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Environmental Technology Verification Report

Groundwater Sampling Technologies

Burge Environmental, Inc. Multiprobe 100

Sandia National Laboratories

ETV ETV ETV

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

EPA
U.S. Environmental Protection Agency

ETV ✓

Sandia National Laboratories

ETV JOINT VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**GROUNDWATER SAMPLING TECHNOLOGIES**
APPLICATION:	**VOC-CONTAMINATED WATER SAMPLING**
TECHNOLOGY NAME:	**Multiprobe 100**
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The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations and stakeholder groups consisting of regulators, buyers, and vendor organizations, with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Site Characterization and Monitoring Technologies Pilot, one of 12 technology areas under ETV, is administered by EPA's National Exposure Research Laboratory. Sandia National Laboratories, a Department of Energy laboratory, is one of the verification testing organizations within the ETV Site Characterization and Monitoring Pilot. Sandia collaborated with personnel from the US Geological Survey to conduct a verification study of groundwater sampling technologies. This verification statement provides a summary of the results from a verification test of the Multiprobe 100 sampler manufactured by Burge Environmental.

DEMONSTRATION DESCRIPTION

In August 1999, the performance of six groundwater sampling devices was evaluated at the US Geological Survey Hydrological Instrumentation Facility at the NASA Stennis Space Center in southwestern Mississippi. Each technology was independently evaluated in order to assess its performance in the collection of volatile organic compound- (VOC) contaminated water.

The verification test design incorporated the use of a 5-inch diameter,100-foot standpipe at the USGS facility. The standpipe, serving as an "above-ground" well, was filled with tap water spiked with various concentration levels of six target volatile organic compounds. The target compounds (1,2-dichloroethane, 1,1-dichloroethene, trichloroethene, benzene, 1,1,2-trichloroethane, and tetrachloroethene) were chosen to represent the range of VOC volatility likely to be encountered in normal sampler use. Water sampling ports along the exterior of the standpipe were used to collect reference samples at the same time that groundwater sampling technologies collected samples from the interior of the pipe. A total of seven trials were carried out at the standpipe. The trials included the collection of low (~20 µg/L) and high (~200 µg/L) concentrations of the six target VOC compounds in water at sampler depths ranging from 17 to 91 feet. A blank sampling trial was also included in the test matrix.

The standpipe trials were supplemented with additional trials at groundwater monitoring wells in the vicinity of sites with VOC-contaminated groundwater at the NASA Stennis facility. The sampling devices were deployed in a number of 2-inch and 4-inch wells, along with co-located submersible electric gear pumps as reference samplers. The principal contaminant at the onsite monitoring wells was trichloroethene. The onsite monitoring provided an opportunity to observe the operation of the sampling system under typical field-use conditions.

All technology and reference samples were analyzed by two identical field-portable gas chromatograph-mass spectrometer (GC/MS) systems that were located at the test site during the verification tests. The GC/MS analytical method used was a variation of EPA Method 8260 purge-and-trap GC/MS, incorporating a headspace sampling system in lieu of a purge and trap unit. The overall performance of the groundwater sampling technologies was assessed by evaluating sampler precision and comparability with reference samples. Other logistical aspects of field deployment and potential applications of the technology were also considered in the evaluation.

Details of the demonstration, including an evaluation of the sampler's performance, may be found in the report entitled *Environmental Technology Verification Report: Burge Environmental Inc., Multiprobe 100,* EPA/600/R-00/074.

TECHNOLOGY DESCRIPTION

The Multiprobe 100 is a discrete, multi-level sampler that is designed for permanent deployment in a well. The sampler is designed for use with a complementary automated wellhead analyzer for TCE called the Optrode. Only the sampling module was evaluated in this test. Optrode performance was not evaluated in this demonstration.

The Multiprobe 100 consists of two units with tubing and wiring interconnections. A upper receiving module which is deployed at the wellhead on top of the well is 18 inches long, 3.25 inches in diameter, and weighs 3 pounds. The lower sampling module, which is inserted into the water column inside the well, is 12 inches long, 3.25 inches in diameter and also weighs 3 pounds. The system is constructed of Teflon, borosilicate glass, stainless steel and Delrin®, a solvent-resistant, acetal homopolymer resin. Electrical solenoid valves are used to select the sampling level and control gas flow to the sampler. Water level sensors in the water chambers of both modules are used to trigger valve changes during the sampling process. A small, battery-operated microprocessor controller is used to control the valves used during the sampling process.

The lower sampling module is filled with water from the selected sampling level by hydrostatic pressure. The water sample is then pushed up to the upper receiving module by pressurizing the sampling chamber headspace with nitrogen gas. Samples can be manually dispensed into analysis vials from the upper receiving module, however, the system is primarily intended for interconnection with automated analyzers, such as the Optrode, which would also be positioned at the wellhead.

The system also has the ability to purge volatile organic compounds from water *in situ* with subsequent analysis by sensors, such as the Optrode, that are positioned in the headspace or at the wellhead. Following the purge, the vapors can also be transported via tubing to the surface for collection and analysis. The *in situ* purge capability of the sampler was not tested in this investigation.

VERIFICATION OF PERFORMANCE
The following performance characteristics of the Multiprobe 100 groundwater sampling system were observed:

Precision: The precision of the sampler was determined through the collection of a series of replicate samples from two standpipe trials using low (~20 µg/L) and high (~200 µg/L) VOC concentrations at 17, 35, 53 and 91-foot depths. Each trial included 6 target VOCs at each of the sampling depths, resulting in a total of 24 cases per trial. Multiprobe 100 precision, represented by the relative standard deviation, for all compounds at all concentrations and sampling depths evaluated in this study ranged from 3 to 21% with a median value of 9.4 %. In 27 of the 48 cases, the Multiprobe 100 was less precise than the reference sample set. The F-ratio test was used to assess whether precision differences between Multiprobe 100 and reference samples were statistically significant. Test results showed that precision differences between the Multiprobe 100 and reference samples were statistically insignificant at the 95% confidence level in 46 of the 48 test cases.

Comparability with a Reference: Multiprobe 100 sampler results from the standpipe trials were compared with results obtained from reference samples that were collected at the same time. Both Multiprobe 100 and reference samples were analyzed by the same method using the same GC/MS system. Sampler comparability is expressed as percent difference relative to the reference data. Sampler differences for all target VOC compounds at all concentrations and sampler depths in this study ranged from -30 to 15%, with a median percent difference of -5%. The t-test for sample means was used to assess whether the observed differences between Multiprobe 100 and reference samplers were statistically significant. These tests revealed that in 31 of 48 trials, differences were statistically indistinguishable from 0% at the 95% confidence level. Of the remaining 17 cases that were statistically different from 0%, 16 showed a negative Multiprobe 100 sampler bias. Statistically significant negative sampler bias ranged from – 10 to – 30%.

Versatility: Sampler versatility is the consistency with which it performed with various target compounds, concentration levels, and sampling depths. In terms of precision, Multiprobe 100 performance was generally consistent at the range of concentrations and collection depths evaluated in this study. The Multiprobe 100 showed a trend toward negative bias for 11DCE and TCE and the sampler showed consistently negative bias for PCE at all concentrations and sampler depths. As a result of its physical size, the Multiprobe 100 cannot be installed in wells with diameters less than 4 inches. In light of these considerations, the Multiprobe 100 sampler in its aqueous sampling mode is judged to have limited versatility.

Logistical Requirements: The Multiprobe 100 is designed for permanent installation in 4-inch or larger wells. The installation would require either custom installation by Burge Environmental personnel or user installation following approximately two days of training. Although the system is optimized for

automated operation, it can also be used in a manual mode. The system is also capable of being removed from one installation for redeployment in a second well however several hours of disassembly and re-assembly time would be required. The system also requires a source of compressed nitrogen at the wellhead.

Overall Evaluation: The results of this verification test show that the Multiprobe 100 multi-level sampler can be used to collect VOC-contaminated water samples that are generally statistically comparable to reference samples. Sampler recoveries for PCE in the aqueous sampling and transfer mode were consistently low when compared to reference samples. Further investigation of sampler performance for this compound may be required. The Multiprobe 100 is a component of an overall automated sampling and analysis system. Only the sampler module was evaluated in this test. A complete system evaluation would be warranted prior its deployment in long term automated monitoring applications.

As with any technology selection, the user must determine if this technology is appropriate for the application and the project data quality objectives. For more information on this and other verified technologies visit the ETV web site at http://www.epa.gov/etv.

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Environmental Technology Verification Report

Groundwater Sampling Technologies

Burge Environmental Inc.

Multiprobe 100

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Notice

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Abbreviations and Acronyms

BNZ	Benzene
DIFF	Difference
EPA	US Environmental Protection Agency
ETV	Environmental Technology Verification Program
GC/MS	Gas chromatograph-mass spectrometer
HIF	Hydrological Instrumentation Facility
MSL	Mean sea level
MW	Monitoring well
NASA	National Aeronautics and Space Administration
ND	Not detected
NERL	National Exposure Research Laboratory
PCE	Tetrachloroethene
PTFE	Polytetrafluoroethylene
QA	Quality assurance
QC	Quality control
RSD	Relative standard deviation
SCMT	Site Characterization and Monitoring Technologies Pilot
SNL	Sandia National Laboratories
SP	Sample port
SSC	Stennis Space Center
TCE	Trichloroethene
USGS	US Geological Survey
VOC	Volatile organic compound
12DCA	1,2-dichloroethane
11DCE	1,1-dichloroethene
112TCA	1,1,2-trichloroethane

Section 1 — Introduction

Background

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations and stakeholder groups consisting of regulators, buyers, and vendor organizations, with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

ETV is a voluntary program that seeks to provide objective performance information to all of the participants in the environmental marketplace and to assist them in making informed technology decisions. ETV does not rank technologies or compare their performance, label or list technologies as acceptable or unacceptable, seek to determine "best available technology," or approve or disapprove technologies. The program does not evaluate technologies at the bench or pilot scale and does not conduct or support research.

The program now operates 12 pilots covering a broad range of environmental areas. ETV has begun with a 5-year pilot phase (1995–2000) to test a wide range of partner and procedural alternatives in various pilot areas, as well as the true market demand for and response to such a program. In these pilots, EPA utilizes the expertise of partner "verification organizations" to design efficient processes for conducting performance tests of innovative technologies. These expert partners are both public and private organizations, including federal laboratories, states, industry consortia, and private sector facilities. Verification organizations oversee and report verification activities based on testing and QA protocols developed with input from all major stakeholder/customer groups associated with the technology area. The demonstration described in this report was administered by the Site Characterization and Monitoring Technologies (SCMT) Pilot. (To learn more about ETV, visit ETV's Web site at http://www.epa.gov/etv.)

The SCMT pilot is administered by EPA's National Exposure Research Laboratory (NERL). Sandia National Laboratories, one of two verification organizations associated with the SCMT pilot, conducted a verification study of groundwater sampling technologies during the summer of 1999. Groundwater sampling technologies are commonly employed at environmental sites for site screening and characterization, remediation assessment, and routine environmental monitoring. Groundwater sampling technologies generally fall into two categories: (1) active systems, including pumping systems and discrete-level grab systems; and (2) passive or diffusional systems. Both types of samplers were evaluated during this verification study.

Demonstration Overview

In August 1999, a demonstration study was conducted to verify the performance of six groundwater sampling devices: SamplEase (bladder pump, Clean Environment Equipment, Oakland, CA), Micro-Flo (bladder pump, Geolog Inc., Medina, NY), Well Wizard Dedicated Sampling System (bladder pump, QED Environmental, Ann Arbor, MI), Kabis Sampler (discrete-level grab sampler, Sibak Industries, Solano Beach, CA), and GoreSorber (diffusional sampler, W. L. Gore and Associates, Elkton, MD). This report contains an evaluation of the

Multiprobe 100 manufactured by Burge Environmental (Tempe, AZ).

The scope of this technology demonstration was purposely limited to sampling device performance parameters such as precision, comparability with a reference measurement, and where applicable, deployment logistics. Several of the systems tested in this study are intended for use with low volume sampling protocols—a relatively new approach to the collection of a representative sample from a groundwater monitoring well. This study was specifically intended to evaluate sampling device performance and was not an evaluation of the merits of a low flow purge and sampling protocol. This protocol has been proposed, tested, and published elsewhere [Puls and Barcelona, 1996] and is beyond the scope of this particular investigation.

The demonstration was conducted in August of 1999 at the National Aeronautic and Space Administration (NASA) Stennis Space Center in southwestern Mississippi. Sandia worked in cooperation with the US Geological Survey (USGS), a federal agency resident at the NASA Stennis site, and used a 100-foot standpipe testing facility associated with the USGS Hydrological Instrumentation Facility (HIF) located on the NASA site. The standpipe, serving as an "above-ground" well, was filled with water spiked with various concentration levels of six target volatile organic compounds (VOCs). Water sampling ports along the exterior of the pipe permitted the collection of reference samples at the same time that groundwater sampling technologies collected samples from the interior of the pipe.

