FIELD ANALYSIS MANUAL

NEW JERSEY DEPARTMENT OF ENVIRONMENTAL PROTECTION
SITE REMEDIATION PROGRAM
HAZARDOUS SITE SCIENCE ELEMENT
CN 413
TRENTON, NEW JERSEY 08625

July, 1994

Dear Citizen,

I am pleased to present the latest edition of the New Jersey Department of Environmental Protection's Field Analysis Manual for the Site Remediation Program. This document is the department's most recent effort to provide technical guidance to the regulated community regarding field analysis of environmental samples. The manual represents our commitment to be fair, predictable, technically consistent and responsive in all our dealings with the public.

This manual will provide technical guidance on how to comply with the Department's Technical Requirements for Site Remediation (N.J.A.C. 7:26E) in regards to field analysis; will promote greater consistency and enhance the Department's ability to evaluate sample results. The procedures and quality assurance/quality control requirements have been placed into one document so that it is clear to those individuals performing field analysis what is expected of them. The manual includes method summaries, advantages and disadvantages, detectable compounds and quality assurance/quality control requirements. Each project contains variables that must be factored into a final field analysis plan, but use of this manual will provide a level of confidence when presenting the field analysis portion of a project plan for the Department's review.

The success of this manual rests on how well you and the Department personnel use and evaluate it. I encourage you to let us know how well it works for you, and to contribute ideas on ways to improve it. I trust you will find it a useful tool in dealing with the technically complex nature of your work.

Sincerely,

Richard J. Gimello
Assistant Commissioner
Site Remediation Program

Mission Statement

The Mission of the New Jersey Department of Environmental Protection is to conserve, protect, enhance, restore and manage our environment for present and future generations. We strive to prevent pollution; ensure the efficient use of safe, environmentally sound and reliable energy resources; provide opportunities for recreation and enjoyment of natural and historic resources; and promote a healthy and sustainable ecosystem.

Guiding Principles

We are guided by these principles in accomplishing our mission:

-To consistently apply and vigorously enforce environmental laws and standards in a fair, timely and predictable manner.

-To be accountable, accessible and helpful to the public.

-To provide clear, prompt and fair guidance and decisions.

-To increase understanding of environmental and energy concerns through effective communication and education.

-To establish regulations and standards consistent with law and public policy and active public dialogue.

-To base our standards, decisions and activities on sound science.

-To promote energy conservation, pollution prevention and consideration of the cumulative impacts of activities in our actions and those of individuals, business and governments throughout the state.

-To maintain a work environment that attracts and retains dedicated, talented people; fully develops and challenges individual abilities; and encourages innovation and teamwork.

-To adhere to the highest standards of personal and professional conduct.

Field Analysis Manual

State of New Jersey
Christine Todd Whitman
Governor

New Jersey Department of Environmental Protection
Robert C. Shinn, Jr.
Commissioner

July, 1994

The Field Analysis Manual (July, 1994) has been printed on recycled paper.

ACKNOWLEDGEMENTS

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TECHNICAL EDITOR

Allan Scott Motter
Division of Responsible Party Site Remediation

DISCLAIMER

This document was prepared by the New Jersey Department of Environmental Protection (NJDEP) and has been subjected to internal Department as well as outside interested party review. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Department.

FOREWORD

The New Jersey Department of Environmental Protection (NJDEP) is committed to streamlining the site investigation and remediation process at contaminated sites. This manual was developed primarily in an effort to expedite the delineation phases of site investigation by providing a means for improving the quality of field analytical data. However, as new field analysis methods are developed and existing methods are improved, many other applications for field analyses will become apparent. Such applications may include clean zone documentation and ongoing monitoring of remedial activity.

The Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b) define the role of field screening methods to be: 1) for delineation when the contaminant identity is known and 2) to bias sample location to the location of greatest suspected contamination. Field screening methods may not be used to determine contaminant identity or clean zones; however, where ten or more samples are required for initial characterization, field screening methods may be used to document that up to fifty percent of the sampling points are not contaminated. In accordance with N.J.A.C. 7:26E-1.6(d), any person responsible for conducting remediation may petition the Department for a variance from specific sections. These petitions will be evaluated by the Department.

This manual begins with an overview of the Data Quality Levels developed by the Department for use in the context of this manual, followed by a compilation of ten field analysis methods. The methods are presented in standard format and include a detailed method review as well as quality assurance and quality control requirements.

The Field Analysis Manual was developed by the NJDEP, Bureau of Environmental Evaluation and Risk Assessment and has been widely distributed within the NJDEP and the regulated community to obtain comments on content and usability. The manual is intended for use by the regulated community and consultants to implement rapid and technically sound site investigations. The Field Analysis Manual will be most useful when used as a complement to the NJDEP Field Sampling Procedures Manual.

The Field Analysis Manual is not intended to include the entire array of field methods that the Department will approve. Field methods not explicitly mentioned in the manual may be employed if sufficient documentation can be provided to the Department to support the proper application of the method. The manual will be updated regularly to reflect changes in this rapidly growing area of environmental technology. Persons wishing to use a field method not addressed in the manual, or to modify methods included in the manual, should submit the proposal to the project team for approval.

The Field Analysis Manual may be reproduced without NJDEP authorization. Comments on the manual may be addressed to:

New Jersey Department of Environmental Protection
Site Remediation Program
Hazardous Site Science Element
CN - 413
Trenton, New Jersey 08625

609-984-3068

Copies of the Field Analysis Manual or the Field Sampling Procedures Manual may be obtained from the NJDEP Maps and Publications Sales Office. The cost for the Field Analysis Manual is $7.00 and the cost for the Field Sampling Procedures Manual is $25. Costs include both postage and handling. Requests for both manuals may be addressed to:

New Jersey Department of Environmental Protection
Maps and Publications Sales Office
Bureau of Revenue
CN - 417
Trenton, New Jersey 08625

609-777-1038

Checks or Money Orders for the manuals should be made payable to:
Treasurer, State of New Jersey

NOTICE

Field screening data are routinely used in site investigations to approximate the contaminated zone and to guide sample location. As an alternative, certified laboratories have suggested that samples be analyzed rapidly and at a lower cost in the laboratory using field analysis methods or approved laboratory methods with limited data deliverables. Samples analyzed by approved laboratory methods with the required data deliverables or a combination of samples analyzed by approved laboratory methods with the required data deliverables and level 2 data with the required data deliverables would still be used to document the clean zone in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E. This approach is acceptable to the Department as long as the certified laboratories specify on each page of the laboratory report that the data were generated using field methods or approved methods with limited data deliverables.

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TITLE: Data Quality Levels for Contaminant Investigation

I. SUMMARY

This guidance document defines the NJDEP Site Remediation Program's Data Quality Levels for contaminant investigation. This document describes a four tiered data quality hierarchy. Data Quality Level 1 consists of field screening methods utilized for contaminant delineation only. Data Quality Level 2 consists of field analytical methods and can be used for clean sample documentation during the site investigation with the required QA/QC deliverables or for delineation without Level 2 QA/QC deliverables. Data Quality Level 3 consists of approved laboratory methods with QA/QC deliverables as required in the Technical Requirements for Site Remediation, N.J.A.C. 7:26E and can be used for clean zone confirmation as well as for delineation during the remedial investigation. Data Quality Level 4 consists of specialty "state-of-the-art" methods developed specifically for a particular site, and are approved on a case by case basis.

The USEPA utilizes a two tiered approach to data quality. The first category "Screening Data with Definitive Confirmation" would include NJDEP Site Remediation Program's Data Quality Levels 1 and 2. The second category "Definitive Data" would include NJDEP Site Remediation Program's Data Quality Levels 3 and 4.

II. PURPOSE AND SCOPE

To guide in the selection of field analysis methods by defining the minimum data quality standards a contaminant investigation plan should meet to receive approval.

III. RESPONSIBILITY

The project team is responsible for the review and revision of all field analytical proposals.

IV. DEFINITIONS AND PURPOSE OF DATA QUALITY LEVELS

1. <u>Data Quality Level 1</u>

A. Level 1 methods are intended to be used for Health & Safety, initial contaminant screening and/or contaminant delineation (i.e. approximation of contaminated zone).

B. Instruments used for Data Quality Level 1 include: PID survey instruments (HNU), FID survey instruments (OVA) and XRF with remote probe (x-met). Methods used for Data Quality Level 1

include: hydrophobic dye test, colorimetric analysis and headspace analysis.

C. The data produced should only be considered an indicator of contamination. Quality control procedures and deliverable requirements are limited to a brief method review, instrument calibration, maintenance logs, field logs, reported data values and background levels.

D. Level 1 methods are real-time, but are semi-qualitative and semi-quantitative, and measurements may be erratic. Therefore, data should only be used for health and safety and to guide sample placement for analysis by higher level methods.

E. Since relatively few quality control procedures are employed compared to higher level field methods, data quality is very much a function of sample handling techniques and analyst skill.

2. Data Quality Level 2

A. Level 2 methods are intended to provide reliable, rapid, contaminant delineation.

B. Level 2 methods can achieve a high degree of reproducibility when required QA/QC procedures are employed.

C. Level 2 methods are typically laboratory methods which have been adapted for field use (i.e. field GC, portable XRF, field IR).

D. In addition to Level 1 requirements, quality assurance deliverables should include:

1) Initial calibration curves

2) Continuing calibration curves (1 per 10 samples)

3) Field Duplicates (1 per 20 samples)

4) Background/Blank data

5) Raw data submission (i.e. chromatograms, recorded instrument readouts, etc.)

6) Chain of Custody Documentation (or field sample tracking sheets)

7) Non-conformance summary listing all deviations

from the approved SOP and QA/QC parameters outside control limits. The non-conformance summary should include an analyst certification statement.

8) Laboratory confirmation data should be submitted along with the field analytical data. At a minimum, 10% of all Data Quality Level 2 data should be laboratory confirmed (both clean and contaminated samples). The Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b) require that 50% of all "clean" samples be laboratory confirmed during the site investigation and 100% of all "clean zone" samples be laboratory analyzed during the remedial investigation. A variance from these requirements may be requested pursuant to N.J.A.C. 7:26E-1.6(d).

9) Results of analyst competency tests (i.e. performance evaluation tests and proof of training) are required.

10) Matrix Spike Recovery (case-by-case)

11) Surrogate Analyte Analysis (case-by-case)

12) Method Blank Analysis (case-by-case)

13) Quality Control Check Sample Analysis (case-by-case)

E. Level 2 methods are quantitative (i.e. providing an estimated value), but only semi-qualitative (definitive contaminant identification is not provided).

F. Level 2 contaminant delineation may be accomplished by providing enough laboratory confirmation data to allow for laboratory-field correlation throughout the entire contaminant concentration range and to confirm the clean zone (i.e. 50% during the SI, 100% during the RI). At a minimum, laboratory confirmation sampling shall be conducted on 10% of all field samples.

G. Environmental samples frequently contain contaminants, most of which are of unknown concentrations. Laboratory data is not one hundred percent accurate, but currently represents the best estimate of the true concentration of a contaminant in an environmental sample. Therefore, a comparison of field and laboratory data can help to

provide some guidance on the validity of the field data.

A laboratory-field correlation of level 2 data has two components and can be calculated by the following regression analysis equation:

$$L = xF + y$$

where:

L = the reported laboratory concentration of a contaminant

F = the reported field concentration of the same contaminant

x = the slope of the correlation of field and laboratory data

y = the intercept of the field and laboratory data (constant)

R squared = fit of equation

The two components of the laboratory-field correlation are: 1) the fit (R squared) and 2) the intercept (y). Given the lack of homogeneity of environmental samples, variation in sample handling and variations inherent in both field and laboratory data, the fit of the equation is not expected to be perfect (i.e. in most cases, R squared≠ 100%); however, R squared and a plot of the scatter graph should be should be developed by the data reviewer and submitted to the Department. An examination of the R squared and scatter graph should be made to determine the usefulness of the field data. Professional judgement should be used when determining whether field data should be used for delineation and/or clean samples.

The intercept (y) is important due to differences in concentrations determined in field verses laboratory data. During the remedial investigation (RI), field based contaminant zone delineation levels may be adjusted per the following equation:

$$C_f = C + y$$

where:

C_f= contamination zone delineation criteria for field generated data

C = cleanup criteria for laboratory data

y = the intercept of the field and laboratory data correlation equation

Final remediation; however, should be based on the site specific cleanup criteria using Data Quality Level 3 methods.

H. Level 2 methods also include published laboratory methods such as USEPA SW-846 laboratory methods which are highly reproducible; however, data are documented using only limited quality assurance deliverables.

I. The quality of Level 2 data generated from laboratory methods with limited deliverables is a function of sample handling, storage and preservation procedures, and analytical instrument maintenance. These data should be reliable if proper sampling and analytical procedures are followed.

3. Data Quality Level 3

A. Level 3 methods are intended to generate the most reliable data practicable.

B. Level 3 data are highly reproducible and can provide the end user with complete QA/QC documentation in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

C. Level 3 methods are the same as Level 2 laboratory methods but are supported with full laboratory data deliverables or reduced laboratory data deliverables in accordance with subchapter 2 and Appendix A of the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

D. Level 3 data can only be generated by a certified or otherwise approved laboratory pursuant to the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1.

4. Data Quality Level 4

A. Level 4 methods are generally "State-of-the-Art" methods developed specifically for a particular site or contaminant.

B. Level 4 methods are used when standard laboratory methods are either unavailable or impractical.

C. Level 4 data may have variable deliverable requirements. These requirements will be proposed by the laboratory or person performing the analysis and approved by the Department for each method proposed. Data produced by methods conforming to these requirements will be acceptable for their intended use.

D. Level 4 data may be accepted to delineate a contaminant, define a "clean zone" or confirm field data per Item C., above.

E. Generation of Level 4 data may neccessitate use of a laboratory which specializes in methods development.

IV. OVERVIEW (DATA QUALITY CLASSIFICATIONS)

DATA QUALITY LEVEL	PURPOSE OF SAMPLE	EXAMPLE METHODS OR INSTRUMENTS
1	Health & Safety, Field use when excavating, Contaminant Screening & Delineation	Portable PID (HNU), Portable FID (OVA), Colorimetric Analysis, XRF with a remote probe (x-met), Headspace Analysis, Hydrophobic Dye Test
2	Field use when excavating, Contaminant Delineation, Clean Sample Confirmation during SI	Portable GC, Portable IR, Portable XRF with Si(Li), Portable AA, Immunoassay, USEPA SW-846 Field Screening Methods Laboratory Analyzed Samples with limited QA/QC requirements, (i.e. USEPA SW-846 Laboratory Methods (3rd or most recent edition))
3	Delineation, Clean Zone Confirmation	Laboratory Analyzed Samples, with full QA/QC documentation, (i.e. USEPA SW-846 Laboratory Methods (3rd or most recent edition))
4	Non-standard	Laboratory Special Services,

method analysis Mobile Laboratory

V. DATA QUALITY DELIVERABLES

LEVEL 1 QA/QC REQUIREMENTS

The following represents the minimum data deliverables required for Level 1 Data. The "Data Quality Deliverables" section of each method will provide specific requirements:

1. A brief method review should be provided.

2. A single point calibration should be conducted prior to any field activities using site-specific standards.

3. Calibration checks should be performed at a minimum of twice daily. If a calibration check falls outside the manufacturer's suggested range, then a complete multi-point calibration is required.

4. A baseline scan (i.e. "clean air", "clean water" or "clean soil" as appropriate) should be run each day prior to analyzing any site samples.

5. An instrument log should be maintained and submitted (where appropriate). This log should include instrument maintenance, blank, and calibration information, including date, time, analyst's name, calibration compounds (CC), CC concentrations, and CC readings.

6. Field logs should document sample ID#, date, time, location, depth, matrix (i.e. soil type, water, air), soil moisture (qualitative estimate where appropriate), and analysis result.

7. A non-conformance summary should state all data inconsistencies and all divergences from the approved sampling/analysis program. The implication of all non-conformances should be clearly explained and quantified (if possible).

LEVEL 2 QA/QC REQUIREMENTS

In addition to the requirements listed for the Level 1 QA/QC Data, the following represents the minimum data deliverables required for Level 2 Data. The "Data Quality Deliverables" section of each method will provide specific requirements:

1. Each project team that uses a Level 2 method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of capability and an ongoing analysis of calibration standards. To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations:

    a) A soil quality control (QC) check sample. The QC check sample should be prepared by the laboratory using stock standards prepared independently from those used for calibration.

    b) An aqueous QC sample, prepared in the same fashion as the soil QC sample, is also required.

    c) Analyze four aliquots of each of the well-mixed QC check samples according to standard procedures.

    d) Calculate the average recovery mean (X) and the standard deviation of the recovery (s) for each parameter of interest in each matrix using the four results.

    e) For each compound, X should be between 60% and 140% of the true value. Additionally, s should be $\pm$ 40% of X.

2. Method blanks (i.e. syringe blanks, equipment blanks, and instrument blanks) should be run at the beginning and during each work day or when carry-over from a prior sample is anticipated. A higher frequency may be required depending upon equipment use and results.

3. Instrument should be 3-point (minimum) calibrated each month and 1-point calibrated each day using laboratory certified standards. The standard species and concentrations should be chosen based on known site contamination and encompass the range of expected concentrations. Surrogate compounds should also be included. Matrix-specific minimum detection limits should be determined for all site specific compounds.

