

US EPA ARCHIVE DOCUMENT



Environmental Technology Verification Report

Field Portable Gas Chromatograph/Mass Spectrometer

Bruker-Franzen Analytical Systems,
Inc. EM640™

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Environmental Technology
Verification Program



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Field Portable Gas Chromatograph/ Mass
Spectrometer

Bruker-Franzen Analytical Systems, Inc.
EM640™

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Sponsored by

U.S. ENVIRONMENTAL PROTECTION AGENCY
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Notice

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency (EPA) under an Interagency Agreement number DW89936700-01-0 with the U.S. Department of Energy's Sandia National Laboratories. This verification effort was supported by the Consortium for Site Characterization Technology, a pilot operating under the EPA's Environmental Technology Verification (ETV) Program. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of corporation names, trade names, or commercial products does not constitute endorsement or recommendation for use of specific products.

In 1995, the U. S. Environmental Protection Agency established the Environmental Technology Verification Program. The purpose of the Program is to promote the acceptance and use of innovative environmental technologies. The verification of the performance of the Bruker-Franzen Analytical Systems, Inc. EM640™ field transportable gas chromatograph/mass spectrometer (GC/MS) system represents one of the first attempts at employing a testing process for the purpose of performance verification. One goal of this process is to generate accurate and credible data that can be used to verify the characteristics of the technologies participating in the program. This report presents the results of our first application of the testing process. We learned a great deal about the testing process and have applied what we learned to improve upon it. We expect that each demonstration will serve to improve the next and that this project merely represents the first step in a complex process to make future demonstrations more efficient, less costly, and more useful.



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Research and Development
Washington, D.C. 20460



**ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT**

TECHNOLOGY TYPE:	FIELD PORTABLE GAS CHROMATOGRAPH/MASS SPECTROMETER
APPLICATION:	MEASUREMENT OF VOLATILE ORGANICS IN SOIL, WATER, AND SOIL GAS
TECHNOLOGY NAME:	EM640™
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The U.S. Environmental Protection Agency (EPA) has created a program to facilitate the deployment of innovative environmental technologies through performance verification and information dissemination. The goal of the Environmental Technology Verification (ETV) Program is to further environmental protection by substantially accelerating the acceptance and use of improved and more cost effective technologies. The ETV is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies. This verification statement provides a summary of the demonstration and results for the Bruker-Franzen Analytical Systems, Inc. EM640™ field portable gas chromatograph/mass spectrometer (GC/MS) system.

PROGRAM OPERATION

The EPA, in partnership with recognized testing organizations, objectively and systematically evaluates the performance of innovative technologies. Together, with the full participation of the technology developer, they develop plans, conduct tests, collect and analyze data, and report findings. The evaluations are conducted according to a rigorous demonstration plan and established protocols for quality assurance. The EPA's National Exposure Research Laboratory, which conducts demonstrations of site characterization and monitoring technologies, selected Sandia National Laboratories, Albuquerque, New Mexico, as the testing organization for field portable GC/MS systems.

DEMONSTRATION DESCRIPTION

In July and September 1995, the performance of two field transportable GC/MS systems was determined under field conditions. Each system was independently evaluated by comparing field analysis results to those obtained using approved reference methods. Performance evaluation (PE), spiked, and environmental samples were used to independently assess the accuracy, precision, and comparability of each instrument.

The demonstration was designed to detect and measure a series of primary target analytes in water, soil, and soil gas. The primary target analytes at the U.S. Department of Energy's Savannah River Site in Aiken, South Carolina, were trichloroethene and tetrachloroethene. The primary analytes at Wurtsmith Air Force Base in Oscoda, Michigan, were

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benzene, toluene, and xylenes. Secondary analytes at the Michigan site included a variety of chlorinated organic solvents. The sites were chosen because they exhibit a wide range of concentrations for most of the analytes and provided different climatic and geological conditions. The conditions at each of these sites represent typical, but not all inclusive, conditions under which the technology would be expected to operate. Details of the demonstration, including a data summary and discussion of results may be found in the report entitled "Environmental Technology Verification Report, Field Portable Gas Chromatograph/Mass Spectrometer, Bruker-Franzen Analytical Systems, Inc. EM640™." The EPA document number for this report is EPA/600/R-97/149.

TECHNOLOGY DESCRIPTION

GC/MS is a proven laboratory analytical technology that has been used in environmental laboratories for many years. The combination of gas chromatography and mass spectrometry enables the rapid separation and identification of individual compounds in complex mixtures. The gas chromatograph separates the sample extract into individual components. The mass spectrometer then ionizes each component which provides the energy to fragment the molecules into characteristic ions. These ion fragments are then separated by mass and detected as charged particles, which constitutes a mass spectrum. This spectrum can be used in the identification and quantitation of each component in the sample extract. For nontarget or unknown analytes the mass spectrum is compared to a computerized library of compounds to provide identification of the unknown. Field transportable GC/MS is a versatile technique that can be used to provide rapid screening data or laboratory quality confirmatory analyses. In most systems, the instrument configuration can also be quickly changed to accommodate different inlets for media such as soil, soil gas, and water. As with all field analytical studies, it may be necessary to send a portion of the samples to an independent laboratory for confirmatory analyses.

The EM640™ is a commercially available GC/MS system that provides laboratory-grade performance in a field transportable package. The instrument is ruggedized and may be operated during transport. It weighs about 140 lbs and can be transported and operated in a small van. The EM640™ used in the demonstration used a Spray-and-Trap Water Sampler, direct injection for soil gas, and heated headspace analysis for soil samples. The minimum detection limit is 1 ppb for soil gas, 1 µg/L for water, and 50 µg/kg for soil. The instrument requires a skilled operator; recommended training is one week for a chemist with GC/MS experience. At the time of testing, the baseline cost of the EM640™ was \$170,000 plus the cost of the inlet system.

VERIFICATION OF PERFORMANCE

The observed performance characteristics of the EM640™ include the following:

- **Throughput:** The throughput was approximately 5 samples per hour for all media when the instrument was operated in the rapid analysis mode. Throughput would decrease if the instrument were operated in the analytical mode.
- **Completeness:** The EM640™ detected greater than 99 percent of the target compounds reported by the reference laboratory.
- **Precision:** Precision was calculated from the analysis of a series of duplicate samples from each media. The results are reported in terms of relative percent difference (RPD). The values compiled from both sites generally fell within the range of 0 to 40 percent RPD for soil and 0 to 50 percent for the water and soil gas samples.

- **Accuracy:** Accuracy was determined by comparing the Bruker GC/MS analysis results with performance evaluation and spiked samples of known contaminant concentrations. Absolute percent accuracy values from both sites were calculated for five target analytes. For soil, most of the values are scattered in the 0-90 percent range with a median of 39 percent. For water, most of the values fall in the 0-70 percent range with a median of 36 percent. The soil gas accuracy data generally fall in the 0-70 percent range with a median of 22 percent.
- **Comparability:** This demonstration showed that the EM640™ produced water and soil gas data that were comparable to the reference laboratory data (median absolute percent difference less than 50 percent). The soil data were not comparable. This was due, in part, to difficulties experienced by the reference laboratory and other problems associated with sample handling and transport.
- **Deployment:** The system was ready to analyze samples within 60 minutes of arrival at the site. The instrument was operated in a van. Warmup and calibration checks were completed in transit to the site.

The results of the demonstration show that the Bruker-Franzen EM640™ can provide useful, cost-effective data for environmental problem-solving and decision-making. The deviation of EM640™ and reference laboratory results for the soil samples, while statistically significant, is not so great as to preclude the effective use of the EM640™ GC/MS system in many field screening applications. We were unable to determine whether the Bruker GC/MS soil data or that of the reference laboratory or both were problematic. Undoubtedly, this instrument will be employed in a variety of applications, ranging from serving as a complement to data generated in a fixed analytical laboratory to generating data that will stand alone in the decision-making process. As with any technology selection, the user must determine what is appropriate for the application and the project data quality objectives.

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NOTICE: EPA verifications are based on an evaluation of technology performance under specific, predetermined criteria and the appropriate quality assurance procedures. EPA makes no expressed or implied warranties as to the performance of the technology and does not certify that a technology will always, under circumstances other than those tested, operate at the levels verified. The end user is solely responsible for complying with any and all applicable Federal, State and Local requirements.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's natural resources. The National Exposure Research Laboratory (NERL) is EPA's center for the investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. NERL's research goals are to (1) develop and evaluate technologies for the characterization and monitoring of air, soil, and water; (2) support regulatory and policy decisions; and (3) provide the science support needed to ensure effective implementation of environmental regulations and strategies.

EPA created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies.

EPA's Superfund Innovative Technology Evaluation (SITE) Program evaluates technologies for the characterization and remediation of Superfund and Resource Conservation and Recovery Act corrective action sites. The SITE Program was created to provide reliable cost and performance data to speed the acceptance of innovative remediation, characterization, and monitoring technologies. One component of SITE, the Monitoring and Measurement Technologies Program, evaluates new and innovative measurement and monitoring technologies. Effective measurement and monitoring technologies are needed to (1) assess the degree of contamination at a site, (2) provide data to determine the risk to public health or the environment, (3) be cost effective, and (4) monitor the success or failure of a remediation process. This program is administered by NERL's Environmental Sciences Division in Las Vegas, Nevada.

Candidate technologies for these programs originate from the private sector and must be market ready. Through the ETV and SITE Programs, developers are given the opportunity to conduct rigorous demonstrations of their technologies under realistic field conditions. By completing the evaluation and distributing the results, EPA establishes a baseline for acceptance and use of these technologies.

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Demonstration preparation and performance also required the assistance of numerous personnel from the Savannah River Technology Center and University of Michigan/Wurtsmith Air Force Base. The contributions of Joe Rossabi and co-workers at the Savannah River Technology Center and Mike Barcelona and co-workers at the University of Michigan are gratefully acknowledged. The Wurtsmith site is a national test site funded by the Strategic Environmental Research and Development Program. Cooperation and assistance from this agency is also acknowledged.

Performance evaluation (PE) samples provided a common reference for the field technologies. Individuals and reference laboratories who analyzed water and soil samples included Alan Hewitt, of the U.S. Army Cold Regions Research and Engineering Laboratory, for soil PE samples; and Michael Wilson, of the U.S. EPA Office of Emergency and Remedial Response, Analytical Operations and Data Quality Center, for the water PE samples.

We also acknowledge the participation of Bruker-Franzen Analytic GMBH, in particular, Ms. Nölke and Mr. Zey who operated the Bruker instrument during the demonstrations.

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Abbreviations and Acronyms

AC	Alternating current
amu	Atomic mass unit
amp	Ampere
APA	Absolute percent accuracy
APD	Absolute percent difference
BTEX	Benzene, toluene, ethylbenzene, xylenes
CSCT	Consortium for Site Characterization Technology
DNAPL	Dense nonaqueous phase liquid
DCE	Dichloroethylene
DIF	Percent difference
DoD	Department of Defense
DOE	Department of Energy
DOT	Department of Transportation
EPA	Environmental Protection Agency
ESD-LV	Environmental Sciences Division of the National Exposure Research Laboratory
ETV	Environmental Technology Verification Program
ETVR	Environmental Technology Verification Report
g	Gram
GC/MS	Gas chromatograph/mass spectrometer
GEL	General Engineering Laboratories
Hz	Hertz
kg	Kilogram
kW	Kilowatt
L	Liter
μ g	Microgram
mg	Milligram
mL	Milliliter
MS	Mass spectrometer
NCIBRD	National Center for Integrated Bioremediation Research and Development
NA	Not analyzed
ND	Not detected or no determination
NERL	National Exposure Research Laboratory
NETTS	National Environmental Technology Test Sites Program
ng	nanogram
NP	Not present
PAH	Polycyclic aromatic hydrocarbons
PCE	Tetrachloroethene
PE	Performance evaluation
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
PQL	Practical quantitation limit
QA	Quality assurance
QC	Quality control
REC	Percent recovery
RPD	Relative percent difference
RSD	Relative standard deviation

SERDP	Strategic Environmental Research and Development Program
SIM	Single ion monitoring
SNL	Sandia National Laboratories
SRS	Savannah River Site
SUMMA®	(Registered trademark for Passivated Canister Sampling Apparatus)
TCA	Trichloroethane
TCE	Trichloroethene
v	Volts
VOA	Volatile organic analysis
VOC	Volatile organic compound
WAFB	Wurtsmith Air Force Base
W	Watt

Section 1

Executive Summary

The performance evaluation of innovative and alternative environmental technologies is an integral part of the U.S. Environmental Protection Agency's (EPA) mission. Early efforts focused on evaluating technologies that supported the implementation of the Clean Air and Clean Water Acts. In 1987 the Agency began to demonstrate and evaluate the cost and performance of remediation and monitoring technologies under the Superfund Innovative Technology Evaluation (SITE) program (in response to the mandate in the Superfund Amendments and Reauthorization Act of 1987). In 1990, the U.S. Technology Policy was announced. This policy placed a renewed emphasis on "...making the best use of technology in achieving the national goals of improved quality of life for all Americans, continued economic growth, and national security." In the spirit of the technology policy, the Agency began to direct a portion of its resources toward the promotion, recognition, acceptance, and use of U.S.-developed innovative environmental technologies both domestically and abroad.

The Environmental Technology Verification (ETV) Program was created by the Agency to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, purchase, and use of environmental technologies. The ETV Program capitalizes upon and applies the lessons that were learned in the implementation of the SITE Program to the verification of twelve categories of environmental technology: Drinking Water Systems, Pollution Prevention/Waste Treatment, Pollution Prevention/ Innovative Coatings and Coatings Equipment, Indoor Air Products, Advanced Monitoring Systems, EvTEC (an independent, private-sector approach), Wet Weather Flows Technologies, Pollution Prevention/Metal Finishing, Source Water Protection Technologies, Site Characterization and Monitoring Technology (a.k.a. Consortium for Site Characterization Technology (CSCT)), and Climate Change Technologies. The performance verification contained in this report is based on the data collected during a demonstration of a field portable gas chromatograph/mass spectrometer (GC/MS) system. The demonstration was administered by the Consortium for Site Characterization Technology.

For each pilot, EPA utilizes the expertise of partner "verification organizations" to design efficient procedures for conducting performance tests of environmental technologies. EPA selects its partners from both the public and private sectors including Federal laboratories, states, and private sector entities. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from all major stakeholder/customer groups associated with the technology area. The U.S. Department of Energy's Sandia National Laboratories, Albuquerque, New Mexico, served as the verification organization for this demonstration.

In 1995, the Consortium conducted a demonstration of two field portable gas chromatograph/mass spectrometer systems. These technologies can be used for rapid field analysis of organic-contaminated soil, ground water, and soil gas. They are designed to speed and simplify the process of site characterization and to provide timely, on-site information that contributes to better decision making by site managers. The two system developers participating in this demonstration were Bruker-Franzen Analytical Systems, Inc.¹ and Viking Instruments Corporation. The purpose of this Environmental Technology Verification Report (ETVR) is to document demonstration activities, present demonstration data, and verify the performance of

¹ The company is now known as Bruker Instruments, Inc.

the Bruker-Franzen EM640™ field transportable GC/MS. Demonstration results from the other system are presented in a separate report.

Technology Description

The Bruker-Franzen EM640™ GC/MS consists of a temperature-programmable gas chromatograph coupled to a mass spectrometer. This field transportable system uses a small gas chromatographic column and accompanying mass spectrometer to provide separation, identification, and quantification of volatile and semi-volatile organic compounds in soils, liquids, and gases. In the demonstration, the system used a spray-and-trap technique for water analysis, as well as direct injection and head space analysis for soil gas and soil analyses, respectively. The column enables separation of individual analytes in complex mixtures. As these individual analytes exit the column, the mass spectrometer detects the analytes, providing a characteristic mass spectrum that identifies each compound. An external computer system provides quantitation by comparison of detector response with a calibration table constructed from standards of known concentration. The system provides very low detection limits for a wide range of volatile and semi-volatile organic contaminants.

Demonstration Objectives and Approach

The GC/MS systems were taken to two geologically and climatologically different sites: the U. S. Department of Energy's Savannah River Site (SRS), near Aiken, South Carolina, and Wurtsmith Air Force Base (WAFB), in Oscoda, Michigan. The demonstration at the Savannah River Site was conducted in July 1995 and the Wurtsmith AFB demonstration in September 1995. Both sites contained soil, ground water, and soil gas that were contaminated with a variety of volatile organic compounds. The demonstrations were designed to evaluate the capabilities of each field transportable system.

The primary objectives of this demonstration were: (1) to evaluate instrument performance; (2) to determine how well each field instrument performed compared to reference laboratory data; (3) to evaluate instrument performance on different sample media; (4) to evaluate adverse environmental effects on instrument performance; and, (5) to determine logistical needs and field analysis costs.

Demonstration Results

The demonstration provided adequate analytical and operational data with which to evaluate the performance of the Bruker-Franzen EM640™ GC/MS system. Accuracy was determined by comparing the Bruker GC/MS analysis results with performance evaluation and spiked samples of known contaminant concentrations. Absolute percent accuracy values from both sites were calculated for five target analytes. For soil, most of the values are scattered in the 0-90% range with a median of 39%. For water, most of the values fall in the 0-70% range with a median of 36%. The soil gas accuracy data generally fall in the 0-70% range with a median of 22%. Precision was calculated from the analysis of a series of duplicate samples from each media. The results are reported in terms of relative percent difference (RPD). The values compiled from both sites generally fell within the range of 0 to 25% RPD for soil and 0 to 50% for the water and soil gas samples. The EM640™ produced water and soil gas data that were comparable to the reference laboratory data. However, the soil data were not comparable. This was due in part to difficulties experienced by the reference laboratory in analyzing soil samples and other problems associated with sample handling and transport.

Considerable variability was encountered in the results from reference laboratories, illustrating the degree of difficulty associated with collection, handling, shipment, storage, and analysis of soil gas, water, and soil samples using off-site laboratories. This demonstration revealed that use of field analytical methods, with instruments such as the Bruker GC/MS, can eliminate some of these sample handling problems.

Performance Evaluation

Overall, the results of the demonstration indicated that most of the performance goals were met by the Bruker GC/MS system under field conditions, and that the system can provide good quality, near-real-time field analysis of soil, water, and soil gas samples contaminated by organic compounds. The system was easily transportable in a van and required only two technicians for operation. A limited analysis of capital and field operational costs for the Bruker system shows that field use of the system may provide some cost savings when compared to conventional laboratory analyses. Based on the results of this demonstration, the Bruker EM640™ GC/MS system was determined to be a mature field instrument capable of providing on-site analyses of water and soil gas samples comparable to those from a conventional fixed laboratory.

Section 2 Introduction

Site Characterization Technology Challenge

Rapid, reliable, and cost-effective field screening and analysis technologies are needed to assist in the complex task of characterizing and monitoring hazardous and chemical waste sites. Environmental regulators and site managers are often reluctant to use new technologies which have not been validated in an objective EPA-sanctioned testing program or similar process which facilitates acceptance. Until field characterization technology performance can be verified through objective evaluations, users will remain skeptical of innovative technologies, despite their promise of better, less expensive, and faster environmental analyses.

The Environmental Technology Verification (ETV) Program was created by the U. S. Environmental Protection Agency (EPA) to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, purchase, and use of environmental technologies. The ETV Program capitalizes upon and applies the lessons that were learned in the implementation of the SITE Program to the verification of twelve categories of environmental technology: Drinking Water Systems, Pollution Prevention/Waste Treatment, Pollution Prevention/Innovative Coatings and Coatings Equipment, Indoor Air Products, Advanced Monitoring Systems, EvTEC (an independent, private-sector approach), Wet Weather Flows Technologies, Pollution Prevention/Metal Finishing, Source Water Protection Technologies, Site Characterization and Monitoring Technology (a.k.a. Consortium for Site Characterization Technology (CSCT)), and Climate Change Technologies. The performance verification contained in this report was based on the data collected during a demonstration of field transportable gas chromatograph/mass spectrometer (GC/MS) systems. The demonstration was administered by the Consortium for Site Characterization Technology. The mission of the Consortium is to identify, demonstrate, and verify the performance of innovative site characterization and monitoring technologies. The Consortium also disseminates information about technology performance to developers, environmental remediation site managers, consulting engineers, and regulators.

For each pilot, EPA utilizes the expertise of partner "verification organizations" to design efficient procedures for conducting performance tests of environmental technologies. EPA selects its partners from both the public and private sectors including Federal laboratories, states, and private sector entities. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from all major stakeholder/customer groups associated with the technology area. The U.S. Department of Energy's Sandia National Laboratories, Albuquerque, New Mexico, served as the verification organization for this demonstration.

Technology Verification Process

The technology verification process is intended to serve as a template for conducting technology demonstrations that will generate high-quality data which EPA can use to verify technology performance. Four key steps are inherent in the process:

- Needs Identification and Technology Selection;
- Demonstration Planning and Implementation;
- Report Preparation; and,
- Information Distribution.

Each component is discussed in detail in the following paragraphs.

Needs Identification and Technology Selection

The first aspect of the technology verification process is to determine technology needs of the EPA and the regulated community. EPA, the U.S. Department of Energy, the U.S. Department of Defense, industry, and state agencies are asked to identify technology needs and interest in a technology. Once a technology need is established, a search is conducted to identify suitable technologies that will address the need. The technology search and identification process consists of reviewing responses to *Commerce Business Daily* announcements, searches of industry and trade publications, attendance at related conferences, and leads from technology developers. Characterization and monitoring technologies are evaluated against the following criteria:

- Meets user needs.
- May be used in the field or in a mobile laboratory.
- Applicable to a variety of environmentally impacted sites.
- High potential for resolving problems for which current methods are unsatisfactory.
- Costs are competitive with current methods.
- Performance is better than current methods in areas such as data quality, sample preparation, or analytical turnaround time.
- Uses techniques that are easier and safer than current methods.
- Is a commercially available, field-ready technology.

Demonstration Planning and Implementation

After a technology has been selected, EPA, the verification organization, and the developer agree to responsibilities for conducting the demonstration and evaluating the technology. The following issues are addressed at this time:

- Identifying demonstration sites that will provide the appropriate physical or chemical attributes, in the desired environmental media;
- Identifying and defining the roles of demonstration participants, observers, and reviewers;
- Determining logistical and support requirements (for example, field equipment, power and water sources, mobile laboratory, communications network);
- Arranging analytical and sampling support; and,
- Preparing and implementing a demonstration plan that addresses the experimental design, sampling design, quality assurance/quality control (QA/QC), health and safety considerations, scheduling of field and laboratory operations, data analysis procedures, and reporting requirements.

Report Preparation

Innovative technologies are evaluated independently and, when possible, against conventional technologies. The field technologies are operated by the developers in the presence of independent technology observers. The technology observers are provided by EPA or a third party group. Demonstration data are used to evaluate the capabilities, limitations, and field applications of each technology. Following the demonstration, all raw and reduced data used to evaluate each technology are

compiled into a technology evaluation report, which is mandated by EPA as a record of the demonstration. A data summary and detailed evaluation of each technology are published in an ETVR.

Information Distribution

The goal of the information distribution strategy is to ensure that ETVRs are readily available to interested parties through traditional data distribution pathways, such as printed documents. Documents are also available on the World Wide Web through the ETV Web site (<http://www.epa.gov/etv>) and through a Web site supported by the EPA Office of Solid Waste and Emergency Response's Technology Innovation Office (<http://clu-in.com>).

The GC/MS Demonstration

In late 1994, the process of technology selection for the GC/MS systems was initiated by publishing a notice to conduct a technology demonstration in the *Commerce Business Daily*. In addition, active solicitation of potential participants was conducted using manufacturer and technical literature references. Final technology selection was made by the Consortium based on the readiness of technologies for field demonstration and their applicability to the measurement of volatile organic contaminants at environmentally impacted sites.

GC/MS is a proven laboratory analytical technology that has been in use in environmental laboratories for many years. The instruments are highly versatile with many different types of analyses easily performed on the same system. Because of issues such as cost and complexity, the technology has not been fully adopted for use by the field analytical community. The purpose of this demonstration was to provide not only an evaluation of field portable GC/MS technology results compared to fixed laboratory analyses, but also to evaluate the transportability, ruggedness, ease of operation, and versatility of the field instruments.

For this demonstration, three instrument systems were initially selected for verification. Two of the systems selected were field portable GC/MS systems, one from Viking Instruments Corporation and the other from Bruker-Franzen Analytical Systems, Inc. The other technology identified was a portable direct sampling device for an ion trap mass spectrometer system manufactured by Teledyne Electronic Technologies. However, since the direct sampling inlet for this MS system was not commercially available, its performance has not been verified. In the summer of 1995, the Consortium conducted the demonstration which was coordinated by Sandia National Laboratories.

The versatility of field GC/MS instruments is one of their primary features. For example, an instrument may be used in a rapid screening mode to analyze a large number of samples to estimate analyte concentrations. This same instrument may be used the next day to provide fixed-laboratory-quality data on selected samples with accompanying quality control data. The GC/MS can also identify other contaminants that may be present that may have been missed in previous surveys. Conventional screening instruments, such as portable gas chromatographs, would only indicate that an unknown substance is present.

An example of compound selectivity for a GC/MS is shown in Figure 2-1. The upper portion of the figure is a GC/MS total ion chromatogram from a water sample containing numerous volatile organic compounds. The total ion chromatogram is a plot of total mass detector response as a function of time from sample injection into the instrument. Many peaks can be noted in the retention time window between 7 and 11 minutes. In many cases the peaks are not completely resolved as evidenced by the absence of a clear baseline. The inset figure shows a reconstructed ion chromatogram for ion mass 146. This corresponds to the molecular ion peak of the three isomers of dichlorobenzene. The relative intensities of these peaks are at a level of about 60,000 with the background considerably higher at an intensity level between 500,000 and 1,000,000. This is an example of the ability of the GC/MS to detect and quantitate compounds in the midst of high background levels of other volatile organic compounds.

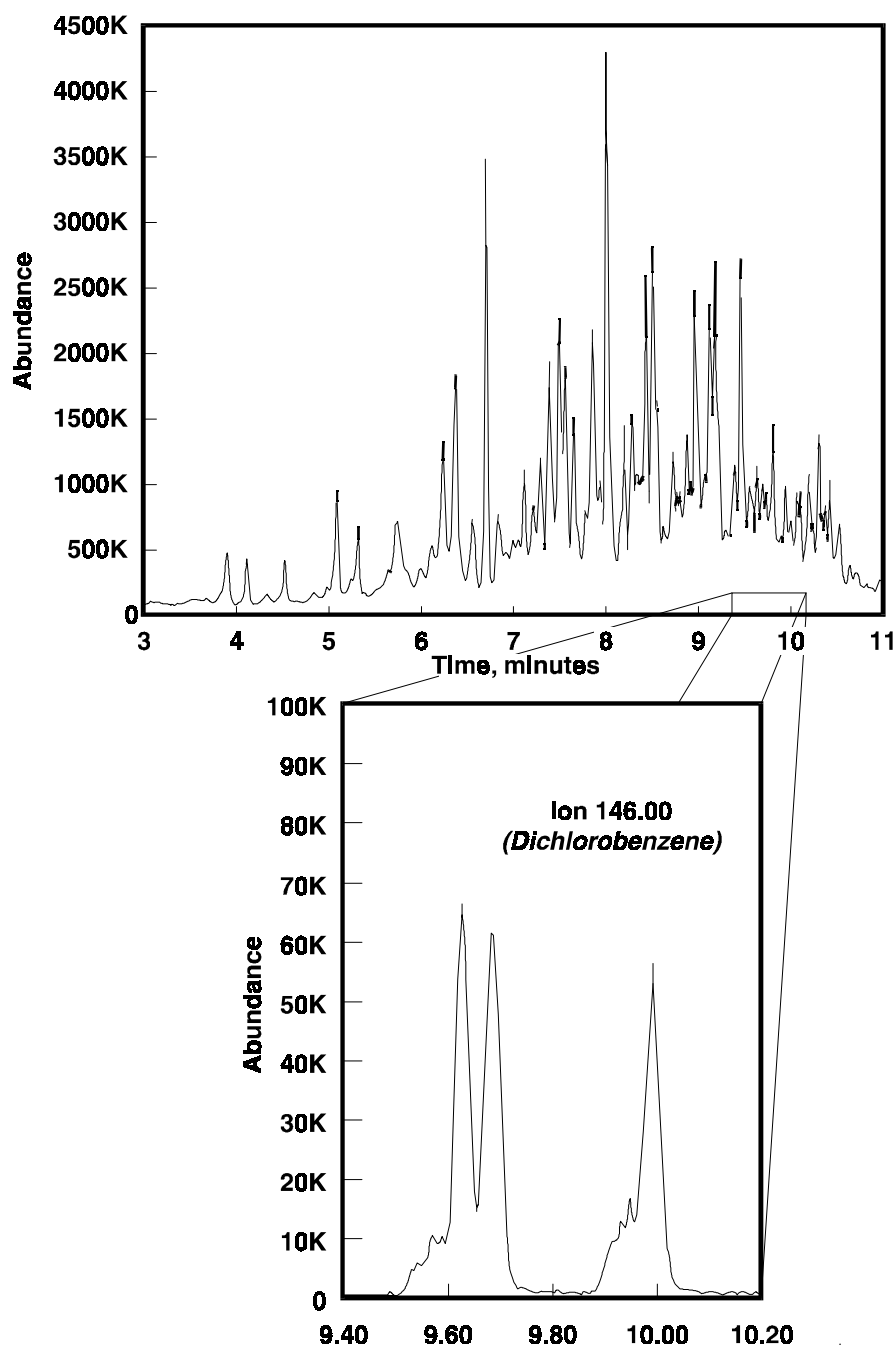


Figure 2-1. Example total ion chromatogram of a complex mixture. The inset shows the ability of the GC/MS system to detect the presence of dichlorobenzenes in a high organic background.

The objectives of this technology demonstration were essentially five-fold:

- To evaluate instrument performance;
- To determine how well each field instrument performed compared to reference laboratory data;
- To evaluate developer goals regarding instrument performance on different sample media;
- To evaluate adverse environmental effects on instrument performance; and,
- To determine the logistical and economic resources needed to operate each instrument.

