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Environmental Technology Verification Report

Groundwater Sampling Technologies

Sibak Industries Ltd. Inc.

**Kabis Sampler
Models I and II**



ETV ✓ ETV ✓ ETV ✓

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Models I and II**

by

Wayne Einfeld
Sandia National Laboratories
Albuquerque, New Mexico 87185

and

Eric N. Koglin
U.S. Environmental Protection Agency
Environmental Sciences Division
National Exposure Research Laboratory
Las Vegas, Nevada 89193-3478



Notice

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**THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM**



ETV JOINT VERIFICATION STATEMENT

TECHNOLOGY TYPE:	GROUNDWATER SAMPLING TECHNOLOGIES	
APPLICATION:	VOC-CONTAMINATED WATER SAMPLING	
TECHNOLOGY NAME:	Kabis Sampler, Models I and II	
COMPANY:	Sibak Industries Ltd. Inc.	
ADDRESS:	P.O. Box 86 Solana Beach, CA 92075	PHONE: (800) 794-6244 (858) 793-6713
WEBSITE:	www.sibak.com	FAX: (619) 793-6713
EMAIL:	sibak@sibak.com	

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 Kabis Model I and II discrete-level point samplers.

DEMONSTRATION DESCRIPTION

In August 1999, the performance of six groundwater sampling devices was evaluated at the US Geological Survey (USGS) Hydrological Instrumentation Facility at the National Aeronautics and Space Administration (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 "aboveground" well, was filled with water spiked with various concentration levels of six target volatile organic compounds. The target compounds (1,2-dichloroethane, 1,1-dichloroethene, trichloroethene (TCE), 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 and an optional "clean-through-dirty" trial were also included in the test matrix. The "clean-through-dirty" test was included to investigate the potential of contaminant carryover as a sampler is lowered through a "dirty" (high VOC concentration) layer of water in order to sample an underlying "clean" (low VOC concentration) layer.

The standpipe trials were supplemented with sampler deployments at groundwater monitoring wells in the vicinity of VOC-contaminated groundwater at the NASA Stennis facility. The Kabis sampling device was deployed in a number of 2-inch and 4-inch wells. Comparison samples were also collected using a submersible electric gear pump. The principal contaminant in the monitoring wells was trichloroethene. The groundwater monitoring test phase provided an opportunity to observe the operation of the sampling device under typical field-use conditions.

All technology and reference samples were analyzed by the same field-portable gas chromatograph-mass spectrometer (GC/MS) system that was 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, with the use of a headspace sampler in lieu of a purge-and-trap unit. The overall performance of the groundwater sampling technologies was assessed by comparison of technology and reference sample results with particular attention given to key performance parameters such as sampler precision and accuracy. Aspects of field deployment and potential applications of the technology were also considered.

Details of the demonstration, including an evaluation of the sampler's performance, may be found in the report entitled *Environmental Technology Verification Report: Sibak Industries Ltd. Inc., Kabis Sampler*, EPA/600/R-00/054

TECHNOLOGY DESCRIPTION

The Kabis Sampler is a discrete-level, grab sampler. The two models evaluated in this test operate on the same principle and only differ in size and sampling capacity. Both samplers are constructed of 321 stainless steel. The Model I is 17.4 inches long, 1.75 inches in diameter, and weighs 6.5 pounds. The Model II is 22.3 inches long, 3.65 inches in diameter and weighs 15.5 pounds. Both samplers have a removable top into which a single (Model I) or three (Model II) 40-mL VOA vial(s) are screwed prior to sampler deployment in the well. The sampler is attached to a measuring tape and is manually lowered into the water column. The size and orientation of the inlet and exhaust ports of the sampler are such that it does not fill while it is being lowered down through the water column in the well. When the sampler is held stationary at the desired sampling depth, it begins to fill under hydrostatic pressure. Fill duration time is about 5 minutes for the Model I and 8 minutes for the Model II.

Air inside the sampler escapes through an exhaust port as the installed sample vials fill from the bottom upward. The vials are flushed with about 6 vial volumes prior to the collection of the final vial volume at the end of the sampling cycle. The flush water flowing through the vials spills into the sampler body through spill ports located in the vial holder in the sampler head. Following completion of the fill cycle, the sampler is manually retrieved to the surface and the sample vials removed. The sample is then preserved, if required, and the vials are capped with positive-displacement-type caps that ensure a bubble-free sample. Sampler decontamination is carried out by rinsing the sampler in the field using a 5-gallon bucket of detergent water followed by several deionized or distilled water rinses.

Costs for the Kabis samplers are \$825 for the Model I and \$1,895 for the Model II. Additional sampler accessories available include a delivery tape, wooden storage box, and positive-displacement VOA vial caps.

The Model I and Model II samplers differ only in their size and number of vials filled during sampling. The samplers were used interchangeably in the study and their performance results are combined. Hereafter, the two sampler models are simply referred to as the Kabis sampler.

VERIFICATION OF PERFORMANCE

The following performance characteristics of the Kabis sampler were observed:

Precision: The precision of the sampler was determined through the collection of a series of replicate samples from four standpipe trials using low (~20 µg/L) and high (~200 µg/L) VOC concentrations at 17-foot and 91-foot collection depths. Each trial included 6 target VOCs for a total of 24 cases. Kabis sampler precision, represented by the relative standard deviation, for all compounds at all concentrations and sampling depths evaluated in this study, ranged from 2.9 to 25.8%, with a median value of 10.7%. Reference method precision ranged from 4.1 to 17.6%, with a median relative standard deviation value of 8.7%. In 16 cases, the relative standard deviation of the Kabis samples was greater than the reference samples, with Kabis precision less than or equal to reference sample precision in the other 8 cases. The F-ratio test was used to assess whether the observed precision differences between Kabis and reference samples were statistically significant. Test results showed that precision differences between Kabis and reference were statistically insignificant at the 95% confidence level in 23 of the 24 cases.

Comparability with a Reference: Kabis sampler results from the standpipe trials were compared with results obtained from reference samples that were collected at the same time. Both Kabis and reference samples were analyzed by the same analytical 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 used in this study ranged from -39 to 18%, with a median difference of -3%. The t-test for two sample means was used to assess whether the observed differences in Kabis sampler and reference sample results were statistically significant. These tests revealed that in 16 of 24 trials, the differences were not statistically different at the 95% confidence level. Of the remaining 8 cases, 5 showed a statistically significant Kabis sampler negative bias; and in 2 of those cases, the negative bias for PCE was in excess of 25%.

Versatility: Sampler versatility is the consistency with which the sampler performed over the ranges of target-compound volatility, concentration levels, and sampling depths. The standpipe tests reveal generally consistent performance with regard to Kabis sampler precision. Kabis sampler results show low recovery for TCE and PCE at the higher (~200 µg/L) concentration at the deeper (91 ft) sampling location used in this evaluation. In light of these results, the Kabis sampler is judged to have limited versatility.

Logistical Requirements: The sampler can be deployed and operated in the field by one person. About 1 hour of training is generally adequate to become proficient in the use of the system. The sampler is

compact and can easily be hand carried to the wellhead for use. Decontamination of the sampler can be carried out in the field by using a detergent water rinse followed by several distilled water rinses. A reasonable degree of manual dexterity is required to remove the sample vials from the sampler head without sample loss. Sampling vials that have been pre-preserved cannot be used in this sampler. Preservative must be added following sample collection, if required.

Overall Evaluation: The results of this verification test show that the Kabis sampler can be used to collect VOC-contaminated water samples that are generally indistinguishable from a reference method with regard to precision. Sampler recovery, relative to reference samples, was acceptable for four of the six target compounds. Test results indicated low sample recovery with the Kabis sampler for TCE and PCE at high concentrations at both shallow and deep sampling locations.

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>.

Gary J. Foley, Ph.D.
Director
National Exposure Research Laboratory
Office of Research and Development

Samuel G. Varnado
Director
Energy and Critical Infrastructure Center
Sandia National Laboratories

NOTICE: EPA verifications are based on evaluations of technology performance under specific, predetermined criteria and appropriate quality assurance procedures. EPA and SNL make no expressed or implied warranties as to the performance of the technology and do not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements. Mention of commercial product names does not imply endorsement.

