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

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August 2003

Environmental Technology Verification Report

Ground-water Sampling Technologies

Geoprobe Inc.

Mechanical Bladder Pump, Model MB470

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**Sandia
National
Laboratories**

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**GROUND-WATER SAMPLING TECHNOLOGIES**	
APPLICATION:	**NARROW-BORE WELL WATER SAMPLING**	
TECHNOLOGY NAME:	**Model MB470 Mechanical Bladder Pump**	
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PROGRAM DESCRIPTION

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 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.

Verification of contaminated site characterization and monitoring technologies is carried out within the Advanced Monitoring Systems (AMS) Center, one of seven ETV verification centers. Sandia National Laboratories, a Department of Energy laboratory, is one of the verification testing organizations within this ETV Center. Sandia collaborated with personnel from the US Geological Survey and Tyndall Air Force Base to conduct a verification study of ground-water sampling technologies for deployment in narrow-bore, direct-push wells at contaminated sites with potential ground-water contamination. This verification statement provides a summary of the results from a verification test of the Model MB470 Mechanical Bladder Pump manufactured by Geoprobe Systems Inc.

DEMONSTRATION DESCRIPTION

The performance of two ground-water sampling technologies was evaluated at the US Geological Survey Hydrological Instrumentation Facility at the NASA Stennis Space Center in southwestern Mississippi and at Tyndall Air Force Base near Panama City, Florida. Each technology was independently evaluated to assess its performance in the collection inorganic cations, commonly encountered in ground-water, as well as volatile organic compound- (VOC) contaminated ground-water.

The verification test, conducted over a one-week interval in February 2003, incorporated the use of a 5-inch diameter,100-foot standpipe at the USGS facility. The standpipe, serving as an “above-ground” well, was filled with tap water spiked with various concentration levels of five target inorganic cations (calcium, iron, magnesium, potassium and sodium) and six volatile organic compounds. Target VOC compounds (vinyl chloride, methyl-tertiary butyl ether, cis-1,2-dichloroethene, benzene, trichloroethene and ethyl benzene) were chosen to represent the range of VOC volatility likely to be encountered in normal sampler use. Target cation concentrations were in the range of 5 to 100 mg/L and VOC concentrations were in the range of 50 to 100 μg/L. Water sampling ports along the exterior of the standpipe were used to collect reference samples at the same time that ground-water sampling technologies collected samples from the interior of the pipe. Trials were carried out at two different inorganic cation concentrations, a single VOC concentration, and sampler depths ranging from 17 to 76 feet. An un-spiked, tap-water, blank sampling trial was also included in the test matrix. A total of 48 cation and 24 VOC samples were collected with the sample count equally split between vendor and reference sampling methods.

The standpipe trials were supplemented with additional trials at six,1-inch internal-diameter, direct-push-installed wells at Tyndall Air Force Base. Sampling at narrow-bore, direct-push wells provided an opportunity to observe the operation of the sampling system under typical field-use conditions. A simple reference sampler was deployed alongside the vendor technology such that co-located, simultaneous samples could be collected from each well. Principal contaminants at the Tyndall monitoring wells included trichloroethene and its degradation products as well as hydrocarbon contaminants such as benzene and ethyl benzene. Ground-water VOC concentrations ranged from low μg/L to low mg/L levels. A total of 96 ground-water samples were collected, with the sample count equally split between vendor and reference methods.

All technology and reference samples were analyzed by an offsite laboratory utilizing EPA SW-846 Standard Methods 3010A (Acid Digestion of Aqueous Samples and Extracts For Total Metals by FLAA or ICP Spectrometry) and 6010B (Inductively Coupled Plasma Atomic Emission Spectrometry) for inorganic cation analysis and EPA SW-846 Standard Method 8260B (Volatile Organic Compounds by Gas Chromatography/Mass Spectroscopy) for VOC analysis. The overall performance of the ground-water sampling technologies was assessed by evaluating sampler precision and comparability with reference samples. Other logistical aspects of field deployment and potential applications of the technology were also considered in the evaluation.

Details of the demonstration, including an evaluation of the sampler’s performance, may be found in the report entitled *Environmental Technology Verification Report: Geoprobe Systems Inc., Mechanical Bladder Pump, Model MB470,* EPA Report Number EPA/600/R-03/086.

TECHNOLOGY DESCRIPTION

The Model MB470 is a narrow-diameter (25.5-inch length x 0.47-inch outside diameter) bladder pump suitable for deployment in direct-push-installed ground-water wells. The pump consists of an internal, concentrically corrugated, flexible bladder that is positioned within a rigid stainless steel tube. The bladder’s internal volume can be reduced by applying a vertical force to collapse the bladder along it longest dimension. The bladder is equipped with one-way inlet and outlet check valves and passively fills with water when the pump is at depth in the well as a result of the hydrostatic pressure exerted by the surrounding water column. Following the bladder fill cycle, a length of rigid tubing running from the pump to the surface is pushed downward at the surface in order to collapse the bladder and push water to the surface. The pumping sequence consists of repeated fill-compress cycles, using either a hand-operated crank or an electric motor and actuator positioned on the top of the well head. The narrow-diameter sampling pump with an inert bladder design offers the advantage of minimizing sample turbulence, which can result in loss of VOCs in the sample, as well as eliminating contact of the water with an air vacuum and further potential VOC losses.