Section 3 Technology Description

Theory of Operation and Background Information

Gas chromatography/mass spectrometry (GC/MS) is a proven laboratory technology that has been in use in fixed analytical laboratories for many years. The instruments are highly versatile, with many different types of analyses easily performed on the same instrument. The combination of gas chromatography and mass spectrometry enables rapid separation and identification of individual compounds in complex mixtures. One of the features of the GC/MS is its ability to detect and quantitate the compounds of interest in the presence of large backgrounds of interfering substances. Using GC/MS, an experienced analyst can often identify every compound in a complex mixture.

The varying degrees of affinity of compounds in a mixture to the GC column coating makes their separation possible. The greater the molecular affinity, the slower the molecule moves through the column. Less affinity on the other hand causes the molecule to elute from the column more rapidly. A portion of the GC column effluent is directed to the MS ion source where the molecules are fragmented into charged species. These charged species are in turn passed through a quadrupole filter which separates them on the basis of their charge-to-mass ratio. The charged fragments are finally sensed at an electron multiplier at the opposite end of the quadrupole filter. The array of fragments detected for each eluting compound is known as a mass spectrum and provides the basis for compound identification and quantitation. The GC/MS mass spectrum can be used to determine the molecular weight and molecular formula of an unknown compound. In addition, characteristic fragmentation patterns produced by sample ionization can be used to deduce molecular structure. Typical detection limits of about 10^{-12} g can be realized with MS.

*Operational Characteristics*¹

The Bruker-Franzen EM640™ shown in Figure 3-1 is a complete GC/MS system that provides laboratory-grade performance in a field transportable package. The system is based on transferring VOCs in liquid or solid samples to the gas phase. General instrument specifications are presented in Table 3-1. VOCs extracted from air, liquid, or solid samples are introduced in the gas phase into a gas chromatograph (GC) for separation. Compounds eluting from the GC column permeate through an inlet membrane into the vacuum chamber of the MS. The molecules are ionized by electron impact and subsequently pass through a mass selective filter. The ions are detected in an electron multiplier that generates an electrical signal proportional to the number of ions. The data system records these electrical signals and converts them into a mass spectrum. The sum of all ions in a mass spectrum at any given instant corresponds to one point in the total detector response (total ion chromatogram) that is recorded as a function of time. A mass spectrum is like a fingerprint of a compound. These fingerprints are compared with stored library spectra and used together with the GC retention times for the identification of the compounds. The signal intensity of selected mass peaks is used for quantitation of pre-selected target compounds.

Recommended ancillary analysis equipment is the Spray-and-Trap Water Sampler (Bruker Analytical Systems Inc., Billerica, MA). The Spray-and-Trap Water Sampler device consists of a mechanical pump to inject a continuous flow of an aqueous sample into a sealed extraction chamber through a spray nebulizer. The droplet formation enormously increases the total interfacial area between the sprayed water and the carrier gas, which supports the transfer of the VOCs into the gas phase. The steadily flowing carrier gas is transferred to a suitable sorbent tube which collects the extracted VOCs. In contrast to the purge-and-trap

¹ The information presented in the remainder of Section 3 was provided by Bruker. It has been minimally edited. This information is solely that of Bruker and should not be construed to reflect the views or opinions of EPA.

method, spray-and-trap utilizes a dynamic equilibrium. During water spray, an equilibrium VOC transfer rate between the droplet surfaces and flowing carrier gas is established.

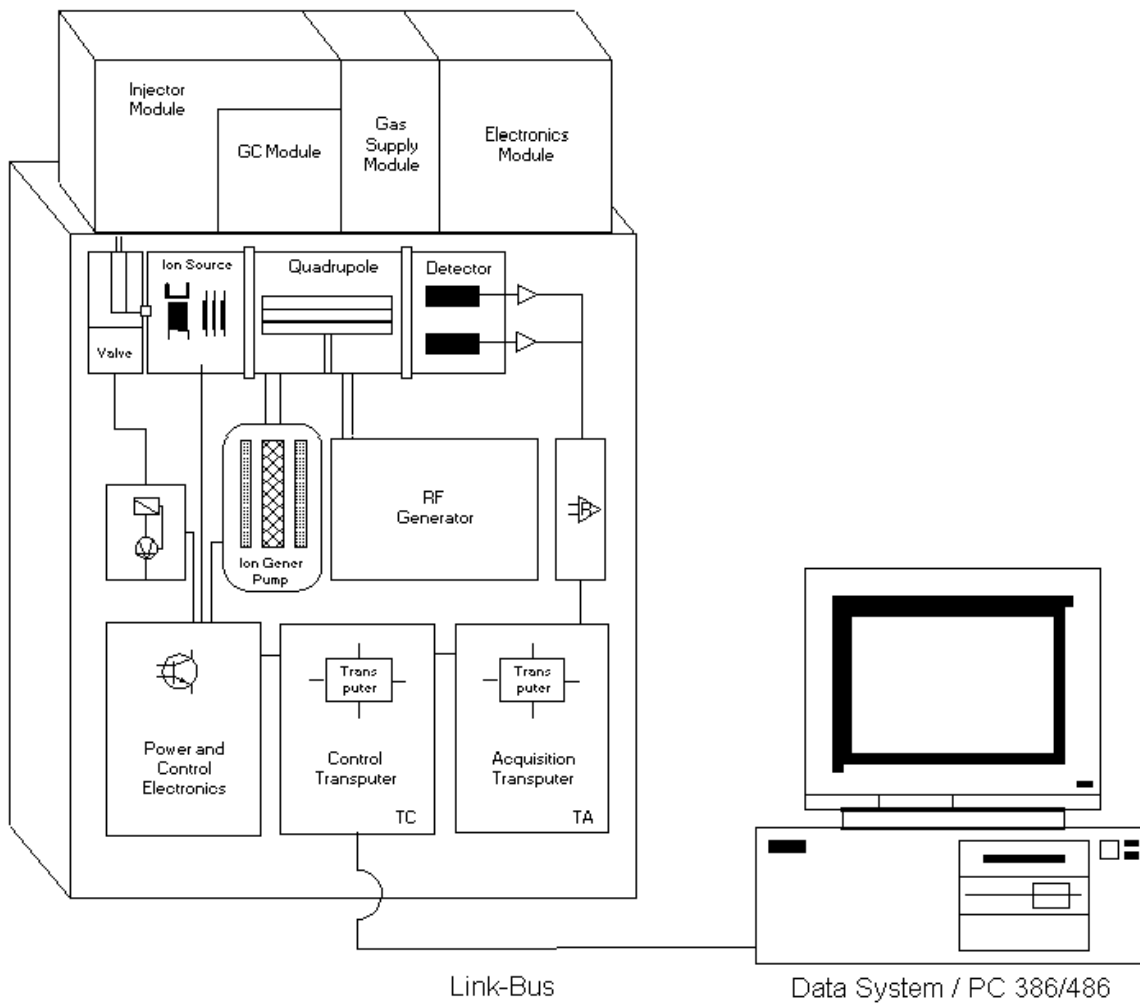


Figure 3-1. Block Diagram of Bruker-Franzen EM640™ GC/MS.

Performance Factors

The following sections describe the Bruker-Franzen EM640™ GC/MS performance factors. These factors include detection limits, sensitivities, and sample throughput.

Table 3-1. Bruker-Franzen EM640™ GC/MS Instrument Specifications.

Parameter	Developer's Specification
Practical Quantitation Limits (scan mode)	20 ppb air (soil gas), 0.1 $\mu\text{g/L}$ water, and 50 mg/kg soil
Mass range	1 - 650 amu
Dynamic Range	4 - 5 orders of magnitude
Sample throughput	10 minutes per sample including analysis time
Maximum scan speed	2000 amu/sec
Temperature range	-10 to 45°C
Power requirements	500 W
Weight	ca. 65 kg
Size	750 x 450 x 350 mm
Operator and training required	Full chemist (1 week operation, method development, evaluation), lab operator (3 weeks execution of methods, protocol)
Support equipment	Spray-and-trap extractor, batteries, power generator (as an alternative to batteries)
Computer requirements	PC with OS/2 multitask software
Cost	Baseline \$170K + cost of inlet system

Practical Quantitation Limits

Detection limits vary depending on compound, media, operation mode of the MS (“scan” or “single ion monitoring”), and sample volume. Generally, for thirty-six of the most common VOCs, the practical quantitation limits (PQL) in the “scan mode” are: 20 ppb for soil gas (100 mL sample volume); 0.1 $\mu\text{g/L}$ for water samples (250 mL sample volume); and, 50 mg/kg for soil samples (6 g sample weight). The “single ion monitoring” (SIM) mode of operation increases the sensitivity by a factor of 10. To express this in absolute values, the mass spectrometer needs 1 ng of a compound to produce a signal-to-noise ratio of 10 in the scan mode.

Dynamic Range

Approximately 4 - 5 orders of magnitude linear dynamic range are possible with the Bruker-Franzen EM640™ depending upon the analyte and the analysis conditions.

Sample Throughput

Sample throughput measures the amount of time required to prepare and analyze one field sample. Bruker-Franzen claims that the complete analysis time is as follows: air and water samples, 8-10 minutes per sample or 6 samples per hour, soil samples, 7 - 10 minutes or 7 - 8 samples per hour. This does not include sample handling, data documentation, or difficult dilutions and concentrations.

Advantages of the Technology

The EM640™ offers the following advantages:

- It is a ruggedized instrument, built for reliability and ease of operation. It is shock and vibration proof and can be successfully transported in a four wheel drive vehicle in rough terrain (a special damping bed with quick release connector is used to mount the instrument).
- The instrument can be calibrated during transport to the site, therefore increasing overall analysis time on site.
- The application of fast analysis runs results in 6 to 8 sample analyses per hour, as a result of the short-column GC analysis technique applied. Incomplete GC separation is compensated for by mathematical separation routines.
- The analysis report for a sample is available within a few minutes after start of the analysis, making it possible to evaluate and direct the sampling strategy in the field. With one or two EM640™ instruments in a small van, the analysis speed can be adapted to the sampling speed of a sampling team. Sampling and analysis can easily progress simultaneously.
- The EM640™ analytical procedures can be optimized with respect to a variety of parameters, e.g. highest analysis speed, safest substance identification, maximum precision, or lowest detection limits.
- The EM640™ GC/MS technology offers low cost sample analysis. Costs should be considerably lower than 25% of those incurred using conventional laboratory analysis.
- The high sample throughput rate allows for the analysis of many QA/QC samples during the day, providing better quality control for the analyses.
- A calibration gas stored inside a small container inside the instrument is the only consumable of the EM640™. The GC column is operated using an ambient air as the carrier gas. There are no pump oils, lubricants, or other maintenance materials. Little maintenance is necessary. No ion source cleaning is required. The high vacuum pump inside the EM640™ does not contain any moving parts, and there is no roughing pump at all. To aid in trouble-shooting, the EM640™ features internal monitoring of all electric functions.
- The preparation of samples is simplified by the use of a large dynamic measuring range, featuring a linear calibration curve over four to five orders of magnitude.
- For soil extraction, a special battery-operated ultra sound extraction method with acetone has been developed, minimizing the use of chlorinated solvents that must be treated as hazardous waste.

Limits of the Technology

Some limitations associated with the EM640™ are listed below:

- *Detection limits in air:* By sampling 500 mL of air on a sorption tube, the limit of detection for toluene is approximately 10 ppb, using the instrument in full-scan mode. The limit of detection for toluene in air is 1 ppm, if measured with the instrument's flexible probe in full-scan mode without any enrichment.
- *Detection limits in water:* Spraying 300 mL of water by the Spray and Trap Water Sampler, which takes about two minutes, a detection limit of 0.1 µg/L is measured for most volatile substances like trichloroethene and perchloroethene. Less polar substances have lower detection limits; more polar compounds have higher detection limits.
- *GC limitations:* The GC usually operates with air as the carrier gas, therefore the maximum temperature of the column is restricted to 240°C. Most analytical separations can be achieved within this temperature limitation by selection of the right type of GC column. Nitrogen can be used to extend the useful temperature range to 300° C if high boiling point semi-volatiles are to be analyzed.

- *Analyte limitations:* The membrane inlet system limits the analytes that can be analyzed. Extremely polar compounds cannot be analyzed with the same sensitivity as non-polar compounds. Some classes of compounds are not easily analyzed.
- *Sample Media Effects:* In general, air and water samples are more easily analyzed than soil by GC/MS instruments. Therefore, accuracy and precision for soil is expected to be lower. Additionally, soil is often more difficult to homogenize, giving rise to additional analytical variation.
- *Spectral Interference:* With GC/MS technology in general, interference can occur with excessive water vapor and with contamination. Water vapor may increase some detection levels; contamination may reside in sampling equipment which must be periodically checked; cross contamination may occur with sequential high and low concentration samples. This can be checked and eliminated by periodically analyzing reagent blanks.

Section 4

Site Descriptions and Demonstration Design

This section provides a brief description of the sites used in the demonstration and an overview of the demonstration design. Sampling operations, reference laboratory selection, and analysis methods are also discussed. A comprehensive demonstration plan entitled "Demonstration Plan for the Evaluation of Field Transportable Gas Chromatograph/Mass Spectrometer" [SNL, 1995] was prepared to help guide the demonstration. The demonstration plan was designed to ensure that the demonstration would be representative of field operating conditions and that the sample analytical results from the field GC/MS technologies under evaluation could be objectively compared to results obtained using conventional laboratory techniques.

Technology Demonstration Objectives

The purpose of this demonstration was to thoroughly and objectively evaluate field transportable GC/MS technologies during typical field activities. The primary objectives of the demonstration were to:

- To evaluate instrument performance;
- To determine how well each field instrument performed compared to reference laboratory data;
- To evaluate developer goals regarding instrument performance on different sample media;
- To evaluate adverse environmental effects on instrument performance; and,
- To determine the logistical and economic resources needed to operate each instrument.

In order to accomplish these objectives, both qualitative and quantitative assessments of each system were required and are discussed in detail in the following paragraphs.

Qualitative Assessments

Qualitative assessments of field GC/MS system capabilities included the portability and ruggedness of the system and its logistical and support requirements. Specific instrument features that were evaluated in the demonstration included: system transportability, utility requirements, ancillary equipment needed, the required level of operator training or experience, health and safety issues, reliability, and routine maintenance requirements.

Quantitative Assessments

Several quantitative assessments of field GC/MS system capabilities related to the analytical data produced by the instrument were conducted. Quantitative assessments included the evaluation of instrument accuracy, precision, and data completeness. Accuracy is the agreement between the measured concentration of an analyte in a sample and the accepted or "true" value. The accuracy of the GC/MS technologies was assessed by evaluating performance evaluation (PE) and media spike samples. Precision is determined by evaluating the agreement between results from the analysis of duplicate samples. Completeness, in the context of this demonstration, is defined as the ability to identify all of the contaminants of concern in the samples analyzed. Sites were selected for this demonstration with as many as fifteen contaminants to identify and analyze and with high background hydrocarbon concentrations. Additional quantitative capabilities assessed included field analysis costs per sample, sample throughput rates, and the overall cost effectiveness of the field systems.

Site Selection and Description

Sandia National Laboratories and the EPA's National Exposure Research Laboratory/Environmental Sciences Division-Las Vegas (NERL/ESD-LV) conducted a search for suitable demonstration sites between January and May 1995. The site selection criteria were guided by logistical demands and the need

to demonstrate the suitability of field transportable GC/MS technologies under diverse conditions representative of anticipated field applications. The site selection criteria were:

- Accessible to two-wheel drive vehicles;
- Contain one or more contaminated media (water, soil, and soil gas);
- Provide a wide range of contaminant types and concentration levels to truly evaluate the capabilities and advantages of the GC/MS systems;
- Access to historical data on types and levels of contamination to assist in sampling activities;
- Variation in climatological and geological environments to assess the effects of environmental conditions and media variations on performance; and,
- Appropriate demonstration support facilities and personnel.

Several demonstration sites were reviewed and, based on these selection criteria, the U. S. Department of Energy's Savannah River Site (SRS) near Aiken, South Carolina, and Wurtsmith Air Force Base (WAFB) in Oscoda, Michigan, were selected as sites for this demonstration.

The Savannah River Site is a DOE facility, focusing on national security work; economic development and technology transfer initiatives; and, environmental and waste management activities¹. The SRS staff have extensive experience in supporting field demonstration activities. The SRS demonstration provided the technologies an opportunity to analyze relatively simple contaminated soil, water, and soil gas samples under harsh operating conditions. The samples contained only a few chlorinated compounds (solvents) with little background contamination, but high temperatures and humidity offered a challenging operating environment.

WAFB is one of the Department of Defense's (DoD) National Environmental Technology Test Site (NETTS) test sites. The facility is currently used as a national test bed for bioremediation field research, development, and demonstration activities. The WAFB demonstration provided less challenging environmental conditions for the technologies but much more difficult samples to analyze. The soil, water, and soil gas samples contained a complex matrix of fifteen target VOC analytes along with relatively high concentration levels of jet fuel, often about 100 times the concentration levels of the target analytes being measured.

Savannah River Site Description

Owned by DOE and operated under contract by the Westinghouse Savannah River Company, the Savannah River Site complex covers 310 square miles, bordering the Savannah River between western South Carolina and Georgia as shown in Figure 4-1.

The Savannah River Site was constructed during the early 1950's to produce the basic materials used in the fabrication of nuclear weapons, primarily tritium and plutonium-239. Weapons material production at SRS has produced unusable byproducts such as intensely radioactive waste. In addition to these high-level wastes, other wastes at the site include low-level solid and liquid radioactive wastes; transuranic waste;

¹ Much of this site descriptive material is adapted from information available at the Savannah River Site web page (<http://www.srs.gov/general/srs-home.html>)

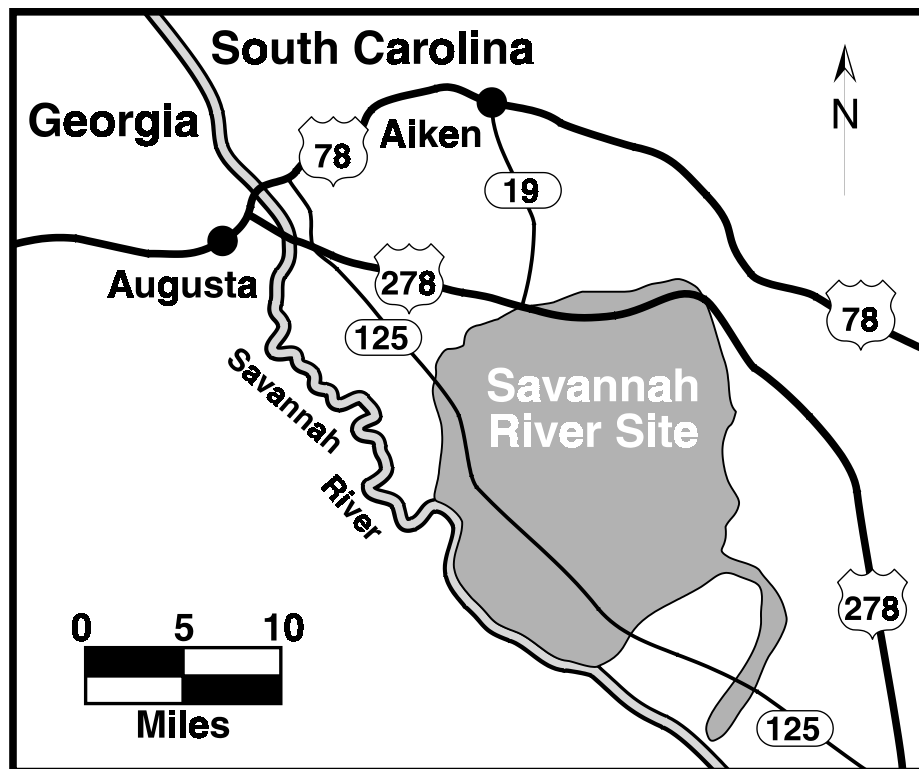


Figure 4-1. Location of the Savannah River Site.

hazardous waste; mixed waste, which contains both hazardous and radioactive components; and sanitary waste, which is neither radioactive nor hazardous. Like many other large production facilities, chemicals have been released into the environment during production activities at SRS. These releases and the common disposal practices of the past have resulted in subsurface contamination by a variety of compounds used in or resulting from production processes.

SRS Geologic and Hydrologic Characteristics

The facility is located on the upper Atlantic coastal plain on the Savannah River, approximately 30 miles southeast of Augusta, Georgia and about 90 miles north of the Atlantic coast. The site is underlain by a thick wedge (approximately 1,000 feet) of unconsolidated Tertiary and Cretaceous sediments that overlay the basement which consists of Precambrian and Paleozoic metamorphic rocks and consolidated Triassic sediments (siltstone and sandstone). The younger sedimentary section consists predominantly of sand, clayey sand, and sandy clay.

Ground water flow at the site is controlled by hydrologic boundaries. Flow at or immediately below the water table is predominately downward and toward the Savannah River. Ground water flow in the shallow aquifers in the immediate vicinity of the demonstration site is highly influenced by eleven pump-and-treat recovery network wells.

SRS Demonstration Site Characteristics

Past industrial waste disposal practices at the Savannah River Site, like those encountered at other DOE weapons production sites, often included the release of many chemicals into the local environment. These releases and early disposal practices have resulted in the contamination of the subsurface of many site areas by a number of industrial solvents used in, or resulting from the various weapons material production processes. The largest volume of contamination has been from chlorinated volatile organic compounds.

The primary VOCs encountered at SRS include: tetrachloroethene (PCE), trichloroethene (TCE), trichloroethane (TCA), Freon 11, and Freon 113.

The area selected for the demonstration is designated the M-Area. The M-Area is located in the northwest section of SRS and consists of facilities that fabricated reactor fuel and target assemblies for the SRS reactors, laboratory facilities, and administrative support facilities. Operations at these and other facilities resulted in the release of the chlorinated solvents previously mentioned. The releases have resulted in the contamination of soil and ground water within the area. The technology staging site was located near an abandoned process sewer line which carried waste water from M-Area processing facilities to a settling basin for 27 years, beginning in 1958. Site characterization data indicate that several leaks existed in the sewer line, located about 20 feet below the surface, producing localized sources of contamination. Although the use of the sewer line was discontinued in 1985, estimates are that over 2 million pounds of these solvents were released into the subsurface during its use.

Typical PCE and TCE concentrations are listed in Table 4-1 for the demonstration wells identified in Figure 4-2. The soil and underlying sediments at the demonstration site are highly contaminated with chlorinated solvents at depths in excess of 50 feet. Identification of the contaminant concentration levels in the soil and sediments has been complicated by the nature of these media at SRS. They have very low organic content, resulting in significant contaminant loss during typical sampling operations. These sampling concerns and limitations, and their influence on the demonstration, are discussed in detail later in this section.

Table 4-1. PCE and TCE Concentrations in SRS M Area Wells.

Conc. Level	Water			Soil Gas		
	Well	PCE ($\mu\text{g/L}$)	TCE ($\mu\text{g/L}$)	Well	PCE (ppm)	TCE (ppm)
Low	MHT-11C	12	37	MHV-2C	10	5
Medium	MHT-12C	110	100	CPT-RAM 15	80	50
High	MHT-17C	3700	2700	CPT-RAM 4	800	350

Wurtsmith Air Force Base Description

Wurtsmith Air Force Base covers approximately 7.5 square miles and is located on the eastern side of Michigan's lower peninsula on Lake Huron, about 75 miles northeast of Midland, Michigan, near the town of Oscoda (Figure 4-3). It is bordered by three connected open water systems; Lake Huron to the east, shallow wetlands and the Au Sable River to the south, and Van Etten Lake to the north. State and National Forest lands surround much of the base. WAFB began operations as an Army Air Corps facility, known as Camp Skeel, in 1923. It was originally used as a bombing and artillery range and as a winter training facility. The WAFB was decommissioned in 1993 and is currently being used as a national test bed for bioremediation field research, development, and demonstration. The National Center for Integrated Bioremediation Research and Development (NCIBRD) of the University of Michigan coordinates these bioremediation activities. Several contaminant features consistent with its history as an Air Force base have

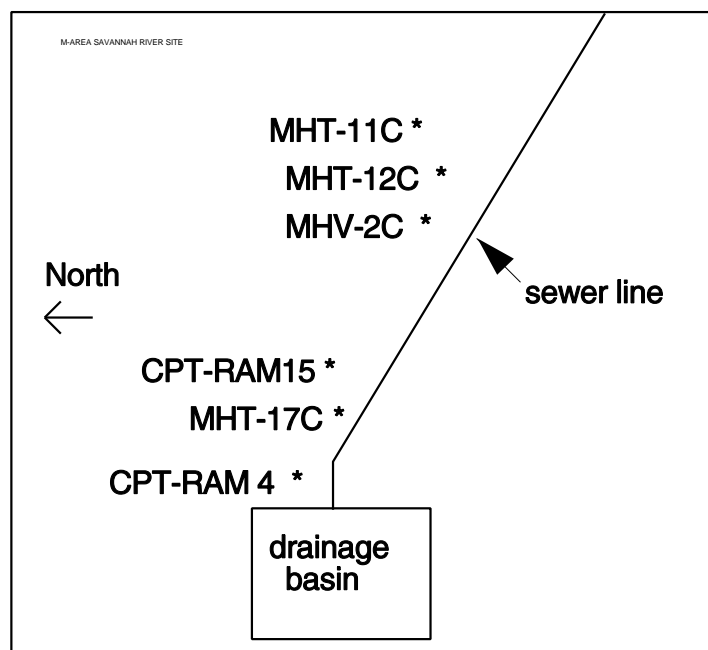


Figure 4-2. SRS M-Area Well Locations.

been identified at WAFB. These include landfills with mixed leachate, gasoline and jet fuel spills, a fire fighting training area, leaking underground storage tanks, an airplane crash site, and pesticide contamination.

Contamination has spread to soil and ground water under approximately 20 percent of the base. A number of VOC contaminants, some of which are identified in Table 4-2, are commingled at the site. The ground water contaminants include: chlorinated solvents such as DCE, TCE, PCE and chlorobenzenes; polycyclic aromatic hydrocarbons (PAHs); aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX); and, other hydrocarbons such as aldehydes, ketones, gasoline, and jet fuel. Many of the VOC contaminants are found in the capillary fringe at the water table as part of a non-aqueous or free phase hydrocarbon medium. Contaminant concentration levels in this medium can be several orders of magnitude higher than in the ground water. Current remediation efforts at WAFB include three pump-and-treat systems using air strippers.

Table 4-2. Historical Ground Water Contamination Levels at WAFB.

Conc. Level	DCE	TCE	PCE	Benz.	Ethyl Benz.	Tol.	Xyl.	Chlorobenzene	DCB
Low	<1	<1	<1	<1	<1	<1	<1	<1	<1
Med	200	<1	<1	20	300	10	200	5	5
High	700	2	<1	250	1200	400	600	30	20

Note: Concentration levels in units of $\mu\text{g/L}$.

WAFB Geologic and Hydrologic Characteristics

The WAFB site rests on a 30-80 foot thick layer of clean, medium-grained sand and gravel sediments formed by glacial meltwater, channel, deltaic and upper shore face-beach depositional processes. This surface layer is underlain by a 100-250 foot thick layer of silty-clay deposited through settlement of the silt

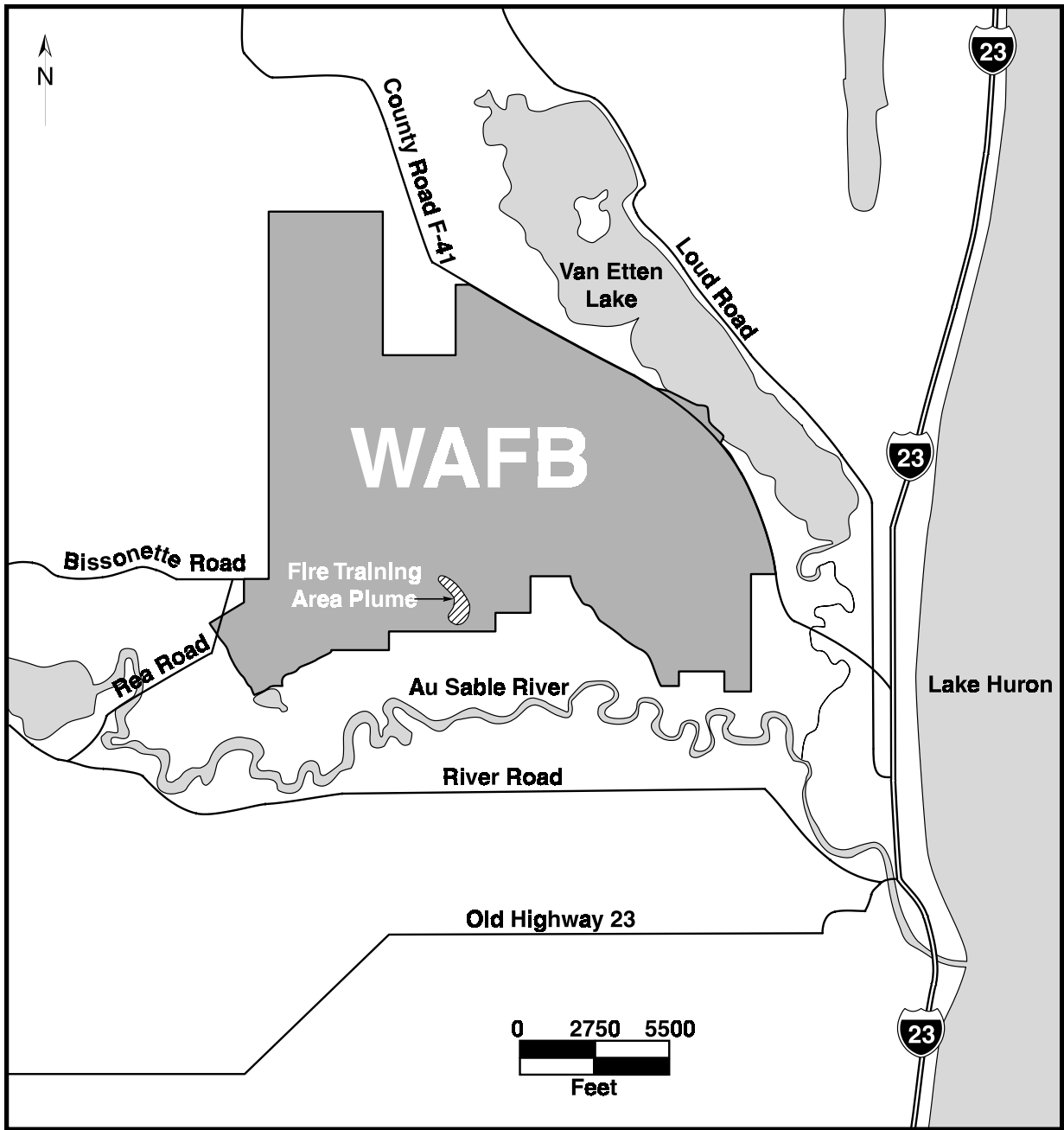


Figure 4-3. Location of Wurtsmith Air Force Base.

and clay-sized particles from glacial meltwater following glacier retreat after the glacial episodes of the Pleistocene Epoch. This layer lies on top of bedrock that consists of Mississippian sandstone and shale formations that have a structural dip to the southwest into the Michigan Basin. The water table ranges from about 5 feet below land surface in the northern regions to 20 feet below land surface in the southern regions. A ground water divide runs diagonally across the base from northwest to southeast. South of the divide, ground water flows toward the Au Sable River, and north of the divide, toward Van Etten Creek and Van Etten Lake. Eventually, all water from WAFB reaches Lake Huron.