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For more information on the Groundwater Sampling Technology Verification Test, contact:

Eric Koglin
Project Technical Leader
Environmental Protection Agency
Environmental Sciences Division
National Exposure Research Laboratory
P. O. Box 93478
Las Vegas, Nevada 89193-3478
(702) 798-2432 (v)
E-mail: koglin.eric@epamail.epa.gov

Wayne Einfeld
ETV Project Manager
Sandia National Laboratories
MS-0755 PO Box 5800
Albuquerque, NM 87185-0755
(505) 845-8314 (v)
E-mail: weinfel@sandia.gov

For more information on the Kabis Samplers contact:

Thomas (Tom) W. Kabis
Sibak Industries Limited Inc.
P.O. Box 86
Solana Beach, CA 92075
800-794-6244 or (858) 793-6713 (v)
e-mail: sibak@sibak.com
tkabis@jps.net

List of 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 (perchloroethene)
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
QA	Quality assurance
QC	Quality control
REF	Reference
RSD	Relative standard deviation
SCMT	Site Characterization and Monitoring Pilot
SNL	Sandia National Laboratories
SP	Sample port
SSC	Stennis Space Center
TCE	Trichloroethene
USGS	US Geological Survey
VOA	Volatile organics analysis
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 Technology (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 systems: Multiprobe 100 (Burge Environmental, Tempe, AZ), SampleEase (Clean Environment Equipment, Oakland, CA) Micro-Flo (Geolog Inc., Medina, NY), Well Wizard (QED Environmental, Ann Arbor, MI), Kabis Sampler (Sibak Industries, Solana Beach, CA), GoreSorber (W. L. Gore and Associates, Elkton, MD), and the Kabis Sampler. This report contains an evaluation of the Kabis Sampler,

Models I and II, manufactured by Sibak Industries Ltd., Solano Beach, CA.

It is important to point out that the scope of this technology demonstration was purposely limited to sampling device performance parameters such as precision, comparability to a reference measurement, and where applicable, deployment logistics. Several of the systems tested in this study are intended for use with low-flow 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 did not evaluate the merits of a low-flow purge 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 Aeronautics and Space Administration (NASA) Stennis Space Center (SSC) 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 (VOC). 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.

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 technologies were deployed in a number of 2-inch and 4-inch wells, along with the reference samplers for comparison. 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 comparing 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 to reference sample results. Aspects of field deployment and potential applications of the technology were also considered.

A brief outline of this report is as follows: Section 2 contains a brief description of the Kabis 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 Kabis sampler technology and provides examples of potential applications of the sampler in site characterization and monitoring situations. Appendix A contains performance data for the reference pump, and Appendix B presents an assessment of quality control data associated with the analytical method used in this study.

Section 2 — Technology Description: Kabis Sampler

This section provides a general description and overview of the capabilities of the Kabis sampler Models I and II manufactured by Sibak Industries. The information used to prepare this section was provided by Sibak Industries.

Two Kabis samplers, the Model I and Model II, as shown in Figure 1, were evaluated in this test. They operate on the same principle and only differ in size and sample capacity. The Model I is 17.4 inch long with a 1.75-inch external diameter and a weight of 6.5 pounds. The Model II is 22.3 inches long with a 3.55-inch external diameter and a weight of 15.5 pounds. Both samplers are constructed of 321 stainless steel and have a removable top into which a single (Model I) or three (Model II) 40-mL volatile organic analysis (VOA) vials are screwed prior to sampler deployment in the well. The sampler is attached to a measuring tape and slowly lowered into the water column. The orientation of the inlet and exhaust ports of the sampler is such that the sampling chamber does not fill while it is being lowered down through the water column. When the sampler is held stationary at the desired sampling depth, it begins to fill by hydrostatic pressure. Fill time is about 5 minutes for the Model I and 8 minutes for the Model II.

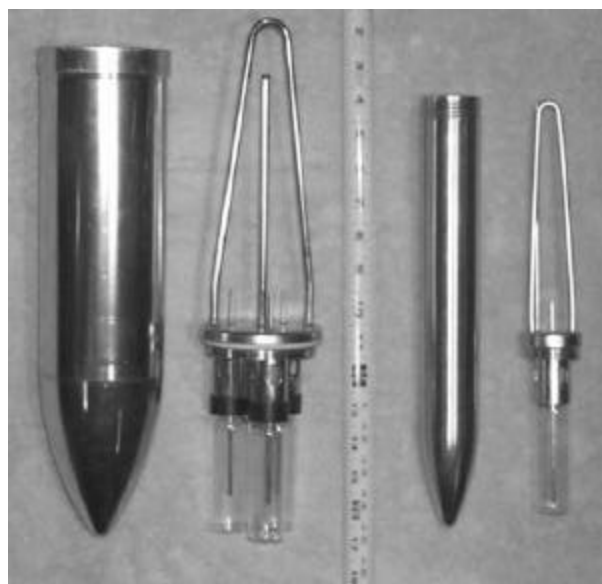


Figure 1. Kabis sampler Model I (right) and Model II (left) .

The Kabis sampler employs simple physics for its operation. As illustrated in Figure 2, water surface tension across the exhaust port (T_1) is equal to the water surface tension across the fill port (T_2). The head pressure (h) imposed by the vertical difference between the fill port (P_1) and the exhaust port (P_2) is only slightly greater than the surface tension across both the fill and exhaust ports. As the sampler is lowered past the air/water interface and down through the water column, the hydrostatic pressure (P) changes across both the fill and exhaust ports at a constant rate. As the hydrostatic head pressure increases, the imposed head pressure (h) tends toward the asymptote of zero. Since h approaches zero, the water surface tension prevents water entry into either sampler port. As the sampler descent rate goes to zero at the desired sampling depth, the imposed head pressure is restored and slowly overcomes the surface tension at the fill port, and the fill cycle begins.

Air inside the sampler escapes through the exhaust port and the installed sample vial(s) fills from the bottom of the vial upward. The vial(s) are flushed with a total of about 6 vial volumes prior to collection of the final vial volume. The flush

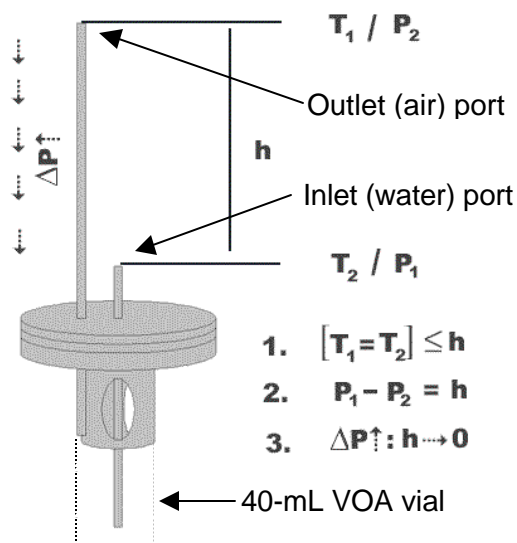


Figure 2. Illustration of the Kabis sampler filling sequence.

water flowing through the vial spills into the sampler body through spill ports located in the vial holder on the sampler head. When the overflow water in the sampler body reaches the bottom of the exhaust port, no more air can escape from the sampler body and the sampler fill cycle is complete. The sampler is then retrieved to the surface. The sampling head is unscrewed from the body of the sampler and the sample vials are then removed from the sample head. If sample preservation is required, few drops of preservative solution can be added. The vial is then capped with a positive-displacement-type cap that ensures a bubble-free sample.

The Kabis sampler is designed to collect a sample from a well at a specific depth chosen by the sampler operator. It is a grab sampler and by virtue of this fact does not incorporate well purging in its use. Well purging, whether by a low-flow method or traditional three-volume purge, may or may not be required in monitoring applications. If site

sampling objectives require well purging, other devices could be used to carry out well purging prior to the use of a Kabis unit for sample collection.

The sampler has no moving parts and requires no maintenance other than routine decontamination. Decontamination procedures consist of a detergent water rinse followed by several distilled water rinses and can be easily carried out in the field.

Costs for the two Kabis samplers are \$825 for the Model I and \$1,895 for the Model II. Sampler accessories, not included in the base price, include a delivery tape, wooden storage box, and positive-displacement VOA vial caps.

Additional information on potential applications of the system for environmental characterization and monitoring can be found in Section 5—Technology Updates and Application.

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 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 Hydrologic Instrumentation Facility supports USGS agencywide 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 1. The standpipe is an aboveground, 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 mixing and transfer of solution. 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 technology samples inside the pipe. As shown in Figure 1, the indoor facility has six levels of access, including the ground floor, and all levels are serviced by a freight elevator. 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 known as Upper Clay, and found at elevations ranging from 10 to 30 feet mean sea level (MSL), overlying a sandy unit named Upper Sand (at 5 to 15 feet 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 interbedded 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.