Pump accessories include a hand-crank mechanical actuator, an electric-motor actuator (currently under development) and various tubing configurations. The measured flow rate of the pump (equipped with the motor-driven actuator) at a depth of 35 feet below the surface with a 30-foot water column above the pump was approximately 100 mL/min. Higher flow rates were observed with the hand-crank actuator accessory.

Costs for the pump and accessories are as follows: pump, $430; mechanical actuator, $240; electrical actuator (undetermined). Concentric tubing sets are priced as follows: HDPE (outer) /FEP (inner), $100 per 50-foot roll; HDPE/LDPE, $54 per 50-foot roll.

VERIFICATION OF PERFORMANCE

The following performance characteristics of the Model MB470 mechanical bladder pump were observed:

Precision: The precision of the sampler was determined through the collection of a series of replicate samples from a number of standpipe trials that included known concentrations of inorganic cations and VOCs. Sampler depths ranged from 17 to 76 feet. Sampler precision, represented by the percent relative standard deviation, for all target cation compounds at all concentrations and sampling depths evaluated in this study ranged from 0.3 to 5.0 percent with a median value of 0.9 percent. Precision for VOCs at a single concentration and multiple sampler depths ranged from 0.2 to 3.4 percent with a median value of 1.2 percent. Pump precision measured in the Tyndall field trials was similar to that observed in the standpipe trials for the target cations. Tyndall monitoring-well field trials revealed considerably more variability in the replicate samples from the pump and co-located reference sampler for VOCs.

Comparability with a Reference: Mechanical bladder pump results from the standpipe trials were compared with results obtained from co-located external reference port samples that were collected simultaneously. Both bladder pump and external port samples were analyzed at an off-site laboratory using standard EPA methods for inorganic cations and VOCs. Sampler comparability is expressed as percent difference relative to the external port data. Sampler differences for all target cations compounds at all concentrations and sampler depths in this study ranged from -12.6 to 3.6 percent with a median percent difference of 0.0. Sampler differences for all VOC compounds at all sampling depths ranged from -5.0 to -0.3 percent with a median value of -2.5 percent.

Two statistical tests, the F-ratio test and the t-test for two sample means, were used to assess whether the observed differences at the standpipe between the mechanical bladder pump and external port sample precision and mean pump and external port target compound concentrations were statistically significant. The tests show that the observed differences between the bladder pump and port samples with regard to both precision and accuracy can be attributed to random variation. Thus, no statistically significant difference exists between the results from the bladder pump and the external port samples.

The comparability of the pump with the reference sampling method for target cations at Tyndall monitoring wells was similar to that observed during the standpipe trials. Comparability results for VOCs were considerably more variable with percent differences ranging from -29.6 to 34.6 percent with a median value of -8.3 percent for all compounds detected at Tyndall. The controlled aspects of the standpipe tests should be considered in combination with the Tyndall field test results for a comprehensive understanding of pump performance.

Versatility: Sampler versatility is the consistency with which it performed with various target compounds, concentration levels, and sampling depths. The mechanical bladder pump performance did not vary with changes in compounds or concentration levels. Deployment of the pump at depths in excess of 50 feet may result in flow rates that are deemed unacceptable for some sampling applications. In general, the Geoprobe mechanical bladder pump is regarded as a versatile technology and applicable for sampling the types of inorganic and VOC contaminants from narrow-diameter direct push wells.

Logistical Requirements: The sampler can be deployed and operated in the field by one person. Several hours of training are adequate to become proficient in the use of the system. The system requires a source of DC or AC power when used with the electric-motor actuator (currently under development). The bladder pump can be used as a dedicated sampler or as a movable sampler; however, decontamination procedures are required when moving the pump from well to well.

Overall Evaluation: The results of this verification test show that the Geoprobe mechanical bladder pump and associated mechanical actuator accessories can be used to collect inorganic cation- and VOC-contaminated water samples from monitoring wells such that results are statistically comparable to reference samples. The system is specifically designed for use in narrow-bore (0.5-inch minimum internal diameter) wells. Furthermore, the pump is compatible with sampling programs that incorporate low-volume purge methodologies.

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

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Office of Research and Development	Sandia National Laboratories

Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), funded and managed, through Interagency Agreement No. DW89826201 with Sandia National Laboratories, the verification effort described herein. This report has undergone peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use of a specific product.

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Acknowledgments

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Abbreviations and Acronyms

AMS	Advanced Monitoring Systems
BNZ	Benzene
DCE	cis-1,2-Dichloroethene
DIFF	Difference
DO	Dissolved oxygen
EPA	US Environmental Protection Agency
EtBNZ	Ethyl benzene
ETV	Environmental Technology Verification Program
FEP	Fluorinated ethylene propylene
GC/MS	Gas chromatograph-mass spectrometer
HIF	Hydrological Instrumentation Facility
HDPE	High-density polyethylene
LCS	Laboratory calibration standard
MS	Matrix spike
MSD	Matrix spike duplicate
MTBE	Methyl tertiary-butyl ether
MW	Monitoring well
NASA	National Aeronautics and Space Administration
ND	Not detected
NERL	National Exposure Research Laboratory
ORP	Oxidation/reduction potential
PCE	Tetrachloroethene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
QA	Quality assurance
QC	Quality control
REF	Reference
RSD	Relative standard deviation
SCMT	Site Characterization and Monitoring Technologies Pilot
SNL	Sandia National Laboratories
SP	Sample port
SSC	Stennis Space Center
TCE	Trichloroethene
USGS	US Geological Survey
VC	Vinyl chloride
VOA	Volatile organics analysis
VOC	Volatile organic compound

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 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," nor approve or disapprove technologies. The program does not evaluate technologies at the bench or pilot scale and does not conduct or support research.

