.

Two types of on-site measurements are available: discrete sampling and flow-through sampling. Discrete samples are collected in the appropriate sample container [e.g., 300-mL biological-oxygen-demand (BOD) bottles or other suitable glass-stoppered bottles capable of preventing entrainment of atmospheric oxygen]. The DO or REDOX sensor is placed in the sample for measurement. Flow-through cells incorporate the sensor in a cell that is in line with a pump. DO and/or REDOX and other primary water quality parameters are continuously monitored as the water flows through the cell. The flow-through technique provides immediate results and minimizes problems resulting from the collection and transport of samples to an on-site laboratory or measurement station. This technique can be used as part of well purging, groundwater quality evaluation, evaluation of corrective action options (e.g., natural attenuation, aquifer bioremediation, *in situ* air sparging), and risk assessment.

Two types of *in situ* measurements are available: short-term continuous monitoring and long-term continuous monitoring (see section on Instrumentation, page 7-7). Once calibrated, positioned at the

desired depth, and equilibrated to the sample conditions, most probes can send continuous readings to surface instrumentation. Meters may display or log these results for a short period of time. A probe designed for long-term monitoring incorporates features to allow the probe to be anchored in place and operated unattended for long periods of time. Long-term monitoring can be useful in evaluating groundwater quality before and during corrective action.

DO/REDOX instruments vary greatly in price, capability, and complexity. Complex probes are available to record DO and REDOX simultaneously along with a variety of other water quality parameters including temperature, specific conductance, turbidity, pH, conductivity, salinity, resistivity, total dissolved solids, and depth. Obviously, capital costs for instruments capable of measuring all of these parameters will be quite high compared with costs for simple DO meters. The cost and complexity of the instrument selected for site characterization or monitoring will depend on the type of sampling required and the parameters to be monitored.

METHOD OVERVIEW

Application and Advantages

The membrane electrode method has been used to monitor DO levels and distribution as part of site characterizations, to monitor DO levels during well purging operations, and to evaluate and monitor *in situ* corrective action technologies (e.g., bioremediation of groundwater, air sparging). Dual DO/REDOX measurements can be complementary. If REDOX measurements indicate a negative or reducing environment, the corresponding DO reading should be low (e.g., <1 mg/L). *In situ* DO/REDOX measurements can also be used to evaluate stratification in an aquifer.

Because DO/REDOX electrodes are very selective, interferences are minimal. DO/REDOX electrodes can provide reliable results in groundwater that is high in dissolved solids and in brackish waters. Table 7-1 presents the capabilities and practical considerations for field DO/REDOX meters.

INTERFERENCES AND LIMITATIONS

REDOX

REDOX measurements cannot be assigned to a specific oxidizing or reducing species in the field unless detailed knowledge of sample composition is available. It is difficult to obtain reproducible REDOX results in poorly buffered water samples.

Table 7-1. Field DO/REDOX Capabilities and Practical Considerations

	Capabilities	
Compounds detected:	Dissolved oxygen - mg/L (preferred units) - % saturation (relative to water-saturated air at sea level) REDOX - mV	
Matrix:	Surface water, well water, and saltwater	
Quantitation range:	Dissolved oxygen	- 0 to 20 mg/L - 0 to 200% saturation
	REDOX	- -999 to +999 mV
Precision:[1]	Dissolved oxygen	- ± 0.05 mg/L - ± 0.5% saturation
	REDOX	Not applicable
Accuracy:[1]	Dissolved oxygen	- 0.1 mg/L
	REDOX	- ± 20 mV
	Practical Considerations	
Cost:	DO meters - Acquisition cost high, maintenance and operation cost quite low. REDOX - Acquisition cost of REDOX electrode for portable pH meters is low; submersible REDOX sensors high, and maintenance and operating cost very low.	
Estimated analytical time:	DO meters - 1 to 5 minutes REDOX - 10 minutes or less	
Quality of data:	Level 2	
Difficulty of procedure:	DO - moderate REDOX - moderate to difficult	
Laboratory equivalent method:	DO - Standard Method 4500-OG REDOX - ASTM Method D-1498-93	

[1] Accuracy and precision estimates given above apply to measurements made with the standard or galvanic cell DO electrodes (these are the electrodes on which Standard Method 4500-OG is based). Modifications of the standard electrode have been developed by manufacturers for specialized applications and to reduce the sensitivity of the probe to flow and fouling. The accuracy and precision of the modified electrodes have not been determined. With rare exception, the standard electrode or galvanic cell is adequate for on-site DO investigations.