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 polyvinyl chloride (PVC) pipe with a 10-foot PVC

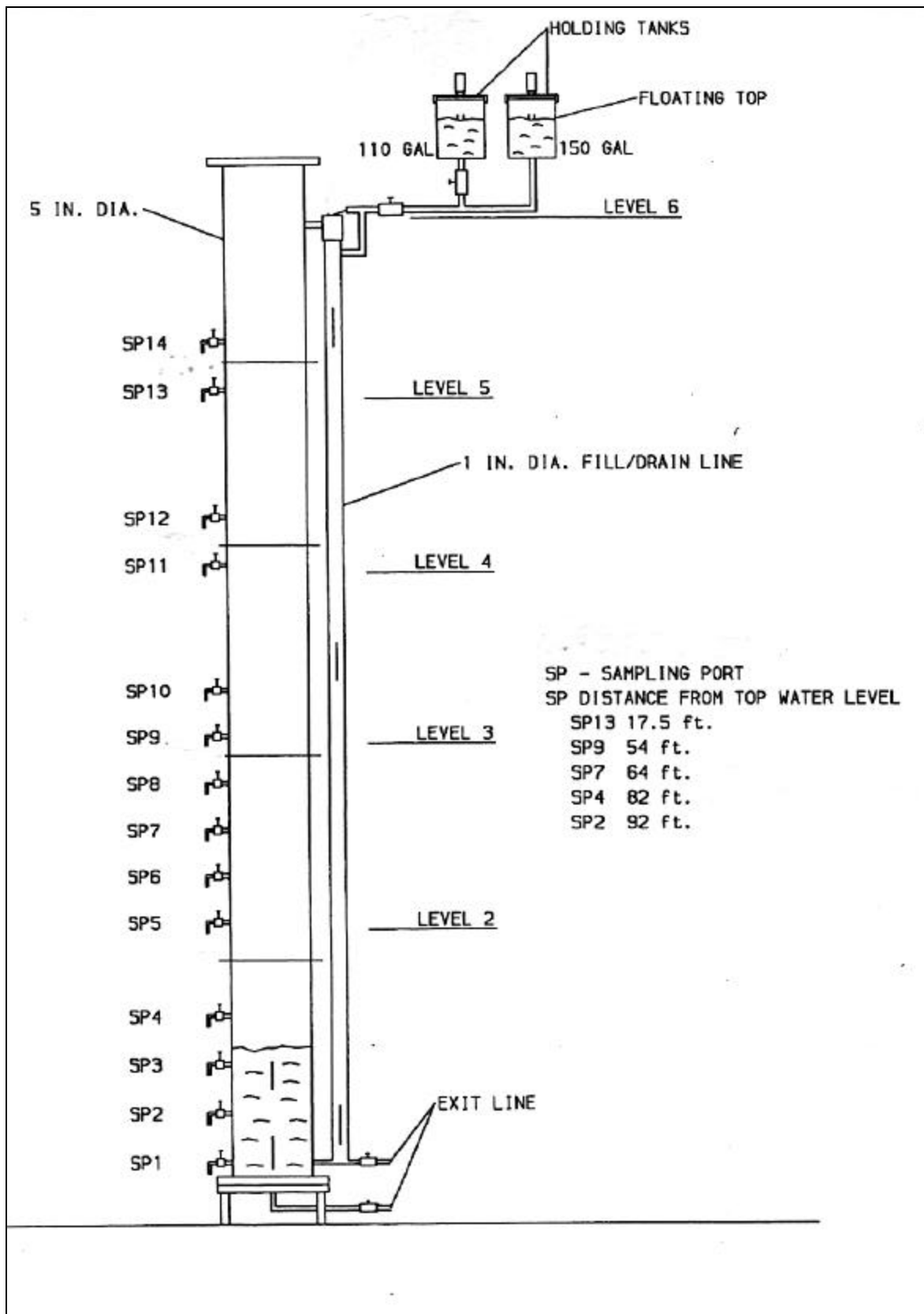


Figure 3. The standpipe at the USGS Hydrological Instrumentation Facility.

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. The depth of the water column above the midscreen 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 sampler performance parameters such as precision and comparability with reference to be evaluated. 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 categories.

Target VOC Compounds—Six target compounds, all regulated under the 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)		Well Dia. (in.)	Install Date	Depth to Water (ft)	Water Level (ft, MSL)	Water Depth Above Screen Midpoint (ft)
			Top	Bottom					
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). Spike solutions of all six target compounds were prepared in methanol from neat compounds. 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 Sample—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 had external sampling ports along its length so that reference samples could be collected simultaneously with the samples from the interior of the pipe with devices 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. The use of multiple sequentially collected samples 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 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 in which 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 could be a 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 from the overlying contaminated layers in the well.

Groundwater Well Reference Samples—Six onsite groundwater monitoring wells were selected for use in the second phase of the study. A submersible electric gear pump (Fultz, Model SP-300) was chosen as a reference sampling device for these additional field tests. Verification studies on the performance of this pump were carried out during the standpipe phase of the experiments to provide technical data substantiating its use as a reference method in the field. A more complete description of the pump along with a summary of these data is given in Appendix A. During field sampling events, the reference pump was co-located in the well with the sampling devices in order to provide simultaneous reference samples from the well. Teflon tubing (¼-inch outside diameter) was used to transport the water sample from the pump outlet to the collection vial at the wellhead. During all sampling, the pump was operated at a low flow rate (100-200 mL/min). During Kabis sampler testing in groundwater monitoring wells, the reference pump and the Kabis sampler could not be simultaneously deployed in the well as a result of space limitations. In these instances, the Kabis sampler was deployed first and replicate samples were collected. Following Kabis sample collection, the reference pump was immediately deployed and a second set of reference samples was collected.

As noted previously, the field sampling trials were not an evaluation of the low-flow purge methodology for well sampling. Consequently, water quality parameters were not monitored in the field sampling trials. The presampling purge was used to flush the reference pump and tubing to ensure that the pump was drawing from the well column water. Whether formation water was

being sampled was of secondary importance in this sampling plan.

Sampler Performance Parameters

Four performance parameters were evaluated in the assessment of each technology. 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* (RSD) 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:

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

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 the assessment of sampler precision, a statistical test was used to assess whether differences between the reference sample precision and the technology sample precision were statistically significant. Specifically, the F-ratio test was used to compare 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 the spike mixtures were mixed and transported 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:

$$\%DIFF = \frac{(\bar{X}_{tech} - \bar{X}_{ref})}{\bar{X}_{ref}} \cdot 100$$

where is \bar{X}_{tech} the average reported concentration of all technology sample replicates and \bar{X}_{ref} is the average reported concentration of all reference sample replicates. The t-test for two sample means was used to assess 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 methods.

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 encountered in both the standpipe and the groundwater monitoring well 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 or at some of the tested sampling depths.

Field Deployment Logistics—This final 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 have 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 sample flow rate when filling the vial with a bladder pump, the cycle times and volume of bladder pump and others may influence overall sample quality. An evaluation of operator influence on sample quality is beyond the scope of this study. All operators were experienced in the use of their technologies and the assumption is made that these operators were operating their sampling devices 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 an 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]. 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 VOCs in water analysis were 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 °C 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 immediately 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- μ L 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 °C 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 in 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 subsequent 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 the internal standard method (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 has 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^{3/4}All sampling activities were documented by Sandia National Laboratories (SNL) field technicians using chain-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*¾Field 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.

*Predemonstration Analytical System Audit*¾Prior to the actual demonstration, a number of samples containing the six target compounds at various concentration levels were prepared at SNL and sent via overnight Express Mail in an ice pack to Field Portable Analytical near Sacramento, CA. They were analyzed by GC/MS analysis 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*¾The 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 B.

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 accepted 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 and GW Well-Sampling Matrix

The sampling matrix for the standpipe sampling phase of the demonstration is given in Table 3. All standpipe and groundwater well testing was carried out sequentially, with the various participants deploying their technologies 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 included seven trials. Trials 1 and 2 were carried out at shallow and deep locations with the a low concentration (10-20 µg/L) standpipe mixture. Trials 3 and 4 were conducted at shallow and deep locations with a high-concentration (175-225 µg/L) standpipe mixture. In all trials, reference samples were collected from external sampling ports simultaneously with sample collection by the device under test.

Trial 5 was a blank mixture measurement at the standpipe to test the cleanliness of each sampler. For this trial, the standpipe was filled with tap water and three replicates were collected by the device under test from the deep location in the pipe while three reference replicates were collected simultaneously from the adjacent exterior sampling port.

Trials 6 and 7 at the standpipe were termed “clean-through-dirty” tests and were designed to evaluate the discrete-level sampling performance of the Kabis sampler. This test was optional for the other

Table 3. Sampler Verification Trials at the Standpipe

Trial No.	Standpipe Collection Port	Sample Collection Depth (ft)	VOC Concentration Level	No. of Replicates per Technology
1	SP14	Low (17)	Low (~20 µg/L)	5
2	SP3	High (92)	Low (~20 µg/L)	5
3	SP14	Low (17)	High (~200 µg/L)	5
4	SP3	High (92)	High (~200 µg/L)	5
5	SP3	High (92)	Blank	3
6	SP3	High (92)	Mixed (high over low)	4
7	SP12	Low (35)	Mixed (high over low)	4

Notes: In each trial, an equal number of reference samples were collected simultaneously with the technology samples from adjacent external standpipe sampling ports. Sample collection points during trials 6 and 7 were from the low VOC concentration region after the sampler was lowered through a high VOC concentration region.

active samplers. Those sampling systems that were intended for permanent deployment in a well were not required to participate in the “clean-through-dirty” sampling trials, although some chose to participate voluntarily. In this test, two mixtures, a high (~200 µg/L) and a low (~20 µg/L), were prepared in the mixing tanks. The pipe was then filled so that the high-level mixture occupied the top 1/3 of the pipe while the low-level mixture was in the bottom 2/3 of the pipe. Water samples were collected at the bottom and approximate midpoint of the pipe after being lowered through the high-level mixture at the top of the pipe. Reference samples were simultaneously collected from the external sampling ports in the same manner as for the previous standpipe trials.