The ETV Program presently consists of seven ETV Verification Testing Centers covering a broad range of environmental application areas. In each of these centers, the EPA utilizes the expertise of partner "verification organizations" to design efficient processes for conducting performance tests of innovative technologies. Verification organizations oversee and report on technology verification testing activities based on testing and QA protocols developed with input from major stakeholder/customer groups associated with the technology area. The verification test described in this report was administered by the Site Characterization and Monitoring Technologies (SCMT) Pilot within the Advanced Monitoring Systems Center and under guidance from EPA's National Exposure Research Laboratory (NERL). More information about the ETV program is available at the ETV web site: http://www.epa.gov/etv.

This particular verification test was administered by Sandia National Laboratories, one of two verification organizations associated with the SCMT Pilot program. Sandia conducted an initial verification study of six different ground-water sampling technologies during the summer of 1999. Verification statements and reports from this initial verification test can be found at the ETV web site. A follow-on study that concentrated on ground-water sampling technologies specifically designed for deployment in narrow-diameter, direct-push-installed wells was subsequently planned and carried out in February of 2003. In this test two ground-water sampling technologies, a mechanically operated bladder pump and a pneumatically driven bladder pump, from Geoprobe Systems, Inc. were evaluated.

Verification Test Overview

This verification test was designed to investigate ground-water sampling devices that are specifically designedfor use in narrow-diameter (less than 2-inch diameter), direct-push-installed wells. Direct-push wells are finding increased acceptance in the environmental monitoring community by virtue of the fact that well installation costs are typically much less that traditional larger diameter wells. This report outlines the testing protocol and the performance results for the Geoprobe Model MB470 Mechanical Bladder Pump.

This verification test was designed to evaluate critical aspects of pump performance such as precision and accuracy and, while the test did employ the use of low-flow sampling protocols, it was not intended to be an evaluation of the merits of a low-flow purge sampling protocol. This protocol and its merits have been proposed, published, and tested elsewhere [Puls et al, 1996].

The demonstration was conducted in February of 2003 and occurred in two phases. The first phase was carried out at a United States Geological Survey (USGS) facility on the grounds of the National Aeronautics and Space Administration (NASA) Stennis Space Center in southwestern Mississippi and a second phase was conducted at Tyndall Air Force Base near Panama City, Florida. A 100-foot, 5-inch diameter standpipe that is part of the USGS Hydrological Instrumentation Facility (HIF) at the NASA site was used for technology testing under relatively well-controlled conditions. The standpipe served as an "above-ground" well and was filled with water spiked with various concentration levels of target cations and volatile organic compounds (VOC). Water sampling ports along the exterior of the pipe permitted the collection of reference samples at the same time and depth that vendor sampling pumps were used to collect samples from the interior of the pipe.

The standpipe trials were supplemented with additional sampling trials at six direct-push installed ground-water monitoring wells at Tyndall Air Force Base. The contaminant mix at the Tyndall site included both chlorinated and non-chlorinated hydrocarbons. In all sampling cases, both at the standpipe and the direct push wells, each vendor-collected sample was matched to a co-located and simultaneously collected reference sample.

All vendor pump and reference samples were analyzed by an off-site laboratory using EPA SW-846 Method 6010 for cations and Method 8260b for VOCs. Ground-water sampling technology performance was assessed by evaluating sampler precision as well as comparability with matched reference samples. Other aspects of field deployment, such as logistical requirements, and potential applications of the technology, are also considered in this evaluation.

A brief outline of this report is as follows: Section 2 contains a brief description of the Geoprobe Model MB470 Mechanical Bladder Pump and its capabilities. Section 3 outlines a short description of the test facilities and a summary of the verification test design. Section 4 is a technical review of the data with an emphasis on assessing overall sampler performance. Section 5 presents an update of the Geoprobe technology and provides examples of representative applications of the device in environmental characterization and monitoring settings. Appendix A includes performance data for the reference sampler and Appendix B includes an assessment of quality control data associated with the analytical methods used in this study.

Section 2 — Technology Description: Geoprobe Model MB470 Mechanical Bladder Pump.

This section provides a description of the technology evaluated in this verification test. The technology description was provided by the technology vendor with some editing by the verification organization.

Background

Geoprobe Systems began development and design of direct-push probing machines and the affiliated tooling in the late 1980s. The initial application for the direct push machines and tools was for collection of soil gas samples. Because of the effectiveness and efficiency of the direct push method, it was soon applied to soil sampling and ground-water sampling for environmental investigations. More recently, Geoprobe Systems has developed the equipment and methods to install small diameter monitoring wells for use in environmental water quality investigations. Because of the small diameter of the direct-push installed temporary ground-water sampling tools and monitoring wells, smaller diameter sampling pumps are needed. Additionally, research has shown that low-flow sampling rates are usually required to obtain representative water quality samples [EPA, 1996a]. This is especially true for volatile organic compounds that are sensitive to pressure and temperature changes and inorganic analytes, such as iron and chromium, that may be affected by elevated levels of turbidity in the sampled ground-water.