For most of the participating technologies, the standpipe trials were supplemented with additional trials at a number of groundwater monitoring wells at sites with VOC-contaminated groundwater at the NASA Stennis facility. The devices were deployed in a number of 2-inch and 4-inch wells and, where possible, reference samples were collected for comparison with each sampling device. The principal contaminant at the site was trichloroethene.

All technology and reference samples were analyzed by the same field-portable gas chromatograph-mass spectrometer system that was located at the test site during the verification tests. The overall performance of the groundwater sampling technologies was assessed by comparison of technology and reference sample results for a number of volatile organic compounds with particular attention given to key parameters such as sampler precision and comparability with reference sample results. Aspects of field deployment and potential applications of the technology was also considered.

A brief outline of this report is as follows: Section 2 contains a brief description of the Multiprobe 100 sampler and its capabilities. Section 3 outlines a short description of the test facilities and a summary of the verification test design. Section 4 includes a technical review of the data with an emphasis on assessing overall sampler performance. Section 5 presents a summary of the Multiprobe 100 sampler and provides examples of potential applications of the sampler in groundwater monitoring settings. Appendix A includes an assessment of quality control data associated with the analytical method used in this study.

Section 2 — Technology Description: Burge Environmental Multiprobe 100 Sampler

This section provides a general description and overview of the capabilities of the Multiprobe 100 multi-level sampler manufactured by Burge Environmental. Burge Environmental provided the information used to prepare this section.

The Multiprobe 100 is a sampler designed for permanent deployment in a well and has the capacity for collecting samples from up to eight discrete levels within a well. The sampler is designed for use with a complementary automated wellhead analyzer for TCE called the Optrode®; however, the Optrode was not evaluated in this demonstration.

The Multiprobe 100 consists of two units with wiring and tubing interconnections (Figure 1). The upper receiving module, which is deployed at the wellhead and on top of the well, is 18 inches long and 3.25 inches in diameter. The lower sampling module, which is inserted into the water column in the well, is 12 inches long and 3.25 inches in diameter. The receiving and sampling modules each weigh about 3 pounds. The system is constructed of Teflon, borosilicate glass, stainless steel and Delrin®, a crystalline plastic composed of acetal resin made by the polymerization of formaldehyde. A microprocessor controller is included in the system to coordinate the valve sequencing during the sampling process.

A more detailed description of sampler configuration and operation follows: The Multiprobe 100 consists of a sampling and a receiving module as shown in Figure 1. The receiving module, shown in Figure 2, consists of a sample chamber with an internal water level sensor, a sample bottle, and several electrical solenoid valves for directing the flow of the water sample. The receiving module is positioned atop the well casing outside the well. The sampling module, shown in Figure 3, consists of a sample collection chamber fitted with an interior water level sensor and four solenoid valves and associated sampling lines that are deployed to different levels within the well. The sampling module is positioned approximately 2 to 3 feet below the static water level in the monitoring well.

The sampling and receiving modules are interconnected by an electrical cable, enabling control of sampling module's valves and water level sensor. The cable also encases a nitrogen gas line used to pressurize the sampling module and a Teflon tubing line that is used to transport the water sample from the sampling module to the receiving module.

The sampling process is initiated by opening one of the four sampling module inlet valves. Each of the four valves is connected to a length of Teflon tubing that is positioned at a pre-determined sampling depth within the monitoring well. When the sampling chamber is vented to the atmosphere, the lower chamber fills through the sampling tube, being driven by the hydrostatic pressure head as shown in Figure 4, Step 1. The water continues to flow into the sample collection chamber until it contacts the water level sensor located near the top of the chamber, whereupon the sampling valve and vent line are automatically closed. Prior to placement into the well, the position of the water sensor inside the sampling module can be set to collect a water volume between 100 to 200 mL. Following sample collection, nitrogen is used to pressurize the headspace in the sampling chamber. The water flows through a bottom port in the sampling module, up through the interconnecting tubing, and into the receiving module, as shown in Figure 4, Steps 2 and 3. The water sample fills the receiving module chamber until a second water-level sensor inside this chamber is activated. At this point, the remaining water and pressurized nitrogen in the tubing is diverted to a waste container. The water sample contained in the chamber is then manually transferred into a sample bottle as shown in Figure 4, Step 4. The upper receiving module serves as a common collection and analysis point from the multiple sampling lines and by inclusion of a headspace in the collection volume, enables analysis of selected VOC contaminants in the headspace volume.

The sampler requires a cylinder of compressed nitrogen at the wellhead. The line pressure required is usually less than 30 psi, allowing the collection of hundreds of samples before cylinder recharge or replacement is necessary. The only

moving parts of the ground-water sampling system are electrically controlled valves. The system is capable of years of operation without replacement of electrical components.

The cost of the four-level groundwater sampling system, as configured for this test, was $3,000. Additional information on potential applications of the system for environmental characterization and monitoring can be found in Section 5—Technology Updates and Application.
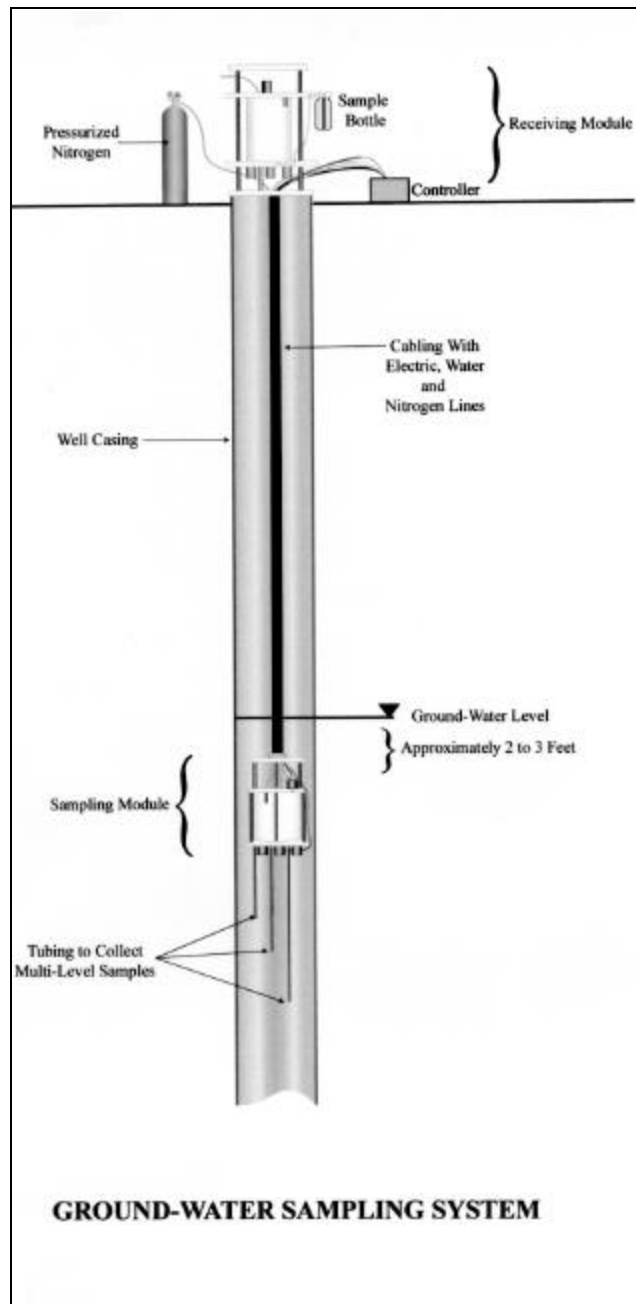
Figure 1. Burge Environmental Multiprobe 100 Sampling System.
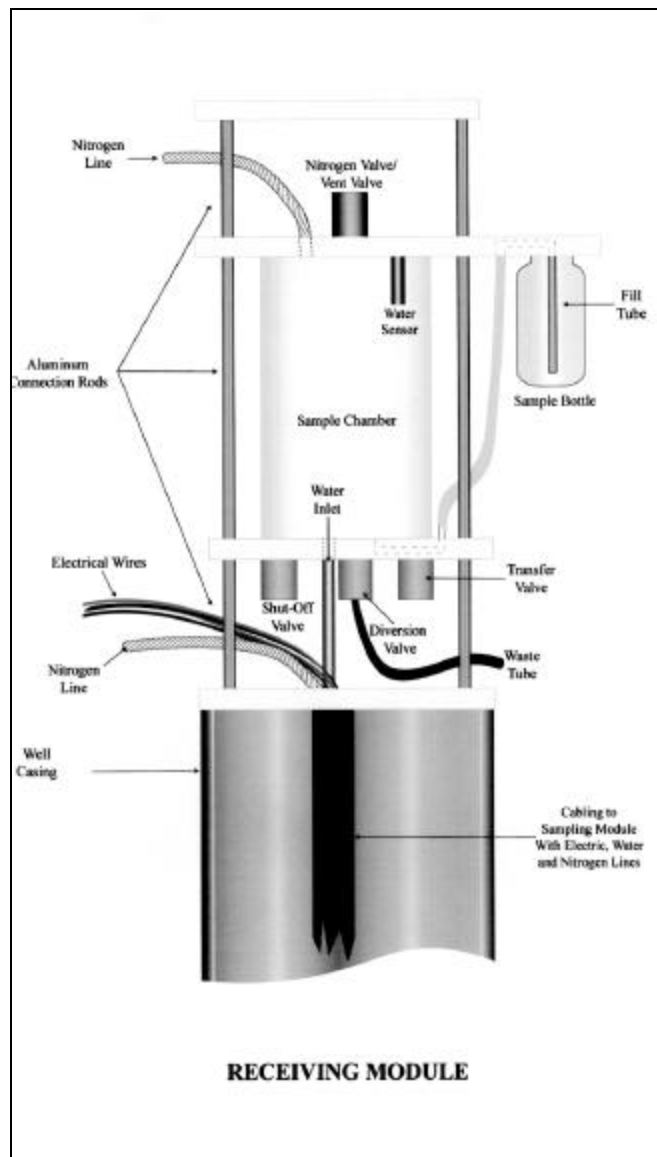
Figure 2. The Burge Multiprobe 100 Receiving Module.

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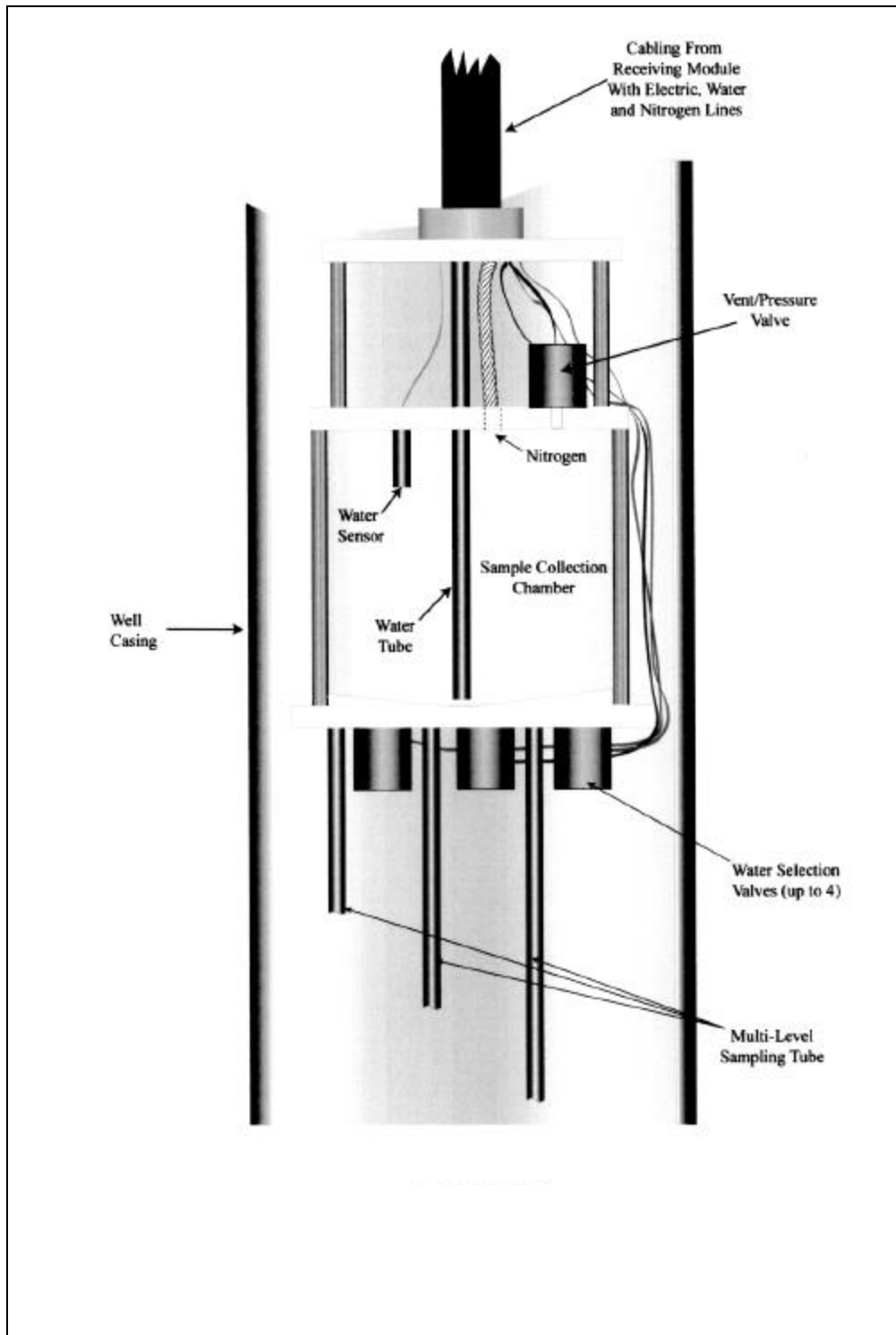
Figure 3. The Burge Multiprobe 100 Sampling Module.
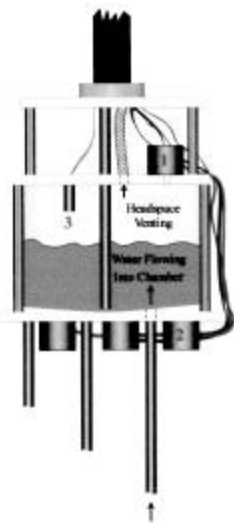
Step One: Filling