The onsite groundwater sampling matrix is shown in Table 4. Two of the wells originally scheduled for use were dropped from the sampling matrix because the TCE concentrations were below the instrument detection limit. The groundwater sampling procedure for the Kabis and reference sampler was as follows: As a result of the limited space available in the 2- and 4-inch diameter wells, the Kabis sampler and reference pump could not be deployed in the well at the same time. A modified sampling protocol was used in which the Kabis sampler was first delivered to the midscreen depth and four replicate samples were collected. In most cases, a single delivery of the Kabis sampler to the well was used and any VOA vials in addition to those installed on the sampler head were filled from the overflow reservoir of the Kabis sampler. Following Kabis sampler retrieval,

the reference pump was installed at the same midscreen level in the well. A purge volume of about 1 to 2 liters was drawn through the reference pump at a flow rate between 100 to 200 mL/minute. Following this purge, four replicate samples were collected.

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 (multilevel 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 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 the 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.

Table 4. Sampler Verification Trials at the Groundwater Monitoring Wells

Trial	Well	Distance from Top of Well to Screen Mid-point (ft)	Water Column Depth (ft)	Approximate TCE Conc. (µg/L)	No. of Replicates per Technology
10	06-20MW	67.7	59.9	<5	4
11	06-11MW	83.1	69.0	500	4
13	06-04MW	35.1	9.8	500	4
14	12-09MW	15.0	5.2	20	4

Notes: Reference samples were collected using a submersible electric sampling pump that was colocated with the Kabis sampler in 4-inch wells and after the Kabis sampler in 2-inch wells.

Well numbers 06-04 and 12-09 were 2-inch diameter wells. All other wells had 4-inch diameters.

Approximate TCE concentrations are derived from NASA contractor quarterly monitoring data. Sampling methodology consisted of a three-well volume purge followed by sample collection with a bailer.

Trials 12 and 15 were no-detect wells and were dropped from the data set.

Sample analysis was performed in a mobile laboratory parked near the standpipe and was carried out 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 instrument variability on the analysis results.

The demonstration technical team observed and recorded the operation of each technology during both standpipe and monitoring well trials to assist in the assessment of logistical requirements and ease of use of the technology. These observations also were used to document any performance anomalies as well as the technical skills required for operation.

Deviations from the Verification Plan

Under most field testing environments, circumstances often arise that prevent a complete execution of the test plan. A list of the deviations from the test plan that are judged to be important are summarized below and an assessment of the resulting impact on the field test data set is included.

Lost/Dropped Samples ¾ 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. No Kabis or Kabis reference samples were lost during the testing.

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 the 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 Kabis 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 tubing carryover contamination was determined to

be the cause of the erroneous screening data. 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 most of the objective parameters of performance, such as sampler accuracy and precision, are derived from the standpipe data.

Questionable Sampling Procedure—In several sampling events at both the standpipe and monitoring wells, the Kabis sampler operator filled some of the replicate sample vials by pouring from the sampler sump instead of deploying the sampler a second time into the standpipe or well. This procedure may have influenced the analysis results; however, since the procedure was done infrequently, the effects on sample quality cannot be ascertained in this study.

Filling sample vials from the sump is not a recommended practice in normal sampler use.

Unverified Performance Claim—One of the performance claims associated with the Kabis sampler is that no well purging is required in order to acquire a sample that is representative of formation water. Performance claims of the various vendor participants in the study associated with the merits of low volume purging or no purging were beyond the scope of this study and were not evaluated. Furthermore, the design and operation of the Kabis sampler is such that a reference sampler could not be co-located in the monitoring wells for comparative purposes. Thus, quantitative comparisons of Kabis and reference samples from the groundwater monitoring wells were not possible in this study.

Section 4 — Performance Evaluation for Kabis Sampler

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. The Kabis Model I and Model II samplers were used interchangeably in these tests. They are identical in design and method of operation and only differ by size of sample collected. All data are combined and reported under the term “Kabis sampler.”

Sampler Precision

The precision for both Kabis and reference samples from the first four standpipe trials is given in Table 5. The first four trials consisted of low (10-20 $\mu\text{g/L}$) and high (175-225 $\mu\text{g/L}$) target compound concentrations, with sample collection at shallow (17 feet) and deep (91 feet) locations in the standpipe, as outlined previously in Table 3. Relative standard deviations are tabulated by compound with 4 test conditions (low concentration at shallow sampling depth, high concentration at shallow sampling depth, and so on) shown for each compound, for a total of 24 cases. The final column in the table is the result of the F-ratio test used to assess whether the technology and reference precision values are statistically different. The value p tabulated in the final column of the table is a measure of the observed difference between the two values in probabilistic terms. Values of p that are close to 1 indicate small differences between the two precision values, and low values of p indicate greater differences. Values of p that are less than 0.05 are indicative of statistically significant differences that 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 being compared 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%. In other words, such an observed difference would be highly unlikely. For

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

The results shown in Table 5 can be summarized as follows. Relative standard deviations from low and high sample concentrations do not significantly vary for both Kabis and reference data. The greatest imprecision in the Kabis and reference results are encountered for 112TCA in the deep collection, low concentration test. Preliminary evaluations of GC/MS performance carried out prior to the field demonstration revealed that this compound had higher analytical uncertainty than the other target compounds, so the observed effect can be attributed to the analytical method and not the sampling process. The median RSD for all compounds and all trials was 10.7% for the Kabis sampler and 8.7% for the reference samples. Sixteen of the Kabis sampler precision values were less precise than the reference values, and 8 were more precise than the reference values. The results of the F-ratio test indicate that only 1 of the 24 cases had a value of p that was less than 0.05. Thus, differences in precision between Kabis and reference samples are statistically insignificant in 23 of the 24 cases.

Comparability to Reference

The comparability of the Kabis sampler data with reference data for standpipe trials 1 through 4 is given in Figure 4 and Table 6 and are expressed as percent differences. Percent difference values were computed for each of the six target compounds in the four standpipe trials for a total of 24 cases. The difference values for the Kabis sampler range from -39 to 18%, with a median value of -3%. By compound, the greatest variability in results is seen for 12DCA, PCE and TCE and the lowest for benzene and 112TCA. Percent difference values for 14 of the 24 results shown in Table 6 were less than zero with another 10 values above zero, thus no consistent bias in either direction is observed when all cases are grouped together. A t-test for two sample means was performed to assess whether the differences between the Kabis sampler and reference mean values could be attributed to random variation or to a systematic bias for each case. As noted previously in the discussion on precision, values of

p that are less than 0.05 are suggestive of a systematic bias between the Kabis and reference sample results. Most of the results (16 of 24) show no statistically significant difference between Kabis and reference results. T-test results for 8 of the 24 cases have values of p less than 0.05. Five of those 8 cases show a Kabis sampler negative bias ranging from -14 to -39% and these all occur at the high VOC concentration levels. Negative bias is judged to be of most importance since only VOC losses are expected during the sampling

process. Negative biases in excess of 25% were observed for 2 PCE cases at high VOC concentrations at both shallow and deep sample collection points. If one were to use a negative sampler bias performance criteria of 25% or greater as unacceptable performance, these results show that the sampler would perform acceptably for all compounds tested except PCE. Actual performance criteria for a particular application may vary and should be established by the site investigator on a case-by-case basis.