WAFB Demonstration Site Characteristics

The demonstration area selected is located at the former Fire Training Area 2, near the southern boundary of the base (Figure 4-4). A wide range of organic contaminants from former fire training and other

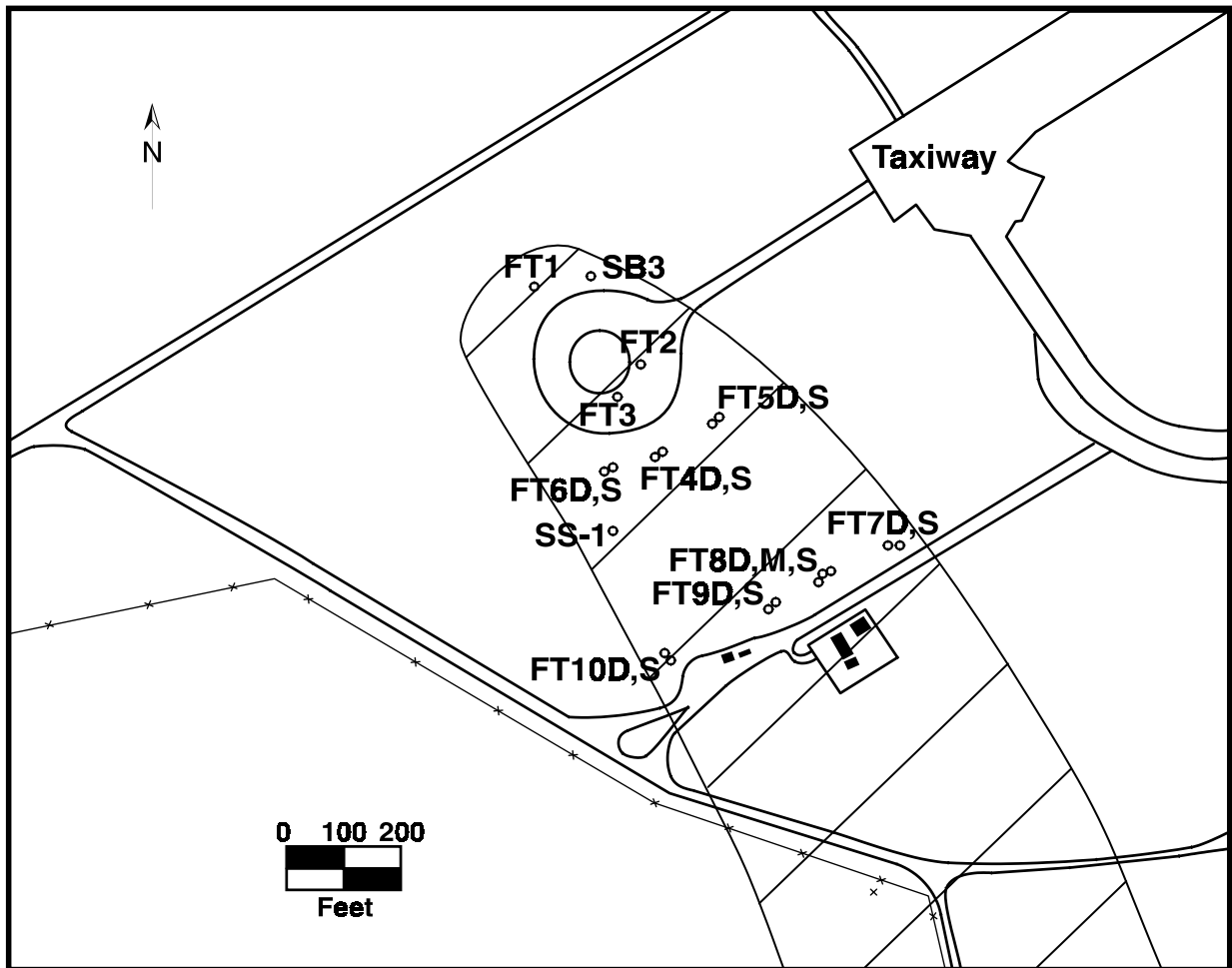


Figure 4-4. WAFB Fire Training Area 2 Sampling Locations. The cross-hatched region shows the approximate location of the below-ground contaminant plume. A number of deep (D), medium (M), and shallow (S) well locations are also shown.

Table 4-3. VOC Concentrations in WAFB Fire Training Area 2 Wells.

Conc. Level	Water			Soil Gas		
	Well	Benzene ($\mu\text{g/L}$)	Toluene ($\mu\text{g/L}$)	Xylenes ($\mu\text{g/L}$)	Well	Total VOCs (ppm)
Low	FT5S	0.24	0.20	20	SB3 at 4'	30
Medium	FT3	20	15	400	SB3 at 7'	55
High	FT8S	225	2	1800	SB3 at 10'	62

activities exist in the soil and ground water at the site. Based on historic data, over fifteen organic contaminants exist at the site. Additionally, high background levels of petroleum hydrocarbons such as jet and diesel fuel exist at the site. Historic contaminant concentration levels are listed in Table 4-3 for the monitoring wells at the Fire Training Area. The monitoring wells at this site are often clustered together with one well screened at a shallow depth, denoted by an (S), and one screened at a deeper depth denoted by a (D). No historical data regarding the expected soil contamination levels were available for the site.

Overview of the Field Demonstrations

The demonstrations were designed to evaluate both the analytical and operational capabilities of the field GC/MS technologies under representative field conditions. The analytical method for the operation of the Bruker GC/MS is provided in Appendix A. The SRS field demonstration was conducted in July 1995 and lasted three days. The technologies arrived at the demonstration site on Monday, July 17. As is typically the case for this part of the country in mid-summer, the weather was hot (up to 95°F) and humid but with no rain. Each day the technologies arrived at the site about 6:30 a.m. They were set-up, calibrated, and ready for sample analysis by about 7:30 a.m. Sample analysis typically lasted through mid-afternoon. Soil vapor samples were prepared and analyzed on-site by the participants on Tuesday, July 18. The water and soil samples were collected and analyzed by the participants on Wednesday and Thursday, respectively. Each developer provided their own transportation, personnel, and equipment needed to conduct their analyses. At SRS, the developers were required to provide their own electrical power as part of their field operations. The field demonstration was completed by Friday, July 21.

The WAFB field demonstration was conducted in September 1995. The participants arrived at the demonstration site on Sunday, September 10. The weather was generally cool, typically 40°F in the mornings, warming to about 70°F during the afternoons. No appreciable precipitation was encountered during the demonstration. Each participant arrived with their respective instrument early in the morning. Following set up and calibration, instruments were ready for sample analysis by 7:30 a.m. Sample collection and on-site analysis took three days, one day for each media. A fourth day was used as a “media day” to showcase the participating technologies. As at SRS, each developer provided their own transportation, personnel, equipment, etc., to conduct the sample analyses.

Overview of Sample Collection, Handling, and Distribution

Soil gas, water, and soil samples were collected during the demonstrations at both sites. Sample splits were provided to the technology developers for on-site analysis the day of the sampling and shipped to reference analytical laboratories for analysis using conventional methods. Formal chain-of-custody forms were used for distribution of the samples to each of the reference laboratories. The samples were collected, numbered, stored, and shipped to the laboratories in accordance with laboratory procedures that incorporate EPA sampling guidelines. Somewhat less formal chain-of-custody records were maintained for distribution of the samples analyzed on site. An overview of the site-specific sampling plans and the procedures for collecting, handling, and distributing the samples is presented below. Additional sampling details can be found in the demonstration plan referenced earlier. A description of the sampling terminology used in the context of this demonstration is presented in Table 4-4.

SRS Sample Collection

A total of 33 samples were collected and analyzed in the SRS demonstration. The samples were distributed among the three sample media, soil gas, water, and soil, as identified in Table 4-5. Sample collection and on-site analysis took place over a three day period in July 1995. Water and soil gas samples were obtained from the six M-Area wells identified in Table 4-1. The principal analytes were TCE and PCE at concentration ranges noted in the table, but other contaminants such as TCA, Freon 11, Freon 113, and their degradation products were sometimes present at lower concentrations in the wells.

SRS Soil Gas Survey

Wells MHV-2C, CPT-RAM 15, and CPT-RAM 4, shown in Figure 4-2, were sampled using Tedlar™ bags and SUMMA™ canisters. The Tedlar™ bags were used for on-site analyses and the SUMMA™

Table 4-4. Sample Terminology and Description.

Term	Description
Method Blanks	Method blanks are samples which do not contain the target analytes. Water blanks consisted of deionized water; Soil blanks consisted of uncontaminated soil representative of the site being sampled; Soil gas blanks consisted of dry nitrogen gas.
Spike Samples	Spike samples are generated by adding a known amount of analyte to a sample matrix. Spike samples are used to evaluate the accuracy of an instrument by comparing the concentration measured to the prepared reference concentration (spike recovery).
Performance Evaluation Samples	<p>Performance evaluation (PE) samples are samples having a certified concentration for specific analytes of interest. PE samples may include dilutions of a certified sample where so noted. PE samples are also used to evaluate the accuracy of a technology or laboratory during sample analysis by comparing the measured concentration to the defined reference concentration.</p> <p>At both SRS and WAFB, water PE samples were obtained, diluted to appropriate concentrations, and submitted for analysis to the developers and the reference laboratories. At SRS, a soil vapor PE sample was generated using a VOC vapor standard from SRS. At WAFB, the soil PE samples were acquired in sealed vials and were submitted to the developers and laboratories. Each laboratory did their own dilutions as appropriate.</p>
Duplicate or Split Samples	A duplicate sample is a split of an initial sample. Duplicate samples are used to evaluate the precision of an instrument by comparing the relative difference between the duplicate measurements. For water and soil gas samples, a duplicate sample is often considered a second sample taken sequentially from the same well.

Table 4-5. SRS Demonstration Sample Type and Count.

Media	Concentration Level	Samples	Duplicates	Spikes	PE Samples	Total
Soil gas	Blank	2				13
	Low	1	1	1	1	
	Medium	1	1	1	1	
	High	1	1	1	1	
Water	Blank	2				13
	Low	1	1	1	2	
	Medium	1	1	1		
	High	1	1	1		
Soil	Blank	1				7
	Low			3		
	Medium					
	High			3		

canisters were sent to the reference laboratory for analysis. For the soil gas survey, soil vapor² from each

² A soil gas survey is conducted to measure the vapor phase concentration of VOC contaminants in a soil sample. This vapor phase contaminant concentration is commonly referred to as the soil gas concentration. The terms soil vapor and soil gas are used interchangeably in this report.

well was pumped sequentially into three Tedlar™ bags. The first bag was used to fill a SUMMA™ canister while the other two bags were used for analysis by the developers. A sample aliquot was taken directly from the Tedlar™ bags by each developer for analysis on a round-robin basis.

Additional aliquots were taken by the SRS on-site laboratory prior to and following drawing developer samples from each bag in order to monitor the stability of both TCE and PCE in the bags during the analysis. A blank sample, a Tedlar™ bag filled with nitrogen, was provided to participants at the beginning and another blank provided at the end of the analyses. Spike samples were prepared by the SRS on-site laboratory by injecting a known volume of TCE and PCE into a Tedlar™ bag filled with a known volume of nitrogen. Two gas PE samples from certified cylinders were metered into Tedlar™ bags for analysis by the participants. Sample aliquots were also taken by the developers from each of the PE and blank sample bags on a round-robin basis.

SRS Water Sampling

Water samples were collected from wells MHT-11C, MHT-12C, and MHT-17C (Figure 4-2). Each well was initially purged and a 2 liter sample collected. Immediately after collection, the sample was sealed and stirred for 10 minutes. The homogenized sample was then split into individual sample vials for distribution and analysis. Two blank samples consisting of deionized water were provided to the participants for analysis. Two water PE samples, prepared for the EPA's Hazardous Substances Evaluation Division in Washington, DC for use in the Contract Laboratory Program, were also provided to the participants for analysis. For on-site analysis, the PE sample ampules were mixed with the appropriate volume of water to obtain the defined reference concentration. For the reference laboratory analysis, the ampules were provided directly to the laboratories without prior dilution.

SRS Soil Spike Samples

Soils and sediments at the demonstration site are highly contaminated with PCE and TCE. Accurate analyses of the sediments at depths greater than 50 feet, where contaminant levels appropriate to the requirements of this demonstration exist, have been difficult because the SRS soils have low organic content and the VOCs do not bind well to the soil matrix. The expense of drilling and sampling at these depths and the composition of the soil at the site indicated that collecting standard soil core samples for analysis was inappropriate for this demonstration. In order to maximize the amount of data that could be derived from the demonstration under these circumstances, the demonstration plan contained a procedure for using spiked soil samples in the place of soil core samples. This procedure called for soil to be collected from an erosion pit at SRS, homogenized, spiked with solutions of TCE and PCE, separated into 5-gram portions, and placed in 40 mL VOA vials equipped with screw-top lids and septa. This vial configuration allowed participants the option of either purge and trap or head space sample introduction and analysis. Actual sample preparation was done differently from that presented in the demonstration plan. These deviations are discussed later in this section.

SRS Sample Handling, Storage, and Shipping

Developers analyzed the samples as soon as practical following collection or preparation, but generally within an hour of sampling. Formal chain of custody protocol was maintained for the reference laboratory samples. The field-analyzed samples had less formal custody procedures, but all transfers were recorded in log books. Samples collected for laboratory analysis were transported to the reference laboratory at the end of each day. Possible loss of VOCs in the samples was a major concern; therefore, all water, soil vapor, and soil samples were stored and shipped in coolers maintained at approximately 40°F.

WAFB Sample Collection

A total of 37 samples were collected and analyzed in the WAFB demonstration. The distribution of the samples from each media, soil, water, and soil gas are presented in Table 4-6. Sample collection and on-site analysis took place over a three day period in September 1995. Water and soil gas samples were obtained from the wells identified in Table 4-3. Historical sampling and analysis data show VOC concentrations ranging from 0.2 to 1800 $\mu\text{g/L}$ in water and total VOC concentrations in soil gas ranging from 30 to 62 ppm.

Table 4-6. WAFB Demonstration Sample Type and Count.

Media	Concentration Level	Samples	Duplicates	Spikes	PE Samples	Total
Soil gas	Blank	2				11
	Low	1	1	1		
	Medium	1	1	1		
	High	1	1	1		
Water	Blank	2			2	13
	Low	1	1	1		
	Medium	1	1	1		
	High	1	1	1		
Soil	Blank	2			2	13
	Low	1	2			
	Medium	1	2			
	High	1	2			

WAFB Soil Gas Survey

Well SB3, shown in Figure 4-4, was sampled at three depths using Tedlar™ bags. At each depth, two bags were sequentially filled. The bags were used for on-site developer analyses and the residual gas in each bag was used to fill SUMMA™ canisters for analysis by the reference laboratory. For on-site analysis, sample aliquots were drawn from the bags by each developer in a round-robin format like that used at SRS. A blank sample, a Tedlar™ bag filled with nitrogen, was used at the beginning and at the end of the soil gas analytical sequence. A spiked sample for each concentration level was made by injecting a known volume of liquid into a Tedlar™ bag filled with a known volume of nitrogen.

WAFB Water Sampling

Water samples were collected from wells FT5S, FT3, and FT8S (Figure 4-4). Each well was purged for ten minutes. Water samples were then drawn to sequentially fill standard 40 mL VOA vials. A blank sample consisting of deionized water was provided to each developer at the beginning and at the end of the analysis run. Two water PE samples were provided to each developer for analysis. Two samples were provided to each participant from each well for duplicate analysis.

WAFB Soil Sampling

Three soil samples were obtained as sub-cores from a sediment boring taken with a two-inch diameter Geoprobe at a location 100 feet south of well FT6, identified as SS-1 in Figure 4-4. On-site photoionization detector readings taken while drilling allowed the core sample to be subdivided into segments having varying levels of VOC contamination. The three segments, 8 to 9, 9 to 10, and 10 to 11 feet below the surface, were each homogenized, split, and placed in vials. All soil samples were weighed using a calibrated balance. The reference laboratory and each developer received splits from the homogenized samples for analysis. Two soil PE samples,

prepared by the Army's Cold Regions Research and Engineering Laboratory in Hanover, New Hampshire were also provided to the participants for analysis.

WAFB Sample Handling, Storage, and Shipping

After the water and soil samples were collected, they were placed in a cooler containing double-bagged ice to maintain an approximate 40°F temperature. The water samples sent to the reference laboratory were preserved with 1 percent sodium bisulfate (NaHSO₄), and placed in an ice-filled cooler for storage and shipment. The soil gas samples for reference laboratory use were transferred to SUMMA™ canisters for shipment to the laboratory. All reference laboratory samples were picked up by the laboratories at the end of each day. All samples collected for on-site analysis during the demonstration were presented to the developers for analysis as soon as practical. Analysis always occurred on the day of sample collection and often within an hour of collection.

Reference Laboratory Selection and Analysis Methodology

One objective of this demonstration was to determine how well each developer's field instrument performed in comparison to conventional laboratory methods and protocols. Standard analytical methods applicable to the sample media and analytes of interest in these demonstrations were selected as the standard of comparison. These include EPA SW-846 Method 8260 *Gas Chromatography/Mass Spectroscopy for Volatile Organics: Capillary Column Technique* for water and soil analyses, and EPA Compendium Method TO-14 *The Determination of Volatile Organic Compounds in Ambient Air Using Summa Passivated Canister Sampling and GC/MS Analysis* for soil gas analyses.

The selection of reference analytical laboratories for this demonstration was based on consideration of several criteria including:

- Certification in one or more states;
- Recommendation from the site manager of prior use;
- Proximity to the site (generally within 3 hours driving time) to minimize sample transport and handling;
- Proven capability to measure VOCs at the required concentration ranges in the appropriate media and in accordance with the selected analytical methodologies as determined from a review of quality assurance (QA)/quality control (QC) data results;
- Proven capability to provide an analytical data package consistent with the requirements of Method 8260 and TO-14 as determined by a review of QA/QC data results; and,
- Passing a pre-demonstration audit by Sandia that included a review of facilities, personnel, QA/QC procedures, protocols, and overall operations.

Based on recommendations from each of the sites, several analytical laboratories were identified for possible use as reference laboratories for the demonstration. Each laboratory identified was asked to provide information on its QA/QC procedures and sample analysis data, using the same methods, for review. Based on a review of this information, discussions with the site managers, and discussions with other users, three laboratories were identified for further evaluation. These were the General Engineering Laboratory, Inc. for the SRS demonstration, and Traverse Analytical Laboratory and Pace Incorporated Environmental Laboratories for the WAFB demonstration.

Further evaluation included a pre-demonstration audit of each of the laboratories. Each pre-demonstration audit included meeting with laboratory personnel; touring the facility; and reviewing laboratory operations, personnel qualifications, and laboratory QC procedures. Chain of custody procedures, sample holding areas and procedures, and analytical equipment operation were also reviewed. During the Traverse pre-demonstration audit, it was determined that soil gas analysis was not routinely conducted at their laboratory and that Traverse

commonly subcontracted soil gas analyses to Pace. Therefore, Pace was considered for soil gas analysis for the WAFB demonstration and was audited in the same manner as GEL and Traverse.

General Engineering Laboratory

General Engineering Laboratory (GEL) is located in Charleston, South Carolina, and is certified in South Carolina, Georgia, Alabama, and Florida. This laboratory is close to the SRS facility and has been used extensively by SRS to analyze environmental site characterization and monitoring samples. GEL provided QA/QC documentation of their operations for review. Based on the results of the pre-demonstration audit, GEL was found to conduct their analyses in accordance with the analytical methods identified for this demonstration and was selected as the reference laboratory for the SRS demonstration. GEL personnel picked up and transported samples daily to their laboratory in Charleston and performed the analyses for all three media. The final data packages provided also included the corresponding QC results.

Traverse Analytical and Pace Environmental Laboratories

Traverse Analytical Laboratory is located in Traverse City, Michigan, and is certified by the state of Wisconsin. Michigan has no laboratory certification program. This laboratory is close to WAFB and had been previously used by WAFB for environmental sample analysis. Traverse provided QA/QC documentation of their operations for review. The pre-demonstration audit by Sandia determined that their analyses were conducted in accordance with the analytical methods identified for this demonstration. Based on these audit results, Traverse was selected as the reference laboratory for soil and water analyses for the WAFB demonstration.

Traverse suggested that Pace in Camarillo, California, conduct the soil gas analyses for the WAFB demonstration. Pace provided QA/QC documentation on their analytical procedures for review. Based on the pre-demonstration audit of the laboratory by Sandia, they were found to conduct their analyses in accordance with the analytical methods identified and were selected as the reference laboratory for soil gas analysis for the WAFB demonstration. Traverse personnel picked up and transported samples daily to their laboratory and conducted the analyses on the water and soil samples. The soil gas samples were shipped from Traverse to Pace for analysis. Both laboratories provided data packages with accompanying QC results.

SRS and WAFB On-Site Laboratories

In addition to the selected reference analytical laboratories, the on-site laboratories at both SRS and WAFB provided rapid analyses to confirm general sample integrity and to ensure that the samples collected contained the expected levels of contamination. Both on-site laboratories use gas chromatograph systems for routine sample analysis. The laboratory analytical methods and corresponding QC protocol were reviewed by Sandia to confirm their use of acceptable laboratory procedures.

Pre-demonstration Sampling and Analysis

Pre-demonstration sampling and analysis were conducted at both demonstration sites to establish that samples from the sites were appropriate for analysis by the GC/MS technologies and that the technology results could be objectively compared to reference laboratory data. The pre-demonstration activities allowed the technology developers an opportunity to refine their systems, revise operating procedures as necessary, and evaluate media effects or interferences that could influence their analytical results. The pre-demonstration sampling events required one field day at each site and took place on June 5, 1995 at SRS and on July 30, 1995 at WAFB. The pre-demonstration samples consisted of one SUMMA[®] canister of soil gas from a medium-concentration soil gas well at each site (CPT-RAM 15 at SRS and SB3 at WAFB), and three water samples from a medium-concentration well (MHT-12C at SRS and FT4S at WAFB). No pre-demonstration soil samples were provided for developer analysis from either site. The soil gas and water samples were split and sent to the developers and the respective reference laboratories for analysis. The reference laboratories used EPA Compendium Method TO-14 for soil gas analysis and EPA SW-846, Method 8260 for water analysis. Unfortunately, the results from these laboratory analyses were not available prior to the SRS demonstration to help guide the technology

developers. The SRS and WAFB pre-demonstration sample analytical results were available to assist the developers prior to the WAFB demonstration. No interpretation or analysis of the analytical results was conducted since these data were intended primarily to assist the developers in refining their operations and procedures for this demonstration.

Deviations from the Demonstration Plan

Several deviations from the demonstration plan occurred as the demonstrations progressed and are discussed below.

Pre-demonstration Activities

The pre-demonstration activities identified in the demonstration plan called for analysis of pre-demonstration samples to allow the technology developers to refine their methodologies, revise operating parameters, and identify matrix effects or interferences. Predemonstration sample analytical results from the reference laboratory were not available prior to the SRS demonstration. Also, no soil samples from either site were provided for evaluation of media effects. The omission of pre-demonstration soil sampling at SRS led to soil sampling problems at SRS during the demonstration.

SRS Soil Spike Samples

A number of deviations occurred in the soil sample preparation procedures used during the SRS demonstration. The demonstration plan deviations were not discovered until the day of the sample analysis. Consequently, new soil spike samples could not be prepared in the allotted time. These deviations in sample preparation were judged to be significant. Consequently, no assessment or comparison can be made between the Bruker GC/MS and the reference laboratory on the results of soil sample analyses.

SRS Soil Gas Survey Evaluation

Of the thirteen soil vapor samples analyzed by GEL, ten were reported as estimated values. In particular, these data were obtained by extrapolation of the calibration curve beyond the normal calibration range of the laboratory instrument used for analysis. This deviation is significant in that no quantitative information on laboratory precision or accuracy can be derived from such data. Consequently, the GEL soil gas data were not used as a reference data set for comparison with the Bruker GC/MS data.

Soil Gas Samples at WAFB

No initial or final analysis of each Tedlar™ bag gas sample was conducted by the field laboratory as called for in the demonstration plan. Therefore, no data are available on the stability of the vapor sample in these bags during the round-robin sampling and analysis by the developers. Based on the results from a similar analysis at SRS where the vapor sample was determined to be very stable, this is not considered a significant deviation.

Condensation was noted by the participants in the Tedlar™ bags from the well samples. It was not possible to determine if this was liquid contaminant or simply water condensation from the samples given that the ambient air temperatures during the morning of the sampling was below the soil temperatures in the sampling well. In either case, the analytical results from these samples could differ as a result of variation in the vapor phase sample constituent concentrations over the sample handling and transfer interval. No determination could be made of the significance of the condensation and its effect on the analytical results.

Appropriate soil gas PE samples could not be obtained from suppliers in time for the WAFB demonstration. Consequently, the number of samples to evaluate laboratory and developer accuracy was limited. To minimize the significance of this deviation, the number of spike samples prepared on-site was increased.

Water Samples at WAFB

The compound 1,4-difluorobenzene was included in the spike mixture used for water samples at WAFB. This compound is normally used as a Method 8260 internal standard by the Traverse reference laboratory. Inclusion of this compound in the spike mixture required the reference laboratory analyst to revert to an external standard method for quantitative measurements of 1,4-difluorobenzene in the spike samples. Reference laboratory data quality was not adversely impacted by use of the external standard method.

Calibration Check Sample Analysis

The demonstration plan called for the participants to run calibration check samples throughout the day in order to facilitate the assessment of instrument stability. Given the intensity of the schedule for analyzing the samples as quickly as they were distributed, periodic analysis of calibration check samples was not completed. The calibration data were not used in evaluating instrument performance, but were only for use by the instrument operator. This deviation was not considered significant.

Section 5

Reference Laboratory Analysis Results and Evaluation

An important objective of this demonstration was to provide the technology developers with a validated data set from conventional laboratory analyses of water, soil, and soil gas samples. Validated laboratory results are essential for direct comparison with the analytical results from the field methods under evaluation. This section describes a number of qualitative and quantitative data quality indicators that were used to evaluate and validate the analytical results from the reference laboratories. Qualitative factors reviewed included adequacy of laboratory QA/QC procedures and deviations from standard procedures. Quantitative factors reviewed included accuracy and precision of the reference laboratories' analyses of reference samples. The laboratories evaluated were the General Engineering Laboratories for the Savannah River Site demonstration, and the Traverse Analytical Laboratory and Pace Inc. Environmental Laboratories for the Wurtsmith demonstration. The on-site SRS laboratory was evaluated to a limited extent as a result of some data limitations encountered with GEL. The National Center for Integrated Bioremediation Research and Development laboratory was used as an on-site screening laboratory and not in a reference capacity at the Wurtsmith demonstration. Consequently, no formal data quality evaluation was done for this laboratory.

Laboratory Operations

General Engineering Laboratories

Prior to the demonstration, GEL provided a quality assurance plan that described laboratory and personnel capabilities, analytical methods, and internal quality control procedures. A complete description of the analytical methods used in the soil, water, and soil gas sample analysis was also included in their plan. The laboratory quality assurance plan was prepared using EPA guidance [U.S. EPA, 1991]. Water and soil analyses were done using EPA SW-846, Method 8260 for purge and trap GC/MS. Soil gas analysis followed EPA Compendium Method TO-14. A number of laboratory performance quality control indicators were provided in the data package including: daily mass spectrometer tuning results, daily calibration check results, daily blank check results, continuing calibration check results, and surrogate compound recovery results.

SRS On-Site Laboratory

The SRS on-site laboratory was intended to provide rapid on-site analysis to assist in determining sample integrity during the demonstration, and was not identified as a reference laboratory in the demonstration plan. Analyses were conducted using a Hewlett Packard 5890 GC with flame ionization and electron capture detectors. Water samples were analyzed using headspace methods, while the soil gas analysis followed EPA Method TO-14. All samples were analyzed on-site the day of the sampling. No formal QA/QC plan was obtained from the SRS laboratory prior to the demonstration. When SRS data were recognized as a possible replacement for GEL data, an informal quality control package was obtained from laboratory personnel that documented the calibration performance of the GC system for several months prior to the demonstration.

Traverse Analytical Laboratory

Prior to the demonstration, Traverse provided a complete quality assurance plan much like that submitted by GEL. Water and soil analyses were conducted using EPA SW-846, Method 8260 for purge and trap GC/MS and samples were analyzed within 14 days of receipt. As a result of equipment limitations, Traverse did not conduct any soil gas analyses. Instead, this activity was subcontracted to Pace Inc. Environmental Laboratories. A number of laboratory performance quality control indicators were provided in the Traverse data package including: mass spectrometer tuning results, daily calibration check results,

blank check results, continuing calibration check results, internal duplicate analysis data, and surrogate recovery analysis data on selected compounds.

Pace Inc. Environmental Laboratories

Pace conducted soil gas analysis for the Wurtsmith demonstration under contract to Traverse. Prior to the demonstration, Pace provided a complete QA package similar to those provided by the other reference laboratories. Complete method descriptions were also given in the QA/QC plan. The analyses were carried out in accordance with EPA Method TO-14. A number of internal laboratory quality control indicators, including blank and internal laboratory gas spike analytical results, were provided in the data package.