1. Vent valve (1) opens to atmosphere.

2. Water selection valve (2) open to desired depth.

3. Water sample flows into sample collection chamber until water sensor (3) is activated.
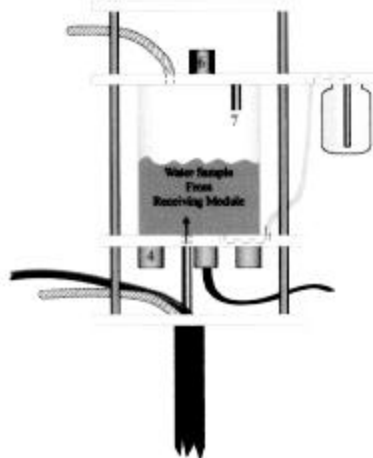
Step Three: Filling

1. Vent valve (6) open to atmosphere.

2. Water from the lower module passes through the shut-off valve (4) filling the sample chamber until water sensor (7) is activated.
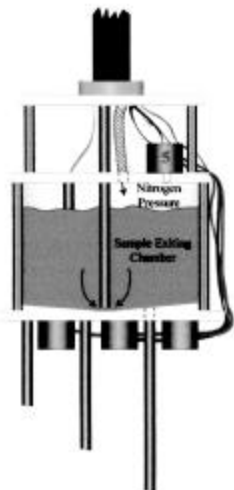
Step Two: Emptying

1. Shut-off valve (4) opens allowing water to be pushed to receiving module.

2. Pressure valve (5) pressurizes the sample collection chamber to push the water sample out of chamber.
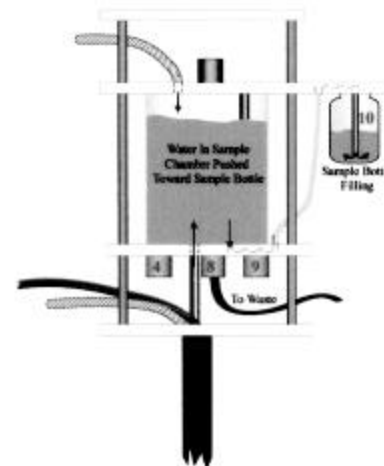
Step Four: Sample Collection

1. Water sensor activated, shutting off water flow to the sample chamber.

2. Diversion valve (8) opens, sending water and nitrogen remaining in tube between upper and lower modules to waste.

3. Transfer valve (9) opens transferring water in sample chamber to sample bottle (10).

SAMPLING MODULE

RECEIVING MODULE

Figure 4. Sampling sequences for the Burge Multiprobe 100 sampler.

Section 3 — Demonstration Process and Design

Introduction

The principal objective of this demonstration was to conduct an independent evaluation of the capabilities of several groundwater sampling technologies for VOC-contaminated water. A number of key performance parameters were chosen to evaluate overall sampler performance. In order to ensure data integrity and authenticity of results, data quality control measures were also incorporated into the study design. The design was developed by personnel at Sandia National Laboratories with concurrence from the various technology vendors participating in the study. Technical review of the study design was also provided by EPA personnel with professional expertise in the area of groundwater sampling. A complete demonstration plan has previously been published [Sandia, 1999].

Site Description

The John C. Stennis Space Center in southwest Mississippi is one of ten NASA field centers in the United States. It is NASA's primary center for testing and flight-certifying rocket propulsion systems for the Space Shuttle and future generations of space vehicles. Over the years, SSC has evolved into a multiagency, multidisciplinary center for federal, state, academic and private organizations engaged in space, oceans, environmental programs and national defense. The USGS is a one of the resident agencies at the NASA-Stennis complex and operates a number of testing facilities as a part of its Hydrologic Instrumentation Facility. This facility supports USGS agency-wide hydrologic data-collection activities through the identification of agency needs, development of technical specifications, and testing and evaluation.

Standpipe Facility – One of the HIF test centers is known as the Standpipe Facility. The facility was designed by Doreen Tai, an HIF chemical engineer, and is housed in a Saturn V rocket storage building at the Stennis complex. A schematic diagram of the standpipe and accessories is shown in Figure 5. The standpipe is an above-ground, 100-foot-long, 5-inch-diameter, stainless steel pipe with numerous external sampling ports along its length. Two large tanks at the top of the standpipe are used to prepare solutions that can then be drained into the standpipe. The tanks are equipped with motor-driven mixing propellers and floating lids to minimize loss of volatile compounds during solution mixing and transfer. An external standpipe fill line at the bottom of the pipe enables the pipe to be filled from the bottom up, thereby minimizing flow turbulence and VOC losses in the prepared solutions. The external access ports allow reference samples to be taken simultaneously with the collection of technology samples inside the pipe. As shown in Figure 5, the indoor facility has six levels of access, including the ground floor, and a freight elevator services all levels. In this demonstration, the standpipe was used in a series of controlled water sampling trials. Technology vendors sampled VOC-contaminated water solutions from the standpipe while reference samples were simultaneously taken from the external ports.

Site Hydrogeology–The second phase of this technology demonstration involved the collection of groundwater samples from six onsite wells at SSC. The site has about 200 wells that have been used for subsurface plume characterization and routine groundwater monitoring. The shallow, near-surface geology where most of the contaminant plumes are located can be summarized as follows [Foster Wheeler, 1998]: The geology generally consists of a thin veneer of clayey sediments know as Upper Clay, found at elevations ranging from 10 to 30 feet above mean sea level (MSL). These overlay a sandy unit named the Upper Sand (at 5 to 15 feet above MSL). The Upper Sand is underlain by a second clayey unit named the Lower Clay and a second sandy unit called the Lower Sand (at –35 to 5 feet MSL). Below the Lower Sand another clayey unit is present which represents an unnamed or undifferentiated Pleistocene deposit. This deposit is underlain by a thick zone of inter-bedded sand and clay deposits that form the Citronelle Formation (at –100 to –40 feet MSL). The VOC contamination is present in the Upper Sand and Lower Sand water-bearing zones; correspondingly, most of the wells selected for use in this test were screened in these zones.
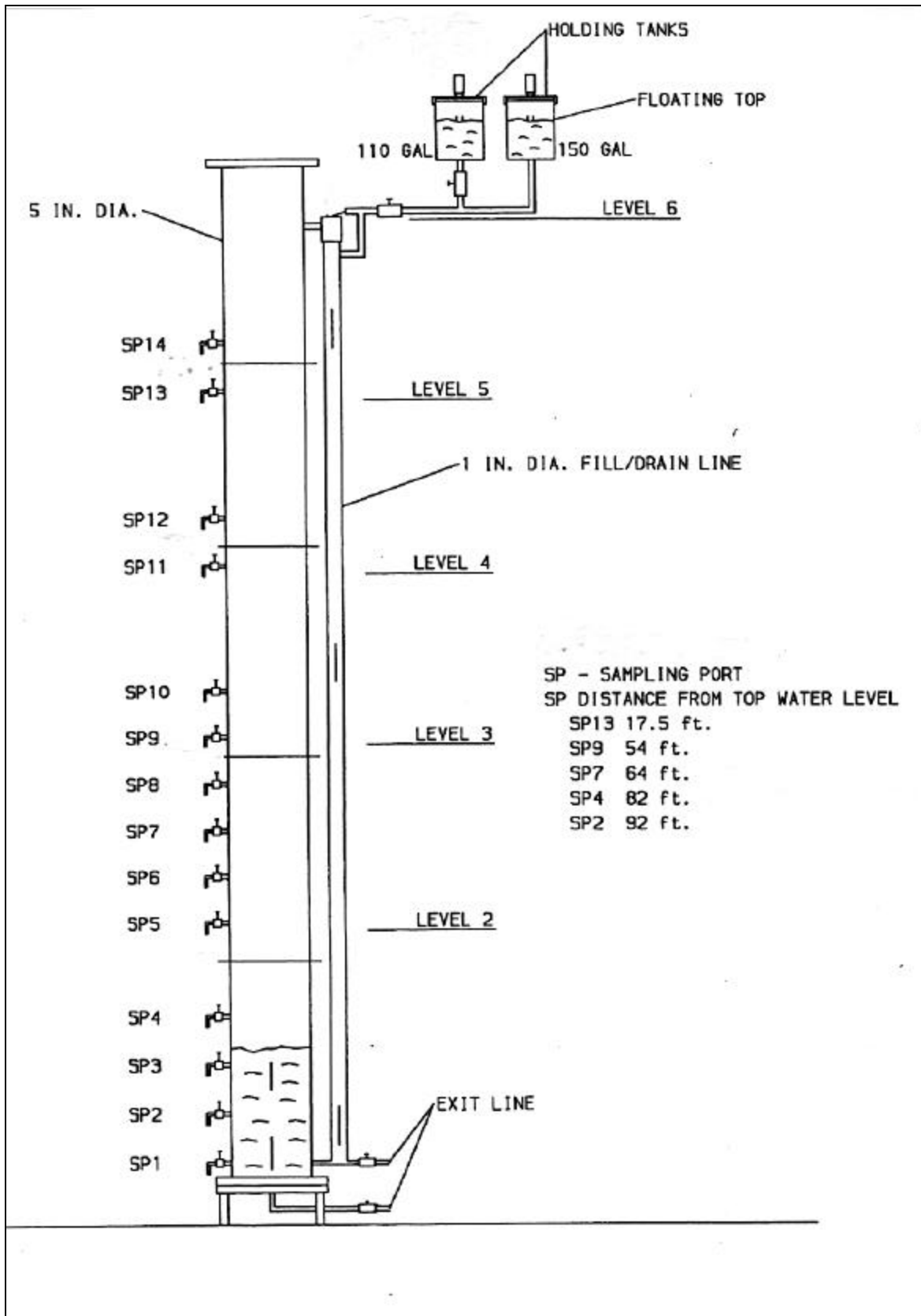
Figure 5. The standpipe at the USGS Hydrological Instrumentation Facility.

Groundwater Monitoring Wells—Construction information for the six wells selected for use in this study is given in Table 1. The wells were constructed with either 2 or 4-inch-diameter PVC pipe with 10-foot polyvinyl chloride (PVC) screen length. All samples were collected at the midscreen level. Typical sampling depths for the wells selected for study ranged from about 15 to 85 feet from the top of the well column to the screen midpoint. Depth of the water column above the mid-screen point ranged from 5 to 68 feet for the wells selected for use in this study.

Verification Test Design Summary

The verification test design consisted of two basic elements. The first was a test matrix, consisting of several trials conducted under carefully controlled sampling conditions at the standpipe. These trials enabled the evaluation of sampler performance parameters such as precision and comparability with reference. The second element was an additional series of tests conducted under actual field conditions with inherently less experimental control. These trials presented an opportunity to observe the technology in actual field use in conditions very similar to those that would be encountered in routine use. Together, these two study elements provided a data set that is adequate for an overall performance assessment of these groundwater sampling devices for applications

specifically involving the sampling of VOC-contaminated groundwater.