Non-dedicated or temporary, small-diameter ground-water sampling tools that are installed by direct-push methods are often used for site assessments and investigations in many geo-environmental projects [Thorton et al, 1997]. In these instances, the temporary sampling devices are installed, samples are collected, and the sampling devices are removed for decontamination and re-use. Such temporary installations provide an efficient and cost effective method for site characterization. Additionally, permanent small-diameter wells installed by direct push methods are substantially growing in use and gaining wider regulatory acceptance for water quality monitoring applications [McCall, 2002]. Traditionally, these small-diameter tools and wells were sampled with peristaltic pumps, inertial pumps (or check valves), and mini-bailers. Each of these sampling methods has significant limitations and often may not provide representative samples [EPA, 1996a] Because of the need for a cost-effective, small-diameter ground-water sampling device that can provide high quality, representative samples from these direct-push tools and wells, Geoprobe Systems has developed a simple mechanically operated bladder pump. Bladder pumps have been found acceptable for sampling of all environmental parameters [ASTM, 2001].

Geoprobe Systems Model MB470 Mechanical Bladder Pump

Device Design—The Geoprobe Model MB470 is a mechanical bladder pump that uses a concentrically corrugated bladder that is open on both ends, as shown schematically in Figure 1. This bladder is alternately compressed and expanded by actuation of the inner concentric tube to pump fluid to the surface. The bladder is fabricated of FEP Teflon® with cuffs on each end that allow for attachment to an upper and lower bladder adapter. The bladder adapters are barbed so the bladder cuffs stay mechanically attached. Stainless steel check valves are also located within the upper and lower bladder adapters. The lower bladder adapter is attached to the pump body so that it is anchored and cannot move during the pump cycle. The upper bladder adapter slides freely inside the pump body and attaches the bladder to the inner tubing adapter and inner tubing so it may be mechanically actuated from the surface. A compression spring is installed above the upper bladder adapter and is held in position with a spring retainer located near the top of the pump body. This spring assists in compressing the bladder and with return of the inner tubing during the downward (or supply) stroke of the pump. Two lines of concentric tubing are positioned between the pump and the top of the well. The outer tubing attaches directly to the upper end of the pump body. This tube may be fabricated of high density polyethylene (HDPE), polypropylene, Kynar® (PVDF), FEP Teflon® or other suitable materials as required by the data quality objectives of the sampling