DO

Insoluble organic and inorganic materials that react, coat, or clog the surface of the membrane will affect the performance of DO probes. This process is called active fouling and can occur in water with high concentrations of sediment and other insoluble materials, oils, and biological growths. Prolonged exposure to reactive gases such as hydrogen sulfide can coat the anode, which will tend to lower sensitivity of DO probes. Frequent cleaning and calibration may be necessary under such circumstances.

Normal operation of the standard and galvanic probes causes chemical changes in the electrolyte concentration and changes to the surfaces of the sensing and reference electrodes. These changes will require the probe to be serviced at regular intervals. In extreme situations, the oxygen-permeable membrane may be torn, requiring replacement and recalibration. Salinity corrections for DO measurements are based on seawater composition. A small error will result in other types of brackish water.

OPERATING PRINCIPLES

Dissolved Oxygen

Probes designed to detect DO consist of reference and sensing electrodes immersed in supporting electrolyte and separated from the sample solution by a selective membrane (Figure 7-1). The oxygen sensor consists of the membrane and a closely fitted electrode. The sensing electrode is considered the cathode where molecular oxygen is reduced, and the reference electrode is considered the anode. Only species that can permeate the membrane and are reduced at the sensing electrode will produce a signal, resulting in the highly selective nature of the DO sensor. Although other gases may permeate the membrane, only oxygen is easily reduced at the cathode. The cell current is linearly proportional to the DO concentration (strictly, the activity of molecular oxygen) and can be converted to concentration by simple calibration procedures.

Temperature and salinity affect the concentration of oxygen dissolved in water. Temperature directly affects the solubility of oxygen, and the permeability of the membrane varies with temperature. Oxygen concentration varies with the ionic strength (salinity) of the test solution versus the standard solution. For these reasons, sample results must be corrected for temperature and salinity factors. Algorithms to calculate the magnitude of these corrections are based on the physical chemistry of dissolved gases and permeation theory. These algorithms are provided in Standard Method 4500.

The field technician does not need to be concerned about these calculations because most portable DO instruments are programmed to apply the algorithms automatically by using information on temperature and salinity that it gathers from sensors in the probe assembly. Temperature and salinity corrections can be made at a later time if the field meter does not have the capability (provided that temperature or conductivity data are available for the samples).