Test Design Elements

The test consisted of a variety of sampling activities carried out under relatively closely controlled experimental conditions at the standpipe, along with field sampling at selected onsite monitoring wells under less controlled conditions. Additional design element descriptions are given below. The participating technologies were split into two categories, *active samplers* and *passive samplers*, with individual sampling trials designed specifically for these two sampler categories.

Target VOCs—Six target compounds, all regulated under the US EPA Clean Water Act, were selected for testing in this study. The compounds were 1,2-dichloroethane (12DCA), 1,1-dichloroethene (11DCE), trichloroethene (TCE), benzene (BNZ), tetrachloroethene (PCE), and 1,1,2-trichloroethane (112TCA). With the exception of benzene, all of these compounds are chlorinated and have regulatory limits of 5 μg/L in water as presented in the Clean Water Act. The six compounds selected encompass a range of volatility, a parameter that is likely to influence sampler performance. Target compound volatility, as represented by Henry's constants and boiling point information, is given in Table 2.

Table 1. Construction Details of Groundwater Monitoring Wells

Well No.	TOC (ft, MSL)	Total Depth (ft)	Screen Elev. (ft, MSL) Top	Screen Elev. (ft, MSL) Bottom	Well Diam. (in)	Install Date	Depth to Water (ft)	Water Level (ft, MSL)	Water Depth Above Screen Midpoint (ft)
06-04	28.8	39.0	-1.3	-11.3	2	04/95	24.6	4.2	10.5
06-10	7.8	87.0	-55.2	-65.2	4	04/95	8.2	-0.4	59.8
06-11	15.3	150.0	-62.8	-72.8	4	05/95	15.2	0.1	67.9
06-20	7.3	75.0	-55.4	-65.4	4	12/96	7.8	-0.6	59.8
12-09	28.0	18.0	18.0	8.0	2	05/95	10.0	18.0	5.0
12-12	28.4	99.0	-11.0	-21.0	4	05/95	11.6	16.8	32.8

Notes: TOC = top of well column; water levels from most recent quarterly well monitoring data

Table 2. Target VOC compounds

Compound	Henry's Constant (kg·bar/mole at 298 K)[a]	Boiling Pt. (°C)
Tetrachloroethene (PCE)	High (17.2)	121
1,1-Dichloroethene (11DCE)	High (29.4)	32
Trichloroethene (TCE)	Mid (10.0)	87
Benzene (BNZ)	Mid (6.25)	80
1,2-Dichloroethane (12DCA)	Low (1.39)	84
1,1,2-Trichloroethane (112TCA)	Low (0.91)	114

[a] Henry's constant data from NIST, 2000.

Test Concentrations—The use of the standpipe facility enabled the preparation of water mixtures containing the six target VOCs in a range of concentration levels. In four standpipe testing trials, the target compound concentration was either low (10-20 µg/L) or high (175-225 µg/L) concentration. Spike solutions of all six target compounds were prepared in methanol from neat compounds. Normally a 5-10 mL volume of the spiking solution was injected into the mixing tank, which was located at the top of the standpipe and contained about 100 gallons of tap water. This solution was covered with a floating lid to reduce volatile losses, gently mixed for 5 minutes, and then drained into the standpipe.

Standpipe Reference Samples--Preliminary studies at the standpipe revealed volatile losses of target compounds during mixing and filling. Consequently calculated spike concentrations could not be used as a reference values in this study. The standpipe has external sampling ports along its length so that reference samples could be collected simultaneously with sampling from the interior of the pipe using the samplers undergoing testing. Each sampling trial consisted of the simultaneous collection of replicate test device and reference samples at a fixed concentration and sampling depth. The reference samples were collected directly into analysis vials with no intervening pumps or filters that could affect the sample. Replicate sampling allowed the determination of test device and reference sample precision. Precision in this context incorporates the variability of the technology and the reference sample in combination with the common analytical method used on both sample types. The reference sample precision is assumed to be the baseline level with which the technology precision

data can be directly compared for each of the sampling trials.

Sampler Blank—The standpipe trials included a blank test where replicate samples were collected from a blank water mixture in the standpipe. This test was conducted to assess whether the construction materials in the various samplers were a possible source of contamination of the sample for the six target compounds used in this study.

Sampler Carryover—One of the intended applications of several of the samplers involved in the study is the collection of a water sample with relatively low VOC levels at a discrete level in a well that may have overlying layers of VOC contamination at higher levels. A so-called clean-through-dirty test was incorporated to assess the degree to which the samplers were contaminated in the high-level layer that was penetrated as the sampler was lowered to a cleaner underlying layer in the well. The results of these trials are also expressed in terms of percent difference from reference samples, with recovery values significantly greater than zero indicating sampler contamination for the overlying contaminated layers in the well. Since the Multiprobe 100 sampler is intended for permanent well installation, it was not included in this optional trial.

Groundwater Well Reference Samples—Six onsite groundwater monitoring wells were selected for use in the second phase of the study. For most of the participating technologies, a reference sampler was co-located in the monitoring well along with the technology to provide a means of comparison. The Multiprobe 100 test was an exception in this case. The 3.75-inch diameter of the Multiprobe 100 sampling module prevented the simultaneous

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deployment of a reference sampler in the well, since limited annular space between the Multiprobe 100 exterior and the internal circumference of the well was available. Deployment of the Multiprobe 100 was done at two wells without co-located samples only for the purposes of observing its deployment and use in actual field settings.

Sampler Performance Parameters

Four performance parameters were evaluated in the assessment of each sampling device. They are briefly outlined in the following paragraphs.

Precision—Sampler precision was computed for the range of sampling conditions included in the test matrix by the incorporation of replicate samples from both the standpipe and the groundwater monitoring wells in the study design. The *relative standard deviation* was used as the parameter to estimate precision. The percent relative standard deviation is defined as the sample standard deviation divided by the sample mean times 100, as shown below:

$$RSD(\%) = \frac{\sqrt{\dfrac{\sum (X_i - \bar{X})^2}{n-1}}}{\bar{X}} \bullet 100$$

Here, X_i is one observation in a set of n replicate samples where $\bar{X}$ is the average of all observations, and n is the number of observations in the replicate set. In assessment of sampler precision, a statistical test was used to assess whether observed differences between the reference sample precision and the technology sample precision are statistically significant. Specifically, the F-ratio test compares the variance (square of the standard deviation) of the two groups to provide a quantitative assessment as to whether the observed differences between the two variances are the result of random variability or the result of a significant influential factor in either the reference or technology sample groups [Havlicek and Crain 1988a].

Comparability—The inclusion of reference samples, collected simultaneously with technology samples from the external sampling port of the standpipe, allows the computation of a comparability-to-reference parameter. The term *comparability* is to be distinguished from the term *accuracy*. Earlier investigations at the standpipe

revealed that volatility losses occurred when mixing and transporting the spike mixtures during standpipe filling. As a result, the "true" concentrations of target VOCs in the standpipe were not precisely known and thus an accuracy determination is not warranted. Alternatively, a reference measurement from the external port, with its own sources of random error, is used for comparison. The term *percent difference* is used to represent sampler comparability for each of the target compounds in the sampling trials at the standpipe. Percent difference is defined as follows:

$$\%DIFF = \frac{\left(\overline{X}_{tech} - \overline{X}_{ref}\right)}{\overline{X}_{ref}} \bullet 100$$

where is $\overline{X}_{tech}$ the average reported concentration of all technology sample replicates and $\overline{X}_{ref}$ is the average reported concentration of all reference sample replicates. The statistical t-test for two sample means was used to assess observed differences between the reference and technology means for each sampling trial [Havlicek and Crain, 1988b]. The t-test gives the confidence level associated with the assumption that the observed differences are the result of random effects among a single population only and that there is no significant bias between the technology and reference.

Versatility—The versatility of the sampler was evaluated by summarizing its performance over the volatility and concentration range of the target compounds as well as the range of sampling depths used in the standpipe trials. A sampler that is judged to be versatile operates with acceptable precision and comparability with reference samples over the range of experimental conditions included in this study. Those samplers judged to have low versatility may not perform with acceptable precision or comparability for some of the compounds at some of the tested sampling depths or concentration levels.

Field Deployment Logistics—This category refers to the logistical requirements for deployment of the sampler under its intended scope of application. This is a more subjective category that incorporates field observations made during sampler deployment at the groundwater monitoring wells. Logistical considerations include such items as personnel qualifications and

training, ancillary equipment requirements, and field portability.

Operator Influence–The sampling technician as well as the sample collection method has an influence on the overall quality of the samples taken. This is particularly true for the active samplers evaluated in this study. Such factors as the time required to collect a sample and the sampler flow rate may influence overall sample quality. An evaluation of operator influence on sample quality is beyond the scope of this study. All sampler operators were experienced in the use of their technologies and the assumption is made that the technologies were being operated under conditions that would yield the highest quality samples.

Sample Analysis
A single analytical method was used for technology and reference samples. All analyses were conducted onsite, using analytical services provided by Field Portable Analytical (Fremont, CA). The onsite instrumentation consisted of two identical field portable gas chromatograph-mass spectrometer (GC/MS) units (Inficon, HAPSITE, Syracuse, NY) equipped with a Inficon Headspace Sampling System. The analysis method used was a modified Method 8260 (purge-and-trap GC/MS) with headspace sampling replacing the purge-and-trap portion of the method [EPA, 1996]. Sample throughput was on the order of 4 to 6 samples per hour per instrument for a daily throughput of 60-70 samples per instrument. The Inficon field-portable GC/MS system with headspace vapor sampling accessory had previously gone through the ETV verification process. Results from this verification study showed that system accuracy and precision for VOC in water analysis was comparable with a conventional fixed laboratory analysis using purge-and-trap sample handling combined with bench-top GC/MS analytical systems [EPA, 1998].

A brief summary of the analytical method follows: Samples were brought to the analysis location in 40-mL VOA vials and kept at temperatures near 4 ºC until they were prepared for instrument analysis. As a result of the relatively high sample throughput and the use of two instruments, sample holding times did not exceed 24 hours in most cases. Consequently, no sample preservatives were used in the study. Immediately prior to analysis, the chilled VOA sample vials were uncapped and transferred to a 50-mL glass

syringe. Half (20 mL) of the sample was then transferred to a second 40-mL VOA vial and the vial was immediately capped. A 5-µL solution containing internal standards and surrogate standards was injected through the septum cap of the vial. The vial was then placed in the headspace sampling accessory and held at 60 ºC for 15 minutes. The original vial was again filled with the remainder of the sample, capped, and held under refrigeration as a spare.) Following the temperature equilibration time, a vapor extraction needle was inserted through the vial's septa cap and into the headspace. A pump in the GC/MS then sampled a fixed volume of headspace gas through a heated gas transfer line and into a fixed-volume gas sampling loop in the GC/MS. Under instrument control, the gas sample was then injected onto the capillary column for separation and detection. An integrated data system processed the mass detector data and output results for the six target analytes plus internal and surrogate standards in concentration format. The method used internal standards (as outlined in Method 8260) for computation of target compound concentrations. Surrogate standard results were used as measures of instrument data quality, along with other quality control measures outlined below.

Data Processing
The results from chemical analysis of both technology and reference samples were compiled into spreadsheets and the arithmetic mean and percent relative standard deviation (as defined in Section 3) were computed for each set of replicate samples from each standpipe and monitoring well trial. All data were reported in units of micrograms per liter for the six target compounds selected. Direct trial-by-trial comparisons were then made between technology and reference sample results as outlined below. All the processed data from the verification study have been compiled into data notebooks and are available from the authors by request.

Data Quality Control
The desirability of credible data in ETV verification tests requires that a number of data quality measures be incorporated into the study design. Additional details on data quality control are provided in the following paragraphs.

Sample Management–All sampling activities were documented by SNL field technicians using chain-

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of-custody forms. To save sample handling time and minimize sample labeling errors in the field, redundant portions of the chain-of-custody forms and all sampling labels were preprinted prior to the field demonstration.

Field Logbooks–Field notes were taken by observers during the standpipe and groundwater well sampling trials. The notes include a written chronology of sampling events, as well as written observations of the performance characteristics of the various technologies tested during the demonstration.

Pre-demo Analytical System Audit–Prior to the actual demonstration, a number of samples containing the six target compounds at various concentration levels were prepared at Sandia National Laboratories and sent via overnight mail in an icepack under refrigeration temperatures to Field Portable Analytical near Sacramento, CA. They were analyzed by GC/MS using the headspace method intended for use in the final field test. Results from this preliminary audit revealed acceptable performance of the GC/MS system and its accompanying method. The written analytical method that was used during the full demonstration was also reviewed and finalized at this time.

Analytical Method–The analytical method was an adaptation of EPA Method 8260B and followed the data quality requirements outlined in the method. Included in the list of data quality measures were: (1) initial calibration criteria in terms of instrument linearity and compound recovery, (2) daily instrument calibration checks at the onset and completion of each 12-hour analysis

shift, (3) blank sample instrument performance checks, (4) internal standard recovery criteria, and (5) surrogate standard recovery criteria. A summary of the GC/MS analysis quality control data for the demonstration period is given in Appendix A.