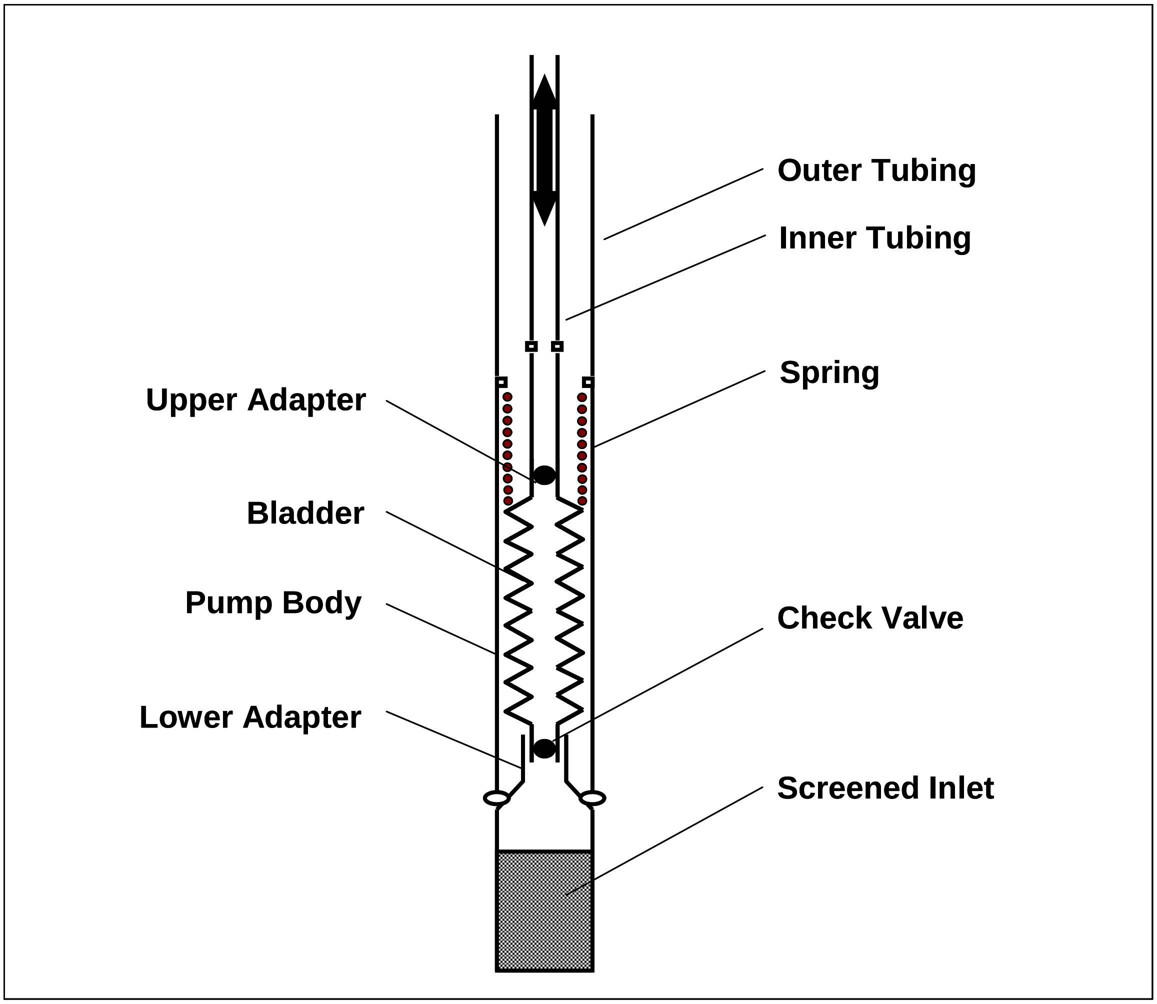

Figure 1. Schematic cross-sectional diagram of the Geoprobe Model MB470 Mechanical Bladder Pump. (Drawing is not to scale.)

program. The inner tube also may be fabricated of HDPE, polypropylene, PVDF, FEP Teflon® or other suitable materials. In the ETV field tests, the outer tubing material was HDPE and the inner tubing material was FEP Teflon. The outer tube is clamped in place at the surface as the inner tube is alternately lowered and raised to operate the pump.

The chemically inert character of FEP Teflon for many environmental contaminants is well documented and known; however, at least two studies [Parker and Ranney, 1997], [Parker and Ranney, 1998] found that Kynar® tubing may be less sorptive than FEP for several of the halogenated compounds, particularly chlorinated volatiles. As Kynar® tubing is more rigid than FEP it may prove to be a better material to use as the inner tube component of the mechanical pump both in terms of longitudinal stiffness and chemical inertness. If the mechanical bladder pump is to be used as a portable sampling device during site characterization with temporary ground-water sampling tools it may be preferable to use less expensive materials for the corrugated bladder and concentric tubing. The bladder and inner tube could be made of polypropylene, which is much less expensive than FEP or Kynar®. Polypropylene is almost as chemically inert as FEP, making it an attractive substitute when the tube and bladder will be used once and discarded for portable applications.

The pump body, check balls and all other metal components of the mechanical bladder pump are fabricated from 304 stainless steel. This material is resistant to corrosion under most ground-water geochemical conditions [EPA, 1991], [Driscoll, 1986] and is recommended for use in the construction and fabrication of well screens and ground-water sampling tools [Parker and Ranney, 1997], [Parker and Ranney, 1998] especially when organic contaminants are the primary analytes of interest.

Field Operation—Operation of the pump can occur by several means. The pump can be operated manually by using one hand to hold the outer tube in position and the other hand to oscillate the inner tube up and down repeatedly. A hand crank mounted on the wellhead can be used to make the physical work easier and help maintain a more consistent flow rate for sampling activities. Additionally, an electric motor may be used to do the work of oscillating the inner-tube up and down, minimizing the physical work required and providing a consistent and adjustable flow rate for purging and sampling activities.

Prior to deployment, the pump is appropriately decontaminated and then assembled according to the manufacturer's instructions. Next the concentric inner and outer tubes are attached to the inner tubing adapter and top of the pump body respectively. Accurate measurement is made and the tubing set is cut at the desired length so the pump intake will be positioned at the desired depth in the well. Following insertion into the well, the outer tube is clamped in position as the inner tube is oscillated up and down to operate the pump and purge water from the well. The outlet of the inner tube may be attached to an in-line flow cell to monitor water quality parameters such as pH, temperature, specific conductance, dissolved oxygen content and oxidation-reduction potential. The discharge flow from the inner tube may also be directed into properly preserved sample containers for sample collection.

Advantages and Limitations

A brief summary of the advantages and limitations of the mechanical bladder pump is provided below. The features of the mechanical bladder pump are discussed relative to other pump designs commonly used for environmental water quality sampling activities.

Advantages

- The pump is small, light weight, and very portable.
- Pump can be operated manually or with manual hand crank with no electrical power requirements.
- Pump can also be driven with an electric motor powered from a vehicle battery, generator or line source.
- An air compressor, pump or supply of compressed gas from cylinders are not required to operate the pump.
- Flow rate can be adjusted to provide the desired flow to meet low flow sampling criteria. For the ½-inch pump, flows can be varied from less than 100 mL/min to over 500 mL/min.
- Low-flow sampling minimizes the amount of pre-sample purge water generated, reducing waste handling and disposal costs.
- Since an air compressor is not used, no problems are encountered with moisture condensation affecting pump operation and air leak testing is not required.
- With a limited number of moving parts and no electrical motor or electrical components in the pump, generation of down-well heat and potential sampling influences are essentially eliminated.
- Cost of the pump is 25 to 50 percent lower than conventional gas-driven bladder pumps.
- The pump can be operated either as a long term dedicated pump or a portable pump.
- Simple construction makes assembly, decontamination and operation easy.
- Bladders can be quickly and easily replaced in the field, thereby simplifying decontamination operations in non-dedicated use.
- For non-dedicated use situations, low-cost polypropylene or HDPE bladders and tubing may be substituted for the more expensive FEP Teflon® components.
- Pump maintenance requirements are minimal and may be easily conducted in the field.
- FEP Teflon® bladders and tubing, and stainless steel construction make this pump acceptable for essentially all environmental water quality sampling requirements.
- The mechanical bladder pump provides an inexpensive and efficient method for obtaining high quality samples from direct-push-installed temporary ground-water sampling tools during initial site characterization activities.