4. If standard curves remain linear over the entire analysis range, only one midpoint standard should be analyzed at a frequency of 1 per 10 samples. If standard curves are not linear over the entire analysis range, a minimum of 2 calibration

standards should be analyzed at a frequency of 1 per 10 samples.

5. Matrix Spike and Matrix Spike Duplicate samples may be required at a rate of one per 20 samples. The project team should determine if MS/MSD samples are required on a case-by-case basis.

6. Chain of custody or sample tracking documentation should be generated for all samples collected and analyzed. This documentation should include a statement certifying that all data were generated following proper procedures.

VI. REFERENCES

1. NJDEPE "Field Sampling Procedures Manual", May, 1992.

2. Technical Requirements for Site Remediation, N.J.A.C. 7:26E, Effective 07/01/93.

3. USEPA CLP-IFB; most recent version.

4. USEPA "Data Quality Objectives for Remedial Response Activities", 1987.

5. USEPA SW-846, RCRA Standard: "Test Methods for Evaluating Solid Waste".

6. 40 C.F.R.136, Atomic Absorption Spectrometry for Trace Metals.

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STANDARD FORMAT FOR FIELD ANALYSIS METHODS

TITLE:

I. SUMMARY

II. PURPOSE AND SCOPE

III. RESPONSIBILITY

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1. Soil Matrix

2. Water Matrix

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VII. HEALTH AND SAFETY CONSIDERATIONS

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IX. APPENDICES

TITLE: Field Screening of Volatile Compounds Using Portable Field Survey Direct Reading Instruments Equipped with a Flame Ionization Detector (FID). (5/94)

I. SUMMARY

Survey instruments are routinely used during site characterization activities to aid in sample placement, or to provide an indication of site contamination. This document provides guidance for using a direct reading FID survey instrument during site activities. The Data Quality Levels on pages two through ten (2-10) should be read prior to using this method.

II. PURPOSE AND SCOPE

This section of the Field Analysis Manual summarizes the minimum procedures a field screening or field delineation (Level 1 Data Quality) sampling proposal should follow.

III. RESPONSIBILITY

The project team is responsible for the review and revision of all site investigation proposals.

IV. METHOD OVERVIEW

A. Applications & Advantages

1. Uses of Method

a. Health & Safety Screening

b. Field Screening of Air, Water, Soils & Sludges

2. Benefits of Method

a. This method provides field personnel with real-time information, which may be used in making field decisions regarding site conditions including selection of samples for higher data quality analysis.

b. This method is recommended for site screening and all excavation activities involving organic contaminants.

c. Humidity will not affect measurement readings on the FID.

B. INTERFERENCES AND LIMITATIONS

1. Restrictions of Method

a. The FID is a non-specific total vapor detector. It cannot be used to identify unknown substances. In an unknown environment it may only be used to confirm the presence of volatile contamination. Quantitative information is not reliable in an unknown environment. During site screening, FID data should be confirmed by a higher data quality level analysis.

b. If a substantial background level is detected, and is determined to be uncontrollable, FID usefulness may be limited.

c. This instrument should not be exposed to precipitation (i.e. rain).

2. Disadvantages of Method

a. In general, the hydrogen flame ionization detector is more sensitive for hydrocarbons than any other class of organic compounds. The response of the FID varies from compound to compound, but gives repeatable results with all types of hydrocarbons (i.e. saturated hydrocarbons [alkanes], unsaturated hydrocarbons [alkenes and alkynes] and aromatic hydrocarbons).

b. Compounds containing oxygen, such as alcohols, ethers, aldehydes, carbolic acid and esters, give a lower response than that observed for hydrocarbons. This is particularly noticeable with compounds having a high ratio of oxygen to carbon, such as the lower members of each series which have one, two or three carbons. With compounds containing higher numbers of carbons, the effect is diminished to such an extent that the response is similar to that of the corresponding hydrocarbons.

c. Nitrogen-containing compounds (i.e. amines, amides and nitriles) respond in a manner similar to that observed for oxygenated materials. Halogenated compounds also show a lower relative response as compared with hydrocarbons. Materials containing no hydrogen, such as carbon tetrachloride (CCl_4), give the lowest response; the presence of hydrogen in the compounds results in higher relative responses. Thus, $CHCl_3$ gives a much higher response than does CCl_4. As in the

other cases, when the carbon to halogen ratio is 5:1 or greater, the response will be similar to that observed for simple hydrocarbons.

d. Caution should be used for headspace analysis to prevent liquids from inadvertently being drawn into the probe.

e. Oxygen deficient environments have been shown to bias FID readings high. Atmospheres where the oxygen is below fifteen percent (15%) will extinguish the flame.

f. Naturally occurring compounds such as terpenes in pine trees may cause elevated readings.

C. Capabilities

1. Compounds Detected: Volatile Organic Compounds.

2. Matrix: Air, Water, Soils, Sludges - Screening Only.

3. Achievable Quantitation Limit - None, compound identification and/or quantitation is generally not possible.

D. Instrumentation

1. A pump provides the sample stream which is measured and passed through a filter before reaching the detector chamber. Inside the detector chamber, the sample is exposed to a hydrogen flame which ionizes the organic vapors. The positively charged particles are collected, measured and the signal amplified to a recorder display.

2. The Flame Ionization detector will detect all flammable compounds.

3. Tables are attached to help determine the usefulness of an FID instrument for specific classes of analytes. It should be noted that an FID will respond differently to various compounds.

E. Practical Considerations

1. Cost per Sample (Approximate): less than $1.00

2. Time Required per Sample: 10 seconds

3. Quality of Data (Level): Poor (Level 1)

4. Difficulty of Procedure: Simple

5. Laboratory Method Equivalent: None

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used during the remedial investigation (RI) for delineation purposes and during the site investigation (SI) for initial characterization sampling to determine that up to fifty percent (50%) of the samples are not contaminated in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b).

2. Soil Matrix - This method should be used primarily to determine site sampling locations for analysis using higher data quality methods (i.e. GC).

3. Aqueous Matrix - This method should be used primarily to screen aqueous samples for analysis using higher data quality methods (i.e. GC).

B. Sampling Procedures

1. Soil Matrix - Sample screening may be performed by holding the probe above the split spoon, or above the native soil. During analysis the probe should be positioned within one (1) inch of the material being screened (Note: For health and safety procedures, the instrument is generally used in the breathing zone for determination of the level of personal protection required).

2. Aqueous Matrix - Sample screening may be performed by holding the probe above the aqueous sample or sample stream. During analysis the probe should be positioned within one (1) inch of the material being screened (Note: see soil matrix note).

3. Use of a polyethylene bag with soil and aqueous samples (see Headspace Analysis section) is another application of this method which will provide results which are quantifiable and reproducible.

C. Field Operations

1. All manufacturer's operation recommendations should be followed. These recommendations, along with an internal Standard Operating Procedure, should be

submitted to the Department as part of the Method's QA/QC program.

2. Generally, several seconds are required to allow analytes to be pumped through the "plumbing" to the detector probe. If a tubing system is used for remote sampling, there should be no pressure drop (flow change) as this may alter instrument response. The response time should be experimentally determined and included as part of the "internal Standard Operating Procedure" referenced in item (C1), above.

3. A background meter reading should be obtained (do not zero to background), at the time of sampling, for all areas where the FID is to be used. This value should be recorded on FID data summary sheets by area of concern. If a substantial background reading is detected, the source of the reading should be determined and controlled.

4. All readings should be recorded in the field logs as "ppm as the calibration gas". These field logs should be used to generate data summary tables. Additionally, all data should be plotted on scaled site maps, if warranted.

D. Quality Assurance/Quality Control

1. A brief method review should be provided. An internal Standard Operating Procedure should be submitted to the Department as part of the method's QA/QC program.

2. An instrument log should be maintained and submitted. This should include all instrument maintenance and calibration information, including date, time, gas select setting (if applicable), analyst's name, calibration compound (CC), CC concentration, and CC meter reading.

3. A single-point calibration should be conducted prior to any field activities. If the type of volatile contamination is known, the instrument may be calibrated to that particular gas.

4. Calibration checks should be performed at a minimum of twice daily. If a calibration check falls outside the manufacturer's suggested range, then a complete multi-point calibration is required.

5. A baseline scan (i.e. "clean air", "clean water" or "clean soil" as appropriate) should be run each day

prior to analyzing any site samples.

6. A non-conformance summary should be submitted. Implications of all such non-conformances should be clearly explained and quantified. This document should also contain a statement of certification (signed by the field analyst), as evidence that proper procedures were followed, and "true" results are reported.

7. Field logs should document sample ID#, date, time, location, depth, soil type (using a soil classification acceptable per the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 3.6(a)2ii), soil moisture (qualitative estimate), and analysis result.

VI. DATA INTERPRETATION AND REPORTING REQUIREMENTS

A. All data summary tables should report raw data, including background. If possible, suspected contaminant species should be reported with an estimate of "actual" concentration(s) based on published or experimentally determined response factors, background readings, and laboratory confirmed concentrations. Examples of the calculations performed should be submitted as an appendix to the Data Report.

B. Data maps may depict background subtracted data, but this should be clearly indicated on the figure. An additional map plotting calculation based, "expected" concentrations may be generated, but is not required. Should this additional map be generated, actual data (i.e. laboratory confirmed) should be clearly differentiated from calculated values.

C. Boring logs should be provided where applicable.

VII. HEALTH AND SAFETY CONSIDERATIONS

A. Potential Physical Hazards - The instrument and the charger should be completely shut down during hydrogen tank refilling operations. Refilling should be done in a ventilated area. THERE SHOULD BE NO POTENTIAL IGNITERS OR FLAME IN THE AREA DURING TANK FILLING.

B. Potential Chemical Hazards - There are no unusual chemical health or safety considerations specifically pertaining to the use of a FID survey instrument. Instrument specific considerations should be obtained from the manufacturer.

VIII. REFERENCES

1. NJDEPE Field Sampling Procedures Manual, May 1992.

2. Gervasio, R., Davis, N.O. "Monitoring in Reduced Oxygen Atmosphere Using Portable Survey Direct Reading Instruments (PID and FID)", Proceedings HMCRI, Washington, D.C., 1989-90.

3. Instruction Manual for Model OVA 128 Century Organic Vapor Analyzer, Foxboro, 1985.

4. Robbins, G.A., Bristol R.d. and Roe, V.D. "A Field Screening Method for Gasoline Contamination Using a Polyethylene Bag Sampling System", GWMR Fall 1989 p. 87-97.

Table I

Relative Response of FID (OVA) Calibrated to Methane

Compound	Response	
Acetone	60	
Acetylene	200	
Benzene	150	
Carbon Tetrachloride	10	
Chloroform	65	
Ethane	90	
Ethyl Alcohol	25	
Ethylene	85	
Hexane	70	
Isopropyl Alcohol	65	
Methane	100	(Reference)
Methyl Alcohol	15	
Methyl Ethyl Ketone	80	
Methyl Isobutyl Ketone	100	
N-Butane	61	
N-Pentane	100	
Propane	64	
Toluene	120	
Trichloroethene	70	
Vinyl Chloride	35	

TITLE: Field Screening of Volatile Compounds Using Portable Field Survey Direct Reading Instruments Equipped with a Photoionization Detector (PID). (12/93)

I. SUMMARY

Survey instruments are routinely used during site characterization activities to aid in sample placement, or to provide an indication of site contamination. This document provides guidance for using a direct reading PID survey instrument during site activities. The Data Quality Levels on pages two through ten (2-10) should be read prior to using this method.

II. PURPOSE AND SCOPE

This section of the Field Analysis Manual summarizes the minimum procedures a field screening or field delineation (Level 1 Data Quality) sampling proposal should follow.

III. RESPONSIBILITY

The project team is responsible for the review and revision of all site investigation proposals.

IV. METHOD OVERVIEW

A. Applications & Advantages

1. Uses of Method

a. Health & Safety Screening

b. Field Screening of Air, Water, Soils & Sludges

2. Benefits of Method

a. This method provides field personnel with real-time information, which may be used in making field decisions regarding site conditions including selection of samples for higher data quality analysis.

b. This method is recommended for site screening and all excavation activities involving organic contaminants.

B. Interferences & Limitations

1. Restrictions of Method

a. The PID is a non-specific total vapor detector. It cannot be used to identify

unknown substances. In an unknown environment it may only be used to confirm the presence of volatile contamination. Quantitative information is not reliable in an unknown environment. During site screening PID data should be confirmed by a higher data quality level analysis.

b. The PID does not respond to certain low molecular weight hydrocarbons, such as methane and ethane. These compounds can interfere with the detection of other active compounds, generally in the form of response suppression. If these compounds are suspected to be present (common in landfills), an alternate field detector that is sensitive to these compounds (i.e. an FID detector), should be used in addition to the PID.

c. This instrument should not be exposed to precipitation (i.e. rain).

2. Disadvantages of Method

a. The PID does not measure the level of contaminants in soil, water or waste, but rather the level of contaminants in the soil gas or gases evolving from the matrix.

b. Certain toxic gases and vapors (i.e. carbon tetrachloride (CCl_4) and hydrogen cyanide (HCN)), can not be detected by the PID, due to their high ionization potentials. In general, compounds with high energy bonds (indicated by differing electronegativities) may not be easily detected by the PID. If these compounds are expected, appropriate precautions (such as the use of an alternate screening instrument) should be taken.

c. Humidity may affect measurement readings. The PID may become unusable under foggy or humid (over 85%) conditions. These types of conditions tend to cloud the lamp, interfering with its ionization potential. An indication of this is the needle dropping below 0, or a slow constant concentration climb on the meter. In addition, low temperatures can effect the battery charge which will effect the readings obtained. Repeated temperature changes (i.e. from a heated vehicle to a low temperature environment) may cause condensation to build up on the lamp which

will effect the readings obtained.

d. If a substantial background level is detected, and is determined to be uncontrollable, PID usefulness may be limited.

e. Caution should be used for headspace analysis to prevent liquids from inadvertently being drawn into the probe.

f. Oxygen deficient environments have been shown to bias PID readings high.

g. Naturally occurring compounds such as terpenes in pine trees may cause elevated readings.

C. Capabilities

1. Compounds Detected: Volatile Organic Compounds, possibly some Semi-Volatile Compounds.

2. Matrix: Air, Water, Soils, Sludges - Screening Only.

3. Achievable Quantitation Limit: None, compound identification and/or quantitation is generally not possible.

D. Instrumentation

1. A field survey instrument is generally equipped with a vacuum pump which transports analyte molecules to an internal detector.

2. The photoionization detector may detect all compounds with ionization potentials below the energy of the internal ionizing lamp, although it should be noted that a PID may detect compounds with energies equal to, or even slightly above the energy of the ionizing lamp.

3. There are a variety of ionizing lamps available, including: 9.5, 10.0, 10.2, 10.6 and 11.7 eV.

4. The standard lamp for most operations should be in the 10.0 to 10.5 eV range, which has been shown to have the greatest sensitivity and durability while being responsive to most compounds.

5. Tables are attached to help determine the usefulness of a PID instrument for specific classes of analytes. These tables may also be useful in source (lamp) selection.

E. Practical Considerations

1. Cost per Sample (Approximate) : less than $1.00

2. Time Required per Sample : 15 seconds

3. Quality of Data (Level) : Poor (Level 1)

4. Difficulty of Procedure : Simple

5. Laboratory Method Equivalent : None

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used during the remedial investigation (RI) for delineation purposes and during the site investigation (SI) for initial characterization sampling to determine that up to fifty percent (50%) of the samples are not contaminated in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b).

2. Soil Matrix - This method should be used primarily to determine site sampling locations for analysis using higher data quality methods (i.e. GC).

3. Water Matrix - This method should be used primarily to screen aqueous samples for analysis using higher data quality methods (i.e. GC).

B. Sampling Procedures

1. Soil Matrix - Sample screening may be performed by holding the probe above the split spoon, or above the native soil. During analysis the probe should be positioned within one (1) inch of the material being screened (Note: For health and safety procedures, the instrument is generally used in the breathing zone for determination of the level of personal protection required).

2. Aqueous Matrix - Sample screening may be performed by holding the probe above the aqueous sample or sample stream. During analysis the probe should be positioned within one (1) inch of the material being screened (Note: see soil matrix note).

C. Field Operations

1. All manufacturer's operation recommendations should be followed. These recommendations, along with an internal Standard Operating Procedure should be submitted to the Department as part of the Method's QA/QC program.

2. Generally, several seconds are required to allow analytes to be pumped through the "plumbing" to the detector probe. If a tubing system is used for remote sampling, there should be no pressure drop (flow change) as this may alter instrument response. The response time should be experimentally determined and included as part of the "internal Standard Operating Procedure" referenced in item (C1), above.

3. A background meter reading should be obtained (do not zero to background), at the time of sampling, for all areas where the PID is to be used. This value should be recorded on PID data summary sheets by area of concern. If a substantial background reading is detected, the source of the reading should be determined and controlled.

4. All readings should be recorded in the field logs as "ppm as the calibration gas". These field logs should be used to generate data summary tables. Additionally, all data should be plotted on scaled site maps if warranted.

D. Quality Assurance/Quality Control

1. A brief method review should be provided. An internal Standard Operating Procedure should be submitted to the Department as part of the method's QA/QC program.

2. An instrument log should be maintained and submitted. This should include all instrument maintenance (i.e. lamp cleaning) and calibration information, including date, time, span setting (if applicable), analyst's name, calibration compound (CC), CC concentration, and CC meter reading.