Verification Test Plan

The preceding information, as well as that which follows, is summarized from the Groundwater Sampling Technologies Verification Test Plan [Sandia, 1999], which was prepared by SNL and met with concurrence by all vendor participants prior to the field demonstration. The test plan includes a more lengthy description of the site, the role and responsibilities of the test participants, and a discussion of the experimental design and data analysis procedures.

Standpipe Sampling Matrix

The sampling matrix for the standpipe phase of the demonstration is given in Table 3. All standpipe and groundwater testing was carried out sequentially, with the various participants deploying their sampling devices one at a time in either the standpipe or the groundwater monitoring wells. A randomized testing order was used for each trial. The standpipe test phase for the Multiprobe 100 included three trials. Trial 1 was carried out at four sampling depths with a low concentration (10-20 μg/L) standpipe mixture. Trial 2 was carried out at same four sampling depths with a high concentration (175-225 μg/L) standpipe mixture. In both of these trials, reference samples were simultaneously collected from external sampling ports adjacent to the Multiprobe 100 inlet locations.

Table 3. Multiprobe 100 Verification Trials at the Standpipe

Trial No.	Standpipe Collection Port	Sample Collection Depth	VOC Concentration Level	Number of Replicates
1	SP14	Low (17 ft)	Low (~20 ppb)	5
	SP12	Mid-Low (35 ft)		5
	SP10	Mid-High (53 ft)		5
	SP3	High (92 ft)		5
2	SP14	Low (17 ft)	High (~200 ppb)	5
	SP12	Mid-Low (35 ft)		5
	SP10	Mid-High (53 ft)		5
	SP3	High (92 ft)		5
3	SP3	High (92 ft)	Blank	3

Notes: In each trial, an equal number of reference samples were collected, from adjacent external standpipe sampling ports, simultaneously with the device samples

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Trial 3 was a blank mixture measurement to test the cleanliness of a new sampler. For this trial, the standpipe was filled with tap water and three replicates were collected by the Multiprobe 100 from the deepest (91 ft) location in the pipe while three reference replicates were collected simultaneously from the adjacent exterior sampling port.

During the groundwater monitoring portion of the test, the Multiprobe 100 was installed and operated at two 4-inch diameter wells, as shown in Table 4. The purpose of these deployments was to observe the installation and operation of the sampling device. The wells at which the Multiprobe 100 was deployed were non-detectable for TCE and the analytical data are not included in this report. The size and configuration of the Multiprobe 100 prevented the simultaneous co-location of a reference sampler in the well, hence no comparison data were collected. The data from the standpipe trials were adequate for performance assessment of such parameters as precision and comparability with reference samples.

Chronological Summary of Demonstration Activities

The demonstration began on Monday, August 9 and concluded on Tuesday, August 17. The first four days of the demonstration were devoted to testing those technologies designated "active samplers." Included in this group were Burge Environmental (multi-level sampler) Clean Environment Equipment (bladder pump), Geolog (bladder pump), QED Environmental (bladder pump), and Sibak Industries (discrete-level grab sampler). The second half of the demonstration

interval was devoted to testing the "passive sampler" category of which W. L. Gore (sorbent sampler) was the only participant. A short briefing was held on Monday morning for all vendor participants to familiarize them with the standpipe facility and the adjacent groundwater monitoring wells. Standpipe testing began for the active sampler category at midmorning on Monday and was completed on the following day. Two days of testing at groundwater wells followed. The passive sampler category tests were begun at the standpipe Thursday, August 12 and were completed on Monday, August 16. The passive sampler category was also deployed at a number of monitoring well sites simultaneously with standpipe testing.

Sample analysis was carried out in a mobile laboratory parked near the standpipe and was done concurrently with field-testing. With the exception of the first day of sample analysis, all technology and matched-reference samples were analyzed on the same instrument and usually on the same day. This approach was taken to minimize the possible influence of day-to-day instrument variability on the analysis results.

The demonstration technical team recorded observations during operation of the devices at the standpipe and monitoring well trials with regard to their logistical requirements and ease of use. These observations also were used to document any performance anomalies as well as the technical skills required for operation.

Table 4. Multiprobe 100 Deployments at Groundwater Monitoring Wells

Well	Well Diameter (in)	Distance from Top of Well to Screen Mid- point (ft)	Water Column Depth (ft)	Approximate TCE Conc. (■g/L)
06-10MW	4	68.0	59.8	< 5
06-20MW	4	67.7	59.9	< 5

Notes: Approximate TCE concentrations are derived from NASA contractor quarterly monitoring data.

Deviations from the Verification Plan

Under most field-testing environments, circumstances often arise that prevent a complete execution of the test plan, and this test was no exception. A list of the deviations from the test plan that are judged to be important are summarized, along with an assessment of the resulting impact on the field test data set.

Lost/dropped samples–Out of over 800 samples, 1 was dropped and lost in the field and 3 were not analyzed either because they were overlooked or lost in handling by the field technicians or analysts. Because 4 or 5 replicates were collected in each sampling trial, the loss of a few samples does not affect the overall study results.

QC-flagged data–Several samples on the first day of GC/MS operation were reported with low internal standard recovery as a result of gas transfer line problems. A close examination of analyses data revealed that these results are comparable with replicate sample results that passed QC criteria. Consequently, these data were used in the final analysis. A note indicating the use of flagged data is included in the appropriate data tables. No flagged data were encountered with regard to the Multi-probe and associated reference samples in this study.

Samples below quantitation limit of GC/MS–One of the wells sampled produced reference and vendor samples that were at or below the practical quantitation limit of the GC/MS system. These data were manually re-processed by the analyst to provide a concentration estimate. Where this occurs, these data are flagged and appropriate notice is given in the analysis section of this report.

Blank GW Monitoring Wells–Six groundwater monitoring wells were selected for study, based on preliminary assessment of observed TCE concentration levels using either historical data or data from previous onsite well screening activities. In three trials, well TCE concentration levels were below the limits of detection, despite evidence to the contrary from preliminary screening. Sampler contamination during preliminary screening carried out prior to the field test was determined to be the cause of erroneously high readings. One of the "blank" wells was kept in the data set to assess sampler blank performance in the field. The other wells were dropped from the list of trials. The impact on the overall data set is not important, since the objective parameters of performance such as sampler precision and comparability with reference are derived from the standpipe data.

Section 4 — Multiprobe 100 Performance Evaluation

Introduction

This section briefly discusses the results of test data analysis and summarizes sampler performance. Sampler precision, comparability with reference sample data, and overall versatility of the sampler for collection of VOC-contaminated water are discussed. Only summary data are given in this report. A complete tabulation of all test data are available from the authors via individual request.

Sampler Precision

The precision for both Multiprobe 100 and the reference samples from the first four standpipe trials is given in Table 5 and Figure 6. These four trials consisted of low (10–20 µg/L) and high (175–225 µg/L) target compound concentrations, with 4 sample collection depths at 17, 35, 53 and 91 feet. Relative standard deviations are tabulated for all of the 6 target compound to give a total of 48 cases. The final column in the table is the result of an F-ratio test used to determine whether the technology and reference sampler precision can be regarded as statistically equivalent. The p value tabulated in the final column of the table is an estimate of the probability of encountering the observed difference in precision, if the assumption is made that the two groups (technology and reference) are equivalent. In statistical terms, this is the null hypothesis and the accompanying assumption is that only random influences are present and no systematic bias is present among the two sets of measurements. Values of p that are close to 1 reflect small differences in precision with a corresponding high probability of encountering differences of these magnitudes under the null hypothesis. On the other hand, values of p less than 0.05 are indicative of statistically significant differences that may warrant a rejection of the null hypothesis. Differences of such magnitude cannot be satisfactorily explained by random variation alone in the two sets of data being compared. If the assumption is made that the two data sets are from the same population, and only random effects are occurring, the probability of observing a difference in two precision values corresponding to a 0.05 value of p is 5%. For values of p less

than 0.05, it is more likely that some systematic bias exists between the two sets of data.

The highest uncertainty in the Multiprobe 100 results is observed for 12DCA at the low concentration and 17-foot depth (Table 5). The lowest uncertainty is observed for PCE at the high concentration and 17-foot collection depth. The median RSD for all compounds in all test cases was 9.5% for the Multiprobe 100 samples and 8.6% for the reference samples. In 27 of the 48 cases, the Multiprobe 100 precision was greater than the reference sampler precision. An even, or nearly even, split of Multiprobe 100 RSD values in the greater and less than categories would be indicative of equivalence between the two sampling methods. From a more formal statistical point of view, the F-ratio test results indicate that the tabulated values of p, with two exceptions, are all greater than 0.05. This indicates that the precision values for the Multiprobe 100 and the reference samples are statistically equivalent and that the observed differences are can be regarded as random variation within a single population.

Sampler Comparability

Percent difference values were computed for each of the six target compounds in the two standpipe trials for a total of 48 cases and the results are given in Table 6 and Figure 7. The percent difference values for the Multiprobe 100 range from –30 to 15% with a median value of –5%. Overall, average percent difference values for 34 of the 48 cases shown in Table 6 were less than or equal to 0% with 14 cases greater than 0%. An even or nearly even split of percent difference values in the greater than zero and less than zero categories would be suggestive of equivalence between the two sampling methods. In this case, a predominance of negative differences is a qualitative indication of negative sampler bias. Negative percent differences are observed for 11DCE, TCE, and PCE under nearly all test conditions. The other three compounds have a more even distribution of positive and negative percent differences.

T-test results show that 31of the 48 trials have values of p that are greater than 0.05 and thus can

be considered statistically indistinguishable from zero percent difference. The other 17 cases have values of p less than 0.05 and with one exception all percent difference values are less than zero. Of particular note is the fact that all tests cases involving PCE show negative differences in the range of –10 to –30%. Additionally, three of the 8 TCE test cases show statistically significant negative differences, ranging from –16 to –24%. The statistically significant low recoveries for TCE and PCE might be attributable to headspace losses or adsorption losses of VOCs in some of the materials used in the construction of the sampler; however, the identification of specific causative factors is beyond the scope of this study.

Table 5. Precision Summary for Multiprobe 100 and Reference Sampler

Compound	Conc. Level	Depth (ft)	Multiprobe 100 Precision (%RSD)	Ref. Precision (%RSD)	F-Ratio Test p
11DCE	Low	17	12.3	9.2	0.64
	Low	35	18.4	9.2	0.30
	Low	53	10.8	8.4	0.88
	Low	91	7.1	14.1	0.20
	High	17	7.9	5.8	0.55
	High	35	9.6	6.4	0.88
	High	53	5.6	6.6	0.77
	High	91	18.1	7.4	0.10
12DCA	Low	17	21.1	10.6	0.20
	Low	35	10.2	17.4	0.30
	Low	53	17.3	13.7	0.77
	Low	91	8.3	11.5	0.65
	High	17	13.0	8.3	0.32
	High	35	9.1	8.5	0.86
	High	53	6.1	14.3	0.13
	High	91	15.4	6.6	0.08
BNZ	Low	17	11.3	3.0	**0.02**
	Low	35	7.7	5.6	0.53
	Low	53	3.5	3.2	0.77
	Low	91	5.0	8.9	0.32
	High	17	9.2	5.2	0.29
	High	35	6.8	5.6	0.89
	High	53	4.4	9.1	0.16
	High	91	16.5	5.9	**0.05**
TCE	Low	17	5.8	11.1	0.14
	Low	35	15.5	16.1	0.57
	Low	53	10.6	14.0	0.29
	Low	91	6.6	11.1	0.29
	High	17	5.5	6.6	0.69
	High	35	5.4	2.0	0.18
	High	53	9.2	6.4	0.52
	High	91	17.2	8.2	0.21
112TCA	Low	17	18.2	15.3	0.78
	Low	35	14.1	14.2	0.88
	Low	53	16.6	11.3	0.80
	Low	91	7.8	6.9	0.62
	High	17	4.4	4.6	0.98
	High	35	17.1	5.9	0.10
	High	53	4.6	8.6	0.22
	High	91	17.8	8.6	0.13
PCE	Low	17	7.1	12.1	0.18
	Low	35	10.3	12.8	0.32
	Low	53	10.0	13.1	0.18
	Low	91	6.8	10.4	0.16
	High	17	3.0	5.4	0.22
	High	35	5.3	3.7	1.00
	High	53	9.7	9.9	0.59
	High	91	16.4	9.2	0.64