Limitations

- When operated in manual mode, maintaining consistent flow rates is difficult to document. Human error can become a factor in flow rates and as such could impact sample quality.
- The pump is not designed to provide high flow rates (e.g. several gallons per minute) but usually is operated at flows of a few hundred milliliters per minute or less.
- In deeper wells (50 feet or more in depth) friction between the relatively long lengths of inner and outer tubing can hinder efficient operation of the pump.
- When FEP tubing is used as the inner tube in deeper wells (50 feet or deeper) elongation of the tubing during the pump cycle can decrease efficiency of the pump. This limitation can be minimized by using a more rigid material for the inner tube (e.g. Kynar /PVDF).

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 — Verification Test Process and Design

Introduction

The principal objective of this verification test was to conduct an independent evaluation of the capabilities of two Geoprobe ground-water sampling technologies designed for deployment in narrow-diameter, direct-push-installed wells. A number of key performance parameters were chosen to evaluate overall sampler performance. In order to insure 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 and Battelle Memorial Institute with concurrence from the technology vendor participating in the study. Technical review of the study design was also provided by EPA personnel with professional expertise in the area of ground-water sampling. A complete verification test plan has previously been published [Sandia, 2003].

Site Descriptions

Verification testing was conducted at the United States Geological Survey (USGS) Hydrological Instrumentation Facility in Southwestern Mississippi and at Tyndall Air Force Base near Panama City, Florida. The following paragraphs briefly describe these two testing sites.

Standpipe Facility – The USGS is one of the resident agencies at the NASA-Stennis complex in southwestern Mississippi and maintains and operates a number of testing facilities as a part of its Hydrologic Instrumentation Facility (HIF). This facility supports USGS agency-wide hydrologic data-collection activities through the identification of agency needs, development of technical specifications, and instrument testing and evaluation. The USGS Standpipe was used during the first phase of this two-phase study. The standpipe was designed by Doreen Tai, a USGS chemical engineer, and is housed in a former Saturn V rocket hangar at the Stennis complex. A schematic diagram of the standpipe and related accessories is shown in Figure 2. The standpipe is an above-ground, 100-foot long, 5-inch diameter, stainless steel pipe with numerous external sampling ports along its length. Two large mixing tanks with tap-water feeds are positioned at the top of the standpipe and are used to prepare spiked solutions which can then be drained into the standpipe. The tanks are equipped with motor-driven mixing propellers and floating lids to minimize loss of volatile compounds during solution mixing and transfer. An external standpipe fill line at the bottom of the pipe enables the pipe to be filled from the bottom up, thereby minimizing flow turbulence and VOC losses in the prepared solutions. External access ports equipped with needle valves allow reference samples to be taken from the standpipe simultaneously with the collection of technology samples inside the pipe. As shown in Figure 2, the indoor facility has six levels of access, including the ground floor, and a freight elevator services all levels. In this verification test, the standpipe was used in a series of controlled, water-sampling trials. The technology vendor deployed pumps in the standpipe and sampled water spiked with inorganic cations and volatile organic compounds while reference samples were simultaneously collected at the external ports.

Direct-Push Ground-water Monitoring Wells- The second phase of this technology demonstration involved the collection of ground-water samples with the vendor pumps from a set of direct-push wells at Tyndall Air Force Base near Panama City, Florida. The Tyndall facility has a number of co-located, direct-push and conventional wells and was part of a nationwide study, sponsored by the Department of Defense Environmental Technologies Certification Program to examine the comparability of direct-push and conventional drilled wells. Numerous conventional and direct-push wells have been installed into relatively shallow contaminated ground-water zones at Tyndall. Contaminants include those arising from hydrocarbon fuel leakage from various aviation fuel storage tanks as well as various chlorinated solvents and their degradation byproducts associated with aircraft maintenance activities at the base.