WAFB On-Site Laboratory

The on-site laboratory at WAFB is the NCIBRD Field Laboratory. The function of this laboratory was much like that of the on-site SRS laboratory during the SRS demonstration. The laboratory was used primarily for on-site, quick-turnaround analyses to help in the assessment of field sample integrity prior to distribution to the participants. Water analyses were conducted using a Perkin-Elmer gas chromatograph with a Tekmar 2016 purge and trap system following EPA Method 502. Samples were analyzed on-site the day of sample collection. A photoionization detector was used for on-site soil gas screening prior to sample distribution to the participants. Soil sample analysis was not conducted by this laboratory.

Laboratory Compound Detection Limits

Detection limits for various compounds are identified for each EPA method. These limits vary both by compound and sample media type. Each of the data packages provided by the reference laboratories defined practical quantitation limits (PQL) for each media and analyte. The PQL is defined as the level at which instrument noise and method inaccuracies have negligible effects on the accuracy and precision of the analytical results. This value is commonly considered to be about three times higher than the method detection limit. The PQLs for each of the laboratories are presented in Table 5-1. Although the PQLs are analyte and method specific, this table is provided to illustrate the range of PQLs for all target analytes in the three media for each of the four laboratories generating reference data used in this demonstration.

Table 5-1. Reference Laboratory Practical Quantitation Limits.

Laboratory	Media	PQL
GEL	Water	2 • g/L
	Soil Gas	10 ppb
	Soil	100 • g/kg
SRS	Water	2 • g/L
	Soil Gas	10 ppb
	Soil	100 • g/kg
Traverse	Water	1 • g/L
	Soil	100 • g/kg
Pace	Soil Gas	10 ppb

Laboratory Data Quality Assessment Methods

All analytical data are subject to some level of inaccuracy and imprecision. This section discusses the methods used in determining the level of confidence placed in the analytical results from the reference laboratories participating in these demonstrations.

Precision Analysis

Precision is a measure of the degree to which repeated analytical measurements of the same sample agree with one another. In the context of this study, precision is indicative of the random errors associated with the measurement process and is intended to yield a measure of the variability encountered in the normal operation of a laboratory or field instrument. In the absence of any inaccuracy or bias in a measurement, repeated determinations of a given analyte in a single sample will be evenly distributed above and below the analyte's true concentration, and the average of several measurements will be a better estimation of the true value than is any individual measurement. A simple way to express precision for duplicate measurements is *relative percent difference* (RPD), which is defined as follows:

$$RPD = \frac{|x_1 - x_2|}{\bar{x}} \cdot 100$$

where x_1 and x_2 are the duplicate measurements and \bar{x} is the average of x_1 and x_2 . The precision of reference laboratory measurements is assessed by using analytical results from duplicate field, PE, or spike samples. However, caution is warranted where sequential samples, often called duplicates, are drawn from a well. These sequential samples may not be equivalent and care must be taken in their evaluation as duplicates.

The standard methods employed in this demonstration generally call for RPD values of 20% or less as an indicator of acceptable analytical precision. In some sampling media these criteria are relaxed to values as high as 50% for selected compounds. The specific acceptance criteria are discussed in more detail in the sections dealing with the laboratory data evaluation.

Accuracy Analysis

In the context of this demonstration, accuracy is defined as the agreement between the measured concentration of a reference sample and the accepted or "true" concentration of the sample. Bias is a term that is related to accuracy. Bias can be either positive or negative depending on whether the measured values are consistently higher or lower, respectively, than the true value, whereas accuracy is normally given in terms of absolute variation with no reference to positive or negative direction. An observed bias indicates the presence of systematic errors in the measurement process. For example, a calibration error in the setup of an instrument may produce a consistent negative or positive bias in the measurement results. Consistently lower values from a particular method may be indicative of evaporation losses, chemical reactions, biological degradation or other analyte loss mechanisms.

Accuracy is often reported in terms of percent recovery. The analysis result from a sample run on an instrument can be compared with the "true" or "reference" value of the sample and expressed in terms of *percent recovery* (REC). The percent recovery is computed as follows:

$$REC = \frac{x_{instrument}}{x_{reference}} \cdot 100$$

where $x_{instrument}$ is the measured concentration by a field instrument and $x_{reference}$ is the true concentration. The evaluation of accuracy is considerably more difficult than the evaluation of precision since there always exists some uncertainty in the "true" value of the reference material's concentration. While precision can be measured in the absence of information about the true concentrations, accuracy cannot be assessed without some level of confidence in the reference value used in the determination.

The accuracy of reference laboratory measurements is assessed by analyzing two types of reference materials, namely, performance evaluation (PE) samples and media spike samples. PE samples are typically purchased chemical standards with an accompanying certification of the chemical composition of

the sample. In some cases, the PE samples require additional preparation in the field, for example, sample dilution prior to distribution. Media spike samples are prepared by adding known quantities of the pure chemicals of interest to uncontaminated samples of the various media. For these demonstrations, the spike samples were prepared by the on-site laboratories and provided to all participants, including the reference laboratories, for analysis. The quality of the prepared media spikes must always be reviewed carefully because of the potential errors that can occur during their preparation. Since they are prepared in the field, a certificate of analysis is not available to confirm the composition of the sample.

Standard EPA methods such as TO-14 and 8260 indicate that appropriate recovery levels for the compounds of interest in this demonstration should generally be in the range of 80-120%. In some cases, the acceptable recovery level range is extended to 50-150% or greater depending on the nature of the media and the analyte. In most cases, these recovery levels are empirically derived by the laboratory during routine method use and are incorporated into the laboratory's QA plan. The specific acceptance criteria for each laboratory are discussed in more detail in the sections dealing with laboratory data evaluation.

Laboratory Internal Quality Control Metrics

Each of the reference laboratories provided internal quality control data along with their analytical results. These data were used as one of several indicators of laboratory data quality. Specific laboratory internal quality control indicators that were evaluated are discussed below.

Blank Analysis

The results from the analysis of blank samples are used primarily as a measure of instrument contamination and as a secondary check on compound detection limits for the laboratory instruments.

Continuing Calibration Check

A continuing calibration verification procedure uses a calibration solution containing target analytes that is periodically analyzed during a sample batch analysis. The analysis results are recorded as a series of percent recoveries relative to the starting calibration value. The procedure gives an indication of the calibration or accuracy drift of the instrument over time. Control limits of $\pm 25\%$ are normally applied for Method 8260 for water and soil and Method TO-14 for soil gas. Values falling outside these limits are suggestive of inadequate analytical process control and questionable data quality.

Internal Duplicate Analysis

The standard methods for water, soil, and soil gas analysis require periodic duplicate analysis of both standards and field samples. These data provide a measure of laboratory precision, often expressed in terms of RPD, as described earlier. The methods used in this demonstration generally call for RPD values of less than 20% in a specified concentration range. For example, Method TO-14 indicates that the RPD for duplicate measurements must be within 20% only for those compounds detected at a level of 5 times greater than the instrument detection level for the compound of interest. Significant variations in duplicate sample measurements are indicative of inadequate analytical process control and questionable data quality.

Laboratory Data Quality Levels

Each of the reference laboratories data were evaluated and assigned one of three levels of data quality based on laboratory internal quality control, accuracy, and precision results. This ranking method identifies those laboratory data that do not meet commonly accepted data quality criteria and therefore are unsuitable or inappropriate for comparison with field technology data. The data quality levels are further described below:

Good Data Quality

- Good laboratory internal quality control⁵ results (e.g., internal blanks, duplicates, continuous calibration, and control samples);
- Analytical accuracy results, based on external (supplied by the project) PE and spike samples, consistently within $\pm 30\%$ of the reference concentrations; and,
- Analytical precision results, as determined by RPD on duplicate samples, consistently less than 30%.

Satisfactory Data Quality

- Satisfactory laboratory internal quality control⁶ results;
- Analytical accuracy results, based on PE and spike samples, consistently within $\pm 50\%$ of the references concentrations; and,
- Analytical precision results, as determined by RPD on duplicate samples, consistently less than 50%.

Unacceptable Data Quality

- Poor or missing internal quality control results; or
- Analytical accuracy results, based on PE and spike samples, consistently exceeding $\pm 50\%$ of the reference concentrations; or,
- Analytical precision results, as determined by RPD on duplicate samples, consistently exceeding 50%.

Laboratory Data Validation for the SRS Demonstration

GEL Data Quality Evaluation

GEL QA/QC procedures were audited by Sandia personnel prior to the demonstration and were found to be operating in accordance with accepted good laboratory practice and the requirements outlined in the standard methods used in analysis of these demonstration samples. GEL analyzed all three sample media types from the SRS demonstration and provided a quality control data package with their analysis results. These results and a discussion of the analytical data are presented below.

Two out-of-limit conditions were identified in the quality control data package sent along with the analysis results. Eight water samples were flagged as missing the maximum holding time by one day. This occurrence was judged not to have significant impact on data quality. Also, ten of thirteen soil gas sample analyses were reported as estimated values since they were outside the calibration range for the species of interest. These reported values were judged to be of unacceptable data quality as further discussed below.

⁵ Good internal lab quality control indicates that a complete QC package was received with the sample analysis data and that the QC data were within method or laboratory guidelines.

⁶ Satisfactory internal lab quality control indicates that an incomplete QC package was received with the sample analysis data but that the available QC data were within method or laboratory guidelines.

GEL Internal Quality Control Data

The quality control data package revealed that the GEL GC/MS passed daily calibration and internal blank checks during analysis of SRS samples. Surrogate chemical spikes were used for all seven soil samples analyzed and recoveries were within the 80-120% range prescribed by Method 8260. Internal laboratory duplicates of soil and water spikes gave RPD values that were less than 20%. Overall, the internal quality control data reveal good laboratory procedures and results.

GEL Accuracy Data

The accuracy results for GEL are presented in Table 5-2 and derived from the analysis of spike and PE samples containing TCE and PCE. EPA Method 8260 calls for empirical derivation of acceptable compound recovery ranges by each lab as they routinely conduct analyses.

Table 5-2. GEL Laboratory Accuracy Data.

Sample Media/Description	Reference Concentration in • g/L		Percent Recovery	
	PCE	TCE	PCE	TCE
Water Low Spike	2.7	2.6	116	220
Water Medium Spike	40.4	38.3	106	210
Water High Spike	270	256	130	276
Water PE Sample 1	NP	NP	-	-
Water PE Sample 2	19.8	46	127	128

Notes: NP = Not Present, TCE or PCE not present in sample

The GEL water analyses results reveal percent recoveries for PCE for all samples within the acceptable range of 64-148% as provided in GEL's implementation of Method 8260 in their QA plan. However, the spike recoveries for TCE in water are in excess of 200%. Recovery limits for TCE, stated in GEL's implementation of Method 8260, are 71-157%. On the other hand, the TCE recovery values for PE Sample No. 2 is within prescribed limits. The result for the PE sample is given precedence over the results from the spike samples since the water spikes were prepared in the field by SRS laboratory personnel and their reference values were not independently certified.

As noted previously in Section 4, problems were encountered in soil spike preparation at the SRS demonstration and the overall quality of the spikes was judged to be unacceptable as reference material.

No accuracy determinations were made for the soil gas samples because all the analytical values reported by GEL were estimates.

GEL Precision Data

The precision analysis results for GEL are presented in Table 5-3 and are based on the results of duplicate sample analyses.

Table 5-3. GEL Laboratory Precision Data.

Sample Media/Description	Reference Concentration in • g/L		Relative Percent Difference	
	PCE	TCE	PCE	TCE
Water Low	10	60	3	22
Water Medium	150	160	2	5
Water High	12,200	6,000	5	2

Precision results for the water duplicate samples show good precision for both PCE and TCE for all three samples. Precision results for the soil gas duplicate samples could not be evaluated since all the reported values were estimated.

GEL Data Quality Summary

The soil gas analysis results from GEL indicate that this data set is unsuitable for comparison with the field technology results. The soil gas analyses are unacceptable because the sample analysis values were estimated values only and cannot be used for comparisons with the field technologies. The precision data for the water analyses were judged to be good. The accuracy data for the water analyses were also good if the recovery data for the TCE spike samples are discounted. The general data quality for the GEL water analyses was considered good and suitable for comparison with the different technologies.

SRS On-Site Laboratory Data Quality Evaluation

As noted previously, the SRS Laboratory analyzed soil, water, and soil gas samples during the SRS demonstration; however, their data were not originally intended for reference use. Because of the semi-quantitative nature of the GEL soil gas data, the SRS on-site soil gas data were evaluated as a possible replacement. A post-demonstration evaluation of their soil gas data and accompanying quality control data was carried out in the hope that the SRS laboratory data were of sufficient quality for comparison with field technology results.

SRS Internal Quality Control Data

The SRS Laboratory Hewlett-Packard Model 5890 gas chromatograph, equipped with dual flame ionization and electron capture detectors, was calibrated daily and internal blank checks showed acceptable performance in terms of detection levels and instrument contamination. The SRS Laboratory also provided a record of calibrations performed on their system for seven chlorinated compounds. These data give an indication of the day-to-day variability of the GC system. Multiple analyses of standard solutions gave relative standard deviations in the range of 2 to 11% for high (1,000 ppm) vapor concentrations; in the range of 5 to 9% for medium (100 ppm) concentrations, and in the range of 6 to 11% for low (10 ppm) concentrations. These data indicate that the SRS GC system meets the 30% precision criteria, indicating good overall quality control procedures and instrument performance.

SRS Accuracy Data

The accuracy data for the SRS Laboratory soil gas analyses are summarized in Table 5-4. The results are based on the laboratory analyses of TCE and PCE spike and PE samples.

Table 5-4. SRS Laboratory Accuracy Data.

Sample Media/Description	Reference Concentration in ppm		Percent Recovery	
	PCE	TCE	PCE	TCE
Soil Gas Low Spike	1.18	1.34	56	78
Soil Gas Medium Spike	118	134	76	77
Soil Gas High Spike	1,182	1,340	99	91
Soil Gas PE Sample 1	1	1.1	61	91
Soil Gas PE Sample 2	93	98	94	95

Accuracy results for the SRS Laboratory soil gas sample analyses show that of the ten analyses conducted, all but two fall within the accepted limits of 75-125% specified in method TO-14, while all of the results are within $\pm 50\%$. Low recovery results are observed for the spike samples nearer the 10 ppm instrument PQL. The SRS Laboratory GC-flame ionization detector data were used for this evaluation since this

system was best suited for analysis of the medium and high level spike and PE sample concentrations. Although the recoveries for these samples are consistently low, they generally indicate satisfactory performance for both PCE and TCE over this wide concentration range.

SRS Precision Data

The soil gas precision data for the SRS Laboratory are presented in Table 5-5. The precision analysis of the soil gas data shows RPD values less than 30% for PCE and TCE at all three concentration levels. This indicates that the performance of the laboratory was good and these data can be used in the verification.

Table 5-5. SRS Laboratory Precision Data.

Sample Media/Description	Reference Concentration in ppm		Relative Percent Difference	
	PCE	TCE	PCE	TCE
Soil Gas Low	1	0.1	8	<1
Soil Gas Medium	80	100	3	3
Soil Gas High	250	500	1	3

SRS Laboratory Data Quality Summary

The accuracy and precision results for the soil gas samples consistently fall within 30% of the reference values. Overall, the soil gas analyses results reveal satisfactory data quality, and are a suitable replacement for the GEL soil gas data.

Laboratory Data Validation for the WAFB Demonstration

At least 15 VOC contaminants are known to exist at the WAFB demonstration site. Typical concentration levels of these major contaminants in soil, water, and gas media were provided to the developers in the demonstration plan [SNL, 1995]. As stated in Section 4, the contaminants at the WAFB Site include BTEX, chlorinated hydrocarbons, and other organics. High background levels of petroleum hydrocarbons (jet fuel) are encountered as well. Based on the information in the demonstration plan and the pre-demonstration activities, each developer chose at least ten of the identified contaminants for analysis. Not all the target contaminants were detected in all of the samples collected and not all of the developers chose to analyze the same contaminants. Therefore, the data quality evaluation of the analytical laboratories participating in the WAFB demonstration were based on the analytical results from five compounds that were analyzed by each of the laboratories and the field technologies. The compounds used for evaluation were benzene, toluene, total xylenes, PCE, and TCE. In a few cases, dichloroethene (DCE) was also included where TCE or PCE was not detected.

Traverse Data Quality Evaluation

The laboratory QA/QC plan had been audited by Sandia prior to the demonstration. Laboratory operations were found to be in accordance with good laboratory practice guidelines and the requirements stated in the various standard methods used in the analysis of samples.

Traverse Analytical Laboratory analyzed soil and water samples from the WAFB demonstration and provided Sandia with complete analysis results and accompanying quality control data package. A complete description of the analytical methods used in the analysis was also included in the quality control package. No out-of-limit quality control conditions were reported in the data package. The internal quality control results and a discussion of the analytical data with respect to accuracy and precision are presented below.

Traverse Internal Quality Control Data

Daily quality control results for the GC/MS instrument used for the sample analyses included mass spectrometer tuning, blank checks, and initial and continuing calibration checks. The quality control results reveal good instrument performance throughout the course of the WAFB demonstration sample analyses. Surrogate chemical spikes were also used for all seven soil samples analyzed and surrogate chemical recoveries were within the 80-120% that is considered acceptable according to Method 8260. Internal laboratory duplicates of selected soil and water spike samples also met the RPD criteria of less than 20%. Overall, the internal quality control results indicate good quality control and instrument performance during the analyses.

Traverse Accuracy Data

The accuracy data for Traverse is presented in Table 5-6 and is based on the results of spike recoveries and PE sample recoveries of the five target analytes for the soil and water media analyzed. Table 5-7 provides the reference concentration levels for each of these analytes.

Table 5-6. Traverse Laboratory Accuracy Data.

Sample Media/ Description	Percent Recovery				
	Benzene	Toluene	Xylenes	PCE	TCE
Soil PE No. 1	89	98	87	154	85
Soil PE No. 2	66	71	65	102	62
Water Low Spike	97	95	112	105	120
Water Medium Spike	119	93	106	96	84
Water High Spike	76	79	81	75	70
Water PE Sample 1	78	NA	101	NA	NA
Water PE Sample 2	81	89	101	76	85

Note: NA = not analyzed; analyte not present in sample

The percent recoveries for eight out of ten soil analyses fall within accepted recovery levels of 65-135%, as given in the Traverse QA documentation. On the basis of these results, overall laboratory accuracy performance is judged to be good. Likewise, the percent recoveries for the water analyses reveal recoveries for the five target analytes, over a wide range of concentrations, well within the laboratory's acceptance limits for all 22 analyses.

Table 5-7. WAFB Water and Soil PE/Spike Sample Reference Concentrations.

Sample Media/ Description	Reference Concentrations				
	Benzene	Toluene	Xylenes	PCE	TCE
Soil PE No. 1 (• g/kg)	61,000	55,000	76,000	91,000	7,900
Soil PE No. 2 (• g/kg)	64,000	59,000	81,000	98,000	8,600
Water Low Spike (• g/L)	59	45	190	63	27
Water Medium Spike (• g/L)	1,180	904	3,790	1,256	715
Water High Spike (• g/L)	66,140	50,620	212,300	70,340	40,040
Water PE Sample 1 (• g/L)	66	NP	158	NP	NP
Water PE Sample 2 (• g/L)	20	20	50	20	46

Note: NP = not present in sample

Traverse Precision Data

The precision data for Traverse is presented in Table 5-8 and is based on the results of duplicate and in some cases triplicate analysis of the analytes in the two media. Table 5-9 shows the reference concentration levels for each of the target analytes evaluated.

Table 5-8. Traverse Laboratory Precision Data.

Sample Media/ Description	Relative Percent Difference				
	Benzene	Toluene	Xylenes	PCE	TCE
Soil PE No. 1	16	8	6	7	6
Soil PE No. 2	<1	9	8	9	8
Soil Low	*	*	*	*	*
Soil Medium	*	*	122	*	*
Soil High	*	13	14	*	*
Water Low	<1	*	<1	<1	*
Water Medium	7	11	8	*	*
Water High	9	*	22	*	*

Note: * = No evaluation as a result of non-detectable levels in one or more samples

Table 5-9. WAFB Water and Soil Duplicate Sample Concentrations.

Sample Media/ Description	Reference Concentrations				
	Benzene	Toluene	Xylenes	PCE	TCE
Soil PE Sample No. 1 (• g/kg)	61,000	55,000	76,000	91,000	7,900
Soil PE Sample No. 2 (• g/kg)	64,000	59,000	81,000	98,000	8,600
Soil Low (• g/kg)	ND	ND	ND	ND	ND
Soil Medium (• g/kg)	ND	ND	5,000	ND	ND
Soil High (• g/kg)	ND	600	55,000	ND	ND
Water Low (• g/L)	2	ND	20	2	ND
Water Medium (• g/L)	40	35	385	ND	ND
Water High (• g/L)	20	2	50	ND	ND

Note: ND = not detected

A number of non-detects were reported for the five target analytes in the soil duplicate samples. Since the soil samples were prepared in triplicate, the RPD values shown are an average of the two or three RPD values. For the available data, except for one high xylene RPD value, the RPD results for the soil analyses are less than 30%.

Low RPD values were observed for the eight water samples that could be evaluated. Unfortunately, most of the samples had non-detectable levels of TCE and PCE and could not be evaluated in terms of precision. Overall, the observed precision for the water samples, where precision determinations were possible, was less than 30% and judged to be good.

Traverse Laboratory Data Quality Summary

The Traverse internal quality control results revealed good laboratory procedures and instrument performance. Accuracy and precision data for the water samples are consistently at values of 30% or less. On the basis of these considerations, the Traverse water data set was judged to be of good quality and suitable for use as reference data. Likewise, the soil accuracy and precision analysis data also are consistently (with one exception concerning the precision of a xylene analysis) within 30% of the reference values; however, evaluations were carried out only at relatively high (>1 mg/kg) compound concentration levels. These data are judged to be of good quality and suitable for reference use, with the caution that soil matrix precision and accuracy are not determined at lower concentrations ranges.

Pace Data Quality Evaluation

The Pace QA plan was audited by Sandia personnel prior to the demonstration. Laboratory operations were found to be in accordance with good laboratory practice guidelines and the requirements stated in EPA Method TO-14.

As noted earlier, Pace analyzed soil gas samples from the WAFB demonstration and provided analysis results and a quality control data package. The results and a discussion of the analytical data are provided below. No out-of-limit quality control conditions were reported in the analysis results data package. As with Traverse, the assessment of precision and accuracy of the analytical laboratory are considered using the data from the five target compounds. Because the results for the soil gas analyses for both PCE and TCE generally showed non-detects, another chlorinated solvent that was detected in the analysis, DCE, was included in the soil gas accuracy and precision analyses.

Pace Internal Quality Control Data

Blank soil gas samples were analyzed in the laboratory and the results were in accordance with performance specified in the TO-14 method. Spiked vapor samples were also run on two different days. Calibration check recoveries for the five target compounds ranged from a low of 94% to a high of 110%, all within the 75-125% acceptance criteria called for in Method TO-14. The quality control data provided in the analysis report indicated good instrument performance.

Pace Accuracy Data

The accuracy data for Pace analysis of Summa™ canisters are presented in Table 5-10 and is based on the results of spike recoveries of the target analytes. Table 5-11 provides the associated reference concentration values for the compounds evaluated. Data from Tedlar bag samples are not included in the analyses since the TO-14 method requires the use of passivated steel canisters for better sample stability and recovery.

Table 5-10. Pace Laboratory Accuracy Data.

Sample Media/ Description	Percent Recovery					
	Benzene	Toluene	Xylenes	PCE	TCE	DCE
Soil Gas Low Spike ¹	112	96	88	107	61	95
Soil Gas Medium Spike	93	NA	82	NA	48	65
Soil Gas High Spike	44	NA	43	NA	20	32

Note: ¹ - recovery values shown corrected by a factor of ten, see text for discussion.
 NA = not analyzed, contaminants not present in spike mixture

Table 5-11. WAFB Soil Gas PE/Spike Sample Reference Concentrations.

Sample Media/ Description	Reference Concentrations in ppm					
	Benzene	Toluene	Xylene	PCE	TCE	DCE
Soil Gas Low Spike ¹	3	2	8	1	1	2
Soil Gas Medium Spike	50	NA	73	NA	50	58
Soil Gas High Spike	250	NA	364	NA	250	291

Note: ¹ - reference values shown corrected by factor of 10, see text for further discussion
 NA = Not applicable; analyte not present in spike mixture

Initial evaluation of the low spike sample recoveries yielded values in the range of 1,000% and were suggestive of a factor of ten error. A calculation error in computation of the reference values was suspected; however, a definite error was not found. Some uncertainty exists, as recorded in laboratory notebooks, as to whether the air volume into which the spike was injected was 1 or 10 liters. A review of the data from each of the field participants showed a similar very high recovery trend, giving further support for the factor of ten error. In view of these combined results, the low spike reference value was increased by a factor of ten as shown in Table 5-11 with resultant changes in Table 5-10. Compound

recovery for Pace is marginal with satisfactory recovery at the low and medium ranges and poor recovery at higher concentration ranges. Recovery is also generally better for non-chlorinated compounds than for chlorinated compounds.

The soil gas spikes were transferred from bags to canisters prior to shipment to the Pace. These transfers, as well as dilution required for the high spike sample analysis, may have caused significant changes in the sample composition. Previous WAFB soil gas survey results presented in Table 4-3 show that the concentration ranges of interest at this demonstration site are generally less than 100 ppm for most VOC compounds. As noted in Table 5-10, recovery data for Pace at contaminant concentration levels less than 100 ppm are generally good. Since the field sample concentration levels are reasonably well matched to the concentration levels at which Pace performance is satisfactory, the laboratory results are considered suitable as reference data for soil gas contaminant concentrations less than 100 ppm.

Pace Precision Data

The soil gas samples used for this analysis were taken sequentially over approximately a two minute period from the monitoring well at each of the three levels selected for sampling. As stated previously, these sequential samples may not be true duplicate samples. As with the other field duplicates taken sequentially from monitoring wells during this demonstration, an assumption is made for the purposes of the precision evaluation that the sequential samples are equivalent. Calculation of RPD values based on these samples then gives an upper limit of the laboratory instrument RPD since some portion of the RPD could be attributable to sample differences. Precision determinations, based on these assumptions for the Pace soil gas analyses, are given in Table 5-12, while Table 5-13 provides the reference concentration levels for the soil gas samples.

The precision data in Table 5-12 show that eight of 11 values fall within 30% margin. Nine of the 11 RPD values fall within the 0-50% range. On the basis of these data, Pace precision performance is judged to be satisfactory.

Table 5-12. Pace Laboratory Precision Data.

Sample Media/Description	Relative Percent Difference					
	Benzene	Toluene	Xylenes	PCE	TCE	DCE
Soil Gas Low	76	NA	66	NA	NA	47
Soil Gas Medium	9	22	5	NA	NA	9
Soil Gas High	3	12	7	NA	NA	7

Note: NA = Not analyzed, contaminant not detected in one or both samples

Table 5-13. WAFB Soil Gas Duplicate Sample Concentrations.

Sample Media/Description	Reference Concentrations in ppm					
	Benzene	Toluene	Xylenes	PCE	TCE	DCE
Soil Gas Low	2	0.1	20	ND	ND	8
Soil Gas Medium	7	0.5	30	ND	ND	10
Soil Gas High	9	1	50	ND	ND	13

Note: ND = not detected

Pace Data Quality Summary

Based on the accuracy and precision results and the concentration ranges shown in Tables 5-11 and 5-13, the Pace soil gas analysis data quality can be regarded as satisfactory for soil gas contaminant concentration ranges between 1 and 100 ppm and are suitable for comparison with the various technologies only within this range.

Summary Description of Laboratory Data Quality

The data quality from each of the laboratory analyses was systematically evaluated for each of the three sampling media selected for study in this demonstration. The results of these evaluations have been previously discussed in detail and are summarized in Table 5-14 for the SRS demonstration and Table 5-15 for the WAFB demonstration. Because of the number of laboratories, evaluation criteria, and media, as previously discussed, an overall data quality grade of *good*, *satisfactory*, or *unacceptable* has been assigned to each of the reference laboratory data sets. Data sets falling into the good or satisfactory categories are considered suitable for comparison with field technologies. An unacceptable data quality ranking indicates that these data are unsuitable for use as reference data.

For SRS each sample media type except soil was determined to have a satisfactory or better reference data set. The data quality for the WAFB demonstration was determined to have a satisfactory or better reference data set for comparison to field analytical results.

Table 5-14. SRS Demonstration Laboratory Data Quality Ranking.

Sample Media	Laboratory	
	GEL	SRS
Soil	No Determination	No Determination
Water	Good	No Determination
Soil Gas	Unacceptable	Satisfactory

Table 5-15. WAFB Demonstration Laboratory Data Quality Ranking.

Sample Media	Laboratory	
	Traverse	Pace
Soil	Good	No Determination
Water	Good	No Determination
Soil Gas	No Determination	Satisfactory

Section 6

Technology Demonstration Results and Evaluation

Introduction

Analytical results and an evaluation of the Bruker GC/MS data collected during the SRS and WAFB demonstrations are presented in this section. Both demonstrations provided an opportunity for analysis of soil, water, and soil gas media by the Bruker GC/MS system. Data from the Bruker GC/MS system are compared to the previously discussed reference laboratory data. Following presentation of the Bruker sample analysis data, instrument performance is assessed using a number of performance goals also described in this section.

Pre-Demonstration Developer Claims

Before the actual field demonstration, the Consortium requested GC/MS instrument performance claims from Bruker. The performance claims provided by Bruker were, to a limited extent, discussed with the Consortium; however, they were not significantly altered prior to their inclusion in the demonstration plan. Since this was a pilot demonstration, the various proposed methodologies for field instrument comparison with reference laboratories were largely unproved. Consequently, the claims made by the developer, although loosely defined at the outset, were accepted with the expectation that specific performance evaluation goals would be developed as experience was gained carrying out the demonstration and the subsequent data analysis. The initial claims made by Bruker for the GC/MS system taken from the demonstration plan prepared prior to the field demonstrations [SNL, 1995] are as follows:

- **Accuracy:** GC/MS data within $\pm 35\%$ of reference laboratory values for soil, water, and soil gas analyses.
- **Precision:** GC/MS relative percent differences less than 30% for water and soil gas analyses; less than 35% for soil analyses.
- **Completeness:** For all samples analyzed, 95% of target VOC compounds detected by reference laboratory also detected by GC/MS system.
- **Sample throughput:** Water and Soil Gas: 8-10 min/sample, 6 sample/hour; Soil: 7-9 min/sample, 7-8 sample/hour.
- **Methodology:** Soil via headspace analysis; Water via spray and trap accessory; Soil gas via sorbent trapping/thermal desorption.
- **Reported Data:** Quantitative results submitted at the end of each run.
- **Deployment:** The GC/MS system can be set up and ready for sample runs within 60 minutes.