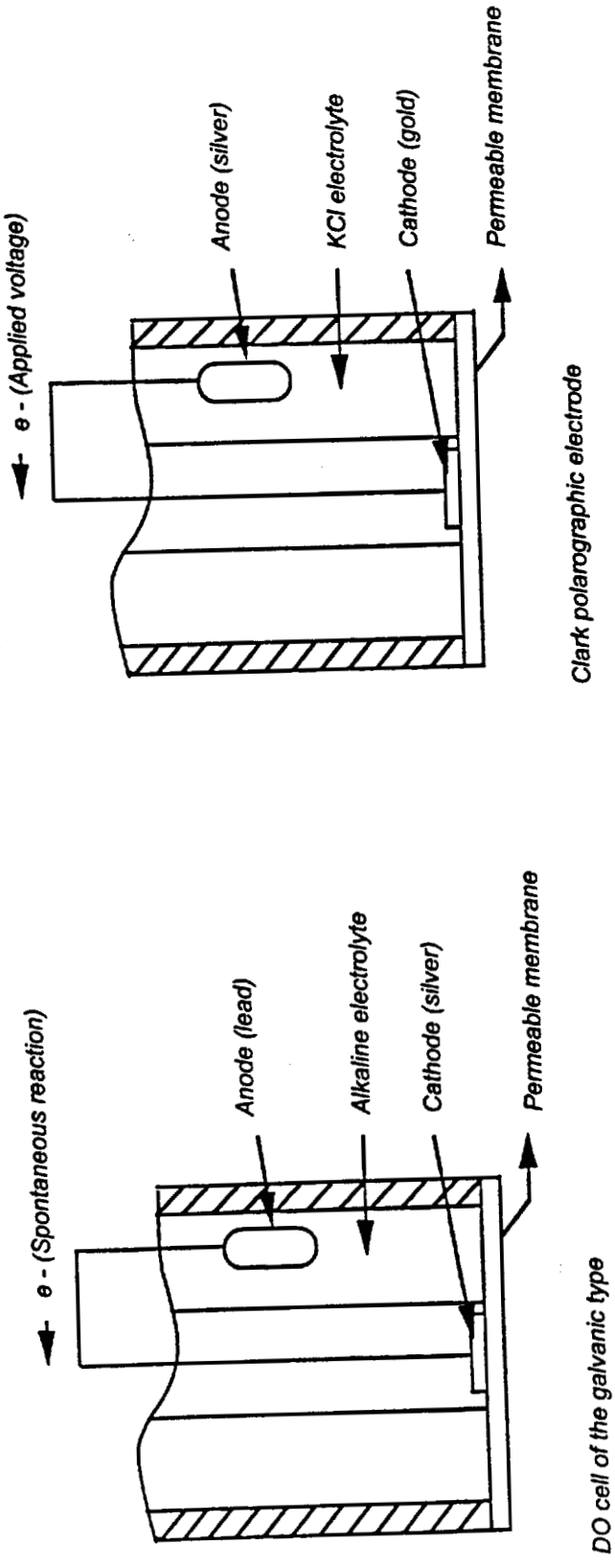


Figure 7-1. Principle of Measurement for Dissolved Oxygen

Several types of DO sensor designs are available depending on the desired application. The most commonly used electrode is the Clark-type polarographic (commonly called the "standard") electrode. The Clark DO probe utilizes an applied potential to reduce molecular oxygen. This device requires circulation of the water being analyzed. If the water is not moving at about 1 foot per second, an error in DO concentration will result. The error is caused by the buildup of a concentration gradient in the vicinity of the DO membrane as oxygen is consumed by the sensor. Circulation of the water replenishes the sample near the sensor. The galvanic cell (Figure 7-1) is less commonly used for detecting DO. The voltage detected by this type of probe is produced by the spontaneous reduction of molecular oxygen at the cathode (analogous to a fuel cell). Because less oxygen is consumed from the sample, this cell is less sensitive to low water flow.

For both types of sensors, molecular oxygen is reduced by a noble metal cathode fitted closely to the permeable membrane. A different type of reference electrode and electrolyte in which the electrodes are immersed is required for each of the two cell types. Chemical changes that occur in the electrolyte and on the surface of the electrode as a result of the chemical reactions in the cell will eventually necessitate cleaning of the electrode surfaces and changing of the electrolyte.

A third type of DO sensor reportedly consumes no oxygen from the sample. The probe consists of three electrodes. Two active electrodes are interspaced on a supporting substrate and covered with an electrolyte. The third electrode (reference) also contacts the electrolyte in order to set the electrochemical potential. The two active electrodes are connected as cathode and anode, and perform oxygen reduction and generation functions. The electrolyte is retained around the electrodes by a gas-permeable membrane, which is covered in turn by silicone rubber.

When the probe is immersed in a sample stream, oxygen diffuses through the membrane and is reduced at the cathode. Simultaneously, an equal amount of oxygen is generated at the anode. The diffusion continues until the oxygen tension on both sides of the membrane is equal and balanced. The current necessary to maintain this equilibrium is converted, by the electrical circuitry of the meter, to a display of the concentration of DO in the solution. In theory, the electrodes are not consumed and the electrolyte remains unchanged. Thus, the life of the cell is greatly extended.

REDOX

REDOX is simply the voltage developed between a noble metal electrode and a standard reference electrode in a test solution (Figure 7-2). The potential depends on the activities of the oxidizing and reducing species in the solution. If the activities of the oxidizing species are greater than those of the reducing species, a voltage greater than the reference electrode voltage will result. If the activities of reducing species predominate, a voltage less than the reference electrode voltage will result. Although REDOX is temperature-dependent, temperature corrections are rarely performed because of theoretical considerations involving the lack of knowledge of the exact nature of the active species in the sample.