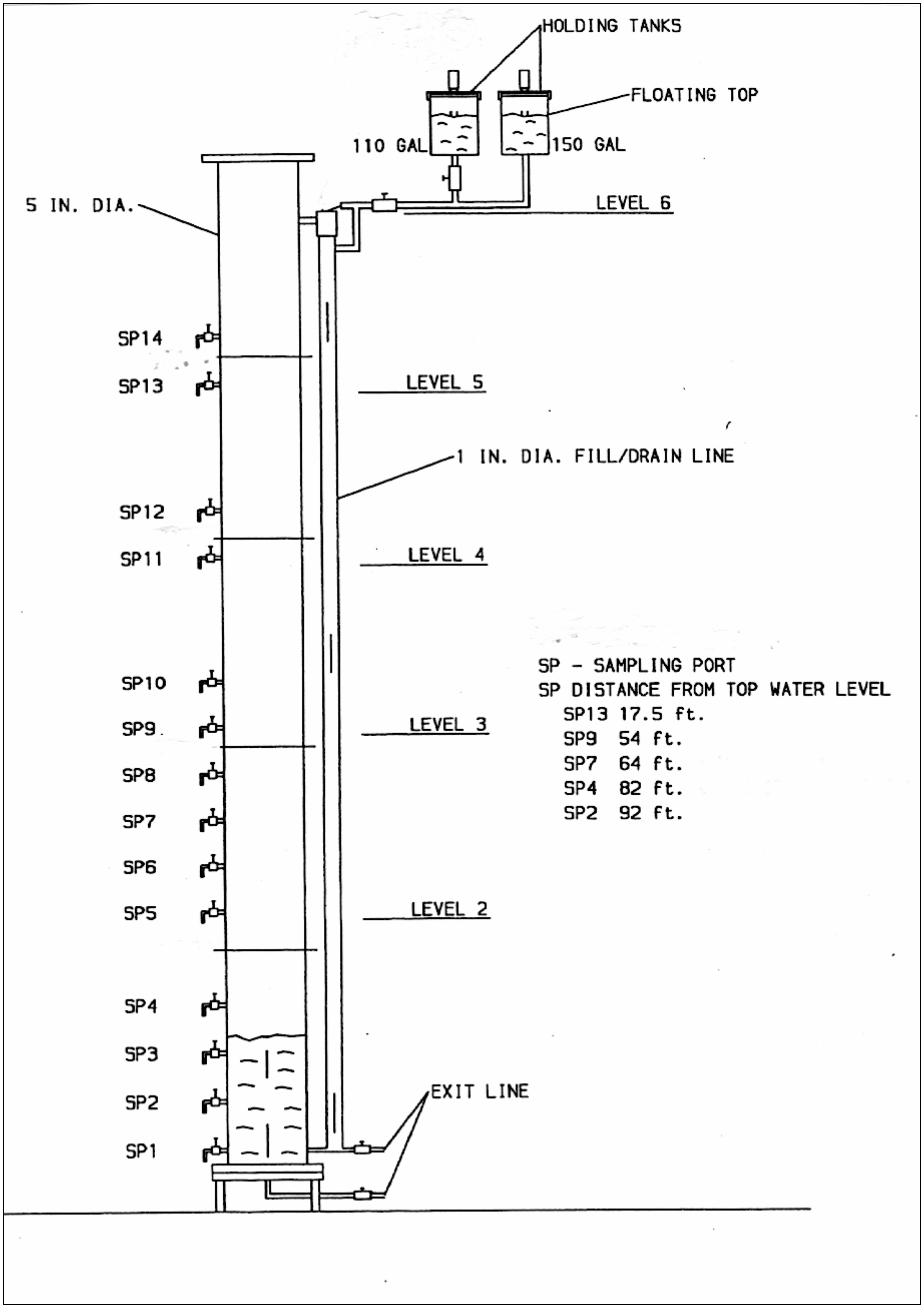

Figure 2. The Standpipe at the USGS Hydrological Instrumentation Facility.

Verification Test Design Summary

The verification test design consisted of two basic elements. The first was a test matrix, consisting of several standpipe trials conducted under relatively well-controlled sampling conditions. These trials enabled sampler performance parameters such as precision and comparability to reference samples to be evaluated. The second element incorporated 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. In an effort to represent pump performance in applications likely to be encountered in typical field use, the suite of contaminants investigated in this study included both non-volatile, inorganic cations as well as a series of volatile organic compounds that covered a range of volatility.

Test Design

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. In both phases of testing, simultaneous, co-located reference samples were collected to enable direct comparison of vendor and reference sample results.

Target Inorganic Compounds - Five inorganic cations were selected for use in the study to assess pump performance for non-volatile species. The cations selected were calcium, iron, magnesium, potassium and sodium. These cations are ubiquitous in most ground-water samples and thereby provide pump performance assessment under conditions of typical use.

Target VOC Compounds - Six target volatile organic compounds with varying degrees of volatility were selected for use in this study. The compounds were benzene (BNZ), ethyl benzene (EtBNZ) methyl-tertiary-butyl ether (MTBE), trichlorethene (TCE), cis-1,2-dichloroethene (DCE), and vinyl chloride (VC). With the exception of MTBE, all of these compounds have regulatory limits dictated by the Safe Drinking Water Act that range from 0.002 mg/L for vinyl chloride to 0.7 mg/L for ethyl benzene. While MTBE is presently not regulated, concern lies in the fact that it is found in ground-water that has been contaminated from leaking hydrocarbon fuel storage tanks containing MTBE as a fuel additive. The six compounds selected also span a range of volatility and solubility; parameters that are likely to influence sampler performance. Target compound volatility and other relevant physical data are given in Table 1.