The performance claims stated above address the critical areas of instrument performance and provide a framework to evaluate the capabilities and utility of the technology. However, the claims as stated do not take such issues as statistical variation in the reference laboratory and the field technology data into consideration. An evaluation based solely on these claims may not fairly evaluate technology performance. For example, the following questions illustrate problems that can arise when considering the above claims:

- Is the instrument accuracy or precision claim considered met if one or two outliers or extreme values do not meet the claim?
- Should reference laboratory data be used for comparison with technology data if significant inaccuracies are encountered in the reference laboratory data?

As a result of these considerations, the original developer claims were used as a basis in formulating more specific performance goals such that instrument performance could be more fairly evaluated. The performance goals incorporated a consideration of the statistical characteristics of the reference laboratory and technology measurements, rather than simply evaluating individual measurements. This approach serves to decrease the effect of an occasional outlier data point on the overall evaluation of the technology or the reference laboratory. The rationale and approach used in setting the performance goals for each of the identified criteria, such as accuracy and precision, generally follows that stated in EPA Method 8260 for water and soil analyses. The development of these performance goals and evaluation criteria are discussed in further detail in the following sections.

Field Demonstration Data Evaluation Approach

A discussion of the methodology and its underlying rationale used for Bruker instrument performance assessment is given in the following paragraphs. The methodology is based on instrument performance in three specific areas: precision, accuracy, and comparability of Bruker data to reference laboratory data. The evaluation methodology uses instrument performance claims made by Bruker as a starting point in the formulation of specific instrument performance goals.

One of the limitations encountered in this particular study is the existence of a limited number of data points for each target analyte in the sample media. For example, analysis of water samples for dichlorobenzene at the Wurtsmith demonstration by Bruker and the reference laboratory produced only five sample pairs that could be compared. A small sample size of five pairs significantly limits the ability to draw conclusions about the performance of the Bruker instrument for this particular compound. One method of dealing with small sample sizes and their associated uncertainties is to pool the data for all analytes in a particular sampling medium and apply statistical techniques to the pooled data set in order to gain an understanding of the overall performance of a field instrument relative to reference data. Many of the factors contributing to measurement uncertainty are random and thus tend to average out when many analysis results are considered together. However, in pooling these data, the assumption must be made that the GC/MS responds to the various target compounds in a similar fashion. As an example, the instrument accuracy and precision for benzene is not assumed to be significantly different than its accuracy and precision for trichloroethene. This is a reasonable assumption for the compounds under investigation in this study. All of the target compounds were either aliphatic or aromatic compounds with a subset of these being chlorinated species with similar chromatographic and detection properties. Compounds with significantly different chromatographic properties, such as alcohols, ethers, ketones, etc., which have different GC/MS response characteristics, were not included in the target analyte list.

Instrument Precision Evaluation

The precision of the field instrument is obtained by the analysis of duplicate samples and is based on the percent difference between the two analytical results. The definition for *relative percent difference* (RPD) is as follows:

$$RPD = \frac{|x_1 - x_2|}{\bar{x}} \cdot 100$$

where x_1 and x_2 are duplicate measurements and \bar{x} is the average of the two measurements. Precision provides a measure of the stability of the instrument under actual field operations and is one of the key indicators of instrument performance. The overall precision claim made by Bruker was that RPD values of 30% or less would be achieved for water and soil gas and less than 35% for soil. Refinement of these claims into more specific performance goals was done following the demonstration in order to incorporate statistical considerations of the data. For a first test, the Bruker RPD data are pooled by sampling media and a determination is made as to whether the median value of the distribution falls in the respective range.

This first precision performance criterion is consistent with that specified in Methods 8260⁷ and TO-14. If this first test criteria is not met, a second evaluation is done. In the second test, the determination is made as to whether the median Bruker RPD value is less than or equal to the 95th percentile of RPD values similarly pooled from the reference laboratory data. The underlying rationale is that Bruker precision is adequate if it is comparable to that observed in the reference laboratory data in this demonstration. Thus, if either precision criteria are met, Bruker precision performance is judged acceptable.

Instrument Accuracy Evaluation

Instrument data accuracy is evaluated by comparing the Bruker GC/MS analysis results from PE and spike samples with known VOC contaminant levels. The spike samples were prepared in the field in soil, water, and gas media from pure compounds or known mixtures. Performance evaluation samples, on the other hand, were purchased or obtained from independent vendors and had undergone extensive analysis by multiple laboratories. They were accompanied by a certificate of analysis in which the concentration levels of the sample components were specified. Often an uncertainty or confidence interval, based upon the multiple laboratory results, was also provided. One way of expressing instrument accuracy, relative to the reference concentration of the PE or spike sample, is by the use of the term *percent recovery* (REC), as described below:

$$REC = \frac{x_{instrument}}{x_{reference}} \cdot 100$$

where $x_{instrument}$ is the measured concentration by a field instrument and $x_{reference}$ is the true concentration. For example, if the benzene content in a PE sample was 100 ppm and the field instrument analytical result was 110 ppm, the percent recovery would be 110%. The *absolute percent accuracy* (APA), also used in these evaluations, is defined as follows:

$$APA = |REC - 100|$$

Acceptable limits of recovery are empirically derived by a particular laboratory during routine use of Methods 8260 and TO-14. Consequently, they vary somewhat among laboratories and compounds. However, recovery values falling within the range of 70 - 130% are considered acceptable in terms of instrument and method quality control [EPA, 1987]. Recoveries that fall outside this range may still be acceptable for some compounds and must be evaluated on an individual compound and laboratory basis.

Initial Bruker claims regarding accuracy were made only in the context of reference laboratory data. Strictly speaking, accuracy assessments should only be made against samples for which a true or certified value is available. Reference laboratory results do not necessarily represent the true VOC contaminant content of the samples. Bruker accuracy performance goals are stated in the context of Bruker and reference laboratory analytical results on PE and spike samples for which reference values were available. They are much like those developed for precision assessment, in the sense that they also include statistical considerations. As with RPD, the absolute percent accuracy values for Bruker are pooled by sampling medium. An initial determination is then made as to whether the median APA value is less than 35%. This initial test criteria closely follows that specified in Methods 8260 and TO-14 for the precision evaluation. For example, Method 8260 specifies that the APA should be less than 30% for most compounds covered by the method. A second evaluation is done if the first criterion is not met. In this test, a determination is

⁷ Paragraph 8.5.5 of Method 8260 states in part: "Results are comparable if the calculated percent relative standard deviation (RSD) does not exceed 2.6 times the single laboratory RSD or 20% whichever is greater and the mean recovery lies within the interval $R \pm 3S$ or $R \pm 30\%$, whichever is greater."

made as to whether the median Bruker APA value is less than or equal to the 95th percentile of APA values similarly pooled from the reference laboratory data. As with the precision assessment, the understanding is that Bruker accuracy should be judged acceptable as long as it is comparable to that observed in the reference laboratory data in this demonstration. Thus, if either criteria are met, Bruker accuracy performance is judged acceptable.

Instrument Comparison with Reference Laboratory Data

A third approach for evaluation of Bruker GC/MS instrument performance entails a comparison of Bruker results with reference laboratory results for paired sample analyses. As described in Section 5, the reference laboratory data were ranked *good*, *satisfactory* and *poor* in terms of overall quality. Only those laboratory results that were ranked good or satisfactory were used for comparison with the field instrument data.

To varying degrees, reference laboratory analytical results possess inaccuracies and uncertainties--a fact which complicates comparisons between laboratory and field instrument data. Uncertainties in analytical results are caused by factors such as sample transport and storage, improper instrument calibration, operator technique, instrument noise, to name a few. Even in cases where sample transportation and storage operations are performed correctly, the sample that reaches the fixed-laboratory analytical instrument may be different in chemical composition from that analyzed by the field instrument because of unavoidable heterogeneities in the sample matrix.

The Bruker to laboratory comparison takes these uncertainties into account by computing the percent difference between the Bruker and reference laboratory results for each duplicate sample pair and examining the distribution of these percent differences for each sample media relative to an absolute accuracy standard--in this case $\pm 50\%$. The *percent difference* (DIF) for each sample pair is mathematically expressed as follows:

$$DIF = \frac{[x_{instrument} - x_{lab}]}{x_{lab}} \cdot 100$$

where $x_{instrument}$ is the measured concentration by the field instrument and x_{lab} is the measured concentration of the same sample by the reference laboratory. The absolute percent difference (APD) ignores the sign of the percent difference value. For this demonstration, the absolute percent difference criterion was set at 50%. Methods 8260 and TO-14 typically specify $\pm 30\%$ as a tolerable range for percent differences of an instrument relative to a PE or spike reference value; however, the reference value (the laboratory result) also has inherent inaccuracy. Consequently the $\pm 30\%$ margin is widened to $\pm 50\%$ to account for this variability. The Bruker to laboratory comparison performance goal stipulates that the median absolute percent difference of the distribution for each sampling media should be in the range of 0-50%. Failure to meet this goal suggests that a significant bias between the Bruker system and the laboratory may exist. An additional bias significance test is performed as described more fully below.

Where a large bias is suspected between the field method and reference laboratory, a statistical technique known as the Wilcoxon Matched Pair test was used to assess the differences encountered between field technology and laboratory data. Both laboratory and field method data include measurement uncertainty as a result of random variability encountered in the sample collection, distribution, and analysis process. A statistical comparison was carried out to determine whether the range of differences encountered between the two methods could be explained by random variability or, alternatively, whether a significant or true bias exists between the two methods. The Wilcoxon Matched Pairs test is a non-parametric test, meaning that no assumptions are made concerning the distribution of the population from which the field instrument and reference laboratory samples are drawn [Iman, 1994; Conover, 1980]. The test produces a test statistic which can be interpreted as the ratio of *observed differences* in the two data sets to expected *random*

differences in the same two data sets. Thus, in very general terms, a large test statistic indicates a significant difference between two instruments or methods. The Wilcoxon test statistic is influenced to a greater extent by the larger values in the data sets being compared, particularly when the data span many orders of magnitude such as encountered in this study. In order to eliminate this undesired effect, the data pairs were normalized by using the percent difference determination for each sample pair, as described earlier. The percent difference computed for each Bruker measurement relative to the paired sample laboratory value is compared against a reference percent difference value of zero in the statistical test.

The quantitative aspect of the Wilcoxon test is given by the p-value, or probability, associated with a computed test statistic. For example, a test result with a p-value of 0.05 indicates that the probability of two equivalent techniques producing the observed differences as a result of random variability alone would be 0.05. By convention, a p-value of 0.05 is often used as the decision point as to whether a statistically significant bias exists between the two sets of measurements. A p-value less than 0.05 is generally understood to indicate differences between two methods that cannot be explained by random variation alone. On the other hand, p-values greater than 0.05, indicate that observed differences between two methods can be explained by random variation alone and that the methods can be considered comparable.

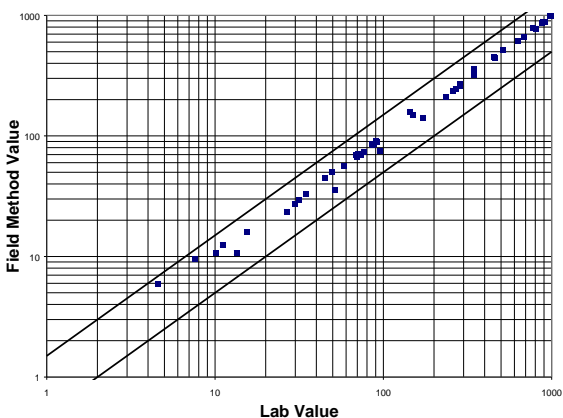
The outcome of the Wilcoxon test is used to make a final decision as to whether one is justified in calling the Bruker field measurements comparable or not comparable to reference laboratory measurement. A Wilcoxon test result with a p-value less than 0.05 indicates that Bruker data are not comparable to reference laboratory data for a particular sampling medium.

In summary then, two criteria are used for assessing Bruker to laboratory accuracy. First a determination is made as to whether the median absolute percent difference is in the range of 0-50%. If this criteria is not met, the Wilcoxon test is performed on the data set to test the significance of the observed bias. If the test result indicates significance, the overall Bruker to laboratory comparison goal is judged not met. Alternatively, if the test indicates no significance, the goal is judged to have been met.

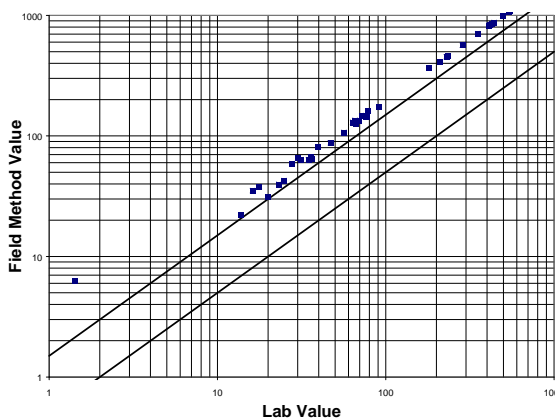
Scatter Plots

Another way to evaluate the performance of the of the Bruker GC/MS with respect to the reference laboratory is through the use of scatter plots. The plots are prepared in log-log format since the data concentrations generally spanned many orders of magnitude. Two solid lines are positioned on each graph which mark the $\pm 50\%$ difference about the zero bias line. As noted in earlier discussion, the $\pm 50\%$ margins are chosen as an indicator of acceptable instrument performance relative to reference laboratory data. The value is derived as follows: If the assumption is made that the uncertainty on field technology and laboratory measurements is $\pm 20\%$, then a worst case percent difference between two measurements at either extremes of the $\pm 20\%$ range would be $\pm 50\%$. As an example, consider a sample with a true concentration of a target analyte of 100 mg/L. The field method reports a value 20% high at 120 mg/L and the laboratory reports the value 20% low at 80 mg/L. The percent difference between these two values is 50%. Thus, the $\pm 50\%$ bias lines denote acceptable tolerances on field instrument comparisons to reference laboratory data.

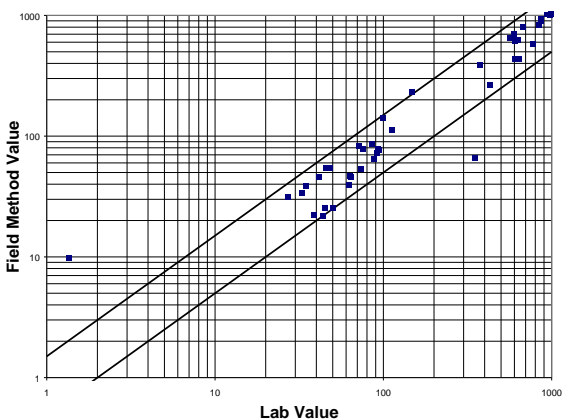
In some cases where the data span five or more orders of magnitude, two plots are used. The plots give the reader an indication of instrument bias and correlation⁸ relative to reference laboratory data. Here, bias is defined as a systematic difference of one method relative to another across a portion of or the entire measurement range of the instrument. Bias is directly related to accuracy. A method with low bias is one with high accuracy. A method with a -10% bias is accurate to within 10%. As an example, Figure 6-1 shows four sets of simulated data with various amounts of bias and random “noise” added. The zero bias line, not shown in the plots, extends from the lower left to the upper right corners of each plot. These findings are based on the assumption that any bias is a constant fraction of the actual value of the result, and that instrument performance is linear over several orders of magnitude.



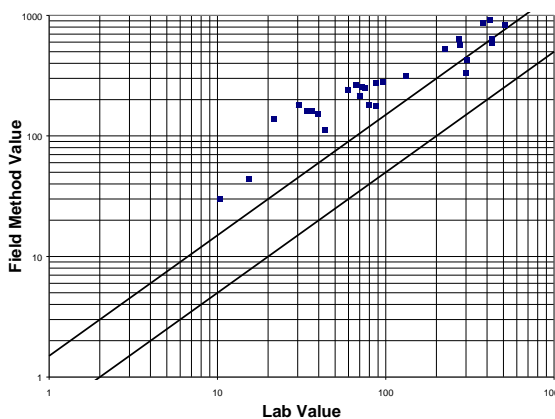
(a) High correlation; low bias



(b) High correlation; positive bias



(c) Low correlation; low bias



(d) Low correlation; positive bias

Figure 6-1. Example scatter plots with simulated data. The four plots illustrate various degrees of measurement correlation and method bias or accuracy. The reference laboratory value is plotted on the x-axis and the paired field technology value on the y-axis. The solid lines mark the $\pm 50\%$ interval about the zero bias line.

Data with low bias and high correlation are shown in Figure 6-1a. The data are closely clustered between the $\pm 50\%$ lines near the zero bias line. A low bias and low correlation example is shown in Figure 6-1c. Most of the data fall within the $\pm 50\%$ lines; however, the scatter is larger than that observed in Figure 6-1a.

⁸ Correlation is a measure of the degree of linear relationship between two variables.

Positive bias is illustrated in Figures 6-1b and 6-1d for high and low correlation data, respectively. In each case, the data are grouped about a line that is shifted well above the zero bias line. As in the other examples, the degree of data scatter is greater for the low correlation case.

Histograms

A final means to evaluate performance is accomplished by computing the percent difference between the field and laboratory value for each paired sample analysis and pooling these data across all compounds by sample medium. These percent difference computations were then tabulated into frequency histograms, examples of which are shown in Figure 6-2. The histogram gives the frequency of occurrence as a function of the percent difference interval and enables a visual evaluation of the field technology data when compared with reference laboratory data. As an example, in Figure 6-2a, nearly all the percent difference computations fall within the $\pm 30\%$ interval, indicating relatively good data correlation. The center of mass of the histogram falls near zero, indicating an average bias near zero. A low correlation, low bias example is shown in Figure 6-2c. In this example, 12 of the 42 total observations fall outside the $\pm 30\%$ range. Although the overall average percent difference falls near zero, the width of the distribution reveals diminished instrument correlation. Figures 6-2a and 6-2c illustrate the same type of data shown in scatter plot format in Figures 6-1a and 6-1c, respectively. Positive bias examples with high and low correlation are illustrated in Figure 6-2b and 6-2d, respectively. In these examples, the center of mass of the histogram falls at a point other than zero, thereby revealing an overall measurement bias. Figures 6-2b and 6-2d illustrate the same type of data shown in the scatter plots in Figures 6-1b and 6-1d, respectively.

Summary of Instrument Performance Goals

The original instrument performance claims, although relevant to the objectives of the demonstration, were determined to be somewhat vague following compilation and evaluation of all demonstration data. For example, should all measurements fall within $\pm 35\%$ of reference laboratory results or should the average results for a particular sample medium meet the 35% criterion? To maintain objectivity in the process of instrument evaluation, instrument performance goals were modified and restated in such a manner that a simple yes or no answer describes whether the goals were met. A summary description of the performance goals, developed in the preceding paragraphs, and how data are evaluated in the context of those goals is presented below.

Accuracy

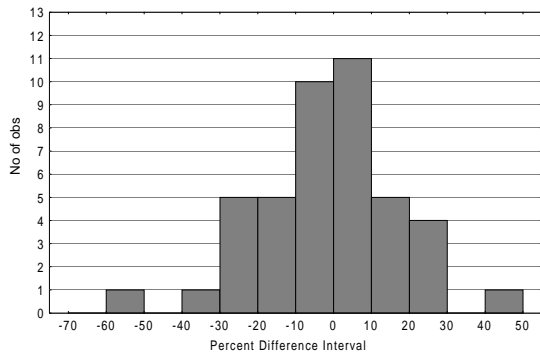
Two goals are stated. If the first goal is met, no evaluation is done relative to the second.

Accuracy Goal 1: Median Bruker absolute percent accuracy for each sampling medium is in the range of 0-35%.

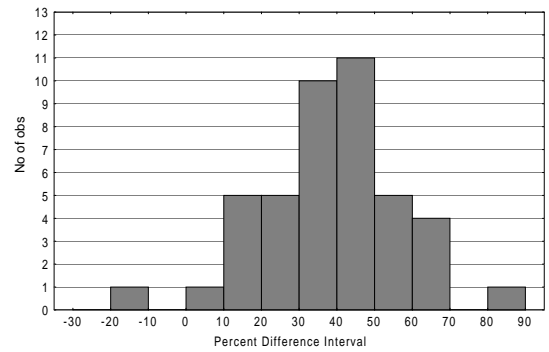
Accuracy Goal 2: Median Bruker absolute percent accuracy for each sampling medium is less than or equal to the 95th percentile of the pooled reference laboratory absolute percent accuracy for each sampling medium⁹.

⁹ The specific accuracy evaluation procedure is as follows:

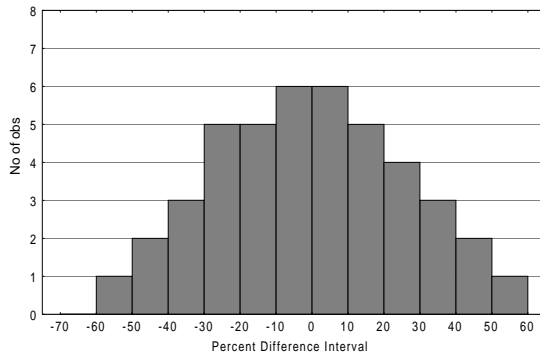
- Pool all the Bruker PE and spike sample analytical results, in terms of absolute percent accuracy, for each sample medium for which a reference value is known. Data from SRS and WAFB are combined in this analysis. All sample data are excluded whose reference values are less than $2 \cdot \text{PQL}_{\text{Bruker}}$
- Compile these data into a frequency histogram and compute the median ($\text{APA}_{.5} \text{Bruker}$), 80th percentile ($\text{APA}_{.8} \text{Bruker}$), and 95th percentile ($\text{APA}_{.95} \text{Bruker}$) values.
- Do the same compilations for the reference laboratory data combined from both demonstration sites by sampling media.
- Apply the following assessment criteria to the absolute percent accuracy distributions:



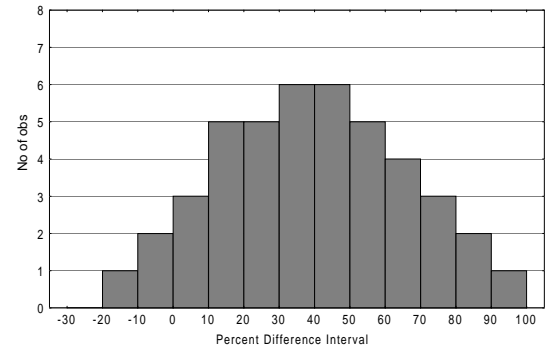
(a) High correlation; low bias



(b) High correlation; positive bias



(c) Low correlation; low bias



(d) Low correlation; positive bias

Figure 6-2. Example histograms with simulated data. Various combinations of measurement correlation and bias are shown.

Precision

In a similar manner as described for accuracy evaluation, two precision goals are stated. If the first goal is met, no evaluation is done relative to the second.

Precision Goal 1: Median Bruker relative percent difference for each sampling medium is in the range of 0-30% for water and soil gas samples and 0-35% range for soil samples.

- (1) If $(APA_{.5})_{Bruker} \leq 35\%$: **Accuracy Goal 1 Met** -- Bruker accuracy performance is better than or equal to that specified in Methods 8260 and TO-14.
- (2) If $Bruker (APA_{.5})_{Bruker} \leq (APA_{.95})_{Lab}$: **Accuracy Goal 2 Met** -- Bruker performs comparably to conventional laboratory using accepted analytical methodologies.
- (3) If $(APA_{.5})_{Bruker} > (APA_{.95})_{Lab}$: **Accuracy Goal 2 Not Met** -- Bruker data does not compare with the reference laboratory data.

Precision Goal 2: Median Bruker relative percent difference for each sampling medium is less than or equal to the 95th percentile of the pooled reference laboratory relative percent differences for each sampling medium¹⁰.

Bruker to Reference Laboratory Comparison

Two goals are stated. If the first goal is met, no evaluation is done relative to the second.

Comparison Goal 1: Median absolute percent difference is in the range of 0-50%.

Comparison Goal 2: If Goal 1 not met, the Wilcoxon test result between Bruker and reference laboratory data should indicate no significant bias ($p > 0.05$)¹¹.

Field Operation Observations

SRS Demonstration

The SRS demonstration consisted of three days of sample analysis by the Bruker analytical team. Following pre-demonstration calibration, the instrument was shipped to the USA from Germany by air freight with no degradation of instrument performance noted following its transport. The instrument was

¹⁰ The specific precision evaluation procedure is as follows:

- Pool all the Bruker duplicate sample results, in terms of relative percent difference (RPD) for each sample medium (soil, water, and gas) for which a reference value is known. Data from SRS and WAFB are combined in this analysis. All sample data are excluded whose reference values are less than $2 \cdot \text{PQL}_{\text{Bruker}}$
- Compile these data into a frequency histogram and compute the median $(\text{RPD}_{.5})_{\text{Bruker}}$, 80th percentile $(\text{RPD}_{.8})_{\text{Bruker}}$, and 95th percentile $(\text{RPD}_{.95})_{\text{Bruker}}$ values.
- Do the same compilations for the reference laboratory data combined from both demonstration sites by sampling media.
- Apply the following assessment criteria to the absolute percent accuracy distributions:
 - (1) If $(\text{RPD}_{.5})_{\text{Bruker}} \leq 30\%$ (water and soil gas), 35% (soil): **Precision Goal 1 Met** -- Bruker precision performance within the range identified in original developer claims and is very near that specified in Methods 8260 and TO-14.
 - (2) If $(\text{RPD}_{.5})_{\text{Bruker}} \leq (\text{RPD}_{.95})_{\text{Lab}}$: **Precision Goal 2 Met** -- Bruker performs comparably to conventional laboratory using accepted analytical methodologies.
 - (3) If $(\text{RPD}_{.5})_{\text{Bruker}} > (\text{RPD}_{.95})_{\text{Lab}}$: **Precision Goal 2 Not Met** -- Bruker precision performance is worse than that reported by reference laboratories despite considerable allowance given for field variability.

¹¹ The specific Bruker to laboratory evaluation procedure is as follows:

- Compute the percent difference and the absolute percent difference for each set of Bruker-laboratory paired sample results.
- Compile the percent difference and absolute percent difference data into frequency histograms and compute the median $(\text{APD}_{.5})_{\text{Bruker-Lab}}$, 80th percentile $(\text{APD}_{.8})_{\text{Bruker-Lab}}$, and 95th percentile $(\text{APD}_{.95})_{\text{Bruker-Lab}}$ values for each distribution.
- Apply the following assessment criteria to the compiled absolute percent differences:
 - (1) If $(\text{APD}_{.5})_{\text{Bruker-Lab}} \leq 50\%$: **Comparison Goal 1 Met** -- Bruker results are consistently within $\pm 50\%$ of reference laboratory results.
 - (2) If $(\text{APD}_{.5})_{\text{Bruker-Lab}} > 50\%$: Proceed to Step (3) for further evaluation.
 - (3) Perform Wilcoxon test to determine if the observed bias is statistically significant. The percent difference values (not absolute percent difference values since the sign of the difference is necessary information in the Wilcoxon Test) are compared to a value of zero percent difference.
 - (a) If p-value for the test > 0.05 : **Comparison Goal 2 Met**
 - (b) If p-value for the test < 0.05 : **Comparison Goal 2 Not Met**

installed in a small air conditioned van and driven to the demonstration site. The instrument was operated from batteries and was also set up for operation during transit from the hotel to the measurement site, a time-saving feature of interest in these field investigations. The Bruker GC/MS was also operated for some portion of the time under ambient air temperatures during the hot afternoons to demonstrate its field versatility. Typical temperatures during the SRS demonstration are shown in Figure 6-3.

On the first day of the demonstration, each developer was provided soil gas samples for analysis. Eighteen GC/MS runs, that included blanks, calibration checks and field samples were completed and data reports were submitted for 16 of these. Two runs were not submitted because power supply problems affected the instruments' performance.

The second day at SRS was dedicated to water analysis. Fifteen blank, calibration and sample runs were completed and data reports were submitted for all runs.

The third day was devoted to soil analysis. Eight runs were completed and data reports were submitted for all runs completed. The Bruker analytical team did their soil analysis using headspace vapor measurements and had calibrated the system using 10 mL vials.

The Bruker team included internal standards in most of their analyses. In nearly all cases, recovery of these compounds was good. However, in some cases, significant changes were noted in the surrogate compounds in water samples. Since much of the sample preparation was done under the changing ambient conditions, the Bruker analysts suspected that the high ambient temperature influenced sample preparation or storage stability. Sample run times were on the order of 12 minutes for all media.

WAFB Demonstration

Analysis at WAFB proceeded much like that at SRS, with soil gas analysis done on the first day, water analysis on the second, and soil analysis on the third. Typical temperatures encountered during the WAFB demonstration are shown in Figure 6-4. Fifteen soil gas runs, including calibration checks, blank analyses, and field sample analyses, were completed on the first day of the demonstration. An instrument breakdown was noted during one run. The problem was resolved and the instrument was brought back on-line in about 60 minutes. Blank soil gas sample analyses results for target analytes were less than 10 ppb.

A total of 17 water sample analysis runs were completed on the second day of the WAFB demonstration. Power problems were encountered during one run which were related to the fact that input voltage to the instrument exceeded the 28 volt maximum for which the instrument was configured. This caused some shifts in calibration data; however, the data were still usable from the run. Blank water sample analyses produced results for the target analytes in the range of 0.1 to 8 $\mu\text{g/L}$.

Eighteen runs were completed on the third day of the demonstration which was devoted to soil sample analysis. Blank soil sample analyses produced results of about 50 $\mu\text{g/kg}$ for the target analytes. The Bruker analysts noted more scatter in the soil analysis results for their internal standards and suspected that to be true for the target analytes as well.