3. The lamp window should be cleaned periodically to ensure detection of air contaminants. Cleaning should be done as per the manufacturer's recommendations, but at a minimum, prior to mobilizing on a new site.

4. A single-point calibration should be conducted prior to any field activities. If the type of

volatile contamination is known, the instrument may be calibrated to that particular gas.

5. Calibration checks should then be performed at a minimum of twice daily. If a calibration check falls outside the manufacturer's suggested range, a complete multi-point calibration is required.

6. A baseline scan (i.e. "clean air", "clean water" or "clean soil" as appropriate) should be run each day prior to analyzing any site samples.

7. A non-conformance summary should be submitted. Implications of all such non-conformances should be clearly explained and quantified. This document should also contain a statement of certification (signed by the field analyst), as evidence that proper procedures were followed, and "true" results are reported.

8. Field logs should document sample ID#, date, time, location, depth, soil type (using a standard soil classification system as described in the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 3.6(a)2ii), soil moisture (qualitative estimate), and analysis result.

VI. DATA INTERPRETATION AND REPORTING

A. All data summary tables should report raw data, including background. If possible, suspected contaminant species should be reported with an estimate of "actual" concentration(s) based on published or experimentally determined response factors, background readings, and laboratory confirmed concentrations. Examples of the calculations performed should be submitted as an Appendix to the Data Report.

B. Data maps may depict background subtracted data, but this should be clearly indicated on the figure. An additional map plotting calculation based, "expected" concentrations may be generated, but is not required. Should this additional map be generated, actual data (i.e. laboratory confirmed) should be clearly differentiated from calculated values.

C. Boring logs should be provided where applicable.

VII. HEALTH AND SAFETY CONSIDERATIONS

A. Potential Physical Hazards - There are no unusual physical health or safety considerations specifically

pertaining to the use of a PID survey instrument. Instrument specific considerations should be obtained from the manufacturer.

B. Potential Chemical Hazards - There are no unusual chemical health or safety considerations specifically pertaining to the use of a PID survey instrument. Instrument specific considerations should be obtained from the manufacturer.

VIII. REFERENCES

1. NJDEPE Field Sampling Procedures Manual, May 1992.

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4. USEPA Environmental Response Team "Standard Operating Procedure #2056", 1989.

IX. APPENDIX

Table I

Relative Sensitivity For Compound Classes (PID)

Class	Relative Sensitivity	Examples
Aromatics	100%	Benzene, Toluene, Styrene
Aliphatic Amines	100%	Diethylamine
Chlorinated, Unsaturated, Aliphatics	50-90%	Vinyl Chloride, Trichloroethylene, Dichloroethene
Carbonyls	70-90%	MEK, MiBK, Acetone, butanone, Cyclohexanone
Unsaturated Aliphatics	30-50%	Acrolein, Propylene, Allyl Alcohol

Sulfides	30-50%	Hydrogen Sulfide, Methyl Mercaptan
Paraffins (C_5-C_7)	10-30%	Pentane, Hexane, Heptane
Ammonia	1-5%	
Paraffins (C_1-C_4)	0%	Methane, Ethane

TABLE II

Relative Lamp Sensitivity

Ionization Potential (eV)	Lamp Energy 9.5 eV	10.2 eV	11.7 eV
8.0 - 9.5	7-10%	100%	7-12%
9.5 - 10.2	5-10%	100%	10-15%
greater than 10.2	0%	100%	10-50%

Table III

Approximate Ionization Potentials For Classes

Class	Approximate IP (eV)	Notes
Paraffins	9.8 - 10.8	CycloParaffins
Alkyl Halides	10.5 - 11.5	Chlorinated Compounds
	9.0 - 10.5	Brominated and Iodinated Compounds
	11.7 - 12.9	Fluorinated Compounds, i.e. Freons
Aliphatics	10.0 - 11.0	Alcohols
	9.2 - 10.0	Ethers

	9.1 - 9.5	Thiols
	8.3 - 8.7	Sulfides
	9.5 - 10.9	Aldehydes
	8.9 - 9.6	Ketones
	10.0 - 11.1	Acids
	10.0 - 11.0	Esters
	7.2 - 9.0	Amines
	8.6 - 10.3	Amides
	10.7 - 11.1	Nitro-aliphatics
	10.4 - 12.2	Nitriles
	9.1 - 13.9	Cyano Compounds
Olefins, Acetylenes	8.9 - 10.5	
Hetero-Cyclics	8.0 - 9.5	i.e. Furans
Aromatics	7.7 - 9.7	
Sulfides	8.2 - 9.7	i.e. Hydrogen Sulfide, Methyl Mercaptan
Ammonia	10.2	

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TITLE: Field Delineation of Volatile Contamination Using Headspace Analysis.(5/94)

I. SUMMARY

Ambient temperature headspace analysis may be used to delineate VO contamination and heated headspace analysis may be used to delineate VO and possibly lighter SVO contamination in soils and to screen for these contaminants in groundwater. This method may employ a field gas chromatograph, or direct reading field survey instrument as the analytical instrument, although a field GC is preferred and more applicable to most situations. When used in conjunction with a field gas chromatograph, the ability to detect VOs and SVOs will generally be greater than that of standard laboratory methods, as analyte loss due to transport and storage is minimal. The Data Quality Levels on pages two through ten (2 - 10) should be read prior to using this method.

II. PURPOSE AND SCOPE

To define the minimum standards for an ambient temperature headspace delineation proposal, consistent with the Data Quality Levels defined on pages two through ten (2-10).

III. RESPONSIBILITY

The project team is responsible for the review and revision of all site delineation proposals.

IV. METHOD OVERVIEW

A. Applications & Advantages

1. Uses of Method

    a. Field Delineation of Soils.

    b. Field Screening of Water.

2. Benefits of Method

    a. Provides field personnel with real-time information which may be used in making field decisions regarding contaminant delineation.

    b. This method is recommended for site screening and contaminant delineation whenever volatile

organic compounds are of concern.

c. This method expedites the delineation process while providing better site definition at a reduced cost.

d. Headspace readings can be correlated to NAPL presence in groundwater and saturated soil samples.

B. Interferences and Limitations

1. Restrictions of Method

a. A field GC must be used to get separation and quantitation on specific analytes.

b. All detector specific (i.e. PID, FID, GC-ECD) information provided in other SOPs and/or in Manufacturer's documentation applies.

c. PID or FID meter readings are not quantitative. These instruments report total organic vapor, although, the detector response differs between compounds which may often lead to a bias in results.

d. Any background or naturally occurring VOs may give false positives (i.e. methane for FID, neighboring sources, terpenes from pine trees).

e. The information obtained is semi-quantitative and may or may not correspond well with laboratory confirmation data; however, the data set should be consistent within itself, thereby being sufficient for delineation and determining a "clean zone" to be laboratory verified. It should be noted that the percentage of compounds present at separate sampling locations may cause the same reading for direct reading survey instruments although the total amount of contaminant present varies due to instrument sensitivity. Also, due to instrument sensitivity, a zero reading may not be indicative of a "clean zone.

f. Effective use of this technology requires that the project team carefully select

laboratory confirmation samples. The goals of laboratory confirmation are to establish a correlation between the field and laboratory data and to maximize the usability of the field analysis results (i.e. laboratory samples should be collected across the entire concentration range [on-site] to generate a calibration curve). Clean zone samples should be laboratory verified. Guidance is given in the "Sampling Considerations" section, below. When used with a field GC, qualitative laboratory data should correlate well with field data; however, quantitative data values may vary due to sample storage and handling. Laboratory confirmation samples should be obtained from the same sample used for the headspace analysis as the volatile compounds and some semi-volatile compounds will be released from the sample matrix.

g. All "clean zone" samples should be analyzed by Level 3 or 4 methods (i.e. certified laboratory methods) as called for by the applicable regulatory program.

h. At a minimum, laboratory samples should be collected to establish calibration throughout the entire range of analysis. In general, 20% of the field samples, including but not limited to, all "clean zone" samples, should be laboratory confirmed.

i. If a field GC is used, a minimum of 10% of the field samples, including but not limited to all "clean zone" samples, should be laboratory confirmed.

2. Disadvantages of Method

a. Since increasing temperature may increase the gas volume and, for volatile compounds, the concentrations of analyte in the headspace, sample results may vary as 'ambient' conditions change throughout the day. Based on the ideal gas law ($PV=nRT$ or $V2=V_1P_1T_2/P_2T_1$), a temperature increase of 18 degrees Fahrenheit may produce, approximately, a 3% error. The field data obtained should be corrected

for all temperature variances throughout the day(s) or the sample should be placed into a constant temperature water bath to eliminate the temperature variation. When three (3) phases are present (solid, liquid and gas), the effect of temperature changes on the equilibrium gas concentration will be given by:

$$d\ln[C_g]/dT=[(V_w/H)(DH_{wg}/RT^2)+M_s(K_d/H)(DH_{sg}/RT^2)]/[V_g+V_w/H+M_s(K_d/H)]$$

where:

C_g = gas concentration
T = temperature (Kelvin)
V_w = liquid volume
R = gas constant
M_s = mass of soil
K_d = water/sorbed partition coefficient
V_g = gas volume
DH_{wg} = water-to-gas phase transfer enthalpy
DH_{sg} = sorbed-to-gas phase transfer enthalpy

b. Heated headspace (using a temperature controlled chamber) may be used to enhance reproducibility without using ideal gas law equations. A portable water bath is the minimum requirement when using this method.

c. As headspace concentration approaches the vapor pressure of the contaminant compounds, readings may be less reliable.

d. Compounds with low Henry's Law Constants (i.e. MTBE), may not partition readily into the headspace from aqueous samples and therefore, may result in low or non-detectable results or will result in high detection limits.

C. <u>Capabilities</u>

1. Compounds Detected: Volatile Compounds; Semi-Volatile Compounds with heated headspace analysis

2. Matrix: Soils - Delineation or Screening
Water - Screening Only

3. Achievable Quantitation Limits - Variable; MDLs as low as 0.1 ppb can be achieved using level 2 instrumentation.

D. Instrumentation

1. The user has a choice of several instruments, depending on data needs.

   a) Survey instruments (i.e. PID, FID) may be used when few compounds are present and/or the area is well characterized. Detector choice should be based on the compounds present. Detector or instrument specific comments can be obtained from the survey instrument sections (pages 13 - 29).

   b) A field GC may be used when exact compound identification is necessary. Detector choice should be based on the compounds of interest. Instrument specific comments can be obtained from the appropriate guidance document.

E. Practical Considerations

1. Cost per Sample (Approximate): $10.00 (Dependent on detector)

2. Time Required per Sample: 20 minutes (Note: When used with a field GC, the time between samples should be longer than the longest eluting compound to avoid buildup on the column.)

3. Quality of Data (Level): Good (Level 1A)

4. Difficulty of Procedure: Simple

5. Laboratory Method Equivalent: Draft Method SW-846 3810

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used during the remedial investigation (RI) for delineation purposes and during the site investigation (SI) for initial characterization sampling to determine that up to fifty percent (50%) of the samples are not contaminated, in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b).

2. To maximize the utility of the information obtained, care should be taken when choosing samples to be laboratory analyzed (i.e. bias to obtain laboratory correlation over the entire concentration range on-site).

3. At least one (1) laboratory sample should be biased to a "hot spot" to correlate field data.

4. Sampling frequency should be twice that recommended in the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, when using a field survey instrument.

5. When comparing field GC results to laboratory results, the field results may be up to 10 times higher in concentration based on past experience with these methods.

B. Sampling Procedures

1. Place a predetermined amount of soil (approximately 25 g) or water (approximately 100 ml) into a one (1) quart zip lock bag equipped with a bulkhead fitting and a small piece of Tygon tubing (or a 40 ml vial may be used). Sample collection methods should minimize soil disturbance, and subsequent volatilization. NOTE: Installation of a valve in the bag may facilitate later sampling.

2. Once filled, immediately seal the bag or vial. Inflate to capacity with a pump or cylinder through the bulkhead fitting.

3. Set samples aside and leave undisturbed at ambient temperature or in a constant heated temperature chamber (i.e. oven, water bath) and out of sunlight for a period of approximately 10 minutes. A constant temperature chamber (i.e. oven, water bath) may be used to provide more consistent and reproducible results. A rise in temperature of $10^{\circ}C$ may double the response to some compounds.

C. Field Operations

1. Following the approximately 10 minute waiting period, shake samples for a minimum of one to three (1-3) minutes. NOTE: It is essential that shaking time be standardized.

2. Place the bag (or capped sample bottle) aside, as in step three, for 1-3 minutes.

3. Withdraw a headspace sample with a syringe and inject into the field GC or measure the headspace directly with a PID or FID through the bulkhead fitting in the bag. An FID or PID probe may be placed into a small opening in the zipper of the bag if the bag does not contain a bulkhead fitting.

4. Record measurements and note the quality of the zip lock or foil seal where appropriate. In the event an analytical anomaly is noted (i.e. a flat-line standard), a vial containing distilled water may be used to check the syringe for blockage. A 100 ml injection should produce approximately 12 discrete bubbles when injected into the distilled water.

D. Quality Assurance/Quality Control

1. A brief method summary is required.

2. For any detector used, QA/QC procedures are described in the Guidance Document for each instrument (i.e. see Guidance Document section for GC). The remainder of this section describes the requirements when using a survey instrument (Note: detector-specific comments are not included below).

3. A single-point calibration should be conducted prior to any field activities. If the type of contamination is known, the instrument may be calibrated to that particular contaminant.

4. A midpoint calibration standard (containing target compounds) and a blank should be rechecked every ten samples, or whenever carry over is expected. These "standards" should be preserved in separate vessels, to limit cross contamination. If, after adjusting for temperature, results of the calibration standard vary by more than 15%, recalibration is appropriate. If the "clean standard" demonstrates elevated levels, rezeroing or system flushing is appropriate.

5. Experimental precision and detection limit(s), for each contaminant of concern, should be determined with site similar materials (i.e. actual site soils).

6. A baseline scan (i.e. "clean air", "clean water" or "clean soil" as appropriate) should be run each day prior to analyzing any site samples.

7. Field logs should document sample ID#, date, time,

location, depth, soil type (using a standard soil classification system as described in the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 3.6(a)2ii), soil moisture (qualitative estimate), and analysis result.

8. A non-conformance summary should state all data inconsistencies and all divergences from the approved sampling/analysis program.

9. Each field team that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of capability and an ongoing analysis of standards. To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations:

   a) Analysis of a quality control (QC) check sample is required and should contain gasoline or appropriate alternate standard at a concentration of 10 ppm in soil. The QC check sample concentrate should be prepared by the laboratory using stock standards.

   b) Prepare an aqueous QC check sample to contain 100-500 ppb of gasoline or appropriate alternate standard.

   c) Analyze four 500-ml aliquots of each well-mixed QC check sample.

   d) Calculate the average recovery X (mean) in μg/L, and calculate the standard deviation of the recovery(ies) in μg/L, for each parameter of interest (i.e. BTEX) using the four results, in each matrix.

   e) For each matrix, (X) should be between 50% and 150% of the true value. Additionally, s should be $\pm$ 50% of X.

VI. DATA INTERPRETATION AND REPORTING

A. A hard copy (i.e. chart recording or down loading of field computer memory) of all Organic Vapor Analyzer readings should be included as a QA/QC Section Deliverable, if available. Hand written copies of instrument readouts are acceptable if the instrument is not capable of down loading.

B. A field data log should include: date, time, soil type,

temperature, location, depth, sample container integrity, field technician's name, field analyst's signature (certifying results), and instrument reading. Calibration procedures performed before and after data collection should be provided.

C. Data summary sheets should be included as a separate section of the site assessment report. These sheets should include: sample location, sample depth, instrument reading, laboratory confirmation results (if available), and "corrected value" (based on data manipulation).

D. Instrument Reading Interpretation - Laboratory data provides speciation, relative concentrations, and quantification. This information, along with known detector response factors and laboratory confirmation results, can be used to elaborate on field instrument results. Even when a field GC is not used, it MAY be possible to infer volatile analyte presence, as well as estimate the relative concentration of volatiles (warning: see Interferences/Limitations section). This information, if generated, should be reported in the data summary sheets. Additionally, example calculations and any other pertinent information should be included as an appendix to the report.

E. All results should be plotted on a scaled area (or site) map. Contour lines should be drawn for each contaminant and total VO content. Note: This may require several maps.

F. Required QA/QC Deliverables

1. Chain of custody documentation or sample tracking sheets for every sample taken and analyzed in the field. Documentation Should be provided at the end of the final data report.

2. Sample Data Packages - should contain the following information: Sample Result Summary, Method Blank Results and Method Detection Limits.

3. Methodology Review - a brief narrative outlining the essential points of each method employed.

4. Non-Conformance Summary Report - in appropriate narrative and tabular form. All data falling outside the quality control criteria specified and approved in the QA plan as a deliverable should be highlighted. The analyst's signature should certify compliance with approved procedures and the recording of actual results.

VII. HEALTH AND SAFETY CONSIDERATIONS

A. Potential Physical Hazards - The instrumentation utilized for this method pose no unusual physical health or safety considerations.

B. Potential Chemical Hazards - There are no unusual chemical health or safety considerations specifically pertaining to the use of headspace analysis; however, the toxicity or carcinogenicity of the compounds used in this method are not always defined precisely. Therefore, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The analytical team is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

VIII. REFERENCES

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TITLE: Field Delineation of Ringed Aromatic Compounds Using Colorimetric Test Kits (12/93).