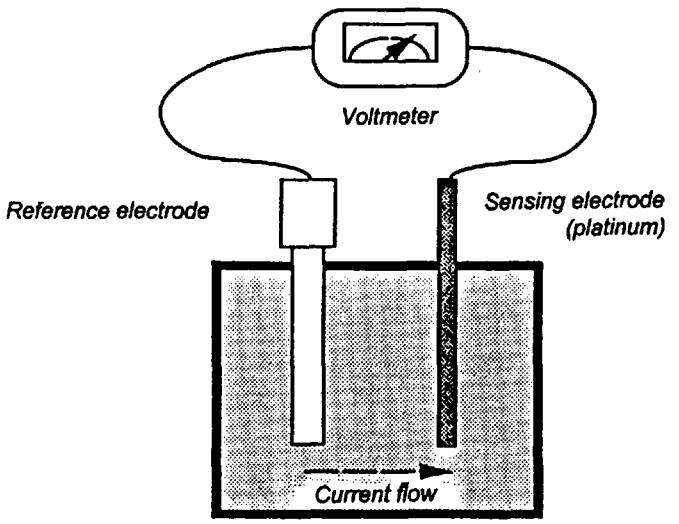


Figure 7-2. Principle of Measurement REDOX

INSTRUMENTATION

DO meters are available that read directly in reportable units and are specifically designed for field use as well as continuous monitoring. Sophistication ranges from hand-held direct-reading meters to PC-compatible meters with computer interface and graphic capabilities. Table 7-2 presents a summary of the portable DO/REDOX instruments and a comparison of the various features of the different models.

Cleaning procedures have been developed to extend the life of both REDOX and DO electrodes. Membranes can be easily exchanged when they become fouled. Replacement membranes, electrolyte, and calibration aids are available in kit form from the suppliers of DO/REDOX instrumentation.

Table 7-2. Summary of DO/REDOX Instruments

	Manufacturer							
Feature:[1]	1	2	3	4	5	6	7	8
Dissolved oxygen	X	X	X	X	X	X	X	X
REDOX (simultaneous meas.)	X	X						
REDOX (separate meter; nonsubmersible probe)			X	X	X	X	X	
Stirrer	X	X			X			
Low-flow cell	X	X	X	X	X		X	X
Flow-through cell	X	X						
Data logger	X	X		X				
Analog output	X	X		X	X	X		X
Computer interface	X	X						
Temperature compensation	X	X	X	X	X	X	X	X
Salinity compensation	X	X		X				
Max cable length, feet	500	500	30	30	300	230	6	20
Probes to fit 2-inch well bores	X							
Probes to fit 4-inch well bores	X	X						
Auto air calibration	X	X	X	X	X			X
Continuous monitors	X	X						

EXPLANATION OF FEATURES[1]

DISSOLVED OXYGEN:
All meters are designed around this parameter.

REDOX:
An X appears in this line only if the instrument can simultaneously measure DO and REDOX using a submersible probe. These probes are called "multi-probes" and are capable of measuring a variety of other parameters in addition to DO/REDOX.

PROBES TO FIT 2-in. OR 4-in. WELL BORES:
Since multi-probes are quite large, it is necessary to note their dimensions in relation to common well bore sizes.

STIRRER:
Stirrers are used in continuous monitoring or low-flow applications. The user will generally have a choice whether to utilize stirring with the standard-type electrode, or to avoid stirring altogether by switching to a low-flow sensor.

ANALOG OUTPUT:
Analog voltage output is available to a printer or to drive external analog devices.

LOW FLOW:
An X indicates that an electrode design is available that is less sensitive to flow than the standard electrode. However, this does not mean the probe can be used for continuous-monitoring applications. Hand-held probes of the galvanic type require little flow, as indicted, and agitation of the probe by the operator is possible if needed.

FLOW-THROUGH CELL:
An X indicates that an off-the-shelf device is available to measure multiple water quality parameters, including DO/REDOX in a flowing sample stream - most often used when pumping water from an aquifer via a sampling well.

DATA LOGGER:
An X means that the display device or the probe itself has nonvolatile memory to record multiple measurements.

COMPUTER INTERFACE:
The instrument can be interfaced to a computer so that data can be transferred from the data logger to the computer and manipulated by standard or custom computer programs. At

(Continued)

EXPLANATION OF FEATURES (Continued)

this point, data can be graphically displayed or further transmitted to networked computers.

TEMPERATURE COMPENSATION (DO):
The meter has a built-in thermistor to measure sample temperature and then correct the DO result for the difference in temperature from when the DO sensor was calibrated.

SALINITY COMPENSATION (DO):
An X indicates that a probe is available with a built-in sensor to record conductivity and convert the reading to salinity. The DO result is corrected for salinity using a standard algorithm. With some meters, the salinity must be entered manually via the keyboard. Then the internal algorithm will calculate the correction factor and apply it to the displayed result. The latter case is not considered an automatic correction in the table.

MAXIMUM CABLE LENGTH AVAILABLE:
The maximum standard cable length available for submersible probes.