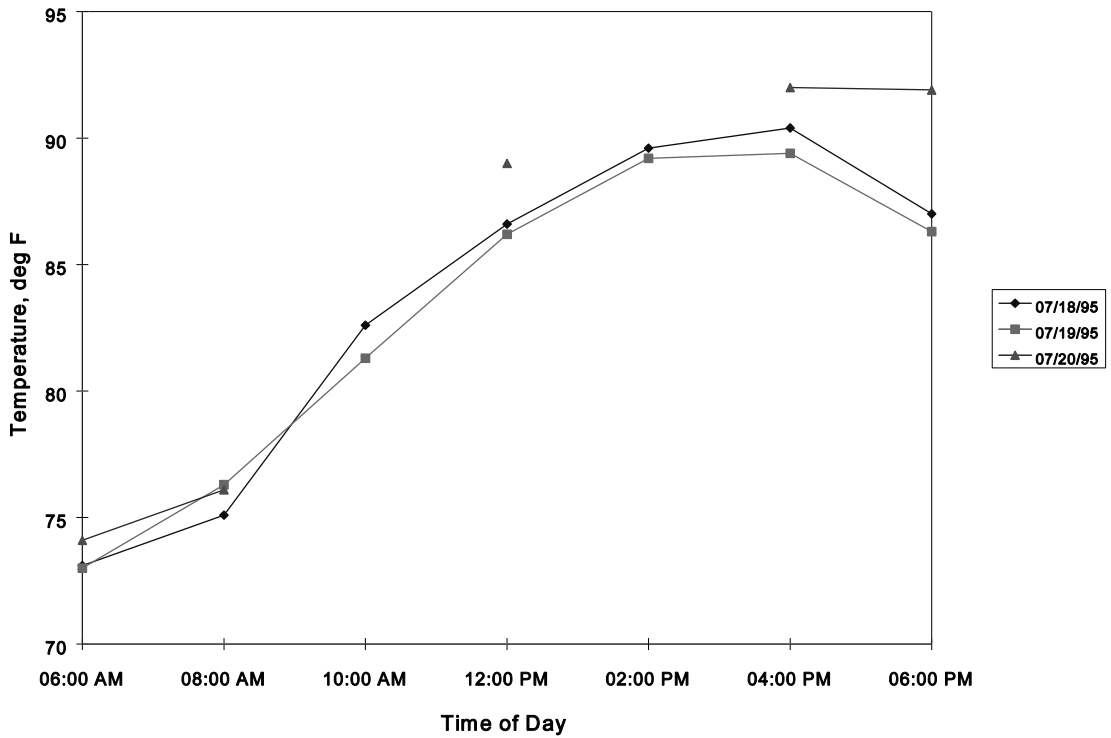


Figure 6-3. Plot of daily temperatures during the SRS demonstration. Note that two data points are missing from July 20, 1995.

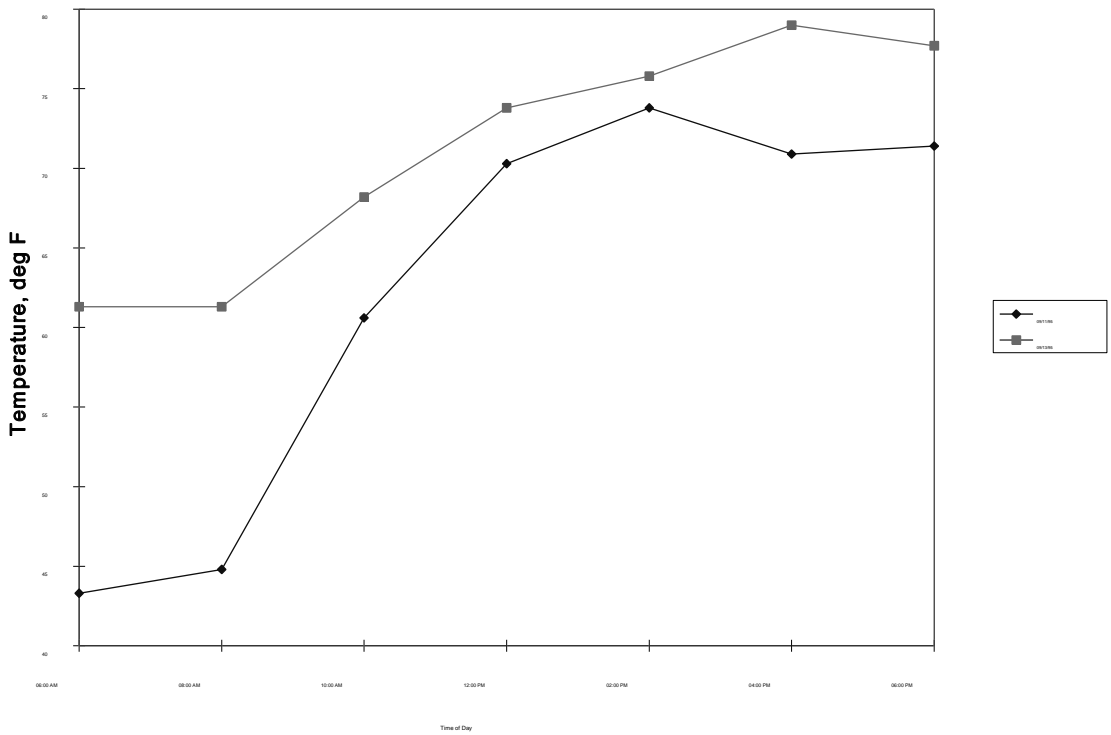


Figure 6-4. Plot of daily temperatures during the WAFB demonstration.

Bruker Accuracy and Precision Results

Bruker Accuracy -- SRS Demonstration

As discussed in Sections 4 and 5, SRS is predominately contaminated with the chlorinated solvents TCE and PCE. Consequently, all of the Bruker GC/MS data and corresponding laboratory data are limited to these two contaminants. Recovery data for the Bruker GC/MS system for SRS spike and PE samples for water and soil gas are presented in Table 6-1. Data from reference values lower than the Bruker PQL are not shown in the table.

Table 6-1. Bruker Recoveries at SRS.

Sampling Medium / Description	Percent Recovery	
	TCE	PCE
Water Medium Spike	102	64
Water High Spike	145	71
Water PE No. 2	78	152
Soil Gas Low Spike	134	195
Soil Gas Medium Spike	52	80
Soil Gas High Spike	36	44
Soil Gas PE No. 1	127	265
Soil Gas PE No. 2	78	51

Because of significant deviations from the demonstration plan, discussed earlier in Section 4, no data are available for assessment of Bruker instrument accuracy on soil samples at SRS.

Percent recoveries for the water spike and PE samples are provided in Table 6-1. Five of the six data points are in the 50-150% range. A recovery value of 145% was obtained for the high TCE spike. The percent recoveries from the reference laboratories for this sample showed similar high recovery results leading to questions about the validity of the reported reference value for this particular sample. The other high value of 152% was for PCE in a PE sample at a relatively low level of 30 $\mu\text{g/L}$.

Recoveries for soil gas measurements are also shown in Table 6-1. The level of confidence in the reference values for the soil gas spike samples is high since they were drawn from gas cylinders with accompanying certificates of analysis. The low spike recoveries are shown since the TCE and PCE content of this sample was above the reported PQL of the Bruker instrument. Recoveries generally fall into two categories: they are high (>100%) for low level spikes and low (<100%) for high level spikes and nearly all the reported values fall outside the 70-130% recovery range. These data suggest questionable accuracy performance for the Bruker system during the SRS demonstration.

Bruker Accuracy -- WAFB Demonstration

The sampling media at the WAFB demonstration site are contaminated with a wide range of VOCs including petroleum hydrocarbons and chlorinated solvents. Approximately fifteen different VOCs were analyzed by both the reference laboratories and the field technologies, though several of these compounds were found in only trace amounts in the different media. To most efficiently evaluate the Bruker GC/MS, a subset of analytes was chosen for accuracy and precision evaluation using the spike and PE samples. The subset included benzene, toluene, ethylbenzene, and xylenes, as well as TCE and PCE. Unless otherwise noted, ethylbenzene is grouped with xylenes in the total xylenes category. Recovery data for the WAFB

demonstration from Bruker GC/MS analysis of PE and spike samples is presented for soil, water, and soil gas samples in Table 6-2.

Two soil PE samples were available for accuracy determinations. These samples were laboratory-prepared in sealed ampules and were judged to be reliable standards. Bruker GC/MS recoveries for the five target compounds fall in the range of 90 to 190%. Computed recoveries from spike and PE water samples, also shown in Table 6-2, are consistently above 100%, and fall in the range of 112 to 177%. The recovery results are similar for all target analytes and indicate no obvious instrument response changes across the range of target compounds.

Soil gas sample recoveries shown in Table 6-2 are all in the range of 60-108% and, in contrast to the SRS recovery data, reveal good accuracy performance during the WAFB demonstration¹².

Table 6-2. Bruker Recoveries at Wurtsmith.

Sampling Medium/Description	Percent Recovery				
	TCE	PCE	Benzene	Toluene	Total Xylenes
Soil PE No. 1	190	143	153	93	101
Soil PE No. 2	174	133	152	134	94
Water Low Spike	153	123	119	142	160
Water Medium Spike	140	112	152	177	145
Water High Spike	132	132	130	156	161
Water PE No. 1	ND	ND	ND	ND	ND
Water PE No. 2	128	136	131	134	144
Soil Gas Low Spike	72	91	79	89	83
Soil Gas Medium Spike	108	ND	87	ND	104
Soil Gas High Spike	82	ND	62	ND	99

Notes: ND = Not detected, compound not present in spike; no recovery data available.

See Tables 5-7 and 5-11 for approximate target analyte concentrations in the various PE/Spike samples.

Overall Bruker Accuracy Performance

The absolute percent accuracy values from both sites were compiled for the target analytes by sampling media and are shown as histograms in Figures 6-5, 6-6 and 6-7 for soil, water, and soil gas, respectively. For soil, most of the values are scattered in the 0-90% range with no clear clustering of results. For water, most of the values fall in the 0-70% range. The soil gas accuracy data generally fall in the 0-70% range.

¹² The Bruker recovery for the lowest soil gas spike sample is shown in Table 6-2 since it is above the reported Bruker PQL. Initially, the computed Bruker recoveries for this particular sample were consistently high by a factor of ten for all target analytes. Results similar to those from Bruker were obtained by other participants, suggesting an error in the reference sample preparation. A review of the laboratory and field data and log books strongly suggest that a factor of ten error occurred in the reference sample concentration computation. The reference values were changed accordingly and the reported Bruker recovery data are based on the corrected values.

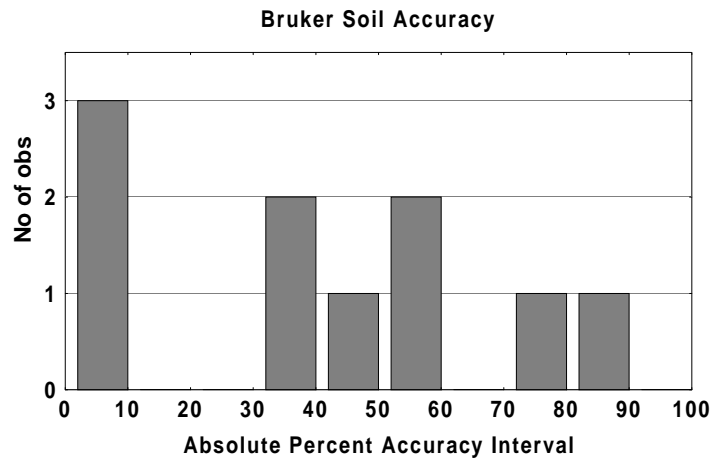


Figure 6-5. Absolute percent accuracy histogram for Bruker soil samples. The number of observations are shown on the y-axis.

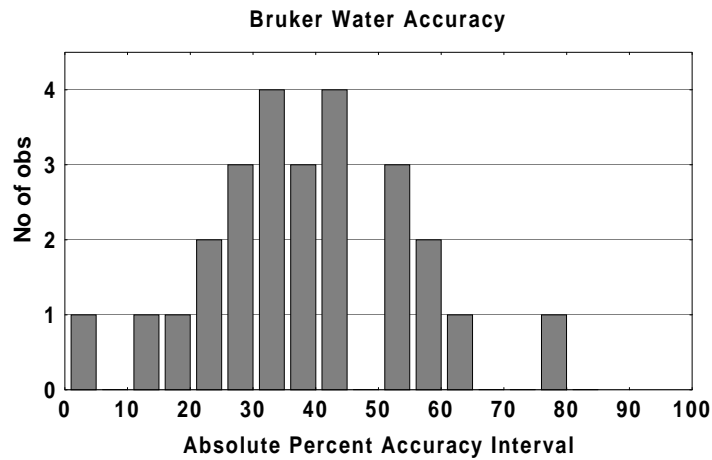


Figure 6-6. Absolute percent accuracy histogram for Bruker water samples.

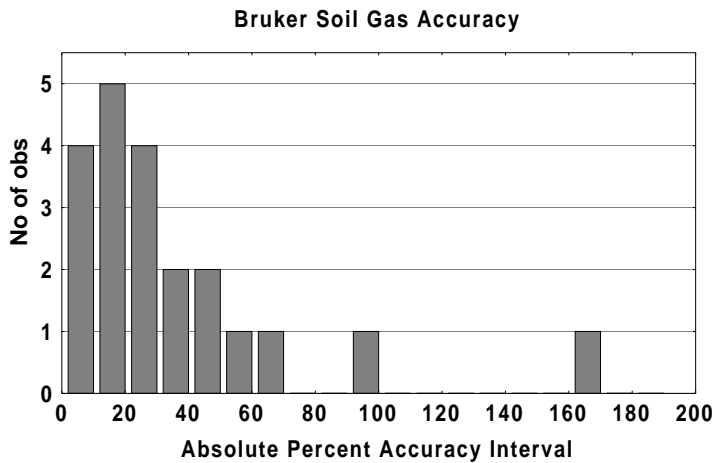


Figure 6-7. Absolute percent accuracy histogram for Bruker soil gas samples.

Summary data from the absolute percent accuracy distributions are shown in Table 6-3 for all media. In general, the lower the number the better the performance. For example, the median absolute percent accuracy was 22% for the pooled reference laboratory soil data. The laboratory's 95th percentile value is 47%. In comparison, the Bruker median absolute percent accuracy for soil samples was 39% and less than the 95th percentile value for the reference laboratories.

Table 6-3. Bruker and Reference Laboratory Accuracy Summary.

Data Set/Media Type	n	Absolute Percent Accuracy		
		x _{.5}	x _{.8}	x _{.95}
Ref. Lab - Soil	10	22	36	47
Bruker - Soil	10	39	57	83
Ref. Lab - Water	30	19	27	116
Bruker - Water	26	36	52	61
Ref. Lab - Soil Gas	24	20	47	66
Bruker - Soil Gas	21	22	49	95

Note: x_{.5} = 50th percentile (median); x_{.8} = 80th percentile; x_{.95} = 95th percentile

Assessment of Bruker performance in terms of the accuracy goals stated previously results in the following determinations:

Soil: (APA_{.5})_{Bruker-Soil} > 35%: **Accuracy Goal 1 Not Met**
 (APA_{.5})_{Bruker-Soil} ≤ (APA_{.95})_{Lab-Soil}: **Accuracy Goal 2 Met**

Water: (APA_{.5})_{Bruker-Water} > 35%: **Accuracy Goal 1 Not Met**
 (APA_{.5})_{Bruker-Water} ≤ (APA_{.95})_{Lab-Water}: **Accuracy Goal 2 Met**

Soil Gas: (APA_{.5})_{Bruker-Gas} < 35%: **Accuracy Goal 1 Met**

Bruker accuracy performance is acceptable in terms of established performance goals for all media. The most stringent performance goals for accuracy were not met for soil and water; however, median Bruker performance was as good as or better than reference laboratory results from similar analyses. Soil gas accuracy performance was better than the most restrictive goal of 35% absolute percent accuracy.

Bruker Precision -- SRS Demonstration

Bruker GC/MS RPD values from the SRS demonstration are presented in Table 6-4 and are based on the results of duplicate field sample analysis. No precision determination was done on SRS soil sample data as discussed previously.

Relative percent differences for water samples, shown in Table 6-4, are from split water samples. The calculated RPD values range from 5-38%. Low concentration samples near the Bruker PQL exhibit the same level of precision as higher concentration samples.

Soil gas duplicate samples were actually gas samples drawn sequentially from each well within a time interval of about 2 minutes. The degree of chemical equivalence of these sequential samples could not be determined since a real-time measure of soil gas species was not made at the wellhead when the

Table 6-4. Bruker Precision for SRS Demonstration.

Sampling Media / Description	Relative Percent Difference	
	TCE	PCE
Water Low Sample	34	38
Water Medium Sample	37	29
Water High Sample	24	24
Soil Gas Low Sample	22	25
Soil Gas Medium Sample	5	10
Soil Gas High Sample	10	14

sequential samples were collected. In this analysis, a worst case precision determination was carried out by assuming that the sequential samples were chemically equivalent. The RPD values for the low, medium, and high vapor samples, provided in Table 6-4, are less than 25%. These data are indicative of good Bruker precision performance.

Bruker Precision -- WAFB Demonstration

The Bruker precision data for the WAFB demonstration are presented in Table 6-5. The tabulated RPD values are based on the analysis of a number of duplicate samples for each media.

Table 6-5. Bruker Precision for Wurtsmith Demonstration.

Sampling Medium / Description	Relative Percent Difference				
	TCE	PCE	Benzene	Toluene	Total Xylenes
Soil Low Sample	ND	ND	ND	ND	ND
Soil Medium Sample	ND	ND	ND	ND	12
Soil High Sample	14	ND	21	12	8
Water Low Sample	5	5	10	27	8
Water Medium Sample	47	21	12	9	8
Water High Sample	120	99	15	119	21
Soil Gas Low Sample	29	ND	26	43	52
Soil Gas Medium Sample	6	ND	7	<1	10
Soil Gas High Sample	108	ND	17	46	11

Notes: ND = not detected; Analyte was either below detection or not present in the sample.

For soil sample analyses, Bruker reported a number of results that were below its PQL of 50 mg/kg. Precision analysis was performed using only those concentrations that were greater than the PQL. The results are shown in Table 6-5.

The low, medium, and high concentration water samples collected at WAFB generally contained only low concentrations of the target analytes (Table 5-9). The RPDs in Table 6-5 are attributed to the fact that the Bruker GC/MS was operating at or very near its PQL. The Bruker operator was told to expect samples that would have analyte concentrations in predetermined ranges, therefore, he performed dilutions based on the expectations. This caused the operator to perform dilutions on low concentration samples, which may have impacted the precision of the measurement.

As noted earlier in the discussion of SRS demonstration results, the duplicate soil gas samples were actually samples drawn sequentially from different levels of the well. The assumption is made that the sequential samples are chemically equivalent. Thus, the RPD value represents a worst-case estimate of

Bruker GC/MS precision since some of the variability encountered in the analysis result may in fact be attributable to variation between two sequential samples. The data in Table 6-5 must be interpreted in light of the target analyte concentrations provided previously in Table 5-13. For example, the reference laboratory reported non-detectable levels of TCE and PCE in all the soil gas samples (low, medium, and high). The Bruker system was able to detect TCE in the samples; however, the levels are near the PQL of the system where precision is not expected to be as good. Taking these considerations into account, the overall Bruker precision for soil gas analyses is satisfactory.

Overall Bruker Precision Performance

The relative percent differences for both sites were compiled by sample media and are shown as histograms in Figures 6-8, 6-9 and 6-10 for soil, water, and soil gas, respectively. For soil, most of the RPD values fall in the 0-25% range. For water and soil gas, nearly all reported values fall in the 0-50% range.

Summary data from the relative percent difference distributions are shown in Table 6-6 for the three sampling media.

Bruker performance with respect to precision goals are as follows:

Soil: $(RPD_{.5})_{\text{Bruker-Soil}} < 35\%$: **Precision Goal 1 Met**

Water: $(RPD_{.5})_{\text{Bruker-Water}} < 30\%$: **Precision Goal 1 Met**

Soil Gas: $(RPD_{.5})_{\text{Bruker-Gas}} < 30\%$: **Precision Goal 1 Met**

Bruker precision performance, relative to these performance goals, is judged acceptable for soil, water, and soil gas analyses.

Bruker to Reference Laboratory Data Comparison

As discussed earlier in this section, comparisons of the Bruker GC/MS analytical data with the reference laboratory analytical data for water, soil, and soil gas samples are presented in a number of formats that include log-log scatter plots, percent difference histograms, and formal performance assessment in light of established goals. All reported values that were less than two times the Bruker GC/MS PQL, although plotted, are not included in any of the statistical analyses. Analytical results from only one of the duplicate or triplicate sample set is included in the statistical analyses since their inclusion would violate requirements for a random sample.

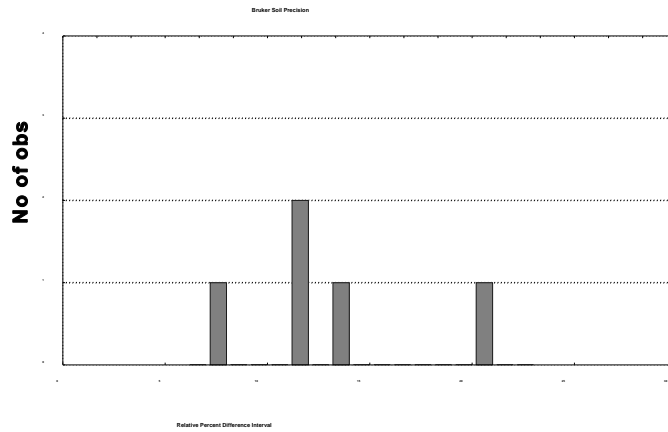


Figure 6-8. Relative percent difference histogram for Bruker soil samples.

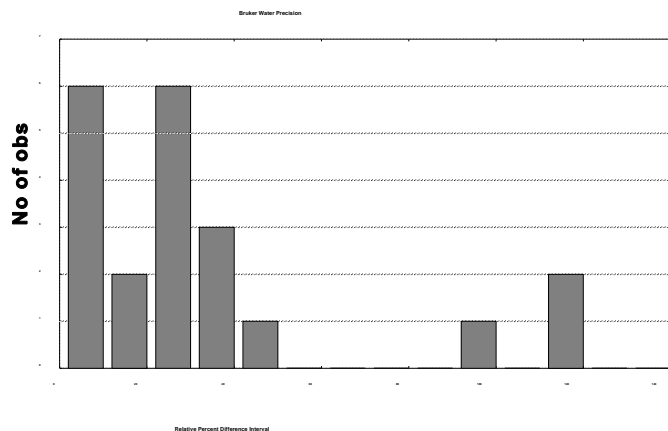


Figure 6-9. Relative percent difference histogram for Bruker water samples.

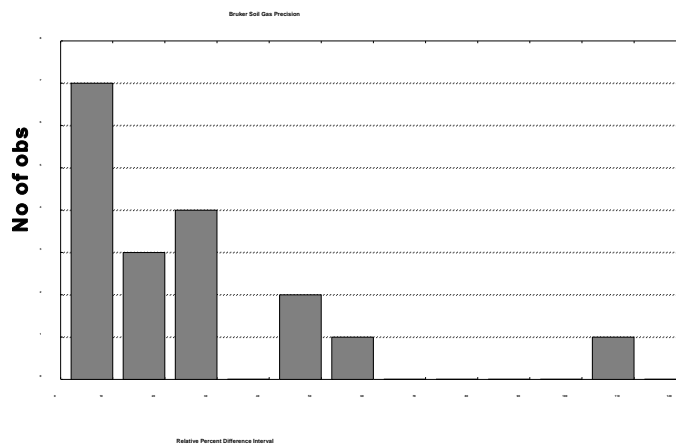


Figure 6-10. Relative percent difference histogram for Bruker soil gas samples.

Table 6-6. Bruker and Reference Laboratory Precision Summary.

Data Set/Media Type	n	Relative percent difference		
		x ₅	x ₈	x ₉₅
Ref. Lab Soil	13	8	13	58
Bruker Soil	5	12	15	20
Ref. Lab Water	14	5	10	22
Bruker Water	21	24	38	119
Ref. Lab Soil Gas	17	7	20	68
Bruker Soil Gas	18	16	37	60

Note: x₅ = 50th percentile (median); x₈ = 80th percentile; x₉₅ = 95th percentile

Scatter Plots/Histograms -- SRS Demonstration

Target analytes at this site were limited to TCE and PCE. The GEL water data are used as the reference data set. The on-site SRS laboratory soil gas data were judged to be an acceptable reference data set.

Plots of Bruker GC/MS water analysis results for TCE and PCE are given versus the laboratory reference data in Figure 6-11 and Figure 6-12 for low (1-100 µg/L) and high (0.1-100 mg/L) concentration ranges, respectively. All but six of the 21 points fall within the ±50% interval about the zero bias line on both the low and high concentration plots.

The distribution of percent difference values is shown as a histogram in Figure 6-13. Differences range from a low of -60 % to a high of 80%.

A plot of the Bruker soil gas data for TCE and PCE relative to the SRS reference laboratory data are shown in Figure 6-14. Half of the data points fall either above or below the 50% bias lines. The accompanying histogram, shown in Figure 6-15, reveals no obvious positive or negative data bias.

Scatter Plots/Histograms -- WAFB Demonstration

As discussed in Section 5, the Traverse laboratory data were given a good ranking for soil sample analyses and a good ranking for water sample analyses. These data are used as reference data for comparison with Bruker GC/MS results. The Pace laboratory data were given a satisfactory ranking for soil gas sample analyses and are used as the reference data set for the soil gas measurements.

Considerably more compounds were detected in the various samples at Wurtsmith AFB than at the Savannah River Site. For the Wurtsmith demonstration, all target analytes have been combined in the plots and statistical analysis. However, duplicate samples are not included in the statistical analysis.

A plot of Bruker data versus Traverse data for all soil analyses is presented in Figure 6-16. Eleven observations fall outside the ±50% margins and 8 fall inside. In general, the Bruker measurements are high with respect to the laboratory data. The percent difference histogram, shown in Figure 6-17, shows nearly all observations on the positive bias side with a significant number in the 120-200% range.

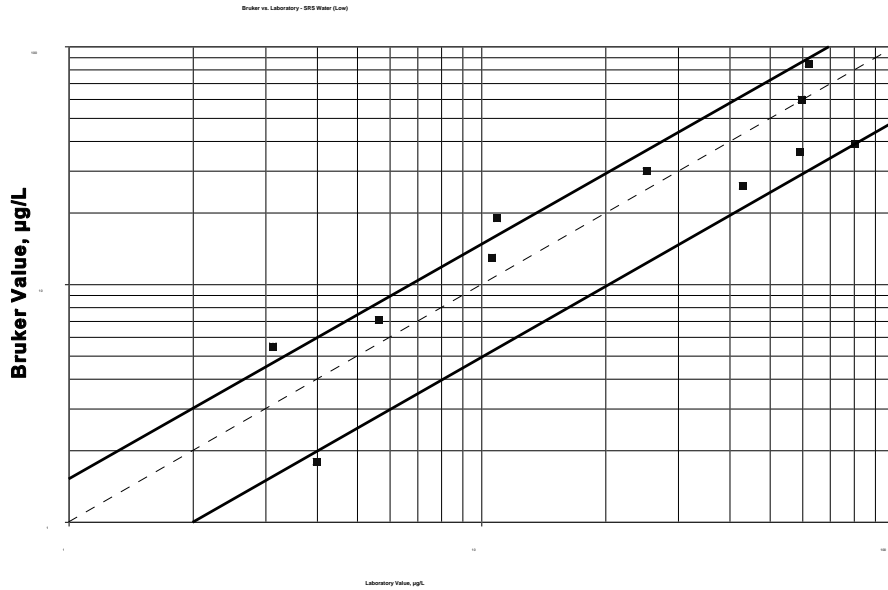


Figure 6-11. Bruker vs. Laboratory data for SRS low concentration water samples. The solid lines show the $\pm 50\%$ range about a zero-bias (dashed) line.

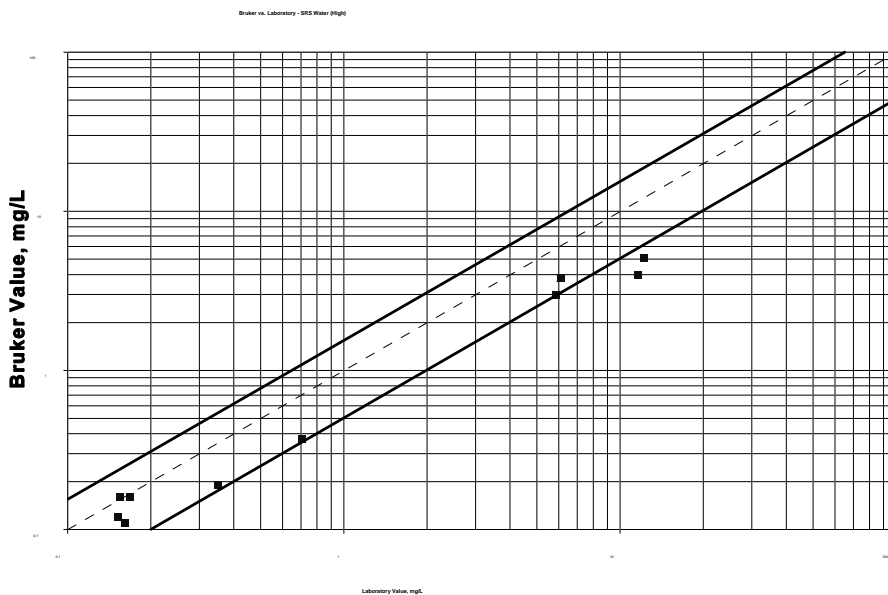


Figure 6-12. Bruker vs. Laboratory data for SRS high concentration water samples. The solid lines show the $\pm 50\%$ range about a zero-bias (dashed) line.