I. SUMMARY:

Colorimetric test kits can be used to detect aromatics, PAHs and PCBs in soil or water. This guidance document should be used as a model for all colorimetric field analysis techniques. The Data Quality Levels on pages two through ten (2 - 10) should be read prior to using this method.

II. PURPOSE AND SCOPE

To define the minimum standards for an acceptable field colorimetric test, delineation plan (Data Quality 1).

III. RESPONSIBILITY

The project team is responsible for the review and revision of all site delineation proposals.

IV. METHOD OVERVIEW

A. Applications & Advantages

1. Uses of Method

a. Field Screening of Soils and Water.

b. Field Delineation of Soils in one phase.

c. This method is recommended for all fuel oil tank excavation activities, or any other activities where elevated PAH compounds are expected.

2. Benefits of Method

a. This method provides field personnel with real-time information, which may be used in making field decisions regarding site delineation.

b. This method becomes cost-effective when greater than 10 samples are to be analyzed.

B. Interferences and Limitations

1. Restrictions of Method

a. Exposure of the colored catalyst to direct sunlight causes the colors to fade to brown. The test tubes containing the test solution

should be protected from direct sunlight.

b. Temperature, pH and eH are likely to affect the efficiency and extent of the reaction. The test should not be performed in extreme conditions.

2. Disadvantages of Method

a. Non targeted ringed compounds which may be present may give false positive results.

b. High chloride content and/or sodium chloride in the matrix will affect the readings.

c. Direct reading results in the Hanby colorimetric test kit are only accurate for monochloride biphenyl. Similar limitations may apply to other colorimetric test kits.

d. Waste solvent is generated and must be disposed properly.

e. Contamination of the samples by chlorinated solvents (i.e. TCE, PCE, methylene chloride) may cause false readings.

C. Capabilities

1. Compounds Detected: Aromatic compounds (i.e. PAHs, PCBs, benzene (and derivatives), naphthalenes, etc.). Standards can be developed to provide adequate quality assurance and quality control.

2. Matrix: Soils/Sludges - Delineation/Screening
Water - Screening Only

3. Quantitation Limit: Detection limits are a function of sample preparation and compounds present. The site specific detection limit should be determined based on the data collected.

D. Chemistry

1. The detection of aromatic compounds is based upon the Friedel-Crafts alkylation reaction. The reagents react with aromatic compounds to produce an intense color.

E. Practical Considerations

1. Cost per Sample (Approximate): $10.00

2. Time Required per Sample: 20 minutes

3. Quality of Data (Level): Fair (Level 1)

4. Difficulty of Procedure: Moderate

5. Laboratory Method Equivalent: None Approved

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used during the remedial investigation (RI) for delineation purposes and during the site investigation (SI) for initial characterization sampling to determine that up to fifty percent (50%) of the samples are not contaminated in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b).

2. Sampling frequency should be approximately twice that which would have been used if all samples were to be laboratory analyzed.

3. Analysis by a higher level method, such as GC, is required to obtain a correlation over the entire concentration range found on-site. This should include a minimum of 3 samples.

4. A minimum of one laboratory sample should be biased to a "hot spot" to correlate field data.

5. Field data should be confirmed by a method of greater data quality (i.e. Level 2, 3 or 4) at a frequency of no less than 20%.

6. Clean zone samples should be laboratory confirmed by methodologies approved in the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

B. Sampling Procedures

The following procedures were developed based on the Hanby colorimetric test kit. Variation in procedures will be appropriate for test kits developed by other manufacturers. The alternate procedures should be submitted to the project team for consideration prior to implementation.

1. Aqueous Samples

a) Collect aqueous samples in one liter brown

bottles, with minimum air space using procedures of NJDEPE Field Sampling Procedures Manual, May, 1992.

b) The sample should be brought to a clean zone in the field for analysis.

2. Soil

a) Collect soil samples in 4 oz. wide mouth brown bottles with minimum air space using procedures of NJDEPE Field Sampling Procedures Manual, May, 1992.

b) The samples should be brought to a clean zone in the field for analysis.

C. Field Operations

1. Analyze samples within 4 hrs (ASAP preferred).

2. Aqueous Samples

a) Pour 500 ml of sample, using a calibrated liter beaker, into a 500 ml separatory funnel. The separatory funnel should be mounted on a tripod or sturdy stand.

b) Break the top of a 5 ml ampule of extraction reagent and pour into separatory funnel.

c) Shake the funnel for 30 seconds then vent the funnel. Continue extracting the sample for 1.5 minutes.

d) Allow the solution phases to separate for 2-3 minutes. Drain the extraction layer into a 16 x 100 mm test tube. Do no allow water into the test tube. Transfer the solvent into a 10 ml graduated cylinder (4.2 ml required). Record the volume and transfer contents to another 16 x 100 mm test tube.

e) Empty the contents of one catalyst vial into the test tube. Stopper the test tube, shake for 30 seconds and compare the color to the color chart.

3. Soil Sample: Low Level, valid up to 400 mg/kg

a) Weigh 100 + 0.1 grams of sample and transfer to a one liter wide mouth bottle.

b) Add one package of clarifying powder and 500 ml of reagent water to bottle, seal and shake soil-water mixture periodically for 20-30 minutes.

c) Pour the mixture into Imhoff cone.

d) Allow the soil to settle and the water layer to clarify for 15-20 minutes.

e) Carefully decant 250 ml of clear water layer into a 500 ml separatory funnel, adding contents of 5 ml ampule of extraction reagent. If 250 ml of clear water layer is not available, record the volume of water transferred.

f) Swirl the funnel for 30 seconds then vent the funnel. Continue extraction of the sample with a swirling motion for 4.5 minutes. Use a cotton swab to remove water from the funnel stem.

g) Allow the solution phases to separate for 2-3 minutes. Drain the extractant layer into a 16 x 100 mm test tube. Do not allow water into the test tube. Transfer the solvent into a clean dry 10 ml graduated cylinder (4.2 ml required). Record the volume and transfer contents to another 16 x 100 mm test tube.

h) Empty the contents of one catalyst vial into the test tube. Stopper the test tube, shake for 30 seconds and compare the color to the color chart. Multiply the results by 20 to obtain the concentration of aromatics in soil in mg/kg. A work sheet for soil calculations comes with the kit.

4. Soil Samples: High Level, valid above 400 mg/kg

a) Measure out 20 ml extraction reagent into clean liter bottle and seal bottle.

b) Place bottle with reagent on balance and tare.

c) Quickly add 10.0 g of soil sample (usually 4-5 ml, volume) to bottle.

d) Chop sample with clean spatula or knife blade until soil is in very small (3 mm) pieces.

e) Seal bottle and swirl (do not shake) soil in

extraction reagent for 5 minutes.

f) Measure out 4.2 ml solvent from the bottle into the graduated cylinder and pour into test tube.

g) Add one catalyst vial and shake well for one minute.

h) Compare to color chart and multiply chart reading by 200 to obtain soil concentration in mg/kg (ppm).

D. Quality Assurance/Quality Control

1. A brief method review should be provided.

2. Experimental precision and detection limit(s), for each contaminant of concern, should be determined with "site-similar" materials.

3. A five-point calibration should be performed at the start of each investigation. Calibration standards (minimum of 5 points covering the entire sample concentration range) should be generated for all sample matrices (i.e. clays, water, sands) analyzed using this colorimetric test. These results should be photographed for reference.

4. Field Duplicates and one blank should be collected and field analyzed at a rate corresponding to the greater of one per day or one per 20 samples.

5. Field logs should document sample ID#, date, time, location, depth, soil type (using a standard soil classification system as described in the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 3.6(a)2ii), soil moisture (qualitative estimate), and analysis result.

6. A non-conformance summary should state all data inconsistencies and all divergences from the approved sampling/analysis program. All data falling outside the quality control criteria, as specified and approved, should be highlighted. The analyst's name and signature should certify the implementation of proper procedures and recording of "true" results.

7. Each project team that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of capability and an ongoing

analysis of aqueous blanks and proof of good color vision. This information should be kept on file, and submitted to the Department upon request. To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations.

a) A quality control (QC) check sample concentrate should contain #2 fuel oil at a concentration of 500 ppm in hexane:acetone. The QC check sample concentrate should be prepared by the laboratory using stock standards prepared independently from those used for calibration.

b) Prepare an aqueous QC sample from the QC check sample concentrate to contain 2000 ppb of fuel oil.

c) Prepare a soil QC check sample to contain 200 ppm of fuel oil.

d) Analyze four 500-ml aliquots of each well-mixed QC check sample according to standard procedures.

e) Calculate the average recovery mean (X) in μg/L, and calculate the standard deviation of the recovery (s) in μg/L, for each parameter of interest using the four results.

f) For each QC check sample, X should be between 50% and 150% of the true value. Additionally, s should be ±50% of X.

VI. DATA INTERPRETATION & REPORTING

A. Summary tables should depict all sample results (field and laboratory). These tables should also include the best estimate of "true values" calculated using the field/laboratory correlation data, surrogate recoveries, soil type, blanks and any other available information. Data correlation should be discussed (a plot of field - versus- laboratory data is highly encouraged). Example calculations, including slope and correlation coefficient, should be provided.

B. Corrected data should be plotted on scaled site maps.

C. Field logs should document sample ID#, date, time, location, depth, soil type, moisture (qualitative estimate), and analysis result.

D. All Quality Assurance/Quality Control documentation should be provided to the Department with the final data report.

E. Calculations

1. Aqueous Samples

$$C\ \mu g/L = \frac{(D)\ (4.2)}{B}$$

D = Chart Reading in µg/L
B = Extract solvent recovered, ml

2. Soil Samples: Low Level (sample weight 100 + 0.1g)

$$C\ mg/kg = \frac{(D)\ (4.2)\ (20)}{(B)\ (A)}$$

A = Fraction of Water recovered (250 ml/volume recovered)

3. Soil Samples: High Level (sample weight 10 + 0.1g)

C mg/kg - (D) (200)

VII. HEALTH AND SAFETY CONSIDERATIONS

A. Potential Physical Hazards - No unusual physical health or safety considerations are posed by this method; however, all manufacturer warnings and cautions should be observed.

B. Potential Chemical Hazards - Several reagents used in this method may pose chemical health or safety considerations. The toxicity or carcinogenicity of the compounds used in this method are not always defined precisely. Therefore, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The analytical team is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Safety practices consistent with that in laboratories is recommended.

All solvent should be properly handled and disposed. Most colorimetric test kit manufactures will accept the spent solvents for disposal.

VIII. REFERENCES

1. Hanby, J.D., "A New Method for the Determination and Measurement of Aromatic Compounds in Water", Written Communication, Hanby Analytical Laboratories, Inc., Houston, Texas, 1989.

2. Miller, M.W.; Stainken, D.M. "Field Method for the Determination of Aromatic Compounds in Water and Soil", Document # OQA-QAM-021-5/90.

3. NJDEPE, Field Sampling Procedures Manual, May 1992.

4. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

5. Roberts, R.M., Khalaf, A.A., Friedel-Crafts Alkylation Chemistry; A Century of Discovery, Macel Dekker, Inc., New York, pp 790, 1984.

6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition 1979.

7. Shriner, R.L., Fuson, R.C. et. al., The Systematic Identification of Organic Compounds, John Wiley and Sons, New York, 1980.

IX. APPENDIX - Table 1, Table 2, and Table 3

TABLE 1: METHOD DETECTION LIMITS

Constituent	Concentration (ppm) Water	Soil
Gasoline and Diesel	0.1	2
BTEX (pure component)	0.05	0.5
PCBs	0.003	0.1

TABLE 2: COLORS & CONCENTRATIONS FOR CLASSES OF COMPOUNDS

Compounds	Color/Concentration Range
Benzene, Toluene, Xylenes, Ethylbenzene	Yellow (1 ppm) to Orange (10 ppm) Orange-Yellow (1 ppm) to Burnt Orange (10ppm)
Gasoline	Beige (5 ppm) to Green (20 ppm)
Diesel	Beige (5 ppm) to Green (20 ppm)

PCBs	Light Pink (0.5 ppm) to Coral (0.2 ppm)
Naphthalates	Light Violet(0.2 ppm) to Blue Violet (2 ppm)

TABLE 3: NOTES

1. Method Detection Limits (MDL) for total aromatics is 50-200 ppb in water and 500-2000 ppb in soil (Table 1). The MDL for a specific waste may differ depending upon the nature of interference in the sample matrix and the type of aromatic compounds present.

2. Type of Matrix: Surface Water, Groundwater, Wastewater, Leachate, Soil, Sediment.

3. Summary of Method - This method uses the reagent packages, and procedures developed by Hanby Analytical Laboratories, Inc. Other procedures will be appropriate for colorimetric test kits available from different manufactures. A water sample is extracted with an alkyl halide solvent. The solvent is treated with a drying agent and a catalyst. When aromatics are present the catalyst develops a color which is compared to a color chart to determine the concentration of aromatic compounds present. Soil samples are extracted with reagent water and the water is extracted with alkyl halide solvent. Soils containing 400 mg/kg of fuel can be directly extracted with alkyl halide solvent.

4. Method Performance

   a. This method is a colorimetric test which can both qualitatively and quantitatively identify the presence of petroleum compounds in soil or water. Table 2 provides a summary of the range of colors and concentrations that each compound or class of compounds represents.

   b. The test is qualitative in that a color shown on the kit chart indicates a particular compound or class of compounds. A mixture of different compounds may result in a color somewhere between the colors shown on the chart.

TITLE: Hydrophobic Dye Test for Determination of NAPL in Saturated Soils and Groundwater Samples (12/93)

I. SUMMARY

The hydrophobic dye test may be used to determine the presence of non-aqueous phase liquids (NAPL) in saturated soils and groundwater. The sample is placed into a polypropylene tube, centrifuged to separate the solid and liquid phases, a hydrophobic dye is added and the mixture is agitated. The liquid phase is then observed to determine whether a NAPL phase is present. The mixture may then be centrifuged again to allow better separation of the liquid phases. Detection capabilities increase as the percent (%) of NAPL increases from one percent to two percent (1% - 2%) or greater. The Data Quality Levels on pages two through ten (2 - 10) should be read prior to using this method.

II. PURPOSE AND SCOPE

To define the minimum standards for a hydrophobic dye test proposal consistent with the Data Quality Levels on pages two through ten (2 - 10).

III. RESPONSIBILITY

The project team is responsible for the review and revision of all site delineation proposals.

IV. METHOD OVERVIEW

A. Application & Advantages

1. Field Screening of Saturated Soils.

2. Field Screening of Groundwater.

3. Provides field personnel with real-time information which may be used in making field decisions regarding site delineation.

4. This method is recommended for site screening when clear, colorless NAPL contamination is of concern.

5. This method expedites the screening process while providing better site definition at a reduced cost.

B. Interferences and Limitations

1. Restrictions of Method

   a. The dye test will not identify dissolved contamination in the aqueous phase.

Therefore, conventional laboratory methods should be employed for dissolved contamination.

b. Up to ten percent (10%) false positives and up to fifty percent (50%) false negatives can be expected in samples with less than one percent (<1%) NAPL. False negatives decrease as the NAPL percentage increases. Samples with greater than one percent (>1%) NAPL indicated only two to eight percent (2% - 8%) false negatives. Therefore, conventional laboratory tests should be used where contamination is suspected but the hydrophobic dye test does not indicate the presence of NAPL.

2. Disadvantages of Method

a. The dye is not analyte-specific but should dissolve in organic NAPL without dissolving in the aqueous phase.

b. Sample matrix may cause false positives.

C. Capabilities

1. Compounds Detected: Non-Aqueous Phase Liquids (NAPL)

2. Matrix: Saturated Soils - Screening
Water - Screening

3. Achievable Quantitation Limits: Dependent on sample conditions, one percent (1%) or less NAPL can be detected.

4. The information obtained is qualitative (i.e. presence or absence of NAPL); however, the density of NAPL relative to water can be determined and the volume of NAPL in the sample can be estimated.

5. Effective Use of this technology requires the project team to select appropriate samples for laboratory confirmation. The goal of the laboratory confirmation is to determine that NAPL has been correctly delineated and identified.

D. Instrumentation

1. This method requires polypropylene tubes and a hydrophobic dye (i.e. Sudan IV, an oleophilic dye, from Aldrich Chemical Co.). A centrifuge is required for saturated soils analysis and is

optional for groundwater samples. Therefore, the method may not be a true field method for saturated soils given that centrifuges are generally not field portable.

E. Practical Considerations

1. Cost per Sample (Approximate): less than $10.00

2. Time Required per Sample: less than 15 minutes

3. Quality of Data (Level): Level 1

4. Difficulty of Procedure: Simple

5. Laboratory Method Equivalent: None Certified

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used only for screening purposes during the initial characterization sampling and monitoring phase to determine the presence of NAPL. Confirmation of the absence of NAPL may be required in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1.

2. Delineation sampling frequency should be in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

3. The results produced by this method are qualitative; however, the density relative to water and approximate volume of NAPL in the sample can be determined.

B. Sampling Procedures

1. Collect one hundred and seventy-five (175) ml of solid or thirty-five (35) ml of liquid sample.

2. Samples should be collected with teflon or stainless steel utensils and placed into polypropylene tubes.

3. Set samples aside for preparation.

C. Field Operations

1. Prepare samples via weighing, centrifuging (soil samples), adding hydrophobic dye and shaking the

tubes. Note: Centrifugation may preclude performance in the field.