AUTO AIR CALIBRATION (DO):
Generally synonymous with "push-button" calibration. The instrument is calibrated quickly and easily in air and the zero point is set electronically without the need to immerse the probe in a zero percent DO solution.

LONG-TERM CONTINUOUS MONITORING:
Probes and associated electronic components are available for applications where continuous unattended operation is desired. The probe can be preprogrammed to take measurements of DO/REDOX as well as other water quality parameters at specified intervals, and hold or transmit the results as requested.

Dissolved Oxygen

Low water flow is a particular problem for the standard electrode because it consumes oxygen in the vicinity of the membrane, and in low-flow situations a concentration gradient is created that can result in a low bias. In general, groundwater flow tends to be low, and some type of circulation is required. Several modifications to the standard polarographic electrode are used. The traditional approach is to add a stirrer to the probe assembly. This technique is effective, but stirrers consume large amounts of battery power and are prone to maintenance problems. These problems have been minimized in the current generation of instruments by stirring only when a measurement is taken. The second approach utilizes changes in the profile of the electrical current supplied to the probe and/or new membrane designs to reduce sensitivity of the probe to low water flow and fouling. Although the new designs are less sensitive to flow, they may be more difficult to work with because of longer equilibration time and faster sensor wear out, and they are not as accurate as the standard electrode.

The galvanic cell is less sensitive to flow because of its design. It simply consumes less oxygen in the vicinity of the membrane and is less likely to induce a concentration gradient in poorly mixed or low-flow water. The third type of DO probe reportedly does not consume oxygen, and is therefore not sensitive to the effects of low water flow.

REDOX

Only two manufacturers make submersible REDOX probes. These probes are part of larger, more expensive multiprobe assemblies. Nonsubmersible REDOX probes are available from several manufacturers. These probes attach easily to field-portable pH meters.

METHOD REQUIREMENTS

Initial Setup

A few simple connections, followed by calibration, are all that is required for initial setup of portable DO/REDOX meters. Units that are interfaced to a computer will require that the operator have a working knowledge of MS-DOS-based operating systems as well as the suppliers' data reduction software. DO meters should be allowed a thorough warm-up period before use if the unit has been in storage.

Sampling Procedures

In situ DO/REDOX measurements are made by lowering "down-hole" probes into a monitoring well and taking a reading. For most groundwater monitoring wells, the hydraulic gradient is usually insufficient for accurate readings (the cells consume oxygen locally around the probe). Typically, an appropriate degree of turbulence is created by either mechanical stirring or pumping water past the probe. The degree of turbulence should be sufficient to allow fresh water to circulate; however, it should not entrain oxygen, which can provide anomalously high readings. Also, the same degree of turbulence should be used for both calibration and measurements. Many probes use a semipermeable membrane that provides a faster response time for low-flow situations. The probe should be recalibrated after replacing the membrane or cleaning the probe.

After the probe is placed in the water, a reading is taken. If the probe does not automatically compensate for temperature changes, the temperature of the water should be recorded at the sample probe during the measurements for later corrections.

On-site measurements using flow-through cells can provide more consistent and accurate DO measurements, depending on the depth at which the sample is collected and the sample transfer system used. The quality of the DO measurement primarily depends on the quality of the sample (i.e., degree of oxygen entrainment during sampling). For 4-inch wells, bladder pumps have been reported to minimize the sample disturbance and oxygen entrainment. Groundwater samples have also been collected from <1-inch drive points, piezometers, small-diameter direct-push points, or direct-push samplers with a variety of pump systems (e.g., peristaltic pump and Tygon™ tubing). Practical considerations should be given to sample transfer system features such as line size, rates of transfer, kind of pump and location, practicality of cleaning the transfer system, and other maintenance. The water flow rate to the cell should be constant and at a flow rate at which oxygen entrainment is

minimized. As the water flows past the probe, readings are recorded. Depending on the probe, the pressure past the cell should not exceed 10 or 15 psi in the flow cell.

For discrete sampling, precautions listed in Standard Method 4500-OG should be followed. This method discusses sampling procedures and precautions as well as appropriate sampling containers. The sample is collected using a sample transfer or pumping system that is generally acceptable for DO sampling (e.g., bladder pumps for withdrawal from monitoring wells, peristaltic pumps with Tygon™ tubing from narrow-diameter points). The sample should be collected and analyzed immediately after sampling. Rapid changes in temperature should be minimized.

