

Compilation of Field Analytical Methods for Assessing Petroleum Product Releases

Health and Environmental Sciences Department
Publication Number 4635
December 1996



One of the most significant long-term trends affecting the future vitality of the petroleum industry is the public's concerns about the environment, health and safety. Recognizing this trend, API member companies have developed a positive, forward-looking strategy called STEP: Strategies for Today's Environmental Partnership. This initiative aims to build understanding and credibility with stakeholders by continually improving our industry's environmental, health and safety performance; documenting performance; and communicating with the public.

API ENVIRONMENTAL MISSION AND GUIDING ENVIRONMENTAL PRINCIPLES

The members of the American Petroleum Institute are dedicated to continuous efforts to improve the compatibility of our operations with the environment while economically developing energy resources and supplying high quality products and services to consumers. We recognize our responsibility to work with the public, the government, and others to develop and to use natural resources in an environmentally sound manner while protecting the health and safety of our employees and the public. To meet these responsibilities, API members pledge to manage our businesses according to the following principles using sound science to prioritize risks and to implement cost-effective management practices:

- ◆ To recognize and to respond to community concerns about our raw materials, products and operations.
- ◆ To operate our plants and facilities, and to handle our raw materials and products in a manner that protects the environment, and the safety and health of our employees and the public.
- ◆ To make safety, health and environmental considerations a priority in our planning, and our development of new products and processes.
- ◆ To advise promptly, appropriate officials, employees, customers and the public of information on significant industry-related safety, health and environmental hazards, and to recommend protective measures.
- ◆ To counsel customers, transporters and others in the safe use, transportation and disposal of our raw materials, products and waste materials.
- ◆ To economically develop and produce natural resources and to conserve those resources by using energy efficiently.
- ◆ To extend knowledge by conducting or supporting research on the safety, health and environmental effects of our raw materials, products, processes and waste materials.
- ◆ To commit to reduce overall emission and waste generation.
- ◆ To work with others to resolve problems created by handling and disposal of hazardous substances from our operations.
- ◆ To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.
- ◆ To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

Compilation of Field Analytical Methods for Assessing Petroleum Product Releases

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4635

PREPARED UNDER CONTRACT BY:

**IT CORPORATION
CINCINNATI, OHIO 45246**

**LAND TECH REMEDIAL, INC.
MONROE, CONNECTICUT 06468**

**TARGET/TEG
COLUMBIA, MARYLAND 21045**

DECEMBER 1996



FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.

NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.

Copyright © 1996 American Petroleum Institute

iii

ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

API STAFF CONTACT

Roger Claff, Health and Environmental Sciences Department

Bruce Bauman, Health and Environmental Sciences Department

MEMBERS OF THE FIELD ANALYTICAL METHODS PROJECT TEAM

Dominic Deangelis, Project Team Chairman, Mobil Oil Corporation

Albert O. Learned, Marathon Oil Company

A.E. Liguori, Exxon Research and Engineering Company

Karl Loos, Shell Development Company

Adolfo E. Silva, Petro-Canada, Inc.

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.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
EXECUTIVE SUMMARY	ES-1
1. INTRODUCTION	1-1
BACKGROUND	1-1
PURPOSE AND SCOPE	1-3
2. DATA QUALITY CLASSIFICATIONS	2-1
DATA QUALITY LEVEL 1A	2-3
DATA QUALITY LEVEL 1B	2-3
DATA QUALITY LEVEL 2	2-4
DATA QUALITY LEVEL 3	2-4
DATA QUALITY LEVEL 4	2-4
3. TOTAL ORGANIC VAPOR DETECTORS AND HEADSPACE ANALYSIS	3-1
SUMMARY	3-1
METHOD OVERVIEW	3-2
Applications and Advantages	3-2
INTERFERENCES AND LIMITATIONS	3-2
OPERATING PRINCIPLES/INSTRUMENTATION	3-5
Flame Ionization Detectors	3-5
Photoionization Detectors	3-6
METHOD REQUIREMENTS	3-8
Initial Setup	3-8
Sampling and Analysis Procedures	3-9
QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENT	3-10
4. FIELD GAS CHROMATOGRAPHS	4-1
SUMMARY	4-1
METHOD OVERVIEW	4-1
Applications and Advantages	4-1
INTERFERENCES AND LIMITATIONS	4-2
OPERATING PRINCIPLES/INSTRUMENTATION	4-3
Detectors	4-4
Field Gas Chromatographs	4-4
METHOD REQUIREMENTS	4-5
Comparative Sample Preparation and Analysis Procedures	4-5

TABLE OF CONTENTS (CONTINUED)