2. Observe the samples directly for evidence of two (2) phases (i.e. one [1] dyed phase and one [1] clear, colorless phase).

3. Centrifuge the liquid phase and observe the samples directly for evidence of two (2) phases. Note: Centrifugation may preclude performance in the field.

D. Quality Assurance/Quality Control

1. A brief method summary is required.

2. The sample location, depth and matrix should be documented along with the sample collection time and date and field analysis time and date.

3. Collection and analysis of uncontaminated samples from site matrix should be performed each day to document matrix interference.

4. Sample duplicates should be performed in the field to document method repeatability at the rate of at least one (1) for every twenty (20) samples.

5. Confirmation of field analysis should be provided in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

6. One (1) method blank and rinsate blank should be field analyzed daily.

7. One (1) blank standard should be performed daily.

VI. DATA INTERPRETATION AND REPORTING

A. A hard copy of all observations of liquid phases should be included as a QA/QC Section Deliverable.

B. A field data log should include: date, time, matrix description (i.e. soil type or groundwater description), temperature, location, depth, field technician's name, field analyst's signature (certifying results), and observations of liquid phases.

C. Data summary sheets should be included as a separate section of the site assessment report. These sheets should include: sample location, sample depth, observation of liquid phases, and laboratory confirmation results (where applicable).

D. All results should be plotted on a scaled area (or site) map.

E. Required QA/QC Deliverables

1. Chain of custody or sample tracking documentation for every sample collected and analyzed in the field. Documentation should be provided at the end of the final data report.

2. Sample Data Packages should contain the following information: Sample results, sample matrix results and blank results.

VII. Health and Safety Considerations

A. Potential Physical Hazards - The instrumentation utilized pose no unusual physical health or safety considerations; however, all manufacturer warnings and cautions should be observed.

B. Potential Chemical Hazards - There are no unusual chemical health or safety considerations specifically pertaining to the use of the hydrophobic dye test; however, the toxicity or carcinogenicity of the compounds used in this method are not always defined precisely. Therefore, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The analytical team is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

VIII. References

1. Cohen, R. M., Bryda, A. P., Shaw, S. T., Spalding, C. P. "Evaluation of Visual Methods to Detect NAPL in Soil and Water", GWMR, Fall 1992. pp. 132-139

2. Cohen, R. M., Mercer, J. W. "DNAPL Site Evaluation", USEPA/600/R-93/022, February, 1993. pp. 7.6, 9.31 and 9.38 - 9.46

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TITLE: Field Screening Using a Field Survey X-ray Fluorescence (XRF) Instrument.

I. SUMMARY

X-ray Fluorescence (XRF) survey instruments may be used to analyze high concentrations (greater than 250 ppm) of metal contamination (instruments with (Si)Li detectors may have lower detection limits). The target metals should be known prior to site use, as instrument calibration is required. Data Quality Levels on pages two through ten (2 - 10) should be read prior to using this method.

II. PURPOSE AND SCOPE

To define the minimum standards of an approvable field XRF delineation plan.

III. RESPONSIBILITY

The project team is responsible for the review, and revision of all site screening proposals.

IV. METHOD OVERVIEW

A. Applications & Advantages

1. Uses of Method

a. Field Screening of Soils.

b. This method is recommended whenever significant metals contamination is suspected.

c. An X-ray Fluorescence Spectrometer (XRF) detects metals (several simultaneously) contamination in solid matrices (soils) or liquid matrices (oil, water).

2. Benefits of Method

a. This method provides field personnel with real-time information, which may be used in making field decisions.

b. The XRF is particularly sensitive to heavy metals, which are commonly found on industrial sites (see Item IX for analyte list and detection limits).

B. Interferences and Limitations

1. Restrictions of Method

a. The use of the hand-held probe is more susceptible to background interferences than are "chamber" type probes. Additionally, the optical configuration of hand held units prevents efficient photon collection, thereby lowering sensitivity, accuracy, and precision.

b. Several metals fluoresce at similar wavelengths (e.g. As and Pb; Hg and Pb). All fluorescence data should be retained so that secondary line (wavelength) analysis may be conducted, if required.

c. The instrument should not be exposed to rain.

2. Disadvantages of Method

a. Hot weather (above 75 degrees) may affect the electronics and battery; however, instrument results may not be significantly affected.

b. The validity of the results is a function of the capability of the technician to reproduce the data. Standardized sample preparation and the minimization of any variations in sample screening techniques is vital to the accurate performance of this test.

c. Detection levels may be above site specific standards for certain metals.

C. Capabilities

1. Compounds Detected - Heavy Metals: Excellent
Other Elements: Variable

2. Matrix: Soils, Sludges, Oil, Water

3. Quantitation Limit: 30-500 ppm; however, quantitation limits are highly dependent on sample matrix. Water and oil detection levels are less than 100 ppm. Soil detection levels are greater than 70 ppm. Since this method does not involve sample preparation, matrix can not be controlled. The site specific quantitation limit should be determined based on the data collected.

D. Instrumentation

1. The detector responds to electromagnetic energy emitted in the process of fluorescence; the energy emitted in the process is characteristic of the

atom irradiated.

2. Two instrument types are available: wavelength dispersive (WD) and energy dispersive (ED). The WD configuration provides very high resolution, at the cost of decreased sensitivity. The ED configuration provides high photon collection efficiency (i.e. sensitivity), but less resolving power. In general, field-portable XRF instruments are energy dispersive due to source and optics limitations.

3. Several x-ray sources, each geared to the analysis of particular elements, are available. Source selection should be based on the specific metals expected on site. Use of more than one source/instrument may be required. Manufacturer's recommendations should guide the selection of a site specific source(s).

4. Detection limits are a function of sample matrix, contaminant species, background radiation levels, and instrumental limitations.

E. Practical Considerations

1. Cost per Sample (Estimate): $6.00

2. Time Required per Sample: 1 - 3 minutes

3. Quality of Data (Level: Poor (Level 1)

4. Difficulty of Procedure: Simple

5. Laboratory Method Equivalent: SW-846 6010 (Solid)
SW-846 200.7 (Aqueous)

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used during the remedial investigation (RI) for delineation purposes and during the site investigation (SI) for initial characterization sampling to determine that up to fifty percent (50%) of the samples are not contaminated in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b).

2. Source choice and rationale should be included in the QA/QC discussion.

3. Sampling frequency should be as great as possible, as the analysis cost is virtually "fixed" per diem. At a minimum, sampling frequency should be consistent with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

4. At a minimum, laboratory samples should be collected to document worst case contamination for use in the delineation phase and to document all clean zone samples.

5. This method may be used to "target" certain areas for higher level analysis (i.e. levels 2-4). In this situation, a reduced deliverable requirement is appropriate.

B. Sampling Procedures

1. Sample screening may be performed by holding the probe on soil on a split spoon, or on the native soil. Variability in the sample results as well as detection limits increase when sample preparation procedures have not been employed. Perform duplicate analysis to obtain an average reading and reduce variability.

2. To keep the probe clean, a piece of plastic wrap should be placed between the probe and sample matrix during analysis.

3. Increased analysis time (i.e. 1-3 minutes) will effect more accurate results.

C. Field Operations

1. All manufacturer's operation instructions should be followed. These instructions, along with an "internal" Standard Operating Procedure should be submitted to the Department as part of the Methods QA/QC program.

2. Generally, 30 to 60 seconds are required to allow sufficient signal averaging to occur; however, increased analysis time (i.e. 1-3 minutes) will effect more accurate results.

3. Background readings should be obtained for all matrices analyzed. This may be done by analyzing a minimum of 3 samples per matrix in non-impacted areas.

4. All readings should be recorded in the field logs.

The field analyst's name and signature should certify the implementation of proper procedures and recording of proper values.

D. Quality Assurance/Quality Control

1. A brief method review should be provided. An internal SOP should be submitted to the Department as part of the method's QA/QC program. Source choice and rationale should be included in a QA/QC Plan and may be included as part of the SOP.

2. The system should be configured and standardized prior to site activities. Standards composed of actual site material should be used for final quantitation. This may be done by collecting "calibration standards" on-site, and back calculating concentrations based on fluorescence intensity readings.

3. Calibration standards (minimum of 5 points covering the entire range of analysis) should be generated for all sample matrices (i.e. clays, sands, etc.) analyzed using the XRF. This five-point calibration should be performed prior to beginning work at a site and at a minimum of monthly in order to assure linearity throughout the entire analysis range. This procedure may be required at a greater frequency if a QC calibration check varies from the "known" value by more than 30%.

4. Midpoint standards (for each matrix) should be rechecked at least every ten to twenty samples. Recalibration (as in 3, above) is appropriate when values obtained vary from the "true" value by greater than 3 times the standard deviation.

5. Experimental estimates of precision and detection limit(s), for each contaminant of concern, should be determined with site-similar (i.e. same matrix or soil type) materials. The measurement time should be established based on these initial site studies. Note: Measurement time has a pronounced effect on precision, accuracy, and detection limits. Longer measurement times (1 to 3 minutes) may be required for most site applications.

6. A baseline scan (i.e. "clean air", "clean water" or "clean soil" as appropriate) should be run each day prior to analyzing any site samples.

7. An instrument log should be maintained and submitted. This log should include instrument

maintenance, blank and calibration information including date, time, work completed, analyst's name, calibration standard(s), source, detection wavelength, standard results in intensity units, and any other pertinent information.

8. Measurement times should be no less than 30 seconds for site screening. Longer times may be required in order to achieve desired accuracy and precision.

9. Field logs should document sample ID#, date, time, location, depth, soil type (using a standard soil classification system as described in the Technical Requirements, N.J.A.C. 7:26E, section 3.6(a)2ii), moisture (qualitative estimate), sampler's name, analyst's name, sampler's & analyst's signature, and analysis result.

10. A non-conformance summary should state all data inconsistencies and all divergences from the approved sampling/analysis program. The implication of all non-conformances should be clearly explained and quantified (if possible).

11. Each project team that uses this method is required to operate a formal quality control program. The minimum requirement of this program is an initial demonstration of capability. This information should be kept on file, and submitted upon request. To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations:

    a) Three soil quality control (QC) check samples, containing a suite of metals (As, Pb, Hg, Cr, Cu, and Ni) at concentrations between 50 ppm and 5000 ppm are required. The QC check samples should be prepared by a laboratory using stock standards.

    b) An aqueous QC sample, containing the above mentioned metals at concentrations between 10 ppm - 40 ppm, is also required.

    c) The field technician(s) should analyze four aliquots of each well mixed QC check sample according to standard analysis procedures.

    d) The average detection, mean (X), and standard deviation (s) should be calculated for each contaminant in each matrix at each concentration using the four results.

e) For each compound and matrix, X should be between 60% and 140% of the true value. Additionally, s should be $\pm$ 40% of X. A plot indicating the linearity of response with respect to concentration is required for each species in each matrix.

VI. DATA INTERPRETATION & REPORTING

A. Summary tables should depict all sample results (field and laboratory). These tables should also include the best estimate of "true values" given the field/laboratory correlation data, surrogate recoveries, and secondary line analysis results. Example calculations should be included.

B. All "corrected" data should be plotted on a scaled site/area map.

C. A hard copy of all data results should be submitted. Many instruments are able to produce contaminant contour diagrams, as well as hard copies of data.

D. All QA/QC deliverables should be submitted as a separate section to the report.

VII. HEALTH & SAFETY CONSIDERATIONS

A. Potential Physical Hazards - The instrumentation utilized should be handled with care, as a radioactive light source is present.

B. Potential Chemical Hazards - There are no unusual chemical health or safety considerations specifically pertaining to the use of field XRF; however, all manufacturer's recommendations and cautions should be followed.

VIII. REFERENCES

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IX. APPENDIX

APPROXIMATE DETECTION LIMITS ATTAINABLE

Element	Portable Laboratory Unit (internal probe)	Mobile Unit (remote probe)
Antimony	5 ppm	50 ppm
Arsenic	10 ppm	25 ppm
Barium	?	30 ppm
Cadmium	5 ppm	35 ppm
Chromium	20 ppm	50 ppm
Copper	20 ppm	40 ppm
Lead	6 ppm	50 ppm
Mercury	5 ppm	30 ppm
Nickel	15 ppm	50 ppm
Selenium	?	25 ppm
Silver	10 ppm	50 ppm
Thallium	?	30 ppm
Vanadium	?	50 ppm
Zinc	15 ppm	50 ppm
Iron	20 ppm	140 ppm
Manganese	25 ppm	50 ppm
Total Chlorine (PCBs)		100 ppm
Calcium	200 ppm	
Potassium	300 ppm	

? Unknown MDLs

* Beryllium and Boron can not be analyzed using an XRF instrument.

** The detection limits reported are the best achievable under ideal conditions. Typical MDLs of three to five times the above stated values should be expected for most sites.

Instruments included in survey:

1. Delta 770 XRF Analyst System
2. Tracor Spectrace 6000
3. Columbia Scientific X-met 840
4. Kevex 7000 x-ray fluorescence system

Approximate Cost of XRF Survey Instrument

Purchase: $40,000-55,000.
Lease : $3,500-5,000 per month.
Rental : $1000/day including analyst.

TITLE: Field Delineation Using a Portable X-ray Fluorescence (XRF) Instrument.

I. SUMMARY

A field portable XRF may accurately detect heavy metals in soil below 50 ppm. Detection limits may be lower in liquid matrices. The Data Quality Levels on pages two through ten (2 - 10) should be read prior to using this method.

II. PURPOSE AND SCOPE

To define the minimum standards for an x-ray fluorescence delineation plan.

III. RESPONSIBILITY

The project team is responsible for the review, and revision of all site delineation proposals.

IV. METHOD OVERVIEW

A. Applications & Advantages

1. Uses of Method

a. Field Delineation of soils.

b. Field Analysis of oils or air samples (contamination collected on a filter).

c. Use of this method is recommended whenever metals contamination is present.

2. Benefits of Method

a. This method provides field personnel with real-time information, which may be used in making field decisions.

b. An X-ray Fluorescence Spectrometer (XRF) accurately detects metals (several simultaneously) contamination in solid matrices, such as soils, or particulates on a filter.

c. The XRF is particularly sensitive to heavy metals, which are commonly found on industrial sites (see Item IX for analyte list and detection limits). Instrumental detection limits for most "List Metals" have been shown to be at or below NJDEP cleanup criteria.

d. Previous studies have shown good correlation (0-30 Percent Difference) between the data generated by XRF, and by current CLP methodologies.

B. Interferences and Limitations

1. Restrictions of Method

a. Hot weather (above 75 degrees) may affect the electronics and battery; however, instrument results may not be significantly affected.

b. Several metals fluoresce at similar wavelengths (e.g. As and Pb; and Pb). All fluorescence data should be retained so that secondary line (wavelength) analysis may be conducted, if required.

c. The instrument should not be exposed to rain.

d. The elemental composition of the analysis chamber should be considered when developing a site specific work plan. Some chambers are made of lead, which may interfere with the analysis of samples containing lead or mercury. Adequate precautions should be outlined to avoid such interferences.

2. Disadvantages of the Method

a. The validity of the results is a function of the capability of the technician to reproduce the data. Standardized sample preparation and the minimization of any variations in sample screening techniques is vital to the accurate performance of this test.

b. Detection levels may be above site specific standards for certain metals.

C. Capabilities

1. Compounds Detected: Heavy Metals - Excellent
Other Elements - Variable

2. Matrices: Soils, Sludges, Oils - Excellent
Water - Good

3. Quantitation Limit: 5-50 ppm; however, quantitation limits are highly dependent on sample matrix and handling. The site-specific quantitation limit should be determined based on

site data.

D. Instrumentation

1. The detector responds to electromagnetic energy emitted in the process of fluorescence; the energy emitted in the process is characteristic of the atom irradiated. Two detectors are available, the counter detector and the Si(Li) detector. The Si(Li) detector is preferred.

2. Two instrument types are available: wavelength dispersive (WD) and energy dispersive (ED). The WD configuration provides very high resolution, at the cost of decreased sensitivity. The ED configuration provides high photon collection efficiency (i.e. sensitivity), but less resolving power. In general, field-portable XRF instruments are energy dispersive due to source and optics limitations.

3. Several sources, each geared to the analysis of particular elements, are available. Source selection should be based on the specific metals expected on site. Use of more than one source/instrument may be required. Manufacturer recommendations should guide the selection of a site specific source(s). X-ray tube sources are preferred, as they are tunable and provide high intensity responses.

4. Detection limits are a function of sample preparation, background radiation levels, and instrument components.

E. Practical Considerations

1. Cost per Sample (Approximate): $20.00 - $40.00

2. Time Required per Sample: 15-25 minutes

3. Quality of Data (Level): Poor (Level 1) Counter
   Good (Level 2) (Si)Li

4. Difficulty of Procedure: Simple - Moderate

5. Laboratory Method Equivalent: SW-846 6010 (Solids)
   SW-846 200.7 (Aqueous)

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used during the remedial investigation (RI) for delineation purposes and during the site investigation (SI) for initial characterization sampling to determine that up to fifty percent (50%) of the samples are not contaminated in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b).

2. In general, laboratory confirmation is required for all "clean zone" samples; however, a variance may be granted on an element and site specific basis. Additionally, laboratory samples should be collected to provide "correlation" across the entire "analysis range".