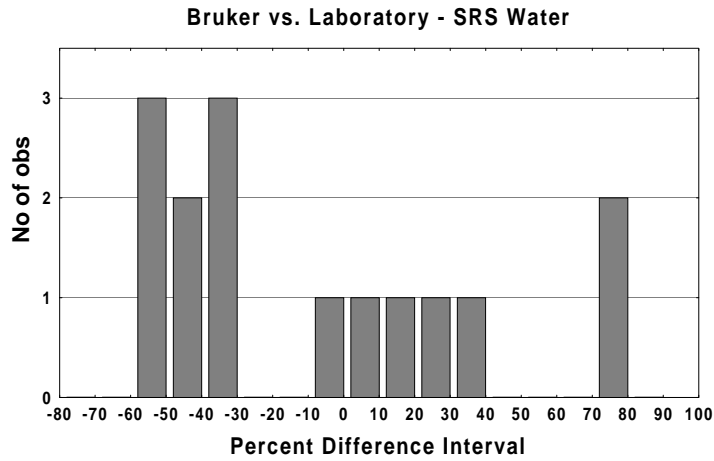


Figure 6-13. Percent difference histogram for SRS water samples.

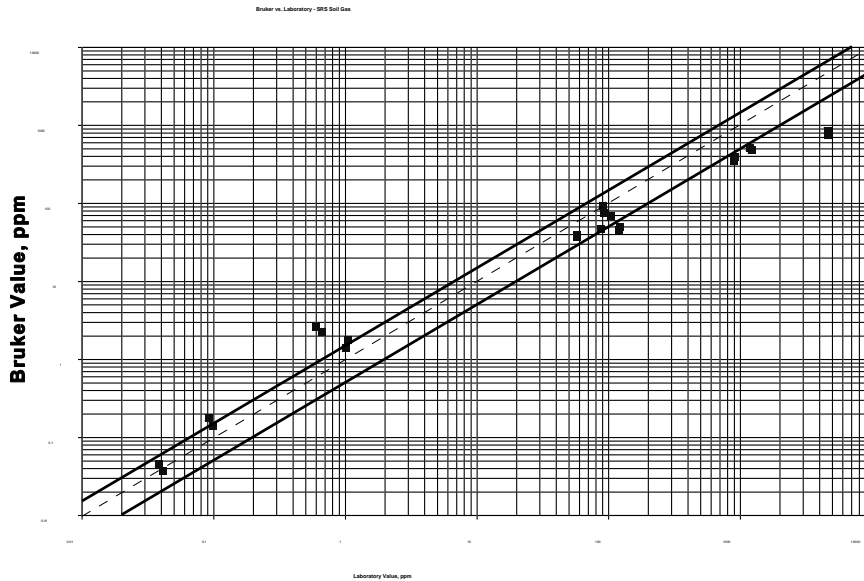


Figure 6-14. Bruker vs. Laboratory data for SRS soil gas samples

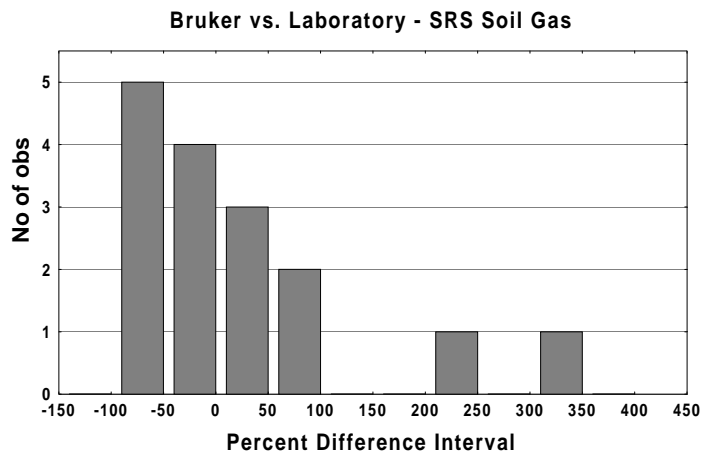


Figure 6-15. Percent difference histogram for SRS soil gas samples.

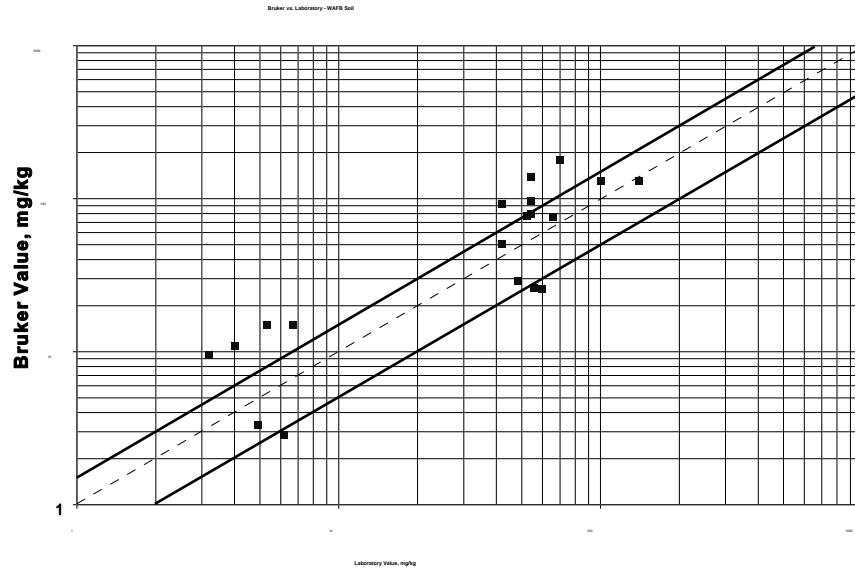


Figure 6-16. Bruker vs. Laboratory data for WAFB soil samples.

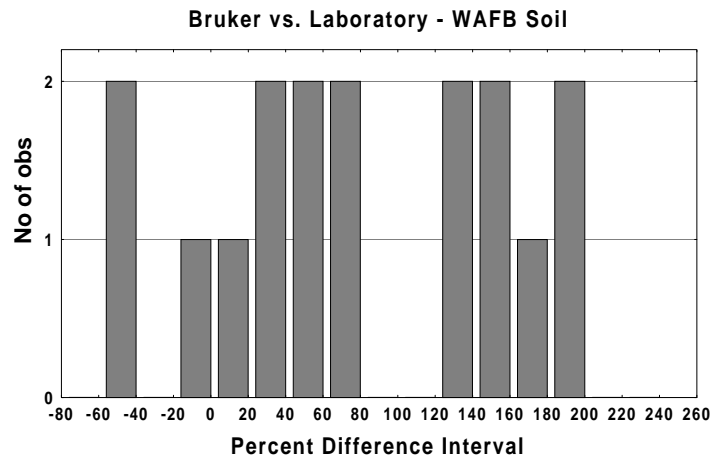


Figure 6-17. Relative percent difference histogram for WAFB soil samples.

Plots of Bruker data versus Traverse data for all water analyses are presented in Figures 6-18 and 6-19 for the low ($\mu\text{g/L}$) and high (mg/L) ranges, respectively. Most Bruker values fall within the $\pm 50\%$ margins on the low concentration plot. In the high concentration plot, 6 observations fall on the high side of the 50% margin and 11 fall inside the margins. The percent difference histogram for the combined data, shown in Figure 6-20, reveals most values in the -20 to 100% range.

A plot of Bruker GC/MS data versus Traverse data for all WAFB soil gas analyses is presented in Figure 6-21. Most of the observations fall inside the $\pm 50\%$ margin lines on the plot, revealing relatively good agreement with the reference laboratory. The histogram, shown in Figure 6-22, shows most observations falling in the 0 to -50% range.

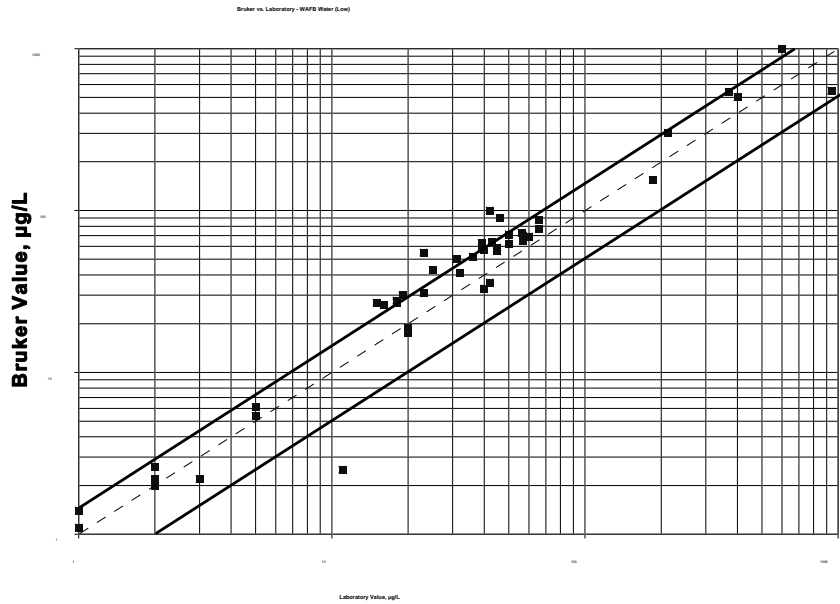


Figure 6-18. Bruker vs. Laboratory data for WAFB low concentration water samples.

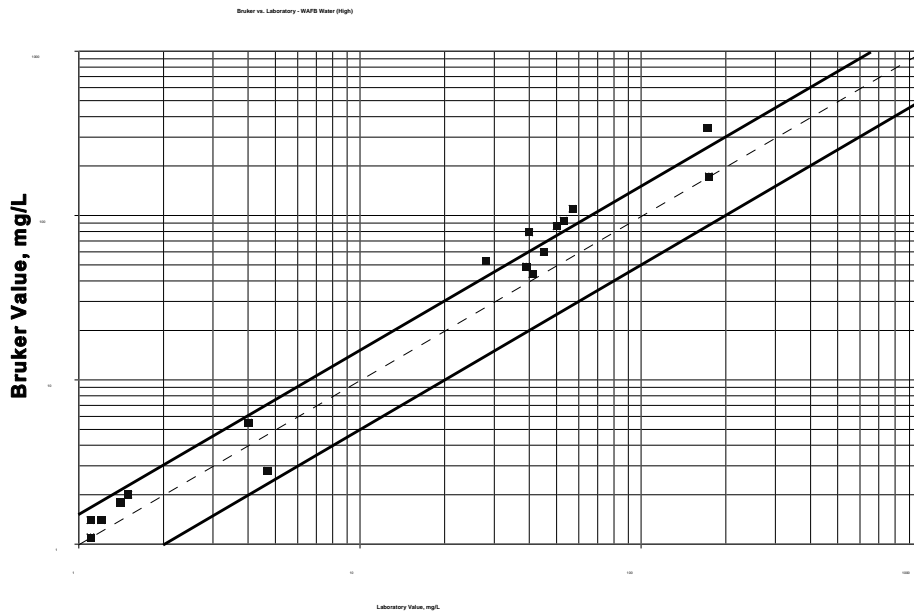


Figure 6-19. Bruker vs. Laboratory data for WAFB high concentration water samples.

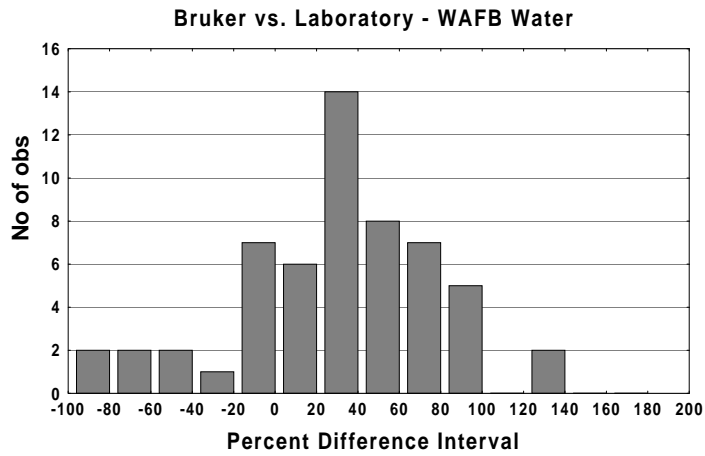


Figure 6-20. Relative percent difference histogram for WAFB water samples.

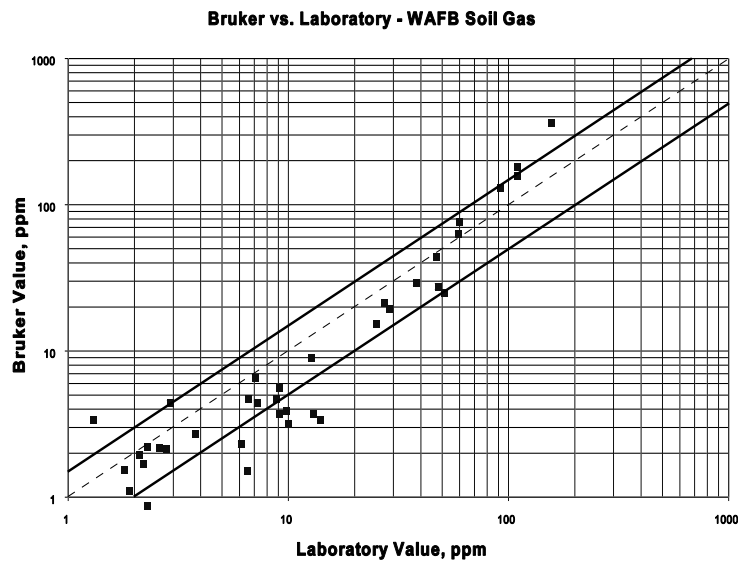


Figure 6-21. Bruker vs. Laboratory data for WAFB soil gas samples.

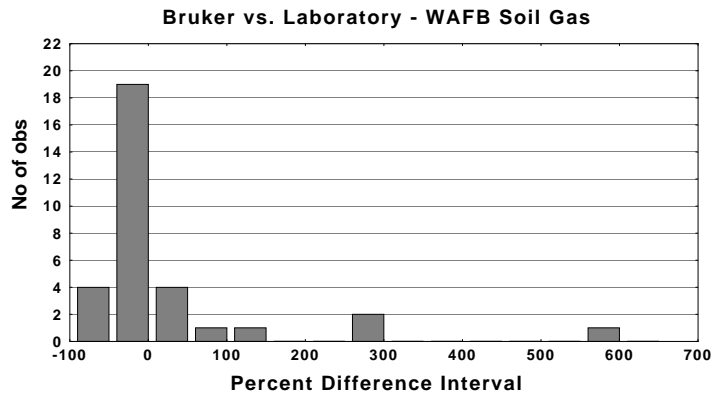


Figure 6-22. Relative percent difference histogram for WAFB soil gas samples.

Overall Bruker to Laboratory Comparison Results

Absolute percent differences from both sites were compiled by sampling media and are shown as histograms in Figures 6-23, 6-24 and 6-25 for soil, water, and soil gas, respectively. For soil, absolute percent differences occur with equal frequency across the 0 to 200% range. Water results are similar with approximately equal distribution across the 0 to 100% range. As noted earlier, soil gas differences generally fall in the 0-50% range.

Summary data from the three absolute percent difference distributions for the three sampled media are shown in Table 6-7.

Table 6-7. Bruker-Laboratory Comparison Summary.

Media Type	n	Absolute Percent Difference		
		$x_{.5}$	$x_{.8}$	$x_{.95}$
Soil	17	72	159	186
Water	71	39	72	95
Soil Gas	49	40	73	275

Note: $x_{.5}$ = 50th percentile (median); $x_{.8}$ = 80th percentile; $x_{.95}$ = 95th percentile

Bruker performance assessment in terms of the comparison goals result in the following determinations:

Soil:	$(APD_{.5})_{\text{Bruker-Lab}}$	> 50%:	Comparison Goal 1 Not Met
	Wilcoxon test result:	$p < 0.05$:	Comparison Goal 2 Not Met
Water:	$(APD_{.5})_{\text{Bruker-Lab}}$	< 50%:	Comparison Goal 1 Met
Soil Gas:	$(APD_{.5})_{\text{Bruker-Lab}}$	< 50%:	Comparison Goal 1 Met

Overall comparison results, in light of established performance goals, indicate that the first goal was met for water and soil gas media. However, the Bruker to laboratory comparison did not meet either the first or second comparison goal for soil. The Wilcoxon test results point to the presence of a significant positive bias of the Bruker data relative to that of the laboratory.

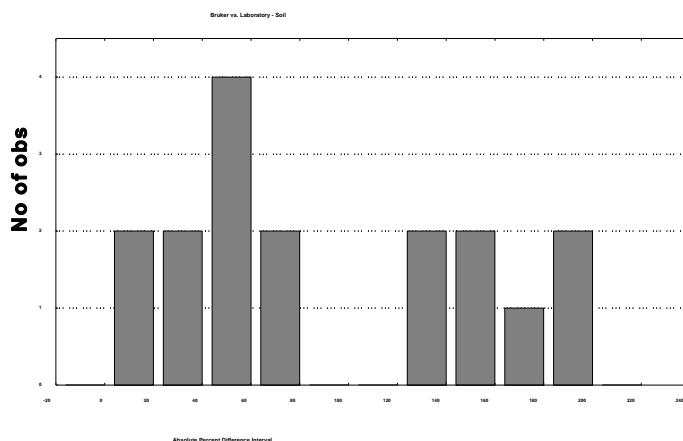


Figure 6-23. Absolute percent difference histogram for soil samples. Data are from WAFB demonstration only.

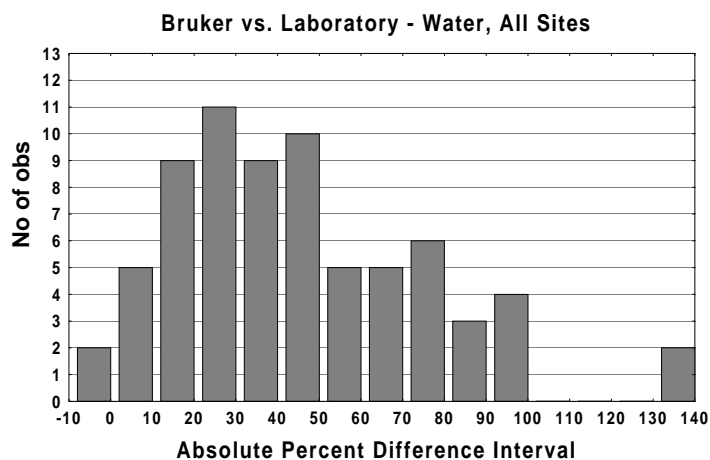


Figure 6-24. Absolute percent difference histogram for water samples.

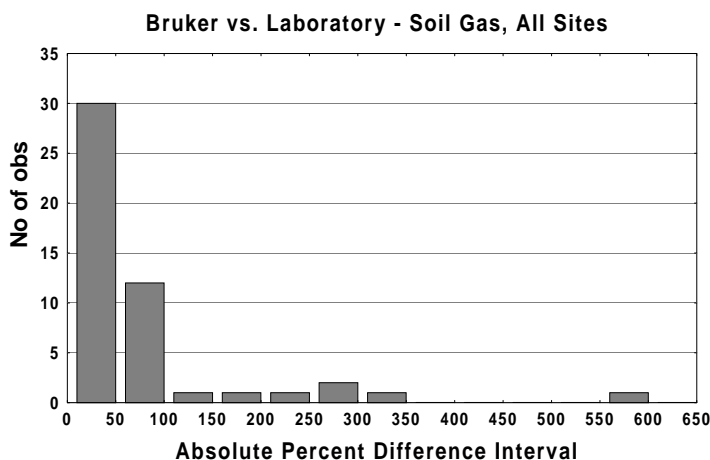


Figure 6-25. Absolute percent difference histogram for gas samples.

Summary of Bruker Accuracy, Precision, and Laboratory Comparison Performance

A summary of Bruker GC/MS performance for both demonstration sites is given in Table 6-8. The results of the foregoing evaluation are summarized with respect to accuracy, precision, and comparison of Bruker and reference laboratory data. The summary information in the table shows that the Bruker GC/MS met performance goals in eight of the nine evaluation categories. Precision was judged acceptable for soil analyses; however, only a very limited sample size (n=5) was available for evaluation. Accuracy of soil analyses also met established goals. Accuracy, precision, and the Bruker to reference laboratory comparison goals were also met for water analyses. For additional insight and evaluation, the data quality rankings of the reference laboratories are given in the table as well. Traverse received a good data quality ranking for soil analyses. The Wilcoxon test result for the soil media indicates that the observed difference between Bruker and reference laboratory data cannot be explained by random variation alone and it is likely that some other factor was causing the Bruker data to be high relative to the laboratory data. Possible Bruker or laboratory factors could be a calibration, sample handling, or injection error by either Bruker or the reference laboratory. For example, the Traverse results on the soil PE samples were consistently low, whereas the Bruker results were much closer to the reference values.

Table 6-8. Summary Performance of the Bruker GC/MS.

Sample Medium	Accuracy ¹ via PE/Spike Samples	Precision ² via Duplicate Analyses	Bruker-Lab Data Comparison ³	Reference Lab Data Quality
Soil	Goal Met	Goal Met	Goal Not Met	SRS: Undetermined WAFB: Good
Water	Goal Met	Goal Met	Goal Met	SRS: Good WAFB: Good
Soil Gas	Goal Met	Goal Met	Goal Met	SRS: Satisfactory WAFB: Satisfactory

Other Bruker GC/MS Performance Indicators

Target Compound Identification in Complex Mixtures

The ability of the instrument to identify a broad range of compounds in complex mixtures was also amply demonstrated with many of the WAFB samples. An example of a Bruker reconstructed ion chromatogram for a selection of target compounds in a water sample containing numerous volatile organic compounds is shown in Figure 6-26. A listing of the identified target compounds, corresponding to the peak numbers shown in Figure 6-26, is presented in Table 6-9. An on-site computerized library search of Bruker GC/MS analysis results from a similar WAFB water sample produced over 100 tentatively identified compounds revealing the complex nature of this particular water matrix.

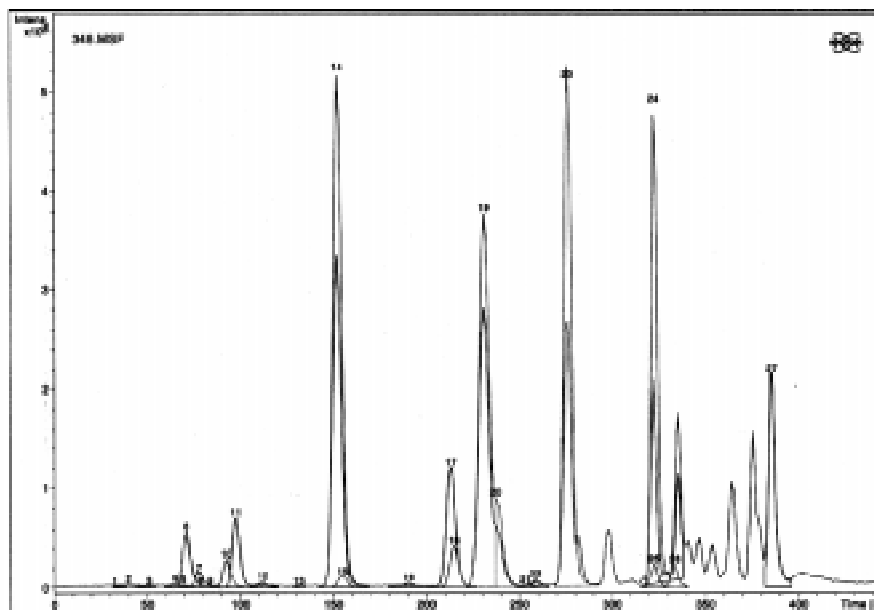


Figure 6-26. Bruker GC/MS reconstructed chromatogram of target analytes in a WAFB water sample.

Field Handling and Operation

The Bruker GC/MS is designed to be shipped to the field and is shock mounted for durability in handling and field use. Prior to the WAFB demonstration, the system was transported by air freight from Germany to the USA. The ruggedized design contributed to stable instrument calibrations over the duration of each demonstration, despite several days of travel on dirt roads during the course of the demonstration. At each site, the system was operated for several days in a row, typically 8-10 hours per day. The instrument was

exposed to ambient temperatures ranging from 40° to 95°F. During both demonstrations, the instrument operated properly and without significant breakdowns or mechanical problems.

Table 6-9. Identified Target Compounds from a Wurtsmith Water Sample Analysis.

Peak No.	Compound
1	Ethene, 1,1-dichloro-
2	Methylene chloride
3	Ethene, 1,2-dichloro-, trans
4	Ethene, 1,2-dichloro-, cis
5	Chloroform
6	Methane, dibromofluoro-
7	Benzene, pentafluoro-
8	Ethane, 1,2-dichloro-
9	Ethane, 1,1,1-trichloro-
10	Benzene
11	Benzene, 1,4-difluoro-
12	Trichloroethene
13	Methyl isobutyl ketone
14	Toluene-d8
15	Toluene
16	Tetrachloroethene
17	Benzene-d5-,chloro-
18	Benzene, chloro-
19	Ethylbenzene / m-Xylene
20	p-Xylene
21	Styrene
22	o-Xylene
23	p-Bromofluorobenzene
24	Benzene-d4, 1,4-dichloro
25	Benzene, 1,2(1,3)-dichloro
26	Benzene, 1,4-dichloro
27	Naphthalene

Note: The peak numbers refer to those given in Figure 6-26.

System set-up was simple and uncomplicated. Set-up procedures involved connecting the ancillary equipment and checking the instrument calibration. Sample analysis time varied according to the sample media and the mode of injection; however, a typical time interval was on the order of 12 minutes per sample. Hard copy data were available at the end of each run.

Overall Bruker GC/MS Performance Conclusions

The Bruker GC/MS system was tested at two locations during this technology demonstration in order to evaluate its capabilities and performance during on-site analysis of VOC contaminated soil, water and soil gas samples. The objectives of the demonstration were: (1) to evaluate instrument performance; (2) to determine how well each field instrument performed compared to reference laboratory data; (3) to evaluate instrument performance on different sample media; (4) to evaluate adverse environmental effects on instrument performance; and, (5) to determine logistical needs and field analysis costs. The system performance goals are summarized in Table 6-10 along with an assessment, based on the data produced in this demonstration, as to whether these goals were met.

As shown in Table 6-10, Bruker GC/MS performance goals were met with two exceptions. Instrument performance in terms of accuracy, precision, and comparison with reference laboratory data met

established performance goals for water and soil gas analyses. The comparison of the Bruker data to the laboratory data was below established goals for soil analyses. Performance goals related to data completeness and data availability were met. The initial Bruker claims of sample throughput rates of 8 samples per hour for soil samples and 6 samples per hour for water and soil gas samples were met during the SRS demonstration. Throughput rates at the WAFB demonstration were about 5 per hour and were not significantly less than the original claims. The sample matrix at WAFB was considerably more complex than that encountered at SRS. This resulted in longer analysis times and reduced sample throughput at WAFB.

Table 6-10. Summary of Bruker Performance Goals and Actual Performance.

Performance Goal	Performance	Goal Met?
ACCURACY: Median absolute percent accuracy within 35% of reference value; or, Median accuracy comparable to reference laboratory accuracy.	Soil gas less than 35% accuracy; Water and soil comparable to reference laboratories.	Water: Yes Soil Gas: Yes Soil: Yes
PRECISION: Median relative percent difference within 30% (water, soil), 35% (soil) or, Median relative percent difference comparable to laboratory precision.	Water, soil, and soil gas RPD less than 30%	Water: Yes Soil Gas: Yes Soil: Yes
REFERENCE LABORATORY DATA COMPARISON: Median absolute percent difference less than 50%; or, if greater than 50% , no significant bias via statistical test.	Water and soil gas differences less than 50%; soil data not comparable	Water: Yes Soil Gas: Yes Soil: No
COMPLETENESS: At least 95% of target compounds detected by reference laboratory also detected by Bruker.	Soil > 99% Water > 99% Soil Gas > 99%	Yes
SAMPLE THROUGHPUT: Method dependent: Soil - 8 samples/hr; Water and soil gas - 6 samples per hour.	Sample throughput met claim at SRS; slightly less than claim (5/hr) at WAFB.	Yes (SRS) No (WAFB)
DATA: Quantitative results submitted at the end of sample analyses.	Data were submitted at the end of each run	Yes
DEPLOYMENT: The Bruker EM640 can be set up and ready to run within 60 minutes.	The system was ready to run samples in 60 min.	Yes

Section 7

Applications Assessment

The Bruker-Franzen EM640™ field portable GC/MS instrument was demonstrated during this verification effort at two geologically and climatologically different sites with a wide range of volatile contaminants. The instrument was used to analyze soil gas, water, and soil samples on-site and in near-real-time. As demonstrated, the Bruker field portable GC/MS system has an application in several field screening and analysis scenarios.

Applicability to Field Operations

From a logistical viewpoint the Bruker-Franzen EM640™ GC/MS has been ruggedized for installation in a van or truck for use in field operations. Since the instrument is not totally self-contained, the van is required to carry the additional equipment needed to support the GC/MS instrument. Required ancillary equipment includes a separate computer system, batteries, or alternatively, a power generator, and a large cylinder of compressed carrier gas. In this configuration, the system can be reliably operated in the field over a wide range of temperatures and relative humidity. Additionally, the system can be operated in a moving vehicle thus increasing the amount of time for on-site sample analysis. System set-up and operation may require a two-person operation for maximum sample throughput. The system uses unique data handling and analysis software.

Capital and Field Operation Costs

On-site field analysis of samples has the potential to reduce overall site characterization and cleanup costs. Real-time and on-site analysis of samples can provide immediate direction to a sampling team during site characterization, thus reducing both the number of sampling trips to the site and the number of samples to be analyzed. Additionally, real-time analysis of samples during site remediation can often minimize the amount of material treated, thus reducing both remediation costs and the time required for site cleanup. The actual cost savings that can be realized from the field analysis of samples depends on many factors. These include: the capital costs of the field analysis system; field operation costs for equipment, supplies, travel, and per diem; labor and overhead costs; sample analysis requirements; and the overall utilization rate of the field instrument.

Capital and field operation costs for the Bruker EM640™ were determined during the demonstration and are presented in Table 7-1. Estimates of sample throughput rates for the single ion monitoring and scanning analysis modes for the Bruker instrument are also provided. Actual sample analysis rates will vary as a function of the media and the contaminants being analyzed. The values provided in Table 7-1 can be used as a guide in assessing the utility and cost effectiveness of using this system for various applications.