Note: Values of p less than 0.05 are shown in bold.
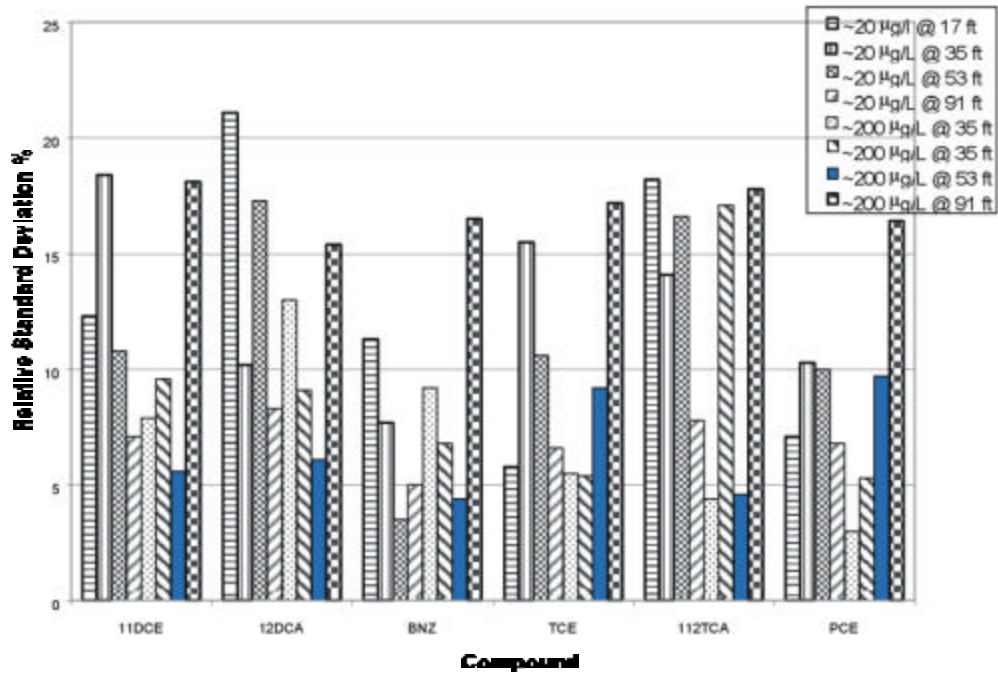
Figure 6. Multiprobe 100 precision from the standpipe trials.
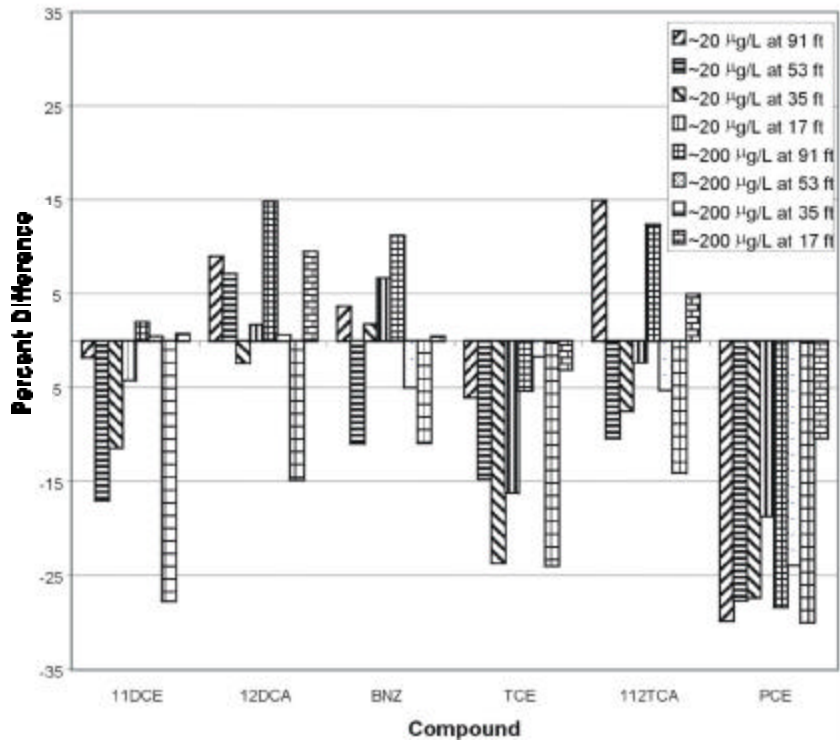

Figure 7. Multiprobe 100 comparability with reference samples from the standpipe trials.

Table 6. Comparability of Multiprobe 100 and Reference Sampler Data from Standpipe Trials

Compound	Conc. Level[a]	Depth (ft)	Multiprobe Difference (%)	t-Test[b] (p)
11DCE	Low	17	−4	0.55
	Low	35	−11	0.21
	Low	53	−17	**0.01**
	Low	91	−2	0.81
	High	17	1	0.87
	High	35	−28	**<0.01**
	High	53	0	0.91
	High	91	2	0.83
12DCA	Low	17	2	0.88
	Low	35	−2	0.80
	Low	53	7	0.47
	Low	91	9	0.21
	High	17	9	0.23
	High	35	−15	**0.02**
	High	53	−5	0.93
	High	91	11	0.12
BNZ	Low	17	7	0.26
	Low	35	2	0.69
	Low	53	−11	**<0.01**
	Low	91	4	0.44
	High	17	0	0.92
	High	35	−11	**0.02**
	High	53	−5	0.30
	High	91	11	0.23
TCE	Low	17	−16	**0.02**
	Low	35	−24	**0.03**
	Low	53	−15	0.07
	Low	91	−6	0.32
	High	17	−3	0.45
	High	35	−24	**<0.01**
	High	53	−2	0.75
	High	91	−5	0.54
112TCA	Low	17	−2	0.84
	Low	35	−7	0.41
	Low	53	−10	0.21
	Low	91	15	**0.02**
	High	17	5	0.12
	High	35	−14	0.08
	High	53	−5	0.26
	High	91	12	0.24
PCE	Low	17	−19	**0.01**
	Low	35	−27	**<0.01**
	Low	53	−28	**<0.01**
	Low	91	−30	**<0.01**
	High	17	−10	**<0.01**
	High	35	−30	**<0.01**
	High	53	−24	**<0.01**
	High	91	−28	**<0.01**

[a] The low-level concentration was in the range of 10 to 20 µg/L for all 6 target compounds. The high-level concentration was in the range of 175 to 250 µg/L.

[b] The t-test was used to compare the mean percent difference of the Multiprobe 100 relative to the reference samples for each compound in each trial. Small values of p (<0.05) shown in bold are suggestive of sampler bias. See text for further details.

Blank Test Results

The analytical results from the blank trial at the standpipe were all reported as non-detectable for all target compounds for both the Multiprobe 100 and the reference samples. These results indicate that a new or decontaminated sampler does not measurably contaminate a clean sample of water.

Monitoring Well Results

As noted in Section 3, the Multiprobe 100 was deployed at two groundwater monitoring wells to observe its operation in a field setting. As a result of the physical configuration of the Multiprobe 100 sampler, a reference pump could not be co-located in the monitoring well and hence no analytical data are available for inter-comparison. The 4-inch diameter wells in which the sampler was deployed were also non-detectable for TCE so Multiprobe 100 precision data were not computed. Observations of Multiprobe 100 deployment and operation in these monitoring wells are summarized in the following section entitled Deployment Logistics.

Sampler Versatility

The data from the standpipe tests reveal that the Multiprobe 100 samples are comparable to reference samples with respect to precision. The comparability data from the standpipe tests reveal a number of statistically significant sampler biases for PCE and to a lesser extent TCE. The physical dimensions of the sampler also prohibit its deployment in wells having diameters less than 4 inches. Based on these considerations the Multiprobe 100 is judged to have limited versatility as a groundwater sampling device. As noted elsewhere in this report, only the sample collection component of this sampling system were evaluated in this test. Further evaluation of the Multiprobe 100 sampler in combination with the automated VOC analysis module are warranted in order to assess the performance of the overall system.

Deployment Logistics

The following observations were made during testing of the Multiprobe 100 at both the standpipe and groundwater monitoring wells.

- Two people were required to configure, install, and operate the sampler. Although the sampler is designed for permanent installation and automatic sampling at timed intervals using a microprocessor/controller, in this test

the automation module was configured for manual control. The ease of programming the controller for automated sampling was not determined in this test. Permanent installation of the overall system would probably be best accomplished by Burge Environmental personnel; however, user installation could be done following some training by Burge personnel.

- The system was configured in a temporary arrangement for this ETV test, with many of the system parts unenclosed. Enclosures were not used since the unit was moved to several different well locations during the test. The interconnections between the sampling and collection reservoirs included wire cables, insulated electrical wires, and narrow-diameter tubing that was not integrated into a single conduit. A permanent deployment of system components at the wellhead would require secure, weather tight enclosures that would be assembled by the supplier to meet local requirements.

- The sampler requires a source of compressed nitrogen at the wellhead.

- The equipment is self-contained and requires no external power to operate.

- The entire system is designed for dedicated use in unattended sampling at groundwater monitoring wells. The sampler can be complemented with an onsite, automated, analysis module for TCE and other halogenated VOCs. However, these components were not evaluated in this test program.

- The sampler's only moving parts are a number of electrical solenoid valves whose long-term performance in a high-humidity environment was not evaluated in this test.

- The sampler can be equipped with up to eight inlet lines so that samples can be collected at multiple levels using a single sampling unit.

Performance Summary

Multiprobe 100 performance is summarized in Table 7. Categories include precision, comparability with reference method, versatility, and logistical requirements. Cost and physical characteristics of the equipment are also included.

The results of this verification test show that the Multiprobe 100 performed in a comparable manner to a reference method with regard to

precision. Absolute comparisons between Multiprobe 100 and reference samples reveal a general trend toward a negative bias in terms of Multiprobe 100 recovery for 11DCE, TCE and particularly PCE. Multiprobe 100 recoveries for the other three target VOC compounds, on average, were closer to zero bias.

The Multiprobe 100 unit is a component of an overall automated sampling and analysis system. This evaluation concentrated on understanding the performance characteristics of the sampling module only. An evaluation of the entire system is warranted in order to assess the overall system performance.

Table 7. Performance Summary for Multiprobe 100

Performance Parameter	Summary
Precision	For 6 target compounds at low (~20 μg/L) and high (~200 μg/L) VOC concentrations and sampling depths of 17, 35, 53, and 91 feet:
	Relative standard deviation range: 3.0 to 21.1% (reference: 2.0 to 17.4%)
	Median relative standard deviation: 9.4% (reference: 8.6%)
	In 46 of 48 standpipe test cases, Multiprobe 100 precision was statistically comparable to reference sampler precision.
Comparability with reference samples	For 6 target compounds at low (~20 μg/L) and high (~200 μg/L) VOC concentrations and sampling depths of 17, 35, 53 and 91 feet:
	Percent difference range: -30 to 15%
	Median percent difference: -5%
	In 31 of 48 test cases, Multiprobe 100 differences relative to reference samples were statistically indistinguishable from 0%. In 16 of the remaining 17 cases sampler differences were statistically significant and less than 0%.
Sampler versatility	The Multiprobe 100 is judged to have limited versatility for groundwater monitoring operations. The sampler's physical dimension prevents deployment wells with diameters less than 4 inches. The observed negative biases of the Multiprobe 100 for 11DCE, TCE and PCE may require further evaluation prior to routine monitoring applications for these compounds.
Logistical requirements	System is designed for permanent installation and would be best installed by the vendor although several days of training would enable user installation.
	System requires a source of compressed air or nitrogen at the wellhead.
	Periodic maintenance requirements associated with long-term unattended use were not evaluated in this test.
Completeness	System was successfully used to collect all of the samples prescribed in the verification test plan.
Purchase cost	Complete sampler: $3,000 per well (does not include automated VOC analysis or installation costs.)
Size and weight	Sampling module: 3.25-inch dia. × 18-inch length, 3 pounds
	Receiver module: 3.25-inch dia. × 12-inch length, 3 pounds
	Microprocessor Controller: 10 × 4 × 4 inches, 5 pounds
Other	System is designed for low-volume purge applications.
	System is designed for use in unattended, automated well-sampling programs when combined with onsite, real-time analyzers for TCE and other chlorinated organics.

Note: Target compounds were 1,1-dichloroethene (11DCE), 1,2-dichloroethane (12DCA), benzene (BNZ), trichloroethene (TCE), 1,1,2-trichloroethane (112TCA), and tetrachloroethene (PCE).

Section 5 — Multiprobe 100 Technology Update and Representative Applications

The Multiprobe 100 sampling system is capable of creating a headspace over a volume of water while under the static water level of the well. This design feature allows various sensors to be placed within a monitoring well without being immersed in water. Alternatively, the sensors can be placed at the top of the well casing or in specially designed, environmentally controlled boxes adjacent to the monitoring wells. A calibration module is available which allows the sensors to be calibrated while positioned inside the monitoring well.