3. Laboratory confirmation should be performed on no less than 10% of all samples analyzed.

B. Sample Collection and Handling

1. Samples should be prepared as outlined below (approximately 15 minutes per sample are required).

   a) Screen with 10-100 mesh sieve.
   b) Dry (air, oven, or heater)
   c) Homogenize sample
   d) Grind to 60-100 mesh (100 mesh is preferred)
   e) Split sample for laboratory, if required

C. Sampling Procedures

1. Sample should be placed in a plastic container.

2. The surface to be analyzed should be covered with Saran wrap which is held in place with a rubber band.

3. The "wrap" surface should be placed over the source.

D. Field Operations

1. All manufacturer's operation instructions should be followed. These instructions, along with an "internal" standard operating procedure should be submitted to the Department as part of a QA/QC program.

2. Generally, 60 seconds may be required to allow sufficient signal averaging to occur; however, longer analysis times may be required to attain

adequate sensitivity and precision.

E. Quality Assurance/Quality Control

LEVEL 1 QA/QC REQUIREMENTS

The following are required for Level 1 Data:

1. A brief method review should be provided. An internal SOP should be submitted to the Department as part of the method's QA/QC program. Source choice and rationale should be included in a QA/QC Plan and may be part of the SOP.

2. The system should be configured and standardized prior to site activities. Standards composed of actual site material should be used for final quantitation. This may be done by collecting "calibration standards" on-site, and back calculating concentrations based on fluorescence intensity readings.

3. Calibration standards (minimum of 5 points covering the entire range of analysis) should be generated for all sample matrices (i.e. clays, sands, etc.) using the XRF. At a minimum, this five-point calibration should be performed monthly and prior to beginning work at a site to assure linearity throughout the entire analysis range. This procedure may be required at a greater frequency if a QC calibration check varies from the "known" value by more than 30%. All contaminants of interest should be represented in these calibration standards for all matrices of interest.

4. Midpoint standards and aqueous blanks should be rechecked at least once every ten samples. Recalibration is appropriate when values obtained vary from the "true" value by greater than 3 times the standard deviation.

5. The use of a "chamber" type probe is required. Hand held probes are more susceptible to background interferences than are "chamber" type probes. Additionally, the optical configuration of hand held units prevents efficient photon collection, thereby lowering sensitivity, accuracy, and precision.

6. Experimental estimates of precision and detection limit(s), for each contaminant of concern, should be determined with site-similar (i.e. same matrix or soil type) materials prior to site sampling.

The measurement time should be established based on these initial site studies (Note: Measurement time has a pronounced effect on precision, accuracy, and detection limits. Longer measurement times [1 to 3 minutes] may be required for most site applications).

7. A baseline scan (i.e. "clean air", "clean water" or "clean soil" as appropriate) should be run each day prior to analyzing any site samples.

8. An instrument log should be maintained and submitted. This log should include instrument maintenance, blank and calibration information including date, time, work completed, analyst's name, calibration standard(s), source, detection wavelength, standard results in intensity units, and any other pertinent information.

9. Field logs should document sample ID#, date, time, location, depth, soil type (using a standard soil classification system as described in the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 3.6(a)2ii), moisture (qualitative estimate), sampler's name, analyst's name, sampler's & analyst's signature, and analysis result.

10. A non-conformance summary should state all data inconsistencies and all divergences from the approved sampling/analysis program. The implication of all non-conformances should be clearly explained and quantified (if possible).

LEVEL 2 QA/QC REQUIREMENTS

In addition to the requirements listed for the Level 1 QA/QC Data, the following are required for Level 2 Data:

1. Each project team that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of capability and an ongoing analysis of calibration standards. To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations:

    a) A soil quality control (QC) check sample containing a suite of metals (As, Pb, Hg, Cr, Cu, and Ni) at concentration between 50 ppm and 500 ppm is required. The QC check sample should be prepared by a laboratory using stock

standards.

b) An aqueous QC sample containing the above mentioned metals at concentrations between 10 ppm - 40 ppm is also required.

c) The field technician(s) should analyze four aliquots of each well mixed QC check sample according to standard analysis procedures.

d) The average detection, mean (X), and standard deviation (s) should be calculated for each contaminant in each matrix using the four results.

e) For each compound and matrix, X should be between 60% and 140% of the true value. Additionally, s should be $\pm$ 40% of X.

2. Field analysis of a performance evaluation (PE) sample is required prior to startup of field analysis.

3. Instrument should be 3-point (minimum) calibrated each month and 1-point calibrated each day using laboratory certified standards. The standard species and concentrations should be chosen based on known site contamination and encompass the range of expected concentrations. Surrogate compounds should also be included. Matrix-specific minimum detection limits should be determined for all site specific compounds.

4. If standard curves remain linear over the entire analysis range, only one midpoint standard should be analyzed at a frequency of 1 per 10 samples. If standard curves are not linear over the entire analysis range, a minimum of 2 calibration standards should be analyzed at a frequency of 1 per 10 samples.

5. Matrix Spike and Matrix Spike Duplicate samples may be required at a rate of one per 20 samples. The project team should determine if MS/MSD samples are required on a case-by-case basis.

6. Field duplicates and field split samples should be collected and field analyzed at a rate of one per 20 samples.

7. A hard copy of all data results should be submitted. Many instruments are able to produce contaminant contour diagrams, as well as hard

copies of data. These maps should NOT be included in the QA/QC section.

8. Chain of custody or sample tracking documentation should be generated for all samples collected and analyzed. This should include a statement certifying that all data was generated following proper procedures.

VI. DATA INTERPRETATION & REPORTING

A. Summary tables should depict all sample results (field and laboratory). These tables should also include the best estimate of "true values" given the field/laboratory correlation data, moisture, surrogate recovery, and secondary line analysis results.

B. All "corrected" data should be plotted on a scaled site/area map.

C. Contour diagrams should be submitted for all contaminants of concern.

D. All QA/QC deliverables should be provided in a separate section of the report.

VII. HEALTH & SAFETY CONSIDERATIONS

A. Potential Physical Hazards - The instrumentation utilized should be handled with care, as a radioactive light source is present.

B. Potential Chemical Hazards - There are no unusual chemical health or safety considerations specifically pertaining to the use of field XRF; however, all manufacturer's recommendations and cautions should be followed.

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IX. APPENDIX

TABLE I

APPROXIMATE DETECTION LIMITS ATTAINABLE

Element	Portable Laboratory Unit (internal probe)	Mobile Unit (remote probe)
Antimony	5 ppm	
Arsenic	8 ppm	15 ppm
Barium	?	25 ppm
Cadmium	4 ppm	30 ppm
Chromium	16 ppm	50 ppm
Copper	16 ppm	30 ppm
Lead	6 ppm	20 ppm
Mercury	1 (?) ppm	25 ppm
Nickel	14 ppm	40 ppm
Selenium	?	20 ppm
Silver	8 ppm	30 ppm
Thallium	?	25 ppm
Vanadium	?	50 ppm
Zinc	11 ppm	30 ppm
Iron	19 ppm	140 ppm
Manganese	21 ppm	50 ppm
Total Chlorine (PCBs)		100 ppm
Calcium	200 ppm	
Potassium	300 ppm	

? Unknown MDLs

* Beryllium and Boron can not be analyzed using an XRF instrument.

** The detection limits reported are the best achievable, based on a survey of current literature. Typical MDLs of three to five times the above stated values should be expected for most sites, if proper QA/QC procedures are followed.

Instruments included:

1. Delta 770 XRF Analyst System
2. Tracor Spectrace 6000
3. Columbia Scientific X-met 840
4. Kevex 7000 x-ray fluorescence system

Costs:

Purchase - $45,000-80,000
Lease - $3,500-5,000 per month

Rental - $1,000-2,000 per day with analyst

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TITLE: Field Delineation of Volatile Contamination Using a Field Portable Gas Chromatograph (12/93).

I. SUMMARY:

A field gas chromatograph may be used to analyze VOs, SVOs, Pesticides, or PCBs in air, water and soil. This guidance document summarizes procedures for analyzing samples using a field portable gas chromatograph. Extraction procedures should be employed prior to analysis. The Data Quality Levels on pages two through ten (2-10) should be read prior to using this method.

II. PURPOSE AND SCOPE

To define the minimum standards a field gas chromatography delineation plan should meet to receive approval.

III. RESPONSIBILITY

The project team is responsible for the review and revision of all site delineation proposals.

IV. METHOD OVERVIEW

A. Applications & Advantages

1. Uses of Method

a. Field delineation of volatile, semi-volatile, pesticide, and PCB contamination.

b. This method is recommended whenever the laboratory analysis method for the contaminants on-site includes gas chromatography. This method should not be used until all contaminants are known or have been characterized using GC/MS analysis.

2. Benefits of Method

b. Field gas chromatography can provide high quality, rapid data when analyzing known volatile organic compounds.

b. This method provides field personnel with rapid information, which may be used in making field decisions.

B. Interferences and Limitations

1. Restrictions of Method

a. Most GC detectors are nonspecific total vapor detectors and therefore cannot be used to identify unknown substances. Many GC units; however, have an internal library which may identify compounds based on retention time index. Retention time index identification is column specific and should only be used as an indicator, in absence of supporting information.

b. These instruments perform best when situated in stable, temperature-controlled environments. When using in the field, it is best to set up in an area up-wind and likely to maintain constant temperature (i.e. out of direct sunlight).

c. This instrument should not be exposed to precipitation.

d. This instrument is difficult to operate and therefore should only be operated by a trained technician familiar with the instrument operation, calibration, matrix preparation and trouble shooting.

2. Disadvantages of Method

a. Readings can only be reported relative to retention times of the calibration standard used, therefore a change in chromatography (which may be brought on by many factors) may disable compound identification and subsequently its quantification. The owners manual (or an Analytical Chemistry text) should be referred to for additional information.

b. A high (C1-C6) alkane concentration in the sample may interfere with the resolution of early eluting alkenes, aromatics, and chlorinated alkenes. Proper column selection is critical in these types of applications.

c. Combustion fumes can contaminate the chromatographic column, and therefore should be avoided.

d. Dilution of samples may be required to elicit separate chromatographic peaks.

e. Certain compounds (i.e. N_2O with a PID) can produce a negative peak.

C. Capabilities

1. Compounds Detected: VOs, BNs, Pest/PCBs, AEs.

2. Matrix: Water, Soil, Air

3. Achievable Quantitation Limit: Water - less than 1 ppb (analyte dependent)

   Soil - 50 ppb

D. Instrumentation

1. The field GC instrument can quantify all volatile compounds which can be identified by its internal detector.

2. Detectors vary with instruments; however, the most common are the Photoionization Detector (PID), the Flame Ionization Detector (FID), the Argon Ionization Detector (AID), and the Electron Capture Detector (ECD) (See Detectors Section).

3. The internal computerized reporting system is generally designed to provide a tentative identification (based on retention time) and an estimated concentration (based on calibration standards) for each compound detected in the sample. See Limitations Section.

E. Practical Considerations

1. Cost per Sample (Approximate): $50-$70

2. Time Required per Sample: 30-40 minutes

3. Quality of Data (Level): Excellent (2)

4. Difficulty of Procedure: Difficult

5. Laboratory Method Equivalent: GC with Similar Detector

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used during the remedial investigation (RI) for delineation purposes and during the site investigation (SI) for initial characterization sampling to determine that up to

fifty percent (50%) of the samples are not contaminated in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b).

2. The separation column should be properly selected based on known site contamination. Proper maintenance, consistent with manufacturer's recommendations, is also required.

3. Detector choice should be based on the contamination present. See Detectors Section for details.

4. A qualified operator is essential to obtaining quality data using a field GC.

5. The data generated using this method is of high quality, particularly for headspace analysis. In general, non-headspace data quality may be a function of field extraction efficiency.

6. In general, laboratory confirmation is required for all "clean zone" samples; however, a variance may be granted on a compound and site specific basis. Additionally, laboratory samples should be collected to provide correlation across the entire analysis range.

7. Laboratory confirmation should be performed on 10% of all samples field analyzed including clean zone samples.

B. Sampling Procedures

1. Samples should be collected in a manner that minimizes sample disturbance and associated volatilization (See NJDEP Field Sampling Procedures Manual and the Technical Requirements for Site Renediation, N.J.A.C. 7:26E).

2. Spiking samples with surrogate compounds is not generally required, but may be necessary (i.e. if a field extraction is to be conducted prior to sample analysis). Spiked samples shall be collected at a rate of 1 per 20 samples.

3. Duplicate samples should be collected at a rate of 1 per 20 samples.

4. Prior to analysis samples should be stored in a cooler (at 4◦C), out of direct sunlight.

5. Field sampling requirements may differ based on the type of sample being collected (i.e. soil-gas samples require collection of a gas sample while soil samples require purging or extraction). Precise details are beyond the scope of this document. In general, sampling should be consistent with the NJDEP Field Sampling Procedures Manual and appropriate sections of the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

C. Field Operations

1. All manufacturer's operation instructions should be followed. These instructions, along with an internal SOP should be submitted to the Department as part of the Methods QA/QC program.

2. Generally up to 35 minutes is required to allow all species to be detected; however, actual run time is dependent on several factors, including flow rate, temperature, column type, and analytes. The exact run time required should be determined using site-similar material.

3. Field operation requirements may differ based on the type of compounds being analyzed (i.e. SVOs and Pesticides/PCBs require extraction). Field operations should mimic laboratory procedures to the greatest extent practicable.

D. Quality Assurance/Quality Control

LEVEL 1 QA/QC REQUIREMENTS

The following are required for Level 1 Data:

1. A brief method review should be provided.

2. A single-point calibration should be conducted prior to any field activities using site-specific standards.

3. Calibration checks should be performed at a minimum of twice daily. If a calibration check falls outside the manufacturer's suggested range, a complete multi-point calibration is required.

4. Experimental precision and detection limits, for each contaminant of concern (on-site), should be determined with site-similar materials prior to site sampling. The sample run time should be established based on these initial site studies.

5. A baseline scan (i.e. "clean air", "clean water" or "clean soil") should be run each day prior to analyzing any site samples.

6. An instrument log should be maintained and submitted. This log should include instrument maintenance, blank, and calibration information, including date, time, analyst's name, calibration compounds (CC), CC concentrations, and CC readings in area units.

7. Field logs should document sample ID#, date, time, location, depth, soil type, soil moisture (qualitative estimate), and analysis result.

8. A non-conformance summary should state all data inconsistencies and all divergences from the approved sampling/analysis program. Retention time drift should be discussed. The implication of all non-conformances should be clearly explained and quantified (if possible).

LEVEL 2 QA/QC REQUIREMENTS

In addition to the requirements listed for the Level 1 QA/QC Data, the following are required for Level 2 Data:

1. Each project team that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of capability and an ongoing analysis of calibration standards. To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations:

   a) A soil quality control (QC) check sample containing gasoline at a concentration of 1-10 ppm is required. The QC check sample should be prepared by the laboratory using stock standards prepared independently from those used for calibration.

   b) An aqueous QC sample prepared in the same fashion as the soil QC sample and containing less than 1000 ppb gasoline is also required.

   c) Analyze four aliquots of each of the well-mixed QC check sample according to standard procedures.

   d) If semi-volatiles (SVOs) are to be analyzed by the field team, steps a, b and c should be

repeated for #4 fuel oil.

e) If pesticides/PCBs are to be analyzed by the field team, steps a, b and c should be repeated for a pesticide and/or PCB mixture, as appropriate.

f) Calculate the average recovery mean (X) and the standard deviation of the recovery (s) for each parameter of interest in each matrix using the four results.

g) For each compound, X should be between 60% and 140% of the true value. Additionally, s should be + 40% of X.

2. Field analysis of a performance evaluation (PE) sample is required prior to startup of field analysis.

3. Method blanks (i.e. syringe blanks, equipment blanks, and instrument blanks) should be run at the beginning and during each work day or when carry-over from a prior sample is anticipated. A higher frequency may be required depending upon equipment use and results.

4. Instruments should be 3-point (minimum) calibrated each month and 1-point calibrated each day using laboratory certified standards. The standard species and concentrations should be chosen based on known site contamination and encompass the range of expected concentrations. Surrogate compounds should also be included. Matrix-specific minimum detection limits should be determined for all site specific compounds.

5. If standard curves remain linear over the entire analysis range, only one midpoint standard should be analyzed at a frequency of 1 per 10 samples. If standard curves are not linear over the entire analysis range, a minimum of 2 calibration standards should be analyzed at a frequency of 1 per 10 samples. If area counts or retention times differ by more than 10, recalibration is necessary.

6. Matrix Spike and Matrix Spike Duplicate samples may be required at a rate of one per 20 samples. The project team should determine if MS/MSD samples are required on a case-by-case basis.

7. Peak integration, area of rejection (threshold) and peak window parameters should be submitted to the

Department as part of the method QA/QC proposal.

8. All chromatograms (i.e. sample, method blank, spikes, and other raw data) should be submitted. All chromatographic peaks should be identified (i.e. integration chart) and labeled. A data summary table should report raw data.

9. Chain of custody or sample tracking documentation should be generated for all samples collected and analyzed. This should include a statement certifying that all data was generated following proper procedures.

VI. DATA INTERPRETATION & REPORTING

A. Unknown peaks in chromatograms may be attributable to contaminants not in the calibration standard. Retention time index identification is semi-qualitative, and has no quantitative value. If laboratory data (GC/MS) confirms this identification and provides sufficient data to determine a response factor (5-point calibration), this data should be included on summary reports. Retention time shift, as monitored by the surrogates, should be considered when identifying compounds. Examples of the calculations performed should be submitted as an Appendix to the Data Report.