Discussion of the Technology

Rapid Analysis

The use of the Bruker field transportable GC/MS system provides near-real-time analysis of samples on-site. This approach is significantly faster than laboratory methods and expedites real-time decision making in the field. This is especially important in guiding sampling activities. Near-real-time analysis of samples on-site may eliminate the need and cost of return trips to the field to collect additional samples. Calibration checks can be done quickly in the field using 24 internal compound standards. As many as five to six laboratory quality sample analyses can be conducted in an hour with this system.

Table 7-1. Bruker EM640™ GC/MS Capital and Field Operation Costs.

<u>Capital Costs</u>	
Bruker-Franzen EM640™ GC/MS (data system and 1 yr. warranty)	\$185K
Ancillary Equipment - Pumps, water sampler, generator	\$25K
Four-year service contract	\$84K
Vehicle	\$35K
Equipment installation	\$15K
Training (2 people for two weeks)	<u>\$6K</u>
<i>Total</i>	\$350K
Annualized system costs for five years (\$350K ÷ 5 years)	\$70K/year
Maintenance (annually 10% of capital equipment costs) Includes new columns, preventive maintenance, software and hardware upgrades, etc:	\$2.5K/year
Five-year annual system and maintenance costs	\$72.5K/year
<u>Field Operation Costs</u>	
Field chemist (\$60K/year including overhead)	\$230/day
Chemical technician (\$50K/year including overhead)	\$190/day
Per diem (lodging and meals - 2 people)	\$200/day
Supplies and consumables (standards, syringes, vials, gas, etc.)	<u>\$ 80/day</u>
<i>Total</i>	\$700/day
<u>Sample Analysis Rates</u>	
Single ion monitoring analysis	60 samples/day
Scanning monitoring analysis	100 samples/day

Sampling and Sample Cost

A major cost savings obtained by the use of field analyses arises from the reduction in time required to obtain the analytical results needed for decision making. In its configuration during this demonstration, the Bruker GC/MS, in most cases, produced good quality data in the field. The ability to generate good quality data in near-real-time allows decisions to be made concerning the extent and completeness of cleanup operations while field equipment is still mobilized. This can result in significant cost reductions by eliminating re-mobilizations or the removal of extra materials to be assured that the cleanup is complete. Similar savings can be achieved during site characterization by eliminating the need for multiple sampling mobilizations as additional sampling efforts can be directed based on real-time data.

Transportability

The ruggedness of the Bruker GC/MS was illustrated by its daily transportation in a vehicle to and from the demonstration sites. Mounted in a small van or truck for field operations, the system is self contained and does not need additional support equipment. This ruggedness and portability provides the system with the ability to perform good quality sample analysis.

Field Screening of Samples

The system's capabilities for transportability and real-time analysis make the instrument useful as a tool for site characterization and monitoring activities. The instrument may be used as a high volume screening tool (scan mode) to guide sampling and remediation efforts or to provide higher quality analyses on selected samples (single ion monitoring mode). The capability to identify unknown compounds with the portable GC/MS enables a site manager to investigate a site for a wide range of contaminants at a single time. The use of the system as a screening tool to guide sampling efforts in the field can provide significant cost savings in terms of the number of samples needed and need for return trips to the field.

Sample Size

The preferred method for water analysis using this system is spray and trap. This process requires a larger than normal sample, at least 250 mL, for water analysis. Since this is significantly larger than normal sample needs, standard sample collection procedures may have to be modified for this system.

Interferences

The presence of contamination can be periodically checked through the analysis of reagent blanks--a procedure normally followed with most laboratory and field GC/MS systems. Since calibration of the system takes only 30 minutes, the sample throughput is not significantly affected by the need to re-calibrate.

Conclusions

The Bruker-Franzen EM 640™ GC/MS can provide good quality sample analysis on-site and in near-real-time. The technology may offer time and cost saving advantages over conventional sampling and laboratory analysis strategies. The system or others like it may never entirely replace conventional laboratory analysis, but the technology can add significant benefits in terms of defining the nature and extent of contamination at a site. The limitations of the system are generally related to the underlying operational considerations associated with the basic use of GC/MS systems.

Section 8 Developer's Forum

These comments were provided by Bruker. Their purpose is to provide the technology developer with the opportunity to share their comments about the verification program. The comments have been minimally edited. The views are solely those of Bruker Instruments Inc. and should not be construed to reflect the views of EPA.

1. Lessons learned:

- It can easily happen in the field, that samples are mistakenly switched, even by official sampling personnel. Therefore: Do not trust the labels on sample tubes, and if you run into saturation with a sample marked “low concentration”, do not immediately start to dilute the samples marked “medium concentration” and “high concentration”, you may have to multiply measured concentrations near the detection limit by extremely high numbers! (It's a wonder that we came out sufficiently well for these samples).
- Don't be proud to deliver results much below the practical detection limit defined by yourself for your method. You may not fulfill the accuracy you claimed with these numbers because these are pitilessly included into the evaluation, even if the reference laboratory claimed these samples as not applicable (non-detectable levels).
- We should not be shy to apply not established but field practical evaluation methods. Example: The calibration check samples for water analysis at WAFB shows average recoveries over 135%. If we had used these recovery rates for continuous corrections of field analytical results, all our results had fulfilled our own accuracy and precision claims ($\pm 35\%$). We are considering to apply this method in the future.

2. How to do better:

- The analytical task should be more specifically and more uniformly defined for all participants in the test. The substances for quantitative measurements should be precisely listed, not given as vague recommendations in order to let the participants select.
- At least two independent reference laboratories should be used. (We simply don't believe in results from reference laboratories, field analytics is better).
- More samples and more duplicates should have been analyzed, especially for Spike and PE samples, which were used to determine the accuracy of each instrument. For example: If 2 of the 5 samples used for accuracy determination are mistakenly switched, this has a tremendous impact on the overall test results.

3. And some criticisms:

- We did not take part in the sampling process, neither in the definition, nor in the real sampling or in the documentation. For example: There were droplets in some of the Tedlar bags used to bring soil air. We doubt that anyone has documented this fact.
- The high cost of the laboratory analyses was defined in the kickoff meeting as the primary reasons for this test of field transportable GC/MS systems. However, later in the evaluation and assessments, costs (and therefore short analysis cycle times) were listed under “secondary objectives”.

- Continuously performed quality assurance measures were not merited in the assessment:
 - Several internal standards and surrogates in all samples
 - Monitoring of mass 40 amu (Argon) throughout all measurements for monitoring the instrument performance.
- PE samples, used to measure the accuracy, should generally be delivered in duplicates.

Section 9

Previous Deployments

Fenstheen, Germany (October 1994). Evaluation of the ability of field GC/MS, in conjunction with other sensor techniques, to detect trace amounts of hazardous contaminants. Bruker contacts John Wronka, USA, Phone: (508) 667-9580, Birgit Nolke, Germany, Phone: 001-49-421-2205-0.

Section 10

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Appendix A

Analytical Method for the Operation of the Bruker EM640™ Gas Chromatograph/Mass Spectrometer System

Prepared by
Bruker Instruments, Inc.
 (Formerly Bruker-Franzen Analytical Systems, Inc.)

1.0 Scope and Application

Using the EM640™ GC/MS system, organic compounds in air (soil gas), water, and soil are qualitatively and quantitatively analyzed. This method applies to the use of the EM640™ for the analysis of volatile compounds in all these three environmental matrices. The compounds in Table A can be determined by applying this method.

Table A. Volatile Organic Compounds Detected with the EM640™

Analyte	CAS No. (a)
Chloromethane	74-87-3
Bromomethane	74-83-9
Vinyl Chloride	75-01-4
Chloroethane	75-00-3
Methylene Chloride	75-09-2
Acetone	67-64-1
Carbon Disulfide	75-15-0
1,1-Dichloroethene	75-35-4
1,1-Dichloroethane	75-34-3
1,2-Dichloroethene (cis)	156-69-4
1,2-Dichloroethene (trans)	156-60-5
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
2-Butanone	78-93-3
1,1,1-Trichloroethane	71-55-6
Carbon Tetrachloride	56-23-5
Vinyl Acetate	108-05-4
Bromodichloromethane	75-27-4
1,2-Dichloropropane	78-87-5
<i>cis</i> -1,3-Dichloropropene	10061-01-5
Trichloroethene	79-01-6
Dibromochloromethane	124-83-1
1,1,2-Trichloroethane	79-00-5
Benzene	71-43-2

TABLE A Continued

trans-1,3-Dichloropropene	10061-02-6
Bromoform	75-25-2
4-Methyl-2-Pentanone	108-10-1
2-Hexanone	591-78-6
Tetrachloroethene	127-18-4
1,1,2,2-Tetrachloroethane	79-34-5
Toluene	108-88-3
Chlorobenzene	108-90-7
Ethyl Benzene	100-41-1
Styrene	100-42-5
<i>p</i> - & <i>m</i> - Xylene	106-42-3,108-38-3
<i>o</i> -Xylene	95-47-6

(a) Chemical Abstract Services Registry Number.

1.1 Principle of Operation

Volatile organic compounds (VOCs) in liquid or solid samples have to be transferred to the gas phase. The gas phase carrying the VOCs extracted from liquid or solid samples, as well as gaseous samples, are introduced into a gas chromatograph (GC) for separation. Compounds eluting out of the GC column permeate through an inlet membrane into the vacuum chamber of the mass spectrometer (MS). In the ion source, the molecules are ionized by electron impact. All ions pass through the quadrupole which filters them depending on their mass-to-charge ratios (m/z). Finally, the ions are detected in an electron multiplier and an electrical signal is generated proportional to the number of ions. The data system records these electrical signals and converts them into a mass spectrum. The sum of all ions in a mass spectrum corresponds to one point in the gas chromatogram (total ion chromatogram). A mass spectrum is like a fingerprint of a compound. These fingerprints are compared with stored library spectra and used together with the GC retention times for the identification of the compounds. The integrated area under a GC peak is used for quantitation.

1.2 Detection Limits

Detection limits vary depending on compound, media, operation mode of the MS (“scan” or “single ion monitoring”) and sample volume. Generally, for most of the compounds in Table A the practical quantitation limits (PQL) in the “scan mode” are 100 ng/L for air (100 mL sample volume) and water samples (250 mL sample volume). For soil samples (6 g) the PQL is approximately 50 mg/kg. The operation mode “single ion monitoring” (SIM) of the MS gives a factor of 10 in sensitivity. To express this in absolute values, the mass spectrometer needs 1 ng of a compound to produce a signal-to-noise ratio of 10 in the scan mode.

2.0 Summary of Method

2.1 Water Samples

Water samples of 250 ML volume are sprayed in a spray chamber. During the spray process volatile compounds are extracted into the gas phase (purified air), transferred to a Tenax tube, and trapped. In the desorption port of the EM640™ the sorbent tube is heated and backflushed with air to desorb trapped

sample components. The analytes are desorbed directly to a capillary for GC/MS analysis (8 m DB5 column; phase: 5 μm ; I.D.: 0.32 μm). The GC-capillary is temperature-programmed. Analytes separated in the capillary are then detected with the quadrupole mass spectrometer interfaced to the gas chromatograph. The mass spectrometer (EM640TM) is equipped with a membrane separator, which can be used with short capillary columns with high carrier gas flows and protects the ion source from contamination. Finally, the detected compounds are automatically identified (library comparison), quantified (internal standard method), and reported.

2.2 Air Samples

100 mL air is drawn through a Tenax tube, where the organic compounds are collected. Desorption and the analysis processes are analogous to those for the water samples.

2.3 Soil Samples

Soil samples are analyzed by a headspace technique. Six grams of soil are weighed in a scrubbed vial. The vial is heated up in a water bath after sealing. Volatile compounds establish an equilibrium between solid and gas phase. The headspace gas is then drawn into the GC/MS. The procedures for separation and detection of the compounds are similar to those for the air and water samples.

Sample sizes are flexible and depend primarily on the contaminant concentration. However, the calibration should be done with the same sample size as in the analysis.

3.0 Interferences

If isomers elute from the GC capillary at the same time and have an equal mass spectrum, they cannot be identified as different compounds. In such cases it is only possible to give the sum of the isomers for quantitation. Another quantitation problem can appear if the target mass of a compound is also found in the media compound that elutes at the same time (for example Benzene- d_6 with the target ion m/z 84 and at the same position in the gas chromatogram is a hydrocarbon that has also an ion with the m/z 84).

Major contaminant sources are volatile substances present on site as well as organic solvents that may be used for sample extraction. The use and frequent replacement of carbon filters on the GC reduces the levels of the on-site contamination during sample analyses.

Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing of the purging apparatus (for water samples) one time between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more calibration blanks should be analyzed to check for cross contamination.

4.0 Equipment and Supplies

4.1 The Spray Extractor

The recommended spray equipment is the Spray-and-Trap Water Sampler (Bruker Analytical Systems Inc., Billerica, MA) or for very sludgy samples the Spray-and-Trap suitcase (ecb ONLINE; Schwerin, Germany). The Bruker Spray-and-Trap Water Sampler device consists of a mechanical pump to inject a

continuous flow of an aqueous sample into a sealed extraction chamber through a spray nebulizer. The droplet formation enormously increases the total interfacial area between the sprayed water and the carrier gas, which supports the transfer of the VOCs into the gas phase. The steadily flowing carrier gas is transferred to a suitable sorbent tube, which collects the extracted VOCs. In contrast to the purge-and-trap method, spray-and-trap utilizes a dynamic equilibrium.

4.1.1 *Purge and Trap*

Alternative to the spray-and-trap, a standard purge-and-trap system can be used to load a sorbent tube.

4.2 The Sorbent Tube

The trap recommended must be a glass tube 110 mm long with an 0.8 mm OD and 0.6 mm ID. The glass should be sealed prior to use to avoid contamination. The trap must contain the following amounts of adsorbents: 1/3 of the trap 2,6-Diphenyl phenylene oxide polymer (Tenax), another 1/3 silica gel, and the last 1/3 Carbopack B. Silanized glass wool is used to separate each adsorbent and also to plug each end to retain the packing material. If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill the 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and Carbopack can be eliminated and the polymer Tenax increased to fill the entire trap.

The polymer alone also can be used if the concentrations are large enough. In this case the breakthrough volumes of the above compounds can easily be reached. A dynamic equilibrium will be formed, where the same amount of a compound that enters the sorbent tube leaves it at the other end. Thus, the sampled amount of the compound does not change with increased sampling time. The only way to use this special method is to always analyze an equal volume and to have a constant flow rate.

4.3 The Injector Systems

4.3.1 *The Desorber Module*

The desorber module is used for air and water analysis. A loaded sorbent tube is inserted into this module and heated up rapidly (400°C/min) to 250°C. After the split injection the tube is backflushed with purified air. Desorption and injection time, desorption temperature, backflush time and temperature and the carrier gas pressure are programmable and controlled by the software .

4.3.2 *The Headspace Module*

At one side of this module is an injection needle. This needle sticks through the septum of a headspace vial. The needle is coupled to an "Ultimet" capillary, which is at its other end directly connected to the GC column. At the downstream side from the inlet membrane of the MS is a pump which regulates the pressure inside this hollow fiber membrane. This pump is used to draw vapor out of the headspace vial (time and flow are programmable) into the GC column in the MS. The Ultimet capillary is heated and backflushed after injection.

4.4 Gas Chromatograph

The GC is temperature programmable and equipped with a flow controller to maintain a constant flow of the carrier gas through the column during operation. Filtered ambient air or nitrogen is used as the carrier gas. The GC is interfaced to the MS with a polysiloxane membrane.

4.4.1 *The GC column*

A 8 m long DB-5 (J&W Scientific) narrow bore capillary GC column with 0.32 mm i.d. and 5 μm film thickness is normally used. The temperature of the column is held at 50=C as starting temperature, then increased to 240=C at 20=C per minute, and held until all expected compounds have eluted. If it is acceptable to have a lesser degree of chromatographic separation (or only a few compounds to be analyzed), the analysis time can be shortened by increasing the slope of the temperature ramp or vice versa. As carrier gas, charcoal filtered air or nitrogen is used.

4.5 The Mass Spectrometer

Mass spectral data are obtained with electron impact ionization at a nominal electron energy of 70eV. The mass spectrometer is capable of scanning from 2 to 640 u in less than half a second (max speed 2000 u/s). To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

4.6 The Data System

The core of the data system is a ruggedized computer, that allows measurements during moving and has an OS/2 multi-tasking software. Thus, data storage and data analysis can take place simultaneously. The software is capable of automated peak picking, comparison with stored library spectra, quantitation, and printing a final report. In addition, all analysis parameters are stored for quality control purposes.

4.7 Microsyringes - 10, 25, 100, 500, and 1,000 μL .

4.8 Balance - Top loading, capable of accurately weighing 0.001 g.

4.9 Disposable pipets

4.10 Vials - 2.0 mL, 5.0 mL, and 22 mL with cap and septum.

4.11 A flow-controlled pump for air sampling.

5.0 *Reagents and Standards*

5.1 Methanol

Methanol should be of a purge-and-trap grade, demonstrated to be free of analytes. It should be stored apart from other solvents.

5.2 Distilled Water

Distilled water must be free of interferents at the method detection limit (MDL) of the analytes of interest.

5.3 Stock Solutions

Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol for water and air (injection in a Tedlar bag) analysis and in ethylene glycol for soil analysis.

5.4 Secondary dilution standards

Using stock standard solutions, use methanol (ethylene glycol for soil) to prepare secondary dilution standards containing the compounds of interest mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace for a maximum of one to two weeks.

5.5 Surrogate standard

A surrogate standard for all described methods is a mixture of three compounds (Dibromofluoromethane, Toluene-d₈ and 4-Bromofluorobenzene) in methanol. This mixture is suggested for EPA method 8260A, and used for the EM640™ methods.

5.6 Internal standard

The internal standard recommended is a mixture of Benzene-d₆ and Xylene-d₁₀ in methanol or, if many hydrocarbons are in the samples, the suggested mixture for EPA method 8260A (Chlorobenzene-d₅, 1,4-Dichlorobenzene-d₄, 1,4-Difluorobenzene and Pentafluorobenzene in methanol). An internal standard spiking solution should be prepared from a stock at a needed concentration. The surrogate spiking solution and the internal standard spiking solution may be combined into one vial.

5.7 Calibration standards

Calibration standards at a minimum of three, preferably 5-10, concentration levels should be prepared from a secondary dilution of stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method. Calibration standards must be prepared daily.

5.8 Media spike standards

Media spike standards can be purchased as certified solutions.

6.0 Procedure

6.1 Initial Calibration

6.1.1 *Tune and Calibration of the MS*

Before the initial calibration the automated mass scale calibration of EM640™ should be started. After finishing this calibration, the automated tune program (tuning of ion source and detectors) can run. In general, a mass scale calibration is only necessary once a month.

6.1.2 *Analyte Calibration*

A set of minimum of three, preferably 5-10, calibration standards containing the method analytes, surrogates, and internal standard are needed. For a calibration over a high dynamic range it is necessary to have two calibration points for each decade. The analytes should be spiked at concentrations above the detection limit through the upper concentration range expected during sample analysis. The surrogate standard should be added in the same amount as the analytes, but the internal standard should remain at a fixed concentration level (6 µg/l for air, 8 µg/l for water and 1 mg/kg for soil samples). Analyze the samples as described in Section 6.3.

6.1.3 *Calibration Curves*

Tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to the internal standard or make a linear regression curve for all compounds also relative to the internal standard.

6.2 **Daily calibration**

Prior to sample analysis a standard (calibration check) should be run that contains all analytes of interest near the midpoint concentration for the working range of the initial calibration. Then calculate the concentrations from all analytes. The software generates a report which contains the percent recovery for all detected and calibrated compounds. If the percent recovery for all analytes is between 65% and 135%, the initial calibration curve are used to calculate sample analyte concentration. If the criterion is not met for any one of the analytes corrective action must be taken. This involves the re-analysis of the continuing calibration standard, using new stock standard solutions, or the generation of a new initial calibration curve. The calibration check standard should be run at least after every 10th analysis. Thus, in the field, where a system recalibration is sometimes not possible, with these standard measurements during the whole day, corrective action to the initial calibration curve have to be made.

6.2.1 *Internal Standard Control*

The internal standard responses in the samples must be evaluated after or during data acquisition. If the Extracted Ion Current Profile (EICP) area for the internal standard from the samples changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the sample must be reanalyzed and the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. Sometimes sample media interferences can adversely affect the internal standard area. If the re-analysis confirms the deviation of a factor of two or more of the internal standard, the sample results should be flagged as questionable due to media interferences. If the EICP is different only for one of the 2 or 4 added internal standard compounds, then use for quantitation only the correct ones. The software allows it easily to change the calculation in a way, that all relations from the incorrect internal standard are changed to one of the correct ones. This is the case for the calculation of the calibration curve (or response factor), as well as for the quantitation of the samples.

6.3 **GC/MS Analysis**

Prior to sample analysis, the mass scale calibration of the MS and the tune parameters of the ion source should be checked. This is performed by a special program in the software.

6.3.1 *Surrogate Control*

For each sample analyzed, the percent recovery of each surrogate in the sample is calculated. If the percent recovery is greater than 65% but less than 135%, the sample analysis is assumed to be valid. If the criterion is not met, the sample must be reanalyzed. Sometimes sample media interferences can adversely affect the surrogate recovery. If the re-analysis confirms the percent recovery being outside the criterion range, the sample results should be flagged as questionable due to media interferences.

6.3.2 *Sample Storage*

The advantage of field instruments is to analyze the samples directly after their collection, which makes sample preservation and storage unnecessary.

6.3.3 *Air Analysis*

If the air samples are in a Tedlar-bag or a similar gas container, add the internal standard and the surrogate mixtures to the gaseous samples. If the samples are collected directly, without any container, inject these mixtures in the sorbent tube (direct on Tenax). Connect a flow-controlled pump to the sorbent tube and sample at least 200 mL purified air (outside air filtered through charcoal) through the tube to get rid of the methanol. Then suck the sample through the tube with a flow of 100 mL/min. The sample volume depends on the expected concentration. A useable range is between 100 and 1000 mL. It is absolutely necessary to use exactly the same sample volume for calibration and for samples, if the internal standard is injected in the tube, if only Tenax is used as sorbent and the sample contains compounds with boiling points under 35=C (Section 4.2). After sampling, insert the sorption tube in the desorption oven and press the start button.

Now, the programmed analysis is running. The sorption tube is heated with a temperature gradient of 400=C/min up to 250=C for 90 s. The desorbed compounds were injected for 20 s. After injection, the tube is backflushed and the GC program starts. The column used and the temperature program depends on the analytical task. For normal fast field analyses use a short 8 m thick film (5 µm) DB 5 capillary with an i.d. of 0.32 µm. Start at a temperature of 50 °C and heat with a gradient of 20 °C/min up to 240 °C. It is recommended to optimize between necessary separation and shortest time, if many samples of the same kind should be analyzed.

Such a temperature program can for example look like this: Start at 50=C and heat with a gradient of 15=C/min up to 80=C. Then continue heating slower with a gradient of 10=C/min up to 100=C, because now, in these special samples, many compounds elute from the GC. After reaching 100=C heat the column with a steep gradient of 45=C/min up to the final temperature of 220=C (This temperature program was used for the GC/MS demonstration at Wurtsmith Air Force Base). The carrier gas (charcoal-filtered air) pressure was 450 mbar and the split is set on 20 mL/min. For screening analysis use a 3 m thinfilm (1 µm) DB 5 capillary and start at 100=C and heat with a gradient of 30=C/min the column up to 240=C (the carrier gas pressure should be not more than 300 mbar). For most separations a 20 m RTX 624 column with a film thickness of 1.8 µm and an i.d. of 0.32 µm can be used. Start at 30=C, hold for 2 min and then heat with a gradient of 10 °C/min or less up to a temperature of 240=C. Analytes separated in the capillary are then detected with the quadrupole mass spectrometer interfaced to the gas chromatograph.

6.3.4 *Water Analysis*

Fill a normal 250 mL laboratory bottle with the water sample. Add the internal standard and surrogate solution and connect the bottle to the water sampler. The cap of this bottle has a hole in the middle,

through which a tubing is fitted. This tubing is connected to the water inlet of the water sampler with a Swagelok ferrule. The sampler has to be driven with an equal carrier gas and water (sample) flow rate as during the calibration. Recommended values are 250 mL/min for the carrier gas flow and 80 mL/min for the water flow rate. An automated program pumps the water sample at the beginning for 15 s over a bypass to fill all sampler tubes with the new sample. Then, the aqueous sample is sprayed for 2 min into the steadily flowing carrier gas in the extraction chamber. The extracted VOCs are trapped in a sorption tube which is placed in the gas outlet stream of the sampler. After finishing the sampling, the tube is inserted in the desorber module of the EM640™. The GC/MS analysis is the same as procedure described in Section 6.3.1.

6.3.5 *Soil Analysis*

Weigh 6 g soil sample in a 22 mL headspace vial and seal it. Inject the internal standard and the surrogate solution through the septum of the vial directly into the soil sample. Do **not** inject the solutions at the walls of the vial. Put the vial for exactly 10 min into a waterbath heated on 80°C. Stick a needle through the septum, to have atmospheric pressure inside the vial, immediately press the start button of the headspace injector module from the EM640™ and with the other hand (at the same time) place the vial under the injection needle of the injector. After 15 s injection time, the vial can be removed from the injector module. The GC/MS analysis is the same as procedure described in Section 6.3.1.

6.3.6 *Qualitative Analysis*

For the evaluation of the data different methods can be selected. An evaluation file is generated with the measurement of the standard. This file contains for every compound a time window for the retention time, the compound's name, and the method for quantitation (for example the target mass of each compound). The GC peak in this time window is detected and an average spectrum of 5 mass spectra is calculated. With this spectrum a library search is activated. Only if the correct compound (the compound out of the evaluation file) is found, the area under the target mass trace is integrated for quantitation. If the identification is not positive, because it is another compound or because the compound is overlapped with a media compound, the data postprocessing switches to a manual mode and the user can take a look at the mass spectrum of this compound by himself. It is the analysts decision to determine if the target ion should be integrated or not (if the compound is the right one or not). In the worst case, the overlapped media compound contains the target ion another target ion has to be selected for this special compound. But, if parameters are changed, a new generation of the calibration curve is needed with the original stored data.

The second mode is completely automated. The dissect algorithm calculates the mass spectra of each GC peak in a defined time window. This special algorithm is capable of separating compounds, even if their GC peaks are almost completely overlapped, as long as the compounds have different mass spectra (at least one significant mass must be different), and as long as their retention time difference is larger than the acquisition time of half a mass spectrum. The calculated mass spectrum of the pure compound is used for the library search. If the identification is positive, then the area under the calculated trace is integrated and used for quantitation of this compound. Negative identification is interpreted in such a way that the compound found, is not the compound out of the evaluation list and therefore, a calibration curve does not exist. Calculated quantitative results are printed out in a report.

All compounds that are not in the evaluation file (not quantified) are detected and identified by the dissect algorithm. In addition, an automatic library search can be done. The result of the evaluation file is to have a complete identification of all compounds in an analysis and a specific one for all compounds (target ion or "dissect" area depends on specification).

6.3.7 *Quantitative analysis*

The concentrations of the compounds are calculated using the determined peak areas. The quantification will take place using the internal standard technique. In the quantitation file (stored calibration curves) it is defined which compound is related to which internal standard.

All compounds that are found by the dissect algorithm but are not in the quantitation file are identified by a library search. These compounds are listed including their “dissected” areas in the report as tentatively identified. The internal standards are also listed with their “dissected” areas. Since the concentration of the internal standards are known, rough concentrations of the compounds can be calculated.

7.0 *Quality Control*

7.1 **Blank Analysis**

Before processing any samples the analyst should demonstrate, through the analysis of a calibration blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of sample is extracted or there is a change in reagents, a reagent blank should be processed as a safeguard against contamination. The blanks should be carried through all stages of sample preparation and measurement.

It is necessary to analyze a reagent blank following a heavily contaminated sample where saturated peaks have occurred. This will eliminate problems of carry over from one sample to the next.

7.2 **Calibration Check Standards**

Calibration check standards should be run at least after every 10th analysis to determine if the GC/MS system is operating properly.

7.3 **System set up**

Prior to sample analysis the mass scale calibration of the MS and the tune parameters of the ion source should be checked. This is done by a special software program.

7.4 **Initial Calibration**

For quantitative analysis, an initial calibration of the GC/MS system must exist as specified in Section 6.1.

7.5 **Surrogates**

For each sample analyzed, the percent recovery of each surrogate in the sample is calculated. For all samples of the same media (of one batch), the average percent recovery (p), and the standard deviation of the percent recovery (sp) for each of the surrogates are calculated.

7.6 **MS Control**

In each analysis run the ion mass 40 (argon, if air is used as carrier gas), or the ion mass 28 (N_2 if nitrogen is used as carrier gas) is measured. These ions are produced by the carrier gas and can be used as internal standard for MS sensitivity. Thus a **permanent** control of the MS system is achieved.

8.0 Method Performance

8.1 Accuracy

The method accuracy for all three matrices (air, water and soil) is 35%. That means 99% of all measured results are between 65% and 135 % of the true values.

8.2 Precision

The method precision for air and water analysis is 30% RPD (relative percent difference). For soil analysis the RPD is 35%.

Method precision and accuracy are determined in a field application for 3 surrogate compounds. The surrogate concentrations added to the samples, were always the same independent of the concentration of the analytes (see table B).

Table B:

Surrogates	RPD1	A.A.1	RPD2	A.A.2	RPD3	A.A.3
		%		%		%
p-Bromofluorobenzene	18.2	91	12.5	105	19.1	104
Dibromofluoromethane	12.5	106	10.2	101	46.5*	135
Toluene-d ₈	07.6	90	09.0	110	20.7	108

RPD: Relative Percent Difference

A.A.: Average Accuracy

1: 10 Air Samples

2: 11 Water Samples

3: 13 Soil Samples

*: This value is out of range. A reason could be the media influence on this compound.

9.0 References

1. Method 8260 - GC/MS for Volatile Organics: Capillary Column Technique. Test Methods for Evaluating Solid Waste Physical/Chemical Methods - Third Edition Proposed Update Package., US EPA, Washington, DC, 1989.
2. Bruker Method B24 (VOA): Gas Chromatography/mass Spectrometry for Volatile Organics: Capillary Column Technique for On Site Analysis.
3. B. Nölke, G. Baykut, "Enhanced efficiency spray extractor for sampling volatile organic compounds in aqueous systems" Rev. Sci. Instrum. **65** (1994) 363.