The Multiprobe 100 sampling unit is designed for multi-level sampling in 4-inch wells. The probe is designed to transport the analyte of interest from the collection point in either the groundwater or as a component in an inert gas phase following its being purged from the groundwater sample. Following its transport to the surface by the sampling system, the analyte can be introduced into sample containers (VOA vials, sorptive tubes) for transport to a laboratory or it can be analyzed onsite through exposure to various sensors located either in the well or at the wellhead. The primary purpose of the Multiprobe 100 is to provide an interface from groundwater to onsite chemical sensing systems. The flexibility built into the Multiprobe 100 that enables one to select the type of transport media (liquid or gas phase) makes this system unique among the sampling systems presently on the market. A totally integrated multi-level groundwater sampling system, as shown in Figure 8, that is interfaced with a chemical sensing system, shown in more detail in Figure 9, allows for the automation of groundwater monitoring and analysis. The errors associated with groundwater monitoring (including the errors observed in this demonstration) can be reduced by automating the sampling and analysis under controlled conditions. The control of errors coupled with the cost savings of automating long-term monitoring may be a significant advantage to this technology. The automation of groundwater sampling and analysis allows sampling to be conducted more frequently than quarterly and it provides near real-time collection and reporting of data from an aquifer. This can be an advantage during remedial action monitoring or the monitoring of possible breakthrough of contaminants at barrier walls. Other advantages of an automated system include the communication of onsite real-time data to a web page or similar format for uncomplicated access by regulators and/or the public.
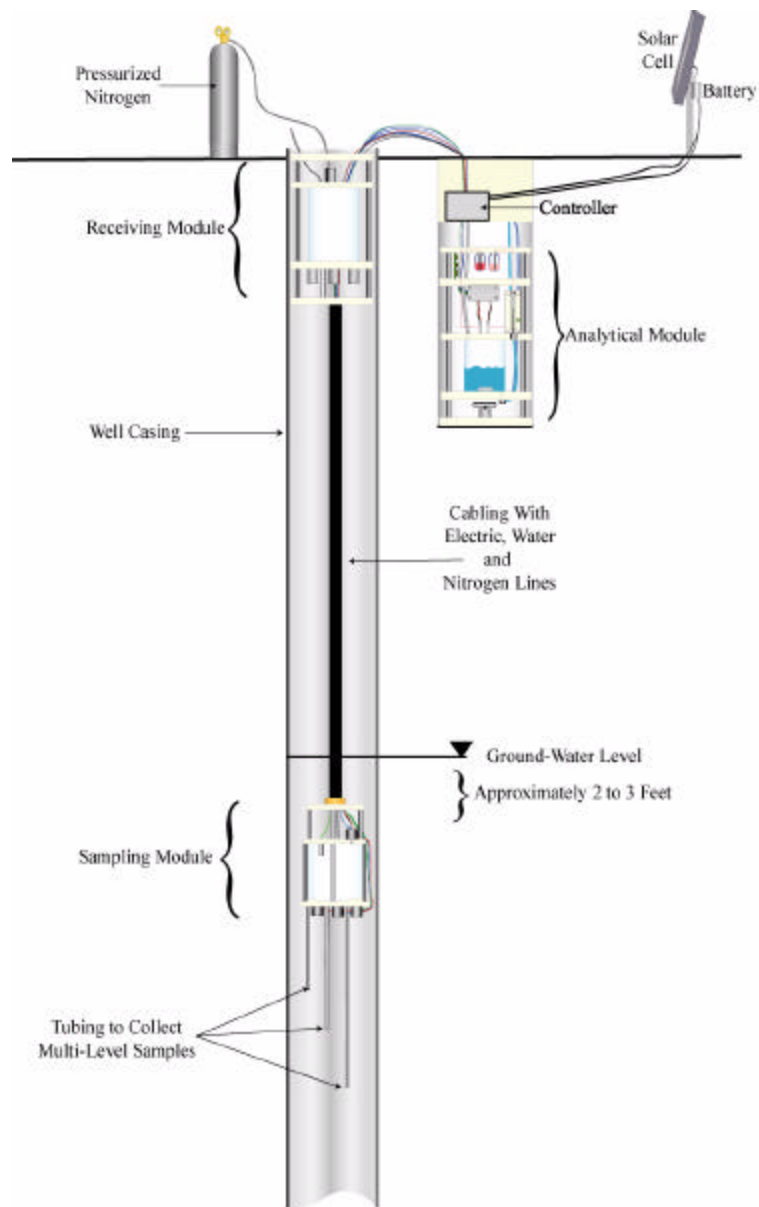
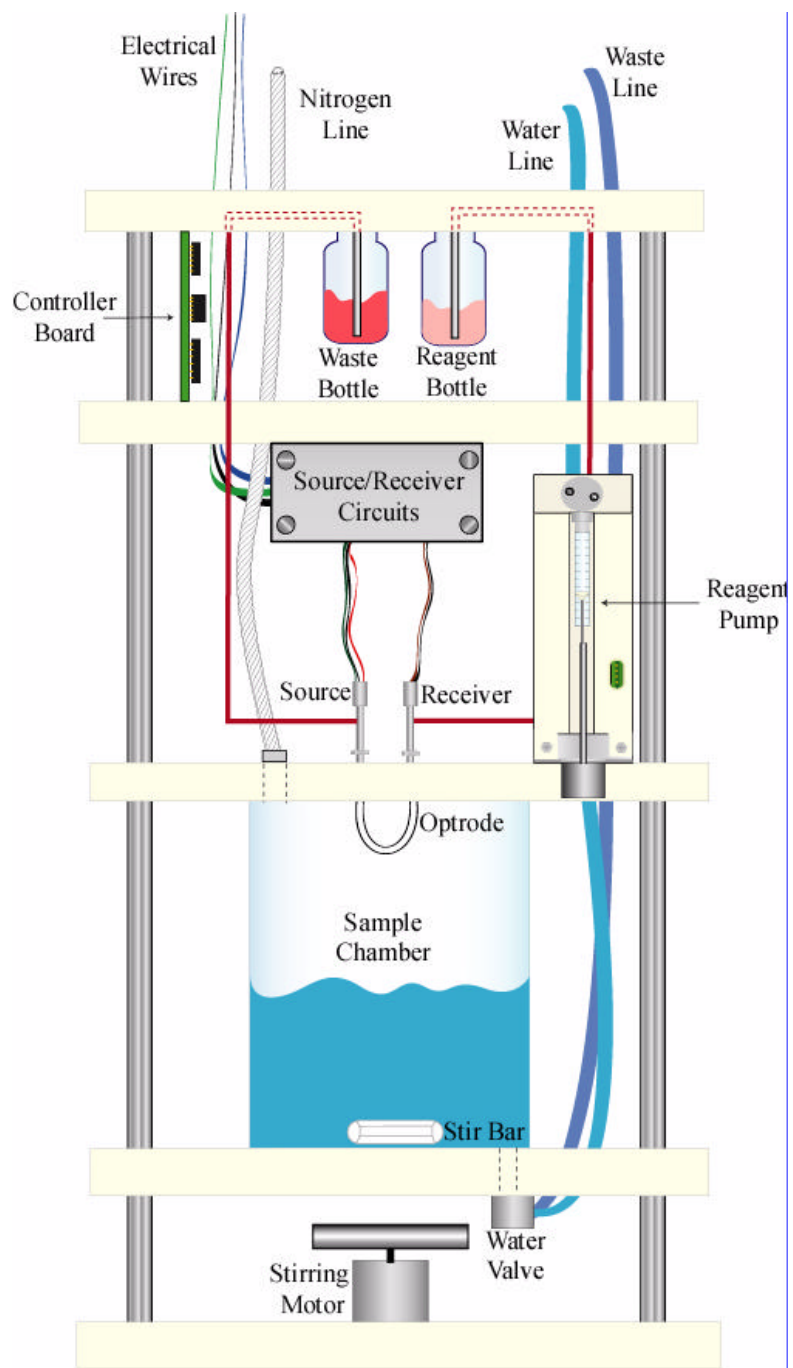**Figure 8. A schematic diagram of the Multiprobe 100 interfaced to an onsite analysis module.**

Figure 9. A schematic diagram of an automated analysis module for TCE

Section 6 — References

EPA, 1996. "Test Methods of Evaluating Solid Waste: Physical Chemical Methods; Third Edition; Final Update III," Report No. EPA SW-846.3-3, Government Printing Office Order No. 955-001-00000-1, Office of Solid Waste and Emergency Response, Washington, DC.

EPA, 1998. Environmental Technology Verification Report, Field Portable GC-MS, Inficon HAPSITE; Report Number EPA/600/R-98/142, US EPA, Office of Research and Development, Washington, DC. (also available at http://www.epa.gov/etv/verifrpt.htm#02).

Foster Wheeler, 1998. "Final Hydrogeologic Investigation Report for the National Aeronautics and Space Administration Stennis Space Center, Mississippi," Office of Environmental Engineering, NASA, Stennis Space Center, Mississippi, 39529.

Havlicek, L.L, and R. D. Crain, 1988a, Practical Statistics for the Physical Sciences, pp 202-204. American Chemical Society, Washington, DC.

Havlicek, L.L, and R. D. Crain, 1988b, Practical Statistics for the Physical Sciences, pp 191-194. American Chemical Society, Washington, DC.

NIST, 2000. National Institutes of Standards and Technology, Standard Reference Database No. 69, R. Sander, editor, available at http://webbook.nist.gov/chemistry.

Puls, R.W., and Barcelona, M. J., 1996, Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures, US EPA Ground Water Issue (April 1996), Publication No. EPA/540/S-95/504, US EPA Office Solid Waste and Emergency Response, Washington, DC.

Sandia, 1999. Groundwater Sampling Technologies Verification Test Plan, Sandia National Laboratories, Albuquerque, NM 87185 (also available at http://www.epa.gov/etv/test_plan.htm#monitoring).

Appendix A — Quality Summary for Analytical Method

Introduction
An onsite GC/MS-headspace method was chosen for analysis of all samples in this study. Two identical GC/MS systems were operated by Field Portable Analytical (Folsom, CA) using a modified EPA Method 8260 (for a summary of the method, see Section 3). Data quality measures were incorporated into all onsite analyses consistent with the guidelines in Method 8260. This appendix summarizes those data quality measures, thereby demonstrating the adequacy of the method for this verification study.

Data Quality Measures
A number of data quality measures were used to verify acceptable instrument performance and the adequacy of the final analytical results throughout the course of the study. These measures are summarized in Table A-1. All data quality measures in this table were followed, with the exception of duplicates. Duplicates were not routinely run since all of the samples from the field were in batches of replicates. Earlier predemonstration studies indicated that the field replicates were the same in composition so that they could be treated as analysis duplicates.

Table A-1. Onsite GC/MS-Headspace Method Quality Control Measures

Quality Control Check	Minimum Frequency	Acceptance Criteria	Corrective Action
MS tune check w/ bromofluorobenzene (BFB)	Every 12 hours	Ion abundance criteria as described in EPA Method TO-14	1) Reanalyze BFB 2) Adjust tune until BFB meets criteria
5-Point (Minimum) calibration	Beginning of each day	%RSD ≤ 30%	Rerun levels that do not meet criteria
Continuing calibration check (CCC)	Beginning of each day	± 25% difference of the expected concentration for the CCC compounds	1) Repeat analysis 2) Prepare and run new standard from stock 3) Recalibrate
End calibration checks	End of each day	± 25% RPD of the beginning CCC	1) Repeat analysis 2) If end check is out, flag data for that day
Duplicates	10% of the samples	Relative percent difference ≤ 30%	1) Analyze a third aliquot 2) Flag reported data
Method blanks	After beginning of day CCC	Concentrations for all calibrated compounds < practical quantification level	Rerun blanks until criteria are met

Data Quality Examples
The following data are examples of system performance throughout the course of the study. In the interest of brevity, all quality control data are not shown in this appendix. A complete tabulation of all quality control data is included in the GW SAMPLING DATA NOTEBOOK and is available for viewing through a request to the ETV Site Characterization and Monitoring Technologies Pilot Manager.

Method Blank Check
Method blanks were run at the beginning of each 12-hour analysis session. Concentration levels of the six target compounds were reported as ND <5 µg/L for all method blank samples.