B. A data summary table should display all data, surrogate recovery, percent moisture, etc.

C. Data maps should clearly depict data indicated on the figure. Laboratory confirmed data, should be clearly differentiated from field values.

VII. HEALTH & SAFETY CONSIDERATIONS

A. Potential Physical Hazards - The instrumentation utilized pose no unusual physical health or safety considerations; however, all manufacturer warnings and cautions should be observed.

B. Potential Chemical Hazards - There are no unusual chemical health or safety considerations specifically pertaining to the use of field GC; however, the toxicity or carcinogenicity of the compounds used in this method are not always defined precisely. Therefore, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The analytical team is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified

in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

VIII. SAMPLE PREPARATION FOR SVOs AND PESTICIDES/PCBs

A. An approved extraction procedure is required. An NJDEP certified laboratory or the Department should be consulted regarding proposed extraction procedures.

IX. DETECTORS

A. Photoionization Detector

1. Applications

a) Selectivity: Minimal - Detects Organic & Inorganic compounds with ionization potentials lower than the energy of the internal lamp.

b) Sensitivity: Very Good - Detection limits are typically 10-50 ppb.

c) Durability: Good

2. Theory

a) A PID is nonspecific and may detect all species with ionization potentials less than the energy of the internal lamp, including inorganic compounds.

3. Comments

a) The PID can not be used to identify unknown substances, without supporting laboratory information. Detector lamp energy selection can provide a degree of compound specificity by limiting the compounds to which the GC system may be sensitive. Attachment 1 provides ionization potential ranges for a variety of compound classes commonly found on industrial facilities.

b) The PID device does not respond to all compounds similarly (i.e. response factors differ substantially). Table I, Attachment 2, is intended to provide an example of this differing response.

c) A single GC/PID instrument may be available with several lamp energies. Although the use

of other lamps may provide some compound specificity, detector response often differs substantially between these detectors. An example of this is provided in Table II, Attachment 2.

4. Interferences

a) The PID does not respond to certain low molecular weight hydrocarbons, such as methane or ethane although these compounds may interfere with the detection of lighter (C1-C6) hydrocarbons.

b) Certain toxic gases and vapors (i.e. carbon tetrachloride and HCN) can not be detected by the PID, due to their high ionization potentials. In general, compounds with high energy bonds (indicated by differing electronegativities) may not be easily detected by the PID.

B. Flame Ionization Detector

1. Applications

a) Selectivity: Minimal - The FID detects any compounds which may burn.

b) Sensitivity: Good - Detection limits are typically in the 10-100 ppb range.

c) Durability: Fair - Gas tanks are required, making the detector cumbersome to use.

2. Theory

a) The FID detector is a non specific total organic vapor detector. The FID may not respond to inorganic compounds.

b) The FID utilizes the principle of hydrogen flame ionization for detection and measurement of organic vapors. Only compounds that burn may be detected.

3. Comments

a) The FID device does not respond to all compounds similarly (i.e. response factors may differ).

4. Interferences

a) Methane may be detected by a FID detector.

C. Electron Capture Detector

1. Applications

a) Selectivity: Moderate - the ECD detector may detect electrophilic volatile organic compounds (i.e chlorinated organics, carbonyls, sulfur, nitrogen). No other organic compounds may be detected.

b) Sensitivity: Good - detection limits in the 10 ppb range can be expected. The ECD is one of the most sensitive gas chromatography detectors currently available.

c) Durability: Moderate

2. Theory

a) The ECD detects compounds by observing a change in "standing current." The standing current is created by passing the effluent over a beta-emitter, thus ionizing it. This ionization causes the production of a burst of electrons, also called the standing current. The current decreases in response to the above mentioned compounds.

b) Linearity is limited to 2 orders of magnitude.

3. General Comments

a) This detector should not be used during initial site screening. The detector may not detect most chemicals.

4. Interferences

a) Moisture has been shown to obscure the resolution of target compound peaks. The reason for this interference has not been determined.

b) In general, this instrument may only detect halogenated, carbonyl, and nitro-compound vapors. Peaks may not be observed for non-electrophilic compounds. High sample concentrations of alkanes may interfere with the detection of early eluting chlorinated alkenes.

D. Argon Ionization Detector

1. Applications

a) Selectivity: Minimal - The AID may respond to the same compounds as the PID.

b) Sensitivity: Fair - The AID is not as sensitive as other detectors.

c) Durability: Excellent - The AID is the most durable detector in this group.

2. Theory

a) An AID detector may detect volatile organic compounds with ionization potentials less than the energy of the internal argon lamp (11.7 eV). Attachment 1 provides ionization potentials for many of the compound classes commonly found on industrial facilities.

3. Comments

a) The AID detector is useful for site screening since most compounds are detected.

4. Interferences

a) High sample (C1-C6) alkane concentration may interfere with the resolution of early eluting alkenes, aromatics, and chlorinated alkenes. Proper column selection is critical in these types of applications.

b) Certain toxic gases and vapors (i.e. carbon tetrachloride and HCN) can not be detected by the AID, due to their high ionization potentials. In general, compounds with high energy bonds (indicated by differing electronegativities) may not be easily detected by the AID.

c) Moisture has been shown to obscure the peak resolution of target compounds. A reason for this has not been determined.

X. REFERENCES

1. Driscoll, J.N., Whalen, M., Wood, C.D., Duffy, M. and Cihak, C.A. "Looking for Pesticides", Soils, January-February 1992.

2. NJDEPE "Field Sampling Procedures Manual", May 1992.

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6. USEPA "Sentex Scentograph G.C. Field Use", Standard Operating Procedures, Guidance Document #1702, December 1988.

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XI. APPENDIX

TABLE 1

Approximate Ionization Potentials For Classes

Class	Approximate IP (eV)	Notes
Paraffins	9.8 - 10.8	Cyclo-Paraffins
Alkyl Halides	10.5 - 11.5	Chlorinated Compounds
	9.0 - 10.5	Brominated and Iodinated Compounds
	11.7 - 12.9	Fluorinated Compounds, i.e. Freons
Aliphatics	10.0 - 11.0	Alcohols
	9.2 - 10.0	Ethers
	9.1 - 9.5	Thiols
	8.3 - 8.7	Sulfides
	9.5 - 10.9	Aldehydes

	8.9 - 9.6	Ketones
	10.0 - 11.1	Acids
	10.0 - 11.0	Esters
	7.2 - 9.0	Amines
	8.6 - 10.3	Amides
	10.7 - 11.1	Nitro-aliphatics
	10.4 - 12.2	Nitriles
	9.1 - 13.9	Cyano Compounds
Olefins	8.9 - 10.5	Acetylenes
Hetero-Cyclics	8.0 - 9.5	(i.e. Furans)
Aromatics	7.7 - 9.7	
Sulfides	8.2 - 9.7	(i.e. Hydrogen Sulfide, Methyl Mercaptan)
Ammonia	10.2	

TABLE II

Relative Sensitivity For Compound Classes

Class	PID Relative Sensitivity	Examples
Aromatics	100%	Benzene, Toluene, Styrene
Aliphatic Amines	100%	Diethylamine
Chlorinated, Unsaturated Aliphatics	50-90%	Vinyl Chloride, Dichloroethane, Trichloroethylene
Carbonyls	70-90%	MEK, MiBK, Acetone, Butanone, Cyclohexanone
Unsaturated	30-50%	Acrolein, Propylene,

Aliphatics		Allyl Alcohol
Sulfides	30-50%	Hydrogen Sulfide, Methyl Mercaptan
Paraffins (C_5-C_7)	10-30%	Pentane, Hexane, Heptane
Ammonia	1-5%	
Paraffins (C_1-C_4)	0%	Methane, Ethane

TABLE III
Relative Lamp Sensitivity

Ionization Potential (eV)	Lamp Energy 9.5 eV	10.2 eV	11.7 eV
8.0 - 9.5	7-10%	100%	7-12%
9.5 - 10.2	5-10%	100%	10-15%
10.2 - 11.7	0%	100%	10-50%
greater than 11.7	0%	0-20%	100%

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TITLE: SW 846 Series 4000 and Alternate Immunoassays for Screening Solid and Liquid Samples

I. SUMMARY

Immunoassays are unique in that each manufacturer produces a distinct antibody which is applied to an independent matrix. Although the technology is the same for each test kit, the differences in application of the technology allow for differences in performance. The draft and approved SW-846 methods have gone through a rigorous evaluation process and have been demonstrated to be capable of producing Data Quality Level 2 data. Likewise, other methods have gone through rigorous evaluation while other methods are fairly new and have not been fully demonstrated to produce consistent Level 2 data. Therefore, non-SW-846 methods will be evaluated on a case specific basis to determine the appropriate data quality level. Once a non-SW-846 test method has been approved for use, the method will automatically be approved for similar use on other cases.

Immunoassay analysis may be used to delineate several groups of organic compounds including PCB, TPH, PCP BTEX, pesticides, TNT and PAH in soils and groundwater. Extraction from solid samples is required and direct analysis of liquid samples may be possible. A colorimetric reaction occurs when antibodies that are not bound by a specific contaminant of concern are exposed to a developing solution. Detection limits range from ppb to ppm, depending on the compound and matrix. The Data Quality Levels on pages two through ten (2-10) should be read prior to using this method.

II. PURPOSE AND SCOPE

To define the minimum standards for the use of immunoassay technology for delineation, characterization and monitoring proposals consistent with the Data Quality Levels.

III. RESPONSIBILITY

The project team is responsible for the review and revision of all site delineation proposals.

IV. METHOD OVERVIEW

A. Application & Advantages

1. Uses of Method

a. Field Delineation of Soils.

b. Field Screening of Water.

c. This method is recommended for site screening, delineation, characterization and monitoring when organic compounds (i.e. PCB, TPH, PCP BTEX, pesticides, TNT and/or PAH) are the known compounds of concern.

2. Benefits of Method

a. Provides field personnel with real-time information which may be used in making field decisions regarding site delineation and remediation.

b. This method expedites the site investigation and contaminant delineation process while providing better site definition at a reduced cost.

c. Can be used by field technician with minimal training.

d. High numbers of samples can be analyzed per day.

B. Interferences and Limitations

1. Restrictions of Method

a. Each kit is analyte specific and may be subject to little interference from other compounds; however, contaminants not targeted by the antibody coated material may not be detected (i.e. PCB test kits may target certain aroclors or have varying detection limits for different aroclors). Each kit should contain a cross reactivity profile.

b. Temperature fluctuations may cause differences in chemical reactions which may give different results. Therefore, standards or references should be run along side of each group of samples analyzed. Samples should not be analyzed outside of the temperature limits or in direct sunlight.

c. Kits should not be exposed to extreme temperatures (i.e. less than 32^{o}F or greater than 100^{o}F - see manufacturer's recommendations) when being stored.

d. Confirmation of field analysis should be provided in accordance with the Technical Requirements for Site Remediation, N.J.A.C.

7:26E . Quantitation of the analyte should be performed by an approved laboratory method from across the range of results including all clean zone samples.

2. Disadvantages of Method

a. Up to twenty percent (20%) false positives and up to ten percent (10%) false negatives can be expected dependent, on test kit used, compound analyzed and matrix. Draft and approved SW-846 methods generally have a lower percent of false positives and false negatives, thereby providing greater confidence.

b. Sample matrix may cause false positives.

c. Solids present in aqueous samples may interfere with antibody/conjugate reactions, thereby giving a false negative result.

C. Capabilities

1. Compounds Detected: (Method dependent) Polychlorinated Biphenyls (PCB) (arochlor dependent), Total Petroleum Hydrocarbons (TPH) (based on fuel products - i.e. gasoline and No. 2, No. 4 and No. 6 fuel oils), Pentachlorophenol (PCP), Benzene, Toluene, Ethylbenzene and Xylene (BTEX) (benzene has a reduced sensitivity compared to the substituted aromatics), pesticides, trinitrotoluene (TNT) and Polynuclear Aromatic Hydrocarbons (PAH). Kits may be available for other compounds.

2. Matrix: Soils - Delineation, Screening and/or Monitoring
Water - Screening and/or Monitoring

3. Achievable Quantitation Limits: Dependent on compound, sample conditions, matrix and test kit used, ppb range to ppm range. See individual test kits for detection limits.

4. The information obtained is either semi-quantitative (i.e. greater than or less than a predetermined value) or quantitative over a specified range.

5. Effective use of this technology requires the project team to select clean zone samples for laboratory confirmation as well as a cross section of the range of results (for quantitative methods). The goal of the laboratory confirmation is to determine that the clean zone has been correctly delineated and values determined are representative of site conditions.

D. Instrumentation

1. Several companies offer immunoassay kits specific to compounds of concern and concentration ranges. Kits are available for PCB, TPH, PCP BTEX, pesticides, TNT, PAH and may be available for other specific compounds.

2. Kits consist of the necessary chemicals to extract the compound of concern (if required), antibody coated materials and color developing chemicals. A photometer/reflectometer or a color chart is required for quantitation.

E. Practical Considerations

1. Cost per Sample (Approximate): $20 - $60

2. Time Required per Sample: less than 30 minutes (multiple samples)

3. Quality of Data (Level): Level 2

4. Difficulty of Procedure: Simple

5. Laboratory Method Equivalent: None

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used during the remedial investigation (RI) for delineation purposes and during the site investigation (SI) for initial characterization sampling to determine that up to fifty percent (50%) of the samples are not contaminated in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b).

2. Delineation sampling frequency should be in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

3. Ten percent (10%) of the results produced by this method should be laboratory confirmed by appropriate laboratory methods in accordance with the Technical Requirementsfor Site Remediation, N.J.A.C. 7:26E.

4. The results produced by this method are either semi-quantitative as they are expressed as a range (i.e. greater than 50 ppm and less than 100 ppm) or quantitative over a specified range.

5. The field technician using the test kit should have proof of training by the manufacturer or their representative.

6. Sampling of the matrix should be consistent with the procedures established in the May 1992 Field Sampling Procedures Manual and appropriate sections of the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

B. Sampling Procedures

1. Collect an appropriate amount of solid or liquid sample according to directions in test kit.

2. Samples should be collected with appropriate equipment and placed into a proper handling vessel.

3. Prepare samples for extraction.

C. Field Operations

Each kit may contain specific instructions for sample preparation and analysis; however, the following provides general guidelines.

1. Prepare samples via weighing or measuring volume, filtering and diluting sample (contaminants may be extracted with laboratory grade methanol, isopropanol, acetone or other solvents as specified by the manufacturer).

2. Add samples and standards along with enzyme conjugate to antibody coated materials.

3. After one to ten (1 - 10) minutes (time may vary with kits), wash the materials and add color developing reagents.

4. Place developed materials into photometer or reflectometer or compare to color chart. Compare

results to standards.

D. Quality Assurance/Quality Control

LEVEL 1 QA/QC REQUIREMENTS

The following are required for Level 1 Data:

1. A brief method summary is required.

2. Standards should be run with each group of samples analyzed.

3. Collection and analysis of uncontaminated samples from each site matrix analyzed should be performed each day to document possible matrix interference.

4. An instrument log should be maintained and submitted (where appropriate). This log should include instrument maintenance, blank, and calibration information, including date, time, analyst's name, calibration compounds (CC), CC concentrations, and CC readings in area units.

5. The raw data (i.e. photometer/reflectometer reading), calibration of photometer/reflectometer (if required), calculations for quantitative results and final results of field analysis for all samples screened (including QC and standard samples) are required.

6. Field logs should document sample ID#, date, time, location, depth, soil type (using a standard soil classification system as described in the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 3.6(a)2ii) or matrix, soil moisture (qualitative estimate if appropriate), and analysis time and result.

7. Sample duplicates should be performed in the field at the rate of at least one (1) for every twenty (20) samples, to document method repeatability.

8. A non-conformance summary should state all data inconsistencies and all divergences from the approved sampling/analysis program. The implication of all non-conformances should be clearly explained and quantified (if possible).

LEVEL 2 QA/QC REQUIREMENTS

In addition to the requirements listed for the Level 1 QA/QC Data, the following are required for Level 2 Data:

1. Field analysis of a performance evaluation (PE) sample or reference sample is required daily.

2. One (1) method blank and rinsate blank (if appropriate) should be field analyzed daily.

3. One (1) matrix spike analysis should be performed daily.

4. Chain of custody or sample tracking documentation should be generated for all samples collected and analyzed. This should include a statement certifying that all data was generated following proper procedures.

5. Additional QA/QC procedures as recommended by the manufacturer.

VI. DATA INTERPRETATION AND REPORTING

A. A hard copy of all photometer/reflectometer readings should be included as a QA/QC Section Deliverable. Handwritten copies of the readouts are acceptable if the instrument is not capable of down loading.

B. A field data log should include: date, time, matrix description (i.e. soil type or groundwater description), temperature, location, depth, field technician's name, field analyst's signature (certifying results), and photometer/reflectometer reading. Calibration procedures performed before and after data collection should be provided (if required).

C. Data summary sheets should be included as a separate section of the site assessment report. These sheets should include: sample location, sample depth, instrument reading, laboratory confirmation results (where applicable) and analysis results (based on calculations and standards).

D. All results should be plotted on a scaled area (or site) map. Contour lines should be drawn for each contaminant.

E. Required QA/QC Deliverables

1. Chain of custody or sample tracking documentation for every sample collected and analyzed in the field. Documentation should be provided at the end of the final data report.