QUALITY ASSURANCE/QUALITY CONTROL

The tolerance limits for bias and response time should be set prior to commencement of field measurements. The tolerance limits will determine the frequency of calibrations and maintenance to be performed in the field.

Response Time

This is the most important quality control check to be made in the field for DO/REDOX systems. It is used to determine the condition of the electrodes, especially those in water with high contaminant concentrations, dissolved inorganic salts, sediments, and other insoluble material. Fouling of the sensing electrodes is the most likely cause of errors in measurement of DO/REDOX.

The condition of the DO sensor can be checked by performing an air calibration and then immersing the probe in a solution in which all of the DO has been chemically reduced. The probe may also be immersed in a pure nitrogen atmosphere. (A zero point is generated by addition of excess sodium sulfite and a trace of cobalt chloride to bring the DO of the actual test water to zero.) The time required for the reading to reach zero can then be compared with that of a clean probe and the required tolerance limits. In addition, the calibration should be verified. A bias from the previous calibration and slow response indicate that the membrane has become fouled and may need to be changed.

The condition of the REDOX probe is verified by recalibration with REDOX standards. Bias from the initial calibration and response time should be noted and compared with that of a clean sensor. Cleaning or more frequent calibrations may be required if the bias or response time is outside tolerance limits.

Calibration

DO probes are most easily calibrated in air saturated with water vapor. Accessories are available to perform this calibration at the actual sample temperature. Calibration of DO probes using the Winkler titration as a standard is not recommended for field work because of inherent errors in the Winkler method and potential errors related to sample handling.

REDOX probes are calibrated with standard REDOX solutions available from the manufacturers. Calibration kits with all the necessary hardware and reagents are available from all the manufacturers listed in Table 7-1. Calibration for DO and REDOX can be performed in the field in less than 30 minutes.

Section 8
EMERGING FIELD ANALYTICAL METHODS

A variety of emerging field analytical methods are being developed and used for evaluating petroleum releases. The emerging methods presented in this section are those that are commercially available and have been tested and used to a limited extent for evaluating petroleum releases. These methods include fiber optic chemical (FOC) sensors, visible UV fluorescence and UV fluorescence spectroscopy, UV absorption spectroscopy, and GC/MS. The number of manufacturers, application at petroleum release sites, and available performance information for most of these methods is limited and still in development. Only mobile laboratory GC/MS has been fully developed and only recently has been applied at petroleum release sites. A brief description of each method and typical use are provided in this section.

FIBER OPTIC CHEMICAL SENSORS

FOC sensors are based on changes of light transmitted along an optic fiber. The outside of a small segment of the optical fiber in the probe is replaced with a chemical coating, which changes the refractive index in the presence of hydrocarbons. The change in the refractive index determines the amount of light transmitted and is proportional to the hydrocarbons present. The probe is located at the end of a cable and can be placed into monitoring wells or other locations to measure hydrocarbons that are in soil vapor and dissolved in groundwater. The sensor can be calibrated to a specific hydrocarbon constituent or mixture.

FOC sensors were initially used for leak detection and measurement of hydrocarbon vapors. Portable FOC sensors that can be used for evaluating dissolved and vapor-phase hydrocarbons have only recently become commercially available. Preliminary evaluations of FOC sensors sponsored by the manufacturer report a high correlation (>95 percent) with EPA modified Method 8015 for TPH, and EPA Methods 624 and 8020 for BTEX. The reported detection limits for these instruments are 50 ppm as xylene in vapor and 3 ppm as xylene in water. The accuracy of FOC sensors can be temperature-sensitive. These portable FOC sensors are currently being evaluated and may be useful in evaluating temporal and spatial variability in hydrocarbon concentrations.

VISIBLE UV FLUORESCENCE AND UV FLUORESCENCE SPECTROSCOPY

Nearly all PNAs tend to fluoresce when exposed to UV light. Saturated aliphatic constituents such as paraffins do not fluoresce. Fluorescence refers to the emission of visible light resulting from the

movement of electrons to higher and lower orbital states after being excited by UV radiation. Both short- and long-wave UV can be used to fluoresce hydrocarbons.