Continuing Calibration Check
The method criterion for the continuing calibration checks run at the beginning and end of each analysis cycle was a value within 25% of the expected value. The results of the TCE continuing calibration checks for both of the GC/MS instruments used in the study are shown in Figures A-1 and A-2. Similarly, the results of the PCE continuing calibration check for both instruments are shown in Figures A-3 and A-4. All check compound recoveries fall within the predefined control interval of 70 to 130%. The control interval is specified in EPA Method SW-846, from which this method is adapted. The relative percent differences between the pre- and post-analysis batch calibration check samples are shown in Figure A-5. In two cases, the relative percent difference falls outside the 25% window. Data from these days were not rejected, however, since the $\pm30\%$ criteria for the calibration check was met.
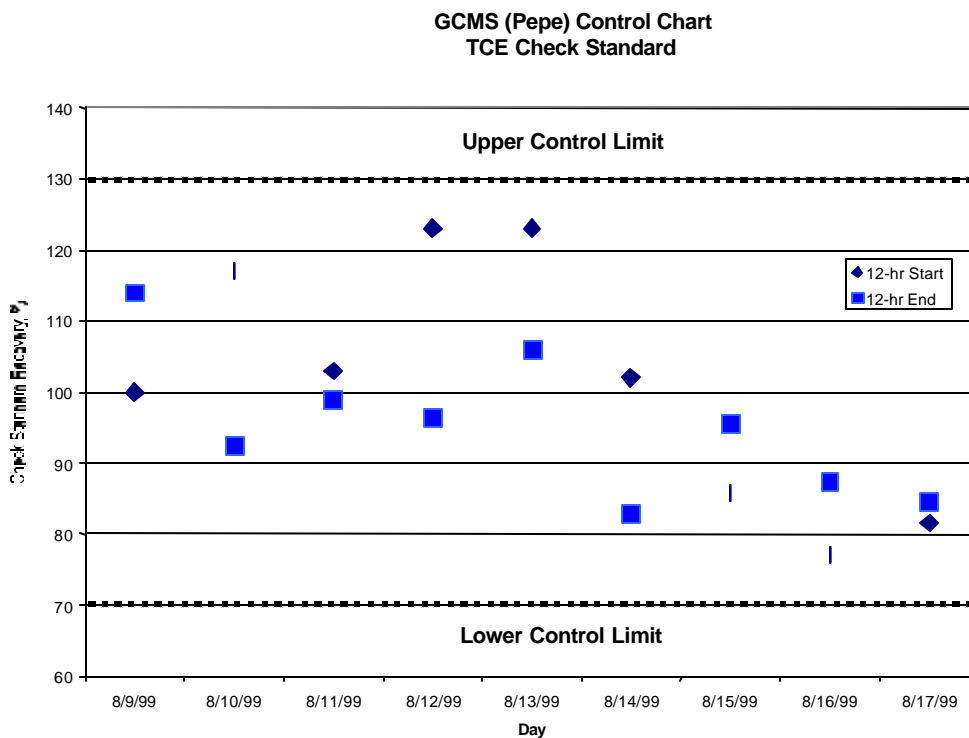

GCMS (Pepe) Control Chart
TCE Check Standard

Figure A-1.   Calibration check control chart for TCE on GC/MS #1.

GCMS (Taz) Control Chart
TCE Check Standard
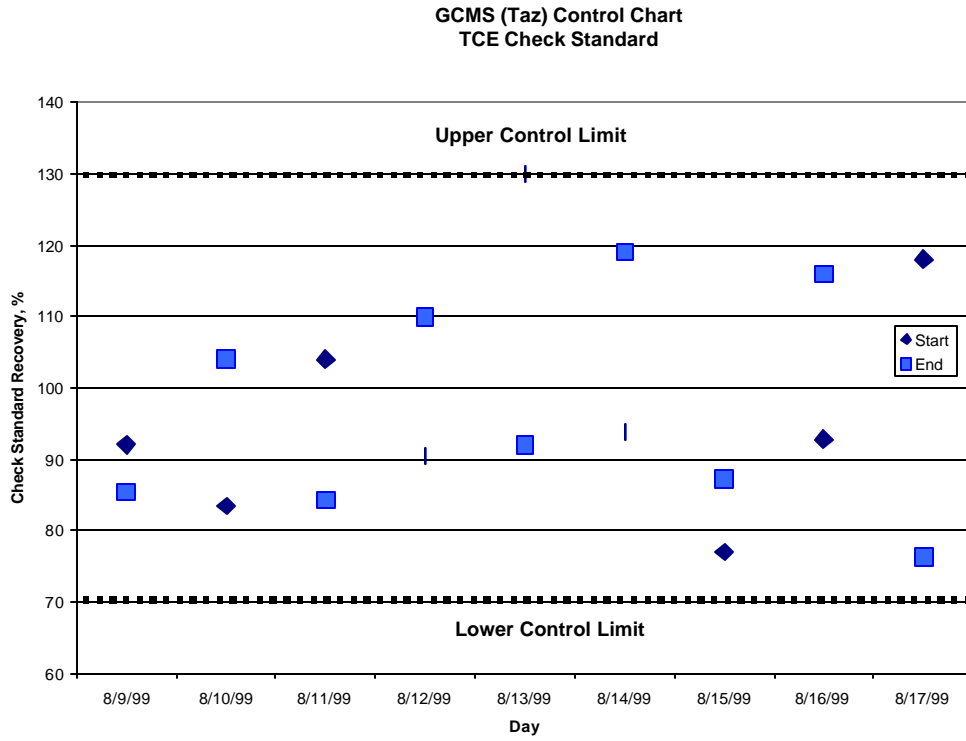
Figure A-2. Calibration check control chart for TCE on GC/MS #2.

GCMS (Pepe) Control Chart
PCE Check Standard
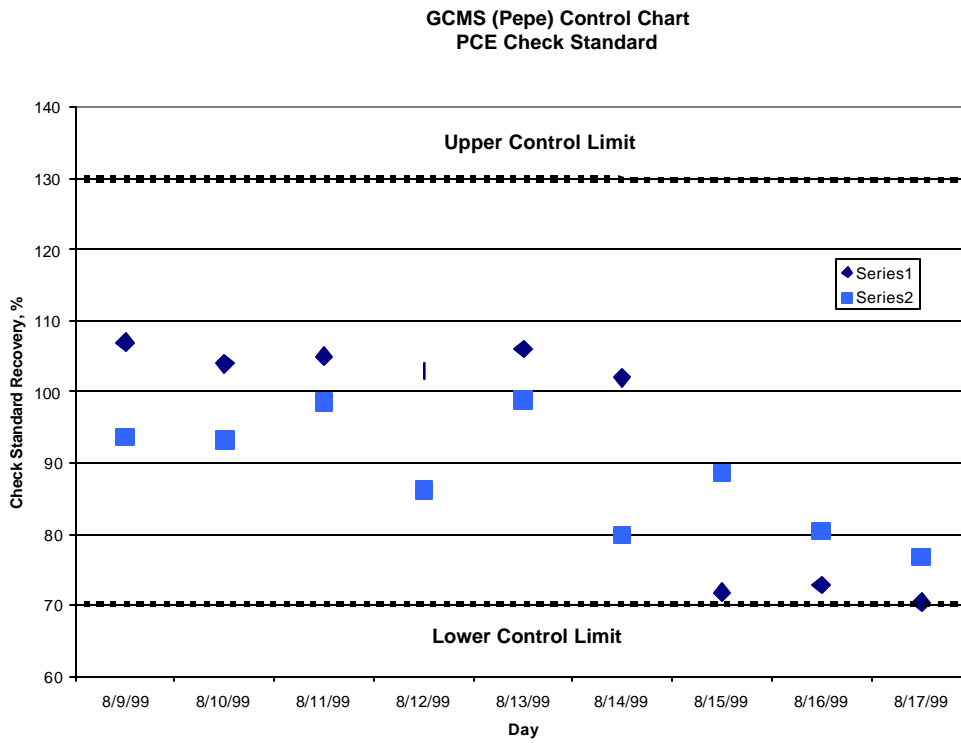
Figure A-3. Calibration check control chart for PCE on GC/MS #1.
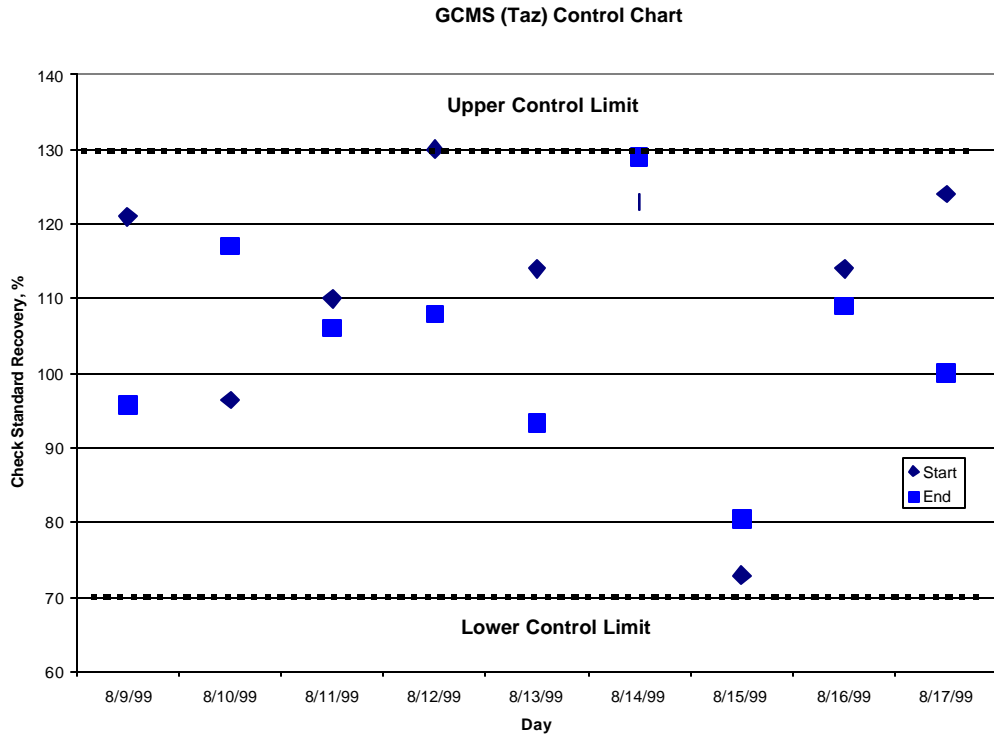
GCMS (Taz) Control Chart

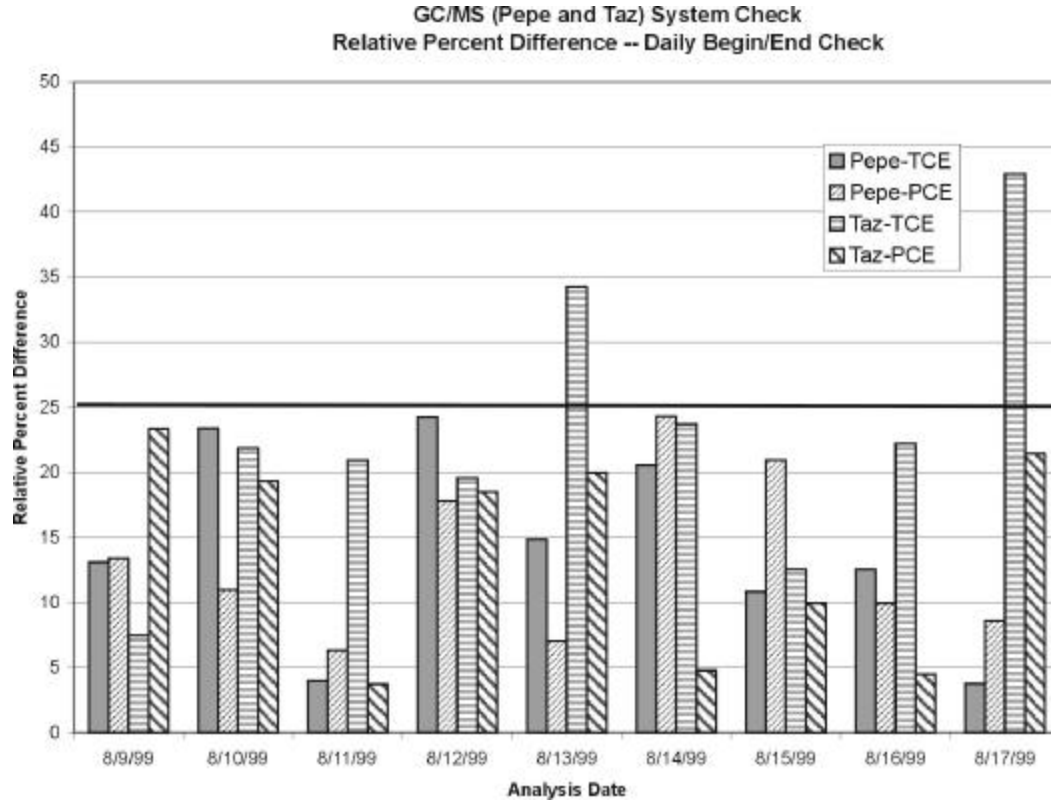**Figure A-4. Calibration check control chart for PCE on GC/MS #2.**

Figure A-5.   GC/MS system check relative percent differences.