Table 5. Precision Summary for Kabis and Reference Sample

Compound	Conc. Level	Sampling Depth (ft)	Kabis Precision (% RSD)	REF Precision (% RSD)	F-Ratio	F-Ratio Test p
11DCE	Low	17	14.1	7.2	3.58	0.24
	Low	91	7.3	11.7	2.32	0.44
	High	17	11.4	7.9	2.14	0.48
	High	91	11.3	9.3	1.08	0.94
12DCA	Low	17	5.6	5.5	1.34	0.78
	Low	91	2.9	9.6	8.79	0.06
	High	17	8.9	4.6	5.15	0.14
	High	91	5.3	10.9	4.34	0.18
BNZ	Low	17	5.8	7.6	1.62	0.65
	Low	91	6.8	7.0	1.04	0.97
	High	17	10.7	4.1	7.36	0.08
	High	91	8.0	9.2	1.68	0.63
TCE	Low	17	6.0	15.3	7.47	0.08
	Low	91	18.0	12.0	2.30	0.44
	High	17	10.6	8.7	1.11	0.92
	High	91	11.4	9.4	1.16	0.89
112TCA	Low	17	15.4	12.1	1.35	0.78
	Low	91	25.8	17.6	2.04	0.51
	High	17	7.5	6.1	1.73	0.61
	High	91	5.7	8.6	1.06	0.39
PCE	Low	17	11.0	4.6	4.78	0.16
	Low	91	19.7	4.9	15.52	0.02
	High	17	13.3	11.2	1.28	0.81
	High	91	12.6	7.5	7.5	0.96

Notes: Values of p less than 0.05 are shown in bold.
REF = reference measurement

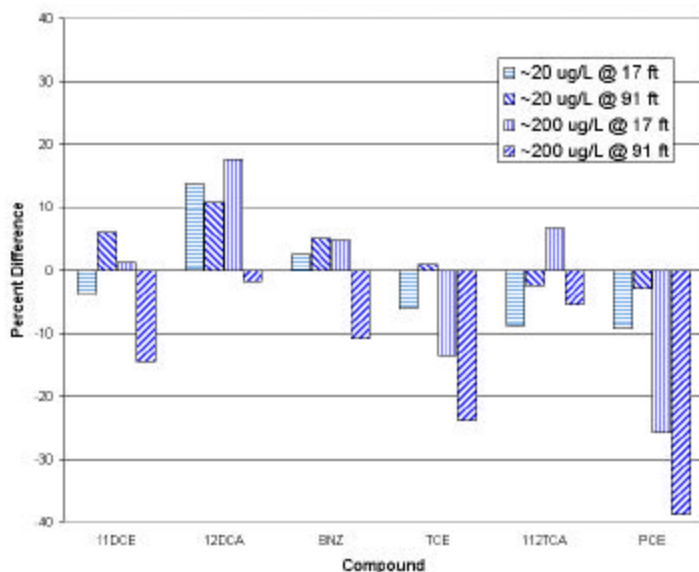


Figure 4. Kabis sampler comparability with reference samples from the standpipe trials.

Table 6. Comparability of Kabis and Reference Sample Data from Standpipe Trials

Compound	Conc. Level ^a	Depth (ft)	Kabis Difference (%)	t-Test ^b <i>p</i>
11DCE	Low	17	-4	0.60
		91	6	0.37
	High	17	1	0.84
		91	-14	0.04
12DCA	Low	17	14	<0.01
		91	11	0.04
	High	17	18	<0.01
		91	-2	0.75
BNZ	Low	17	3	0.58
		91	5	0.30
	High	17	5	0.41
		91	-11	0.07
TCE	Low	17	-6	0.42
		91	1	0.92
	High	17	-14	0.04
		91	-24	<0.01
112TCA	Low	17	-9	0.31
		91	-2	0.87
	High	17	7	0.18
		91	-5	0.26
PCE	Low	17	-9	0.10
		91	-3	0.76
	High	17	-26	<0.01
		91	-39	<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 225 µg/L.

^b The t-test was used to compare the differences between the Kabis and the reference results for each compound in each trial. The value *p* yields a quantitative estimate in probabilistic terms of the likelihood of the difference being attributable to random variation alone. See text for further details.

Blank and Clean-through-Dirty Performance

The results from standpipe trials using blank solutions show that the Kabis sampler reported nondetectable levels for all six target compounds. These results indicate that a Kabis sampler, when decontaminated using the procedures specified in Section 2, will not contaminate a sample with chemical carryover from previous use.

The results of the clean-through-dirty test at the standpipe are shown in Table 7. The sampler was lowered through a layer of relatively high (~200 µg/L) target VOC concentrations at the top of the standpipe for sample collection at a depth of 35 and 91 feet in water with lower (approximately 15 to 50 µg/L) VOC concentrations. The tabulated results are shown in terms of percent difference relative to the reference samples collected simultaneously with the Kabis samples. Note that the tabulated difference levels for this trial are raw values in the sense that they are not normalized with the percent difference levels shown in Table 6. Difference levels for the Kabis sampler for all compounds at both depths vary from 38 to 187%, giving evidence that the sampler is either entraining contaminants from the dirty layer or it

is collecting a partial sample as it is lowered through the dirty layer. This carryover may be of concern when the sampler is deployed at a multiscreened well with high levels of contaminants overlying lower contaminant levels at the desired sampling depth.

Monitoring Well Results

Kabis sampler results from groundwater monitoring samples collected at four wells are shown in Table 8 alongside reference data from the same wells. Four replicate samples were taken with the Kabis sampler and the reference sampler (a submersible electric gear pump), and relative standard deviation values are also given in the table. A few general observations from these data are warranted: First, the field trials were carried out primarily to provide an opportunity to observe the deployment and operation of the technology under actual field conditions. Second, formal statistical analyses of these data have not been carried out since the standpipe trial data set is judged to be a superior data set for the determination of precision and comparability to a reference measurement. The data are shown for qualitative comparison with the standpipe results, and significant differences are noted where appropriate.

Table 7. Clean-through-dirty Test Results for the Kabis Sampler

Compound	Sampling Depth (ft)	Kabis Average Concentration (mg/L)	Kabis Precision (%RSD)	Reference Average Concentration (mg/L)	Reference Precision (%RSD)	Kabis Percent Difference
11DCE	35	71.2	4.2	31.9	18.2	123
	91	23.4	9.8	13.3	11.6	75
12DCA	35	102.3	14.9	38.7	18.1	164
	91	32.7	18.2	14.2	16.7	130
BNZ	35	85.6	5.3	37.6	29.0	127
	91	28.2	12.4	13.7	6.7	106
TCE	35	67.7	11.5	33.2	2.9	104
	91	25.5	18.0	13.8	12.6	85
112TCA	35	102.2	20.2	41.1	7.7	149
	91	43.3	19.9	15.1	10.6	187
PCE	35	83.1	6.3	51.8	9.6	160
	91	31.0	13.6	22.5	7.0	38

Table 8. Kabis Sampler and Reference Pump Results from Groundwater Monitoring Wells

Well No.	Kabis Average TCE Concentration (mg/L)	Kabis Precision (%RSD)	Reference Average TCE Concentration (mg/L)	Reference Precision (%RSD)
06-11 MW	386	3.5	480	5.1
06-04 MW	338	14.7	596	6.4
12-09 MW	11.2	10.8	11.2	10.8
06-2 MW	ND (<5)	--	ND (<5)	--

Note: ND = not detected.

The data in Table 8 reveal that sampler precision in the field was similar to that observed at the standpipe. No assurances can be given that the concentration of TCE in the well was stable over the duration of the sampling event in each well; thus formal comparisons between the two sets of data are not done. Both the Kabis sampler and the reference pump samples were nondetectable for the well with no TCE. These blank results indicate that the Kabis sampler, when decontaminated using normal procedures, is not a potential source of contamination in low-level sampling operations.

Sampler Versatility

The performance parameters for the Kabis sampler discussed previously reveal that it can collect water samples contaminated with VOCs of varying volatility at a range of sampling depths. However, some evidence of a significant systematic bias is observed when results are compared with those of a reference method. Evidence of negative sampler bias is judged to be of greatest importance since it may result in underreporting of actual groundwater concentrations. Observed cases of negative sampler bias in excess of -25% occur for high concentrations of PCE and TCE. A statistically significant negative sampler bias of a lesser magnitude is also observed for 11DCE and TCE cases. In light of these considerations, the Kabis sampler is judged to have limited versatility.

Deployment Logistics

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

- Only one person is required to operate the sampler. Training requirements are minimal,

with about 1 hour of training required for a technician to become proficient in routine field use of the equipment.

- The equipment is lightweight, compact, and requires no external power to operate.
- A moderate level of manual dexterity is required when removing the filled VOA vials from the sampler. Care must be taken to keep both the sampler and the vials upright when removing and capping. Failure to do so may result in spilled samples, resulting in unwanted air bubbles in the capped vial. Dexterity is also required in adding a dilute acid preservative prior to capping the sample.
- The sampler is designed for portable use at multiple wells and can be decontaminated in the field with a detergent rinse followed by several distilled water rinses.
- The sampler is maintenance free, with no moving parts.
- The sampler is not suitable for well purging. In instances where well purging is required, an alternative means of purging is required.
- The sampler cannot be used where sampling protocols require the use of pre-preserved sampling vials or Teflon-lined septum caps in vials.

Performance Summary

Kabis sampler performance is summarized in Table 9. 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 Kabis sampler can be used to collect VOC-contaminated water samples that are statistically comparable to a reference method with regard to

both precision and accuracy. Some indications of significant sampler bias were observed in selected trials. Low recoveries were observed for TCE and PCE at high VOC concentrations at the deeper (91 feet) sampling depth evaluated in this study.

The clean-through-dirty trials also gave evidence that the sampler may carry over contaminants from an overlying dirty layer in a water column. See Section 5 for vendor suggestions to remedy this limitation.