UV fluorescence has been used for decades in the petroleum industry to identify the presence of petroleum products in drilling mud, cuttings, and soil cores. Two types of UV fluorescence methods are currently being evaluated: visual methods and UV spectroscopy. The visual observation of fluorescent colors can be generally interpreted to estimate the density of crude oils (Table 8-1). Several methods use a viewing chamber lit by UV light to determine the intensity of fluorescence in the sample. Different amounts of solvent can be added to ("cut") soil samples to distinguish petroleum fluorescence from mineral fluorescence, to displace the petroleum product into solution for observation, and to increase the sensitivity of the method. Several studies have reported the practical use of this method as a screening tool for identifying the presence of hydrocarbons. Correlations of the intensity of the fluorescence response and hydrocarbon concentrations, however, have not been made. In addition, possible interference of soil type or organic content has not been documented.

Table 8-1. Fluorescence Color of Crude Oils

API Gravity	Color of Fluorescence
Below 15	Brown to none
15-25	Orange to cream
25-35	Cream yellow to cream
35-45	White
Over 45	Blue-white to violet

UV fluorescence spectroscopy uses an energetic UV light source such as a laser to excite the sample and may employ an optical fiber for transmitting the fluoresced light to a photodiode array detector. A spectrum is produced and the intensity of the spectral band is proportional to the constituent concentration. The ability to distinguish specific constituents may be limited due to overlapping spectral bands, and the inherent nonlinearity of fluorescence emission makes quantitation difficult. However, the method is sensitive to the low ppm range.

Most UV spectrophotometers utilize a nitrogen laser capable of detecting three or more ring aromatic compounds. Because UV fluorescence spectroscopy detects PNAs, results from soil vapor analyses may not correlate with other analytical methods that primarily detect light aromatics. A higher energy light source must be used to detect BTEX and naphthalene. In practical terms, this means that a variable-wavelength light source must be used to measure the full range of aromatic hydrocarbons.

This method has limited application at petroleum release sites. It is being developed for use with a cone penetrometer for mapping PNA concentrations in the subsurface. The aromatic compounds naphthalene and BTEX are much more rapidly attenuated in the fiber optic cables.

UV ABSORPTION SPECTROSCOPY

UV derivative or absorption spectroscopy uses a derivative spectrometer to provide first and second derivatives of the intensity of the light versus the wavelength referred to as the absorption spectrum. Some instruments mathematically produce the derivative while others produce the derivatives optically. This method is being developed primarily to detect BTEX in soils. The instruments are mounted in a mobile laboratory and analyze the volatile constituents purged from a heated soil sample. The absorption bands of each aromatic hydrocarbon are detected and compared with a calibration spectrum. The range of operation is reported to be 5 to 500 ppm by weight BTEX. Initial field results indicate a high correlation with EPA purge-and-trap methods.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

The application of GC/MS to the analysis of petroleum hydrocarbons in the laboratory is well known. EPA Methods 624 and 8240 (BTEX) and 8270 (PNAs) describe the laboratory methods. Several commercial bench-top instruments are small enough to be placed in relatively secure, stationary field laboratories. Replacement of the rotary-vane oil-filled vacuum pumps with molecular drag/diaphragm pumps has been successfully attempted in the field and is a simple modification to make the vacuum system more durable and reduce power consumption.

Portable GC/MS instruments are in various stages of development. Two suppliers offer off-the-shelf battery-operated models for specialized applications, but most of the literature describes modified commercial instruments designed by private research laboratories and academic institutions. The modifications focus on reducing the size, weight, and power consumption of the GC/MS and the associated vacuum system. These instruments are also designed to be mounted in a trailer, but are more modular than laboratory-grade GC/MS and may be operated under generator power.

Novel sample introduction systems have been reported in the literature to be developed for portable GC/MS. Miniature purge-and-trap, direct injection of semivolatile extracts, and thermal-extraction techniques for soils have been reported. Because the inlet systems are designed to be modular, very little downtime is necessary when switching from one to another. Short, narrow-bore GC columns

operated with the split-injection technique provide fast separations and short analytical runs. Normal length capillary columns may be used for regular GC separations. Application software for these portable GCs is currently under development.

Portable GC/MS can distinguish specific hydrocarbon constituents or can be used to identify unknown contaminants. Petroleum hydrocarbons (e.g., BTEX, fuel types, and PNA constituents) can be identified. Very heavy oils, tar, and greases will not be recovered from normal GC columns and inlet systems and therefore will not be measured. Detection limits are typically as low as mobile laboratory GCs and lower than other screening techniques (i.e., 1 ppb and less). In general, GC/MS is well suited for PNAs. GCs are typically used for lighter molecular weight constituents.