<u>Section</u>	<u>Page</u>
4. FIELD GAS CHROMATOGRAPHS (Continued)	
METHOD REQUIREMENTS	
Solvent Extraction	4-5
Purge-and-Trap Method	4-5
Static Headspace Method	4-6
Headspace/GC and Soils	4-7
Total Petroleum Hydrocarbon Analysis Using Field GCs	4-7
QUALITY ASSURANCE/QUALITY CONTROL	4-8
5. IMMUNOASSAY FIELD TEST KITS	5-1
SUMMARY	5-1
METHOD OVERVIEW	5-2
Application and Advantages	5-2
INTERFERENCES AND LIMITATIONS	5-3
False Positives/False Negatives	5-5
Temperature Ranges for Storage and Operation	5-5
Calibration Standards	5-6
OPERATING PRINCIPLES	5-6
METHOD REQUIREMENTS	5-10
QUALITY ASSURANCE/QUALITY CONTROL	5-12
Calibration	5-12
Method Blank	5-12
Duplicate Field Analyses	5-13
Confirmation by Reference Method	5-13
Matrix Blanks	5-13
6. PORTABLE INFRARED DETECTORS	6-1
SUMMARY	6-1
METHOD OVERVIEW	6-1
Application and Advantages	6-1
INTERFERENCES AND LIMITATIONS	6-2
OPERATING PRINCIPLES/INSTRUMENTATION	6-4
METHOD REQUIREMENTS	6-5
Initial Setup	6-5

TABLE OF CONTENTS (CONTINUED)

<u>Section</u>	<u>Page</u>
6. PORTABLE INFRARED DETECTORS (Continued)	
METHOD REQUIREMENTS	
Sampling and Analysis Procedures	6-6
QUALITY ASSURANCE/QUALITY CONTROL	6-7
7. DO/REDOX ELECTRODES	7-1
SUMMARY	7-1
METHOD OVERVIEW	7-2
Application and Advantages	7-2
INTERFERENCES AND LIMITATIONS	7-2
REDOX	7-2
DO	7-3
OPERATING PRINCIPLES	7-4
Dissolved Oxygen	7-4
REDOX	7-7
INSTRUMENTATION	7-7
Dissolved Oxygen	7-9
REDOX	7-9
METHOD REQUIREMENTS	7-10
Initial Setup	7-10
Sampling Procedures	7-10
QUALITY ASSURANCE/QUALITY CONTROL	7-11
Response Time	7-11
Calibration	7-12
8. EMERGING FIELD ANALYTICAL METHODS	8-1
FIBER OPTIC CHEMICAL SENSORS	8-1
VISIBLE UV FLUORESCENCE AND UV FLUORESCENCE SPECTROSCOPY	8-1
UV ABSORPTION SPECTROSCOPY	8-3
GAS CHROMATOGRAPHY/MASS SPECTROMETRY	8-3
REFERENCES	R-1
GLOSSARY	G-1



LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
3-1	Apparatus Setup for the Polyethylene Bag Sampling System	3-11
5-1	Antibody Terminology	5-7
5-2	Competitive Binding Immunoassay	5-9
7-1	Principle of Measurement for Dissolved Oxygen	7-5
7-2	Principle of Measurement REDOX	7-8

LIST OF TABLES

<u>Table</u>		<u>Page</u>
2-1	Data Quality Levels for Field Analytical Methods	2-2
3-1	TOV Headspace Analysis Capabilities and Practical Considerations	3-3
3-2	Relative Response of One Type of FID Calibrated to Methane	3-6
3-3	Summary of TOV Instrument Characteristics	3-7
3-4	PID Response to Different Hydrocarbon Groups	3-8
3-5	Summary of Suggested Calibration and Quality Control Requirements for Analytical Systems	3-12
4-1	Capabilities and Practical Considerations of Field GCs	4-2
4-2	Summary of Field Gas Chromatograph Characteristics	4-3
5-1	Hazardous PNA Compounds	5-3
5-2	Immunoassay Capabilities and Practical Considerations	5-4
5-3	Summary of Specifications for Immunoassay Test Kits	5-11
6-1	Field IR Capabilities and Practical Considerations	6-2
6-2	Summary of Field IR Instruments	6-4
7-1	Field DO/REDOX Capabilities and Practical Considerations	7-3
7-2	Summary of DO/REDOX Instruments	7-8
8-1	Fluorescence Color of Crude Oils	8-2



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 C₄ to C₈ 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 $>70^\circ\text{C}$);
- 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

<u>Capabilities</u>		
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
<u>Practical Considerations</u>		
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.