2. Sample data packages should contain the following

information: Sample results summary, standard results and detection limits.

3. Non-conformance summary report in narrative and/or tabular form. All data falling outside of the QC criteria specified and approved in the QA plan as a deliverable should be highlighted. The analyst's signature should certify compliance with approved procedures and recording of actual results.

VII. HEALTH AND SAFETY CONSIDERATIONS

A. The toxicity or carcinogenicity of the compounds used in this method are not always defined precisely. Therefore, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The analytical team is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Disposal of materials should be in accordance with local, state and federal requirements.

VIII. REFERENCES

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TITLE: Infrared Method for Analysis of Total Recoverable Petroleum Hydrocarbons (TRPH) (12/93)

I. SUMMARY

The infrared method may be used to delineate light petroleum fuel hydrocarbons in both soils and groundwater. Extraction from both aqueous and solid samples is required. Absorbance at the 3200 to 2700 cm^{-1} is indicative of hydrocarbon presence with the C-H bond absorbance occurring in the range of 2930 cm^{-1} to 2950 cm^{-1}. Detection limits are in the range of 1 - 5 ppm dependent on the conditions and matrix. The Data Quality Levels on pages two through ten (2-10) should be read prior to using this method.

II. PURPOSE AND SCOPE

To define the minimum standards for an infrared absorption delineation proposal consistent with the Data Quality Levels.

III. RESPONSIBILITY

The project team is responsible for the review and revision of all site delineation proposals.

IV. METHOD OVERVIEW

A. Application & Advantages

1. Uses of Method

a. Field Delineation of Soils.

b. Field Screening of Water.

c. This method is recommended for site screening and delineation when extractable petroleum hydrocarbons are the compounds of concern. Most accurate results are obtained when the compound has twelve or more (>12) carbons.

2. Benefits of Method

a. Provides field personnel with real-time information which may be used in making field decisions regarding site delineation.

b. This method expedites the delineation process while providing better site definition at a reduced cost.

c. The method can be used in a mobile laboratory.

B. Interferences and Limitations

1. Restrictions of Method

a. The method is not appropriate for quantifying non-alkylated aromatics such as benzene and naphthalene.

b. The Freon-113 solvent does not dissolve heavy oils and asphalts completely. Therefore, the extraction and analysis of these compounds will be biased low.

c. Confirmation of field analysis should be provided in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E. Quantitation of the analyte should be performed by an approved laboratory method (i.e. 418.1, 413.2) from across the range of results including clean zone samples.

2. Disadvantages of Method

a. The sensitivity for alkylated aromatics such as toluene and xylenes is very low.

b. False negative results may be caused by poor sensitivity for aromatic compounds. Fuels can contain fifteen to twenty percent (15% - 20%) aromatic compounds. Light fuels (i.e. gasoline) may not be detected.

c. False positive results may be caused by certain soil types including weathered limestone, clays and silts.

d. The method does not give specific compound information.

e. Emulsions which are hard to break down may form during extraction.

f. The method detects compounds that are not petroleum compounds. These compounds are measured as part of the TRPH.

g. If the shaking method of agitation is used and the container is vented, volatile organics may escape and the results may be biased low.

C. <u>Capabilities</u>

1. Compounds Detected: Extractable Petroleum

Hydrocarbons

2. Matrix: Soils - Delineation or Screening
Water - Screening

3. Achievable Quantitation Limits: Dependent on sample conditions and matrix, 1 - 5 ppm.

4. The information obtained is quantitative, but not compound specific and therefore, should be laboratory confirmed in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

5. Effective use of this technology requires the project team to select clean zone samples for laboratory confirmation as well as a cross section of the range of results. The goal of the laboratory confirmation is to determine that the clean zone has been correctly delineated and values determined in the field are representative of site conditions.

D. Instrumentation

1. Glassware, filter paper, centrifuge, pipette, paint or lateral shaker, infrared spectrometer (scanning or fixed wavelength)

2. Distilled water, hydrochloric acid, Freon-113 or substitute, sodium sulfate, activated silica gel, fused silica cells, hydrocarbon standards

E. Practical Considerations

1. Cost per Sample (Approximate): $20 - $60

2. Time Required per Sample: less than 30 minutes

3. Quality of Data (Level): Level 2

4. Difficulty of Procedure: Moderate

5. Laboratory Method Equivalent: 418.1, 413.2, OQA-QAM-005-12/89

V. METHOD PROCESS

A. Sampling Considerations

1. This method may be used for delineation purposes during the remedial investigation (RI) and for initial characterization sampling during the site

investigation (SI) to determine that up to fifty percent (50%) of the samples are not contaminated in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 2.1(b).

2. Delineation sampling frequency should be in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

3. Ten percent (10%) of the results produced by this method should be laboratory confirmed by appropriate laboratory methods in accordance with the Technical Requirements for Site Remediation, N.J.A.C. 7:26E.

4. The results produced by this method are quantitative; however, not compound specific.

B. Sampling Procedures

1. Collect an appropriate amount of solid or liquid sample (i.e. 20 g of soil) required per analysis.

2. Samples should be collected with appropriate equipment and placed into a proper handling vessel (i.e. soil should be placed into a 16 oz french square bottle with minimum exposure).

3. Samples which are not to be analyzed within four (4) hours should be preserved utilizing HCl for aqueous samples and cooling to four degrees centigrade ($4^{o}C$) for both aqueous and solid samples.

4. Set samples aside for extraction and preparation.

C. Field Operations

Specific procedures may be modified dependent on the instrumentation utilized and compound array suspected. The following general guidelines should be observed.

1. Place approximately 20 g of soil in a 16 oz french square bottle with minimum exposure, along with 50 ml of distilled water and adjust pH to 3 with HCl. Cap the bottle tightly using a Teflon lined cap and shake mildly for 1 to 2 minutes to disperse the soil.

2. After shaking, pipette 25 ml of Freon-113 into the bottle and shake well for 15 minutes using a paint or lateral shaker. At the end of the shaking period, let stand to permit contents of bottle to

separate into distinct layers. NOTE: Venting the bottles at the beginning of this procedure may avoid pressure buildup; however, a loss of volatile organic compounds may result.

3. If Freon forms an emulsion that fails to dissipate, it can be broken by centrifugation or by adding 1 g of sodium sulfate into a filter paper cone and slowly draining the emulsion through the salt.

4. Using a pipette, remove about 10 ml of Freon from the appropriate layer and filter it through a column of 5 grams of activated silica gel directly into a 1 cm pathlength fused silica cell. Fill a matched reference cell with clean Freon-113.

5. Place the cells in the appropriate beams of the instrument and scan from 3200 to 2700 cm^{-1} using medium scan speed (Note: a fixed wavelength IR may be used at 2930 cm^{-1} or 2950 cm^{-1}). Drawing a horizontal from the baseline, measure the net absorbance at 2930 cm^{-1} (3.42 μm) or 2950 cm^{-1} (3.39 μm). If the absorbance exceeds 0.80, dilute as needed and re-analyze.

6. Prepare the standards of a known hydrocarbon in Freon in the concentration range of approximately 50 to 5000 mg/l. It is important to choose a standard that most closely resembles the scan of the unknown in the 2700 to 3200 cm^{-1} region, specifically the absorbance at about 2880, 2930 and 3040 cm^{-1}. Appropriate standards may include: 1) EPA standards of reference chlorobenzene, isooctane and hexadecane, 2) reference gasoline that is known to be involved in the spill and which has been weathered (evaporated) to be between 25 and 50% by volume, 3) distillate fuel oil, fresh or weathered and 4) heavier products such as oils and residual fuels.

7. Analyze the standards in a similar fashion as the samples. Prepare a calibration curve by plotting the net absorbance values versus the concentration in mg oil/ml Freon on linear graph paper and drawing a straight line of best fit.

8. Calculate the concentration of hydrocarbons in the solid samples as follows:

$$\text{mg of hydrocarbons/kg of soil} = \frac{C \times V \times D \times 1000}{W}$$

where:

C = concentration of hydrocarbons obtained from the calibration curve (mg oil/ml Freon),
V = volume of Freon 113 used for extraction (ml)
D = dilution factor, if any, and
W = weight of soil sample (g).

* Results are on a wet weight basis.

Calculate the concentration of hydrocarbons in the aqueous samples as follows:

$$\mu g \text{ of hydrocarbons/l of water} = \frac{C \times V \times D}{V_2}$$

where:

C = concentration of hydrocarbons obtained from the calibration curve (mg oil/ml Freon),
V = volume of Freon 113 used for extraction (ml)
D = dilution factor, if any, and
V_2 = volume of aqueous sample (l).

D. Quality Assurance/Quality Control

LEVEL 1 QA/QC REQUIREMENTS

The following are required for Level 1 Data:

1. A brief method summary.

2. A single point calibration should be conducted prior to any field activities using site-specific standards.

3. Calibration checks should be performed at a minimum of twice daily. If a calibration check falls outside the manufacturer's suggested range, a complete multi-point calibration is required.

4. A baseline scan (i.e. "clean air", "clean water" or "clean soil" as appropriate) should be run each day prior to analyzing any site samples.

5. An instrument log should be maintained and submitted (where appropriate). This log should include instrument maintenance, blank, and calibration information, including date, time, analyst's name, calibration compounds (CC), CC concentrations, and CC readings in area units.

6. Field logs should document sample ID#, date, time, location, depth, soil type (using a standard soil

classification system as described in the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, section 3.6(a)2ii), soil moisture (qualitative estimate), and analysis result.

7. The raw data (i.e. absorbance reading), calibration of spectrophotometer (if required), calculations for quantitative results and final results of field analysis for all samples screened (including QC and standard samples) is required.

8. Sample duplicates should be performed in the field at the rate of at least one (1) for every twenty (20) samples, to document method repeatability.

9. A non-conformance summary should state all data inconsistencies and all divergences from the approved sampling/analysis program. The implication of all non-conformances should be clearly explained and quantified (if possible).

LEVEL 2 QA/QC REQUIREMENTS

In addition to the requirements listed for the Level 1 QA/QC Data, the following are required for Level 2 Data:

1. Each project team that uses a Level 2 Method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of capability and an ongoing analysis of calibration standards. To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations.

   a) A soil quality control (QC) check sample. The QC check sample should be prepared by the laboratory using stock standards prepared independently from those used for calibration.

   b) An aqueous QC sample prepared in the same fashion as the soil QC sample is also required.

   c) Analyze four aliquots of each of the well-mixed QC check sample according to standard procedures.

   d) Calculate the average recovery mean (X) and the standard deviation of the recovery (s) for each parameter of interest in each matrix using the four results.

e) For each compound, X should be between 60% and 140% of the true value. Additionally, s should be ± 40% of X.

2. Field analysis of a performance evaluation (PE) sample is required prior to startup of field analysis.

3. One (1) method blank and rinsate blank should be field analyzed daily.

4. Instrument should be 3-point (minimum) calibrated each month and 1-point calibrated each day using laboratory certified standards. Choice of the standard species and concentrations should be based on known site contamination and encompass the range of expected concentrations. Surrogate compounds should also be included. Matrix-specific minimum detection limits should be determined for all site specific compounds.

5. If standard curves remain linear over the entire analysis range, only one midpoint standard should be analyzed at a frequency of 1 per 10 samples. If standard curves are not linear over the entire analysis range, a minimum of 2 calibration standards should be analyzed at a frequency of 1 per 10 samples.

6. One (1) matrix spike analysis should be performed daily.

7. Chain of custody or sample tracking documentation should be generated for all samples collected and analyzed. This should include a statement certifying that all data was generated following proper procedures.

VI. DATA INTERPRETATION AND REPORTING

A. A hard copy of all spectra should be included as a QA/QC Section Deliverable.

B. A field data log should include: date, time, matrix description (i.e. soil type or groundwater description), temperature, location, depth, field technician's name, field analyst's signature (certifying results), and calibration procedures performed before and after data collection.

C. Data summary sheets should be included as a separate section of the site assessment report. These sheets should include: sample location, sample depth, field

results and laboratory confirmation results (where applicable).

D. All results should be plotted on a scaled area (or site) map. Contour lines should be drawn for each contaminant.

E. Required QA/QC Deliverables

1. Chain of custody or sample tracking documentation for every sample collected and analyzed in the field. Documentation should be provided at the end of the final data report.

2. Sample data packages should contain the following information: Sample results summary, sample spectra, standard results and detection limits, and QA/QC sample results.

3. Non-conformance summary report in narrative and/or tabular form. All data falling outside of the QC criteria specified and approved in the QA plan as a deliverable should be highlighted. The analyst's signature should certify compliance with approved procedures and recording of actual results.

VII. HEALTH AND SAFETY CONSIDERATIONS

A. The toxicity or carcinogenicity of the compounds used in this method are not always defined precisely; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The analytical team is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

VIII. REFERENCES

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GLOSSARY

Accuracy - the ability of a technique to detect the true concentration of the analyte.

AID - argon ionization detector.

Aliquot - a portion of a sample.

Alkylated Aromatics - the class of ringed aromatic compounds containing one or more aliphatic side chains.

ATH - ambient temperature headspace.

Calibration - the process by which data can be made to correlate with known standards.

Certified Laboratory - a laboratory that is currently certified pursuant to N.J.A.C. 7:18, the Regulations Governing Laboratory Certification and Standards of Performance, to perform laboratory analysis for a specific certification category and a specific parameter within the certification categories.

Clean Zone - a series of contiguous samples collected at a frequency consistent with the requirements of the Technical Requirements for Site Remediation, N.J.A.C. 7:26E, which are analyzed and determined to be below the cleanup criteria (a single sample may constitute a clean zone for small contaminated areas).

Colorimetric test - a test in which color is used to obtain qualitative or quantitative information.

Contaminant - as defined in N.J.A.C. 7:26E, currently: any hazardous substance, hazardous constituent, hazardous waste or pollutant discharged by any individual or entity.

Contaminant Delineation - the systematic collection and analysis of samples from a point of known contamination to determine the vertical and horizontal extent of contamination.

Contaminant Screening - the analysis of environmental media by non-selective instrumentation or methods to gain a preliminary estimate of contaminant extent.

Corrected Results - the results obtained when instrumental results are adjusted to account for laboratory confirmation values and/or other quality control criteria.

ECD - electron capture detector.

FID - flame ionization detector.

Field Portable - an instrument which is durable and relatively

simple to move between facilities for on-site analysis.

Fluorescence - the emission of radiation (i.e. visible light) by a substance during exposure to external radiation (i.e. light or X-rays).

Full Laboratory Data Deliverables - the data deliverables as required in N.J.A.C. 7:26E, section 1.8 and Appendix A.

GC - gas chromatograph(y)

Headspace - in a sealed vessel, the vapor/air mixture trapped above a solid or liquid sample.

Heavy Metals - the class of metallic elements with relatively high atomic weights (i.e. Pb, Hg, As, Cd, Cr, Zn).

Hydrophobic - having little or no affinity for water.

Immunoassay - a test for a contaminant or class of contaminants based on the antibody/antigen reaction.

Instrument Log - a manual which documents all instrument outputs, calibration, and maintenance.

Ionization Potential - the energy which is required to ionize a particular molecule.

Isoconcentration - more than one sample point exhibiting the same analyte concentration.

Isopleth - the line or area represented by an isoconcentration.

Lamp Window - the lens through which a light source is passed.

LC - liquid chromatograph(y).

Limited Laboratory Data Deliverables - data deliverables with less QA/QC documentation than those required under Appendix A of N.J.A.C. 7:26E.

MDL (method detection limit) - the minimum concentration of a substance that can be measured and reported with a 99 percent confidence that the analyte concentration is greater than zero and is determined from the analysis of a sample in a given matrix containing the analyte.

PID - photoionization detector.

PQL (practical quantitation level) - the lowest quantitation level of a given analyte that can be reliably achieved among laboratories within the specified limits of precision and accuracy

of a given analytical method during routine operating conditions.

Precision - the ability of a method to provide reproducible results from sample to sample.

Quality Assurance - documentation designed to assure that proper sampling and/or analysis protocol are being followed.

Quality Control - the implementation of protocols designed to assure that the final sampling or analytical results are reliable.

Reduced Laboratory Data Deliverables - the data deliverables as required in N.J.A.C. 7:26E, section 1.8 and Appendix A.

Response Factor (Relative Response Factor) - a measure of the relative response of the instrument detector to an analyte compared to an internal or external standard. Relative Response Factors are determined by the analysis of standards and are used to calculate the concentrations of analytes in samples.

Retention Time - in chromatography, the time between when a sample is injected and the time the chromatographic peak is recorded.

Semi-Qualitative - identification of a compound by class rather than identification of the specific compound (i.e. semi-qualitative would identify aromatic hydrocarbons whereas qualitative would identify benzene).

Semi-Quantitative - numeric values which only approximate the true concentration of the analytes.

Site Screening - rapidly surveying a site, possibly employing some chemical analysis instrumentation or methods, in an effort to estimate worst case environmental conditions.

Site-similar material - material containing the same chemical and physical characteristics of native material found on-site and should include actual site material used for the prescribed purpose.

Survey Instrument - an instrument which detects compounds with little or no selectivity.

Total Recoverable - the amount of a contaminant which is extracted from the sample.

Traditional Site Evaluation - the initial characterization, delineation and clean zone confirmation of a site by collection and analysis of samples by certified methods with appropriate data deliverables.