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GLOSSARY

Accuracy - The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a systematic error (or bias) component.

Bias - The deviation due to matrix, and other, effects of the measured value from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of a contaminant spiked into a sample (matrix spike).

BTEX - Benzene, toluene, ethyl benzene, and o-, m-, and p-xylene. Aromatic volatile organic compounds found in motor fuels.

Cross Reactivity - The potential for compounds similar to immunoassay target analytes to bind or cross-react with the antibody. The presence of any cross-reacting compounds will lead to measurement of apparently higher target analyte levels than are actually present.

Data Quality Objectives - A statement of the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data.

Detection Limit (DL) - The minimum concentration of an analyte (parameter) that the analyst using the field analytical method will detect in the specific matrix being analyzed. The detection limit used for field analytical methods is compared to a practical quantification limit (PQL) in a laboratory.

Dissolved Oxygen (DO) - The concentration of molecular oxygen dissolved in water. DO is expressed in units of mg/L or percent saturation. The concentration of oxygen, as described by Henry's Law, is directly related to atmospheric pressure and inversely related to water temperature and salinity. The solubility of oxygen increases proportionately with hydrostatic pressure, hence depth. Because of the pressure dependence, the saturation of oxygen can exceed 100 percent.

False Positive/False Negative - A field measurement should reliably give a positive result when the sample constituent concentration is *above* the stated detection limit, and should give a negative result when the concentrations is *below* the detection limit. A positive reading or result when the constituent concentration is below the detection limit (sensitivity) is a false positive; conversely, a negative result when the concentration is above the detection limit is a false negative.

Instrument Detection Limit (IDL) - The smallest signal above background noise that an instrument can reliably detect.

Laboratory Control Samples (LCS) - A known matrix spiked with constituent(s) representative of the target analytes. This is used to document laboratory performance.

Linear Dynamic Range - Linear dynamic range is the range over which the detector response to a compound is directly proportional to the amount of compound injected. Detectors vary in the range of

component concentrations over which they are linear. Wide linear dynamic range is desirable because it simplifies quantitation of samples having widely different concentrations.

Matrix - The component or substrate (e.g., surface water, drinking water, soil) that contains the analyte of interest.

Matrix Duplicate - A split sample that is used to document the precision of a method in a given sample matrix.

Matrix Spike - An aliquot of sample spiked with a known concentration of the target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the precision and bias of a method in a given matrix.

Matrix Spike Duplicates - Split samples spiked with identical concentrations of target analyte(s). Analysts can use the recovery of these constituents to evaluate sample matrix interferences that may influence quantitation or detection of the target constituent.

Method Blanks - A sample consisting of analyte-free water, soil, or soil vapor that is carried throughout the analytical process. The method blank will confirm the presence or lack of contamination by the analysis process.

Method Interference - Any constituent beside the parameter of interest that, if present, will influence the method response.

PNA - Polynuclear aromatic hydrocarbon.

Precision - The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the detection limit, and may involve the use of matrix spikes.

Recovery Efficiency - The performance of an analytical methodology based on the analysis of a sample or clean matrix spiked with a known amount of analyte. Recovery efficiency is the ratio, expressed as percent recovery, of the measured concentration to the unknown or actual concentration.

Redox Potential - The potential developed by a metallic electrode when placed in a solution containing species in two different oxidation states.

Reference Electrode - That half of an electrode pair which provides a constant potential regardless of solution composition. The potential developed by the oxygen or REDOX sensing electrode is measured against this reference potential to give an overall system potential that can be converted to the oxygen concentration or REDOX potential in the sample.

Screening Test - A procedure that identifies the presence or properties of a substance above a specified value. The test determines if a parameter is present at the level of interest.

Selectivity or Specificity - Selectivity refers to the responsiveness of the detector to the compound of interest. Detectors responding to a wide range of classes of compounds are termed universal or nonselective detectors. Those that respond only to specific compounds or classes of compounds are termed selective detectors.

Sensitivity - Sensitivity refers to the relationship between the detector response and the quantity of the subject compound present. It is the smallest detectable quantity of compound, usually considered to be the amount that produces a response equal to twice the baseline noise of the detector.

TPH - Total petroleum hydrocarbon.

Total Recoverable Petroleum Hydrocarbon (TRPH) - The fluorocarbon-113 extractable hydrocarbons that remain after removal of polar nonpetroleum hydrocarbons and that are measured by IR analysis at a wavelength of 3.4 μm.

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