Table 9. Performance Summary for Kabis Sampler

Parameter	Summary
Precision	For 6 target compounds at low (20 µg/L) and high (200 µg/L) concentrations and at 17-foot and 91-foot sampling depths: Relative standard deviation range: 2.9 to 25.8% (reference: 4.1 to 17.6%) Median relative standard deviation: 10.7% (reference: 8.7%) In 23 of 24 standpipe test cases, Kabis precision was statistically comparable to the reference sample precision.
Comparability with reference samples	For 6 target compounds at low (20 µg/L) and high (200 µg/L) concentrations at 17-foot and 91-foot sampling depths, Kabis and reference differences are summarized as follows: Percent difference range: -39 to 18% Median percent difference: -3% In 16 of 24 standpipe test cases, Kabis differences relative to reference samples were statistically indistinguishable from 0%. Statistically significant negative sampler biases in excess of 25% were observed for PCE in 2 cases.
Sampler versatility	The Kabis sampler demonstrated consistent performance across the tested range of compound volatility and sampler depth with regard to precision. Some statistically significant sampler biases were observed for PCE and TCE. In light of these biases, the sampler is judged to have limited versatility.
Logistical requirements	System can be operated by one person with a few hours of training. System is lightweight and portable, with no power requirements.
Completeness	Sampler was successfully used to collect all of the samples prescribed in the test plan.
Purchase cost	Model I \$825 Model II \$1,895
Size and weight	Model I: 1.75-inch external diam. x 17.4-inch length, 6.5 pounds Model II 3.56-inch external diam. x 22.3-inch length, 15.5 pounds
Other	Sampler cannot be used to purge a well. Other purging system must be provided if purging is required. Clean-through-dirty tests reveal that sampler may carryover contamination from an overlying dirty water column into cleaner underlying water. In all test cases, sample recovery in excess of 100% was observed. Sampler percent differences, relative to reference samples, ranged from 38-187%.

Note: Target compounds were 1,1-dichloroethene, 1,2-dichloroethane, benzene, trichloroethene, 1,1,2-trichloroethane, and tetrachloroethene.

Section 5 – Kabis Sampler Technology Update and Representative Applications

Note: The following comments were provided by the vendor and have not been verified as a part of this ETV test. They have been edited only for editorial consistency with the rest of the report.

Vendor Observations on Clean-Through-Dirty Sampling

The Kabis Sampler, under certain conditions, may intake a small amount of air/water interface water, or whatever other liquid may be at the surface during delivery. Fortunately, the sampler flushes the sample container an average of about six vial volumes before taking the actual sample. If the surface layer is composed of extremely high concentrations, occasionally minute quantities of the surface contaminant remain in the sample, possibly giving the indication of a false positive. A field modification that can be performed under these conditions involves the following: a $\frac{3}{16}$ inch ID by 2½-inch long piece of Tygon tubing which has been heat pinched over a braided nylon cord at one end is lightly pushed over the intake port of the Kabis Sampler. Enough cord is included to accommodate the sampler delivery depth from the surface. The Tygon tubing effectively seals the intake port from water intrusion until it reaches the desired sampling depth, at which time the nylon cord is pulled, removing the external plug from the fill port, allowing the sampler's fill cycle to begin. This modification was not employed during the clean-through-dirty field trial of the Kabis Sampler that was carried out to assess the degree of contaminant carryover that occurs when lowering the sampler through a high VOC concentration layer into a low VOC concentration layer.

The Kabis Sampler may be used in nearly any environment. The single exception is an acid environment, due to the sampler's stainless steel construction. Although the sampler was primarily designed for delivery and use in groundwater monitoring wells, it is equally used in water supply wells, lakes, rivers, streams, ponds, bays, and in the open ocean. In addition, the Kabis Sampler has been used with success in storage tanks containing high-energy radionuclides, food processing vats, beer and other beverage process vats, and on a variety of other liquids in various industries. Wherever the need to sample liquids at a specific depth is encountered, the Kabis Sampler can be used or adapted for use.

Example Field Applications

Recent projects where the Kabis Sampler has been deployed include chlorinated hydrocarbons at Watervliet Arsenal in New York; DNAPL contaminants at the Hanford facility in Washington; light fraction hydrocarbons of gasoline in Raccoon Creek, Pennsylvania; and methyl-tertiary-butyl ether and perchlorates associated with rocket fuel production at a former Rocketdyne plant in California. The Kabis Sampler samples directly into the sample container under laminar flow and provides little disturbance of the well as it is inserted; it is therefore suitable for sampling dissolved minerals, heavy metals, and salts of all kinds. The Kabis Sampler, because of its sampling methodology, cannot be classified as a bailer, though it is a grab-type sampling device; it is a true discrete-point interval sampler. Its applicability, though, unlike other discrete-interval point samplers, covers a broad range of environments and contaminants.

Section 6 - References

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Appendix A — Reference Pump Performance

Introduction

In addition to the sampling at the standpipe, the verification test design included the collection of vendor samples from onsite groundwater monitoring wells. During monitoring well sampling, a reference pump was colocated in the well with the vendor sampler. Both vendor and reference samples were collected simultaneously to enable a comparison of the results. This appendix summarizes the reference sampler chosen and outlines its performance and acceptability as a reference sampling technique.

System Description

The reference pump selected for use in this verification study was a submersible electric gear pump (Fultz, Model SP-300, Lewistown, PA). Pump construction materials are stainless steel and Teflon, and pump dimensions are 7.5 inches in length by 1.75 inches in diameter. This pump is a positive displacement device. Water is introduced into the pump through a 60-mesh inlet screen into a stainless steel cavity. Two Teflon gears inside the cavity push the water to the surface through 100 feet of ¼-inch outside diameter Teflon tubing. An electronic controller is used to regulate the flow rate of the pump. Nominal sample collection flow rates were in the range of 100–200 mL/min.

Performance Evaluation Method

The gear pump was tested during the standpipe trials in the same manner as the other vendor pumps. Water samples were collected from the interior of the standpipe in four separate trials with both low (~20 µg/L) and high (~200 µg/L) target concentrations at low (17 feet) and high (91 feet) sampling depths (see Section 3 for additional details). Reference samples were collected from external sampling ports simultaneously with the pump samples. In each trial, five replicate pump samples and five replicate port samples were collected. Following collection, all samples were analyzed using the same onsite GC/MS system.

Pump Precision

A summary of pump precision is given in Table A-1. The percent relative standard deviation results for each of the six target compounds in the four standpipe trials (low concentration—shallow, low concentration—deep, and so on) for the gear pump and the external sampling port are given in columns 4 and 5, respectively. The relative standard deviation range for the pump was 3.2 to 16.3%, with a median value of 7.6%. The port precision data ranged from 2.8 to 16.2%, with a median value of 10.1%. The final column in the table gives the value of p associated with the F-ratio test (see Section 3 for a description of this test). Values of p less than 0.05 may indicate that significant, nonrandom differences exist between the two estimates of precision.

Out of 24 trials, only 2 show values of p less than 0.05. These data indicate that pump precision was not statistically different from the precision obtained from the reference samples taken directly from the standpipe external ports.

Table A-1. Precision of Gear Pump and Reference Samples in Standpipe Trials

Compound	Conc. Level	Depth (ft)	Gear Pump Precision (%RSD)	Port Precision (%RSD)	F-Ratio	F-Ratio <i>p</i>
11DCE	Low	17	15.7	14.2	1.11	0.46
	Low	91	3.5	14.4	14.7	0.01
	High	17	4.0	8.6	4.81	0.08
	High	91	7.6	9.7	1.28	0.41
12DCA	Low	17	15.4	12.5	2.35	0.21
	Low	91	3.2	13.2	14.1	0.01
	High	17	5.1	9.0	3.18	0.14
	High	91	6.0	10.4	2.38	0.21
BNZ	Low	17	8.1	11.8	1.71	0.31
	Low	91	7.6	12.9	2.30	0.22
	High	17	3.7	8.4	5.02	0.07
	High	91	6.1	9.4	1.83	0.29
TCE	Low	17	16.3	10.5	2.41	0.21
	Low	91	5.9	12.1	3.12	0.15
	High	17	6.4	2.9	4.82	0.08
	High	91	9.6	8.6	1.55	0.34
112TCA	Low	17	9.4	16.2	3.38	0.13
	Low	91	8.4	15.0	2.81	0.17
	High	17	7.6	3.5	4.76	0.08
	High	91	11.0	6.5	3.43	0.13
PCE	Low	17	12.9	9.6	1.36	0.39
	Low	91	9.0	11.7	1.50	0.35
	High	17	4.5	2.8	2.28	0.22
	High	91	12.7	8.8	2.38	0.21

Pump Comparability with Reference Samples

Gear pump comparability is expressed as the percent difference relative to the reference sample concentration by subtracting the average reference value from the average gear pump value, dividing the result by the average reference value, and multiplying by 100. The percent differences for each of the 24 trials are given in Table A-2. They range from -13 to 14% with a median value of 7%. A t-test for two sample means was used to evaluate the statistical significance of the differences between the gear pump and reference samples. The tabulated values of *p* give a quantitative measure of the significance of the observed difference in probabilistic terms. Values of *p* less than 0.05 suggest that a statistically significant bias may exist for the trial. With five exceptions, all values of *p* are greater than 0.05, indicating that overall, the differences between the two sampling methods are statistically indistinguishable.

Table A-2. Comparability of the Gear Pump with the Reference Samples in Standpipe Trials

Compound	Conc Level ^a	Depth (ft)	Difference (%)	t-Test ^b <i>p</i>
11DCE	Low	17	-4	0.64
	Low	91	7	0.31
	High	17	-3	0.54
	High	91	13	0.05
12DCA	Low	17	24	0.05
	Low	91	10	0.13
	High	17	-2	0.71
	High	91	12	0.06
BNZ	Low	17	11	0.13
	Low	91	13	0.11
	High	17	0	0.98
	High	91	14	0.03
TCE	Low	17	0	0.99
	Low	91	16	0.04
	High	17	0	0.95
	High	91	11	0.10
112TCA	Low	17	-6	0.51
	Low	91	7	0.41
	High	17	1	0.77
	High	91	10	0.15
PCE	Low	17	-13	0.08
	Low	91	6	0.37
	High	17	-6	0.03
	High	91	6	0.42

^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 differences between Well Wizard and reference samples for each compound in each trial. Small values of *p* (<0.05) are shown in bold and are suggestive of a statistically significant difference. See text for further details.

The percent recovery data for the gear pump are also shown graphically by target compound in Figure A-1 for each of the four standpipe trials. The horizontal dark line in the figure shows the 100% recovery level.

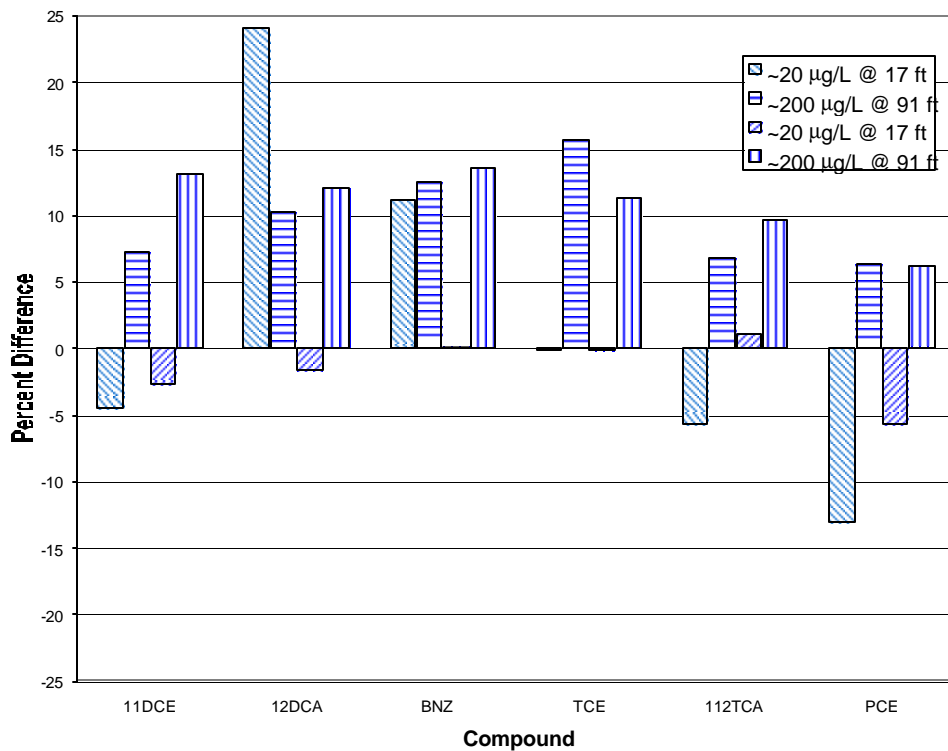


Figure A-1. Percent recoveries of the reference pump by compound for the four standpipe trials.

Reference Pump Performance Summary

The test data for the reference pump reveal considerable variability for PCE and 12DCA. However, the variability and comparability for TCE, the only compound encountered in the field trials, are acceptable. The mean relative standard deviation for TCE was 9.6% and the mean percent difference for TCE was 7%. The data presented for TCE show that the pump is equivalent to the reference sampling method in terms of both precision and accuracy and is acceptable for use as a reference standard.

Appendix B — 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 B-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 prefield demonstration studies indicated that the field replicates were the same in composition so that they could be treated as analysis duplicates.

Table B-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 \leq 30%	Rerun levels that do not meet criteria
Continuing calibration check (CCC)	Beginning of each day	\pm 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	\pm 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 \leq 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 Pilot Project Officer.

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 B-1 and B-2. Similarly, the results of the PCE continuing calibration check for both instruments are shown in Figures B-3 and B-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 postanalysis batch calibration check samples are shown in Figure B-5. In two cases, the relative percent difference falls outside the 25% window. Data from these days were not rejected, however, since the ±30% criteria for the calibration check was met.

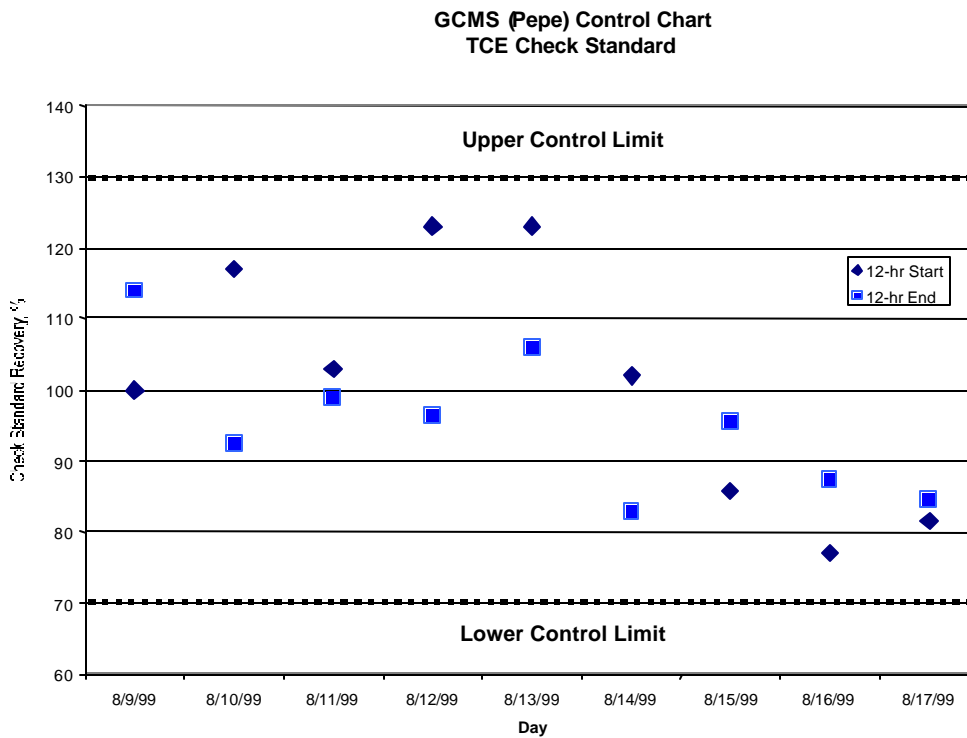


Figure B-1. Calibration check control chart for TCE on GC/MS #1.

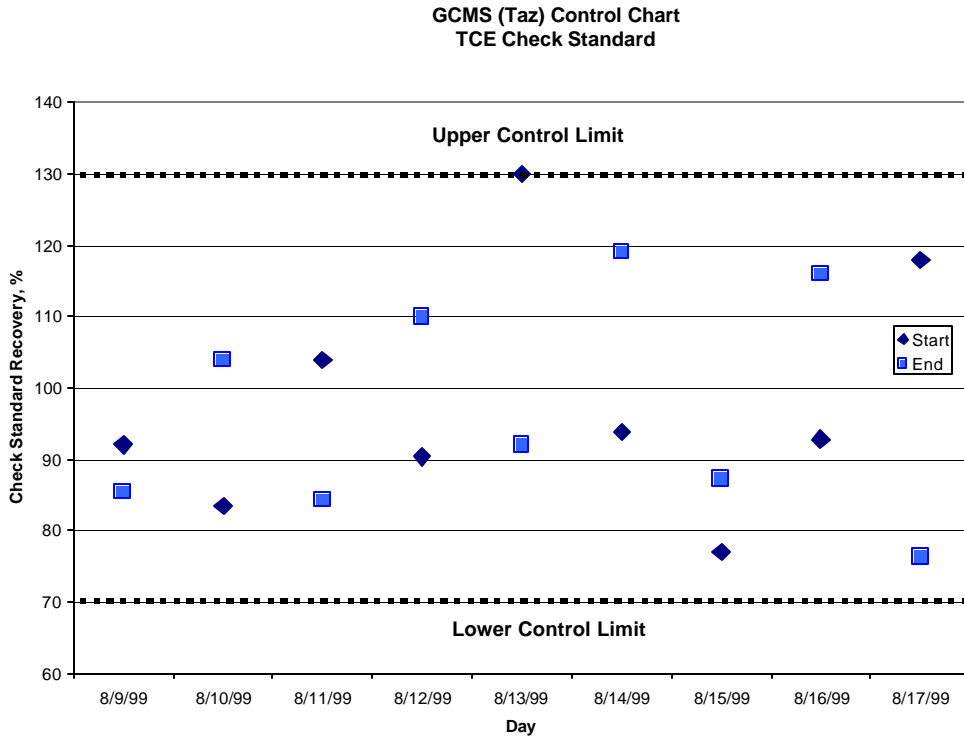


Figure B-2. Calibration check control chart for TCE on GC/MS #2.

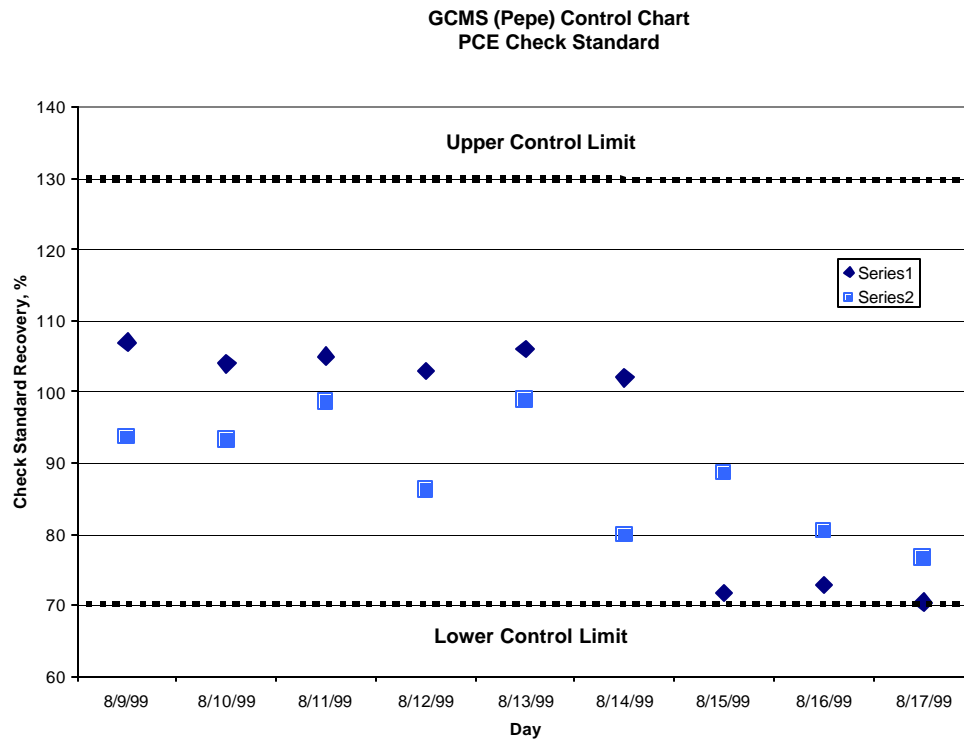


Figure B-3. Calibration check control chart for PCE on GC/MS #1.

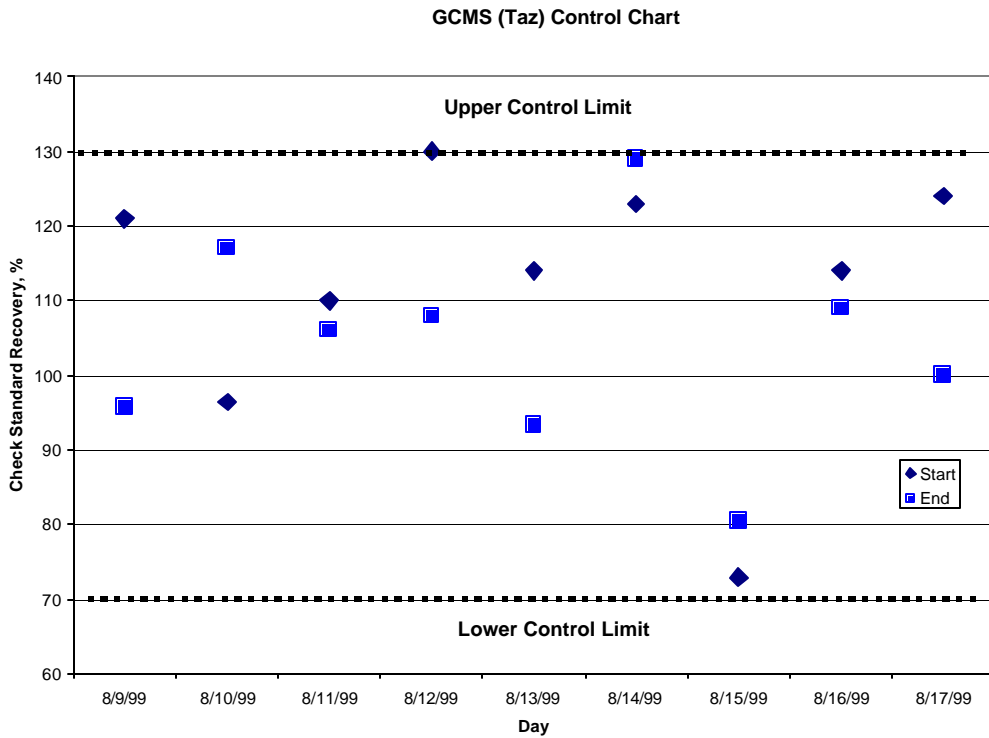


Figure B-4. Calibration check control chart for PCE on GC/MS #2.

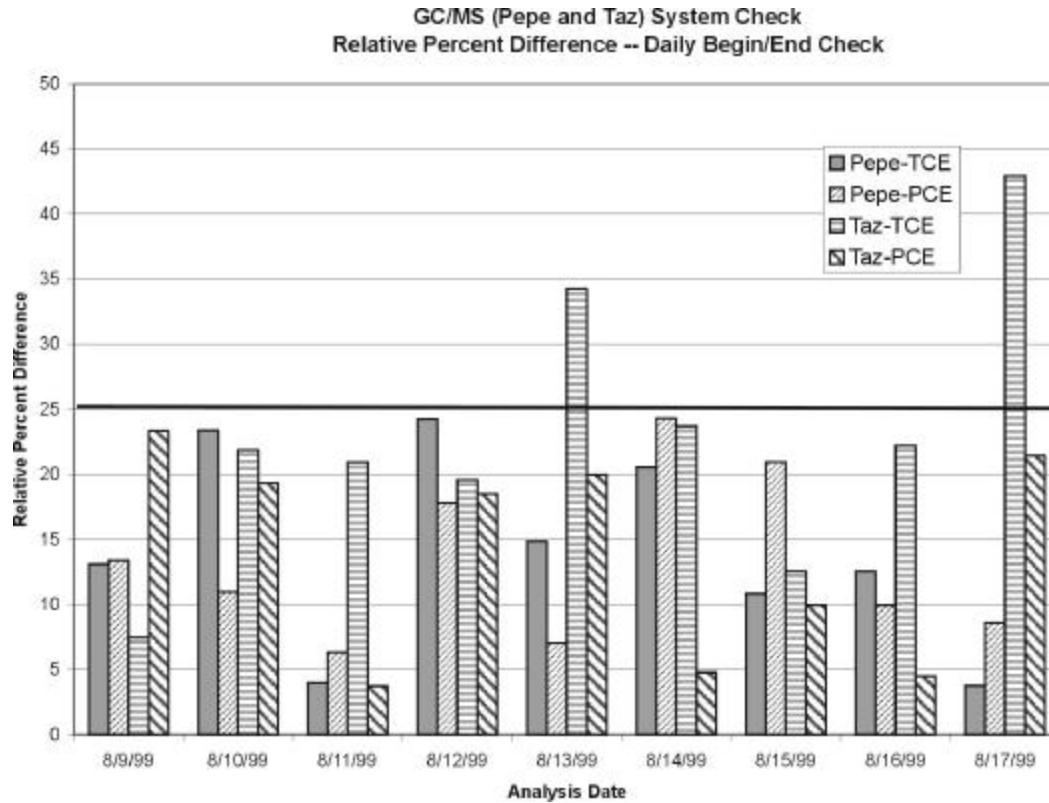


Figure B-5. GC/MS system check relative percent differences.