Table 1. Target VOC Compounds

Compound	Volatility (Henry's Constant, Atm/Moles x Liter^{-1})	Boiling Pt. (ºC)
Methyl tertiary-butyl ether	0.6	55
Benzene	5.6	80.1
cis-1,2-Dicholoroethene	7.8	60.3
Ethyl Benzene	8.3	136
Trichloroethene	9.1	86.7
Vinyl Chloride	22	13.9

Test Concentrations - The use of the standpipe facility enabled the preparation of water mixtures containing the target inorganic cations at two concentration levels and VOCs at one concentration level. Spiked solutions of both inorganic and VOC compounds were prepared by diluting special-order stock solutions. The inorganic certified stock solution was prepared by Accustandard (New Haven, CT) at a concentration level of 5000 μg/mL for each component in 10 percent nitric acid. The custom VOC certified stock solution was also prepared by Accustandard in methanol at a nominal concentration level of 2000 μg/mL for each mixture component. The

VOC solutions were stored in sealed 20-mL glass ampoules that were refrigerated until use. An appropriate volume of either the inorganic or VOC stock mixture was injected into the mixing tank which was pre-filled with tap water. The solution was then gently mixed for 5 minutes prior to draining into the standpipe. Preliminary studies have shown the loss of some of the VOC compounds during mixing and standpipe filling. Consequently spike concentrations were not used as a reference values in this study. Alternatively, the study design included the collection of simultaneous and co-located reference samples from standpipe external sampling ports for a direct comparison with vendor-collected samples.

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

Deep Water Sampling - In all but one test, the standpipe was completely filled and sampling was performed at water depths of 17 and 35 feet. In one test, the pipe was filled to the half-way point (approximately 50 feet below the standpipe top) and samples were drawn from a depth of 76 feet relative to the top of the standpipe in order to evaluate the lift capacity of the pump under water column head conditions near the upper limit of the useful range of the pump.

Standpipe Port Samples - The standpipe included external sampling ports along its length such that reference samples could be collected simultaneously, and at the same depth, with the collection of vendor technology samples from the interior of the standpipe. Each sampling trial consisted of the simultaneous collection of paired technology and port samples. The reference samples were collected directly into analysis vials with no intervening pumps, filters or other devices that could potentially affect the sample. The use of multiple sequentially collected samples at each sampling location allowed the determination of sampler and reference sample precision. The resulting precision data reflects the overall uncertainty in the measurement and includes variability of the technology and the reference sample in combination with the common analytical method. The reference sample precision is used as a baseline against which the vendor technology precision can be directly compared for each of the sampling trials.

Ground-water Well Reference Samples - Use of six onsite monitoring wells in the second phase of the study posed a technical challenge for the collection of reference data with which to compare the technology data. A simple tube sampler with a check valve positioned at the tube inlet was chosen as the reference method. The configuration of this sampler enabled the collection of simultaneous co-located samples from the direct push wells chosen for study in this investigation. Verification studies on the performance of this tube sampler 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 tube sampler and how it was deployed is given in Appendix A. Performance data on the sampler obtained during the standpipe trials are also included in this Appendix.

Low-Flow Sampling Protocol - In all field-sampling trials, a low-flow sampling protocol [Puls and Barcelona, 1996] was used during sampling events and water quality parameters were continuously monitored until stability was achieved in the field sampling trials. In three of the six wells selected for study, the water quality parameters were simultaneously monitored on both the reference and the vendor sampling systems to insure that comparable results were obtained with both sampling methods. For the other three wells, water quality parameters were only measured on the reference sampling line. In all cases, sample collection procedures were not initiated until stability of the critical water parameters was achieved.

Sampler Performance Parameters

Four performance parameters were evaluated in the assessment of this 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 ground-water monitoring wells in the study design. The *relative standard deviation* was used as the parameter to estimate precision. The percent relative standard deviation is defined as the sample standard deviation divided by the sample mean times 100, as shown below:

$$\%RSD = \frac{\sqrt{\frac{\sum\left(x_i - \bar{x}\right)^2}{n-1}}}{\bar{x}} \bullet 100$$

Here, X_i is one observation in a set of n replicate samples where $\bar{x}$ is the average of all observations, and n is the number of observations in the replicate set. In our assessment of sampler precision, we used a statistical test to assess whether observed differences between the reference sample precision and the technology sample precision are statistically significant. Specifically, the F-ratio test compares the variance (square of the standard deviation) of the two groups to provide a quantitative assessment as to whether the observed differences between the two variances are the result of random variability or the result of a significant influential factor in either the reference or technology sample groups [Havlicek, 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 parameter, p*ercent difference,* was used to represent sampler comparability for each of the target compounds in the sampling trials at the standpipe. Percent difference is defined as follows:

$$\%Diff = \frac{\left(\bar{x}_{tech} - \bar{x}_{ref}\right)}{\bar{x}_{ref}} \bullet 100$$

where $\bar{x}_{tech}$ is the average reported concentration of all technology sample replicates and $\bar{x}_{ref}$ is the average reported concentration of all reference or port sample replicates. The statistical t-test for two sample means was used to assess observed differences between the reference and technology means for each sampling trial [Havlicek, 1988b]. The t-test gives the confidence level associated with the assumption that the observed differences between technology and reference mean values are the result of random effects among a single population and that no significant bias between the technology and reference is observed. Following the convention in statistical analysis, a value of *p* that is 0.05 or less is taken to indicate that a statistically significant difference does exist.

Sampler 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 ground-water 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 sampling depths.

Field Deployment Logistics - This final category refers to the relative ease of deployment of the sampler in its intended scope of application. This is also a less objective category and incorporates field observations such as personnel numbers and training required for use, ancillary equipment requirements, portability, and others.

Sample Analysis

Two types of sample analysis were carried out during these trials. At the standpipe, selected samples were collected from the pipe during the various trials and hand-carried to an onsite laboratory for quick-turnaround analyses. Analysis results were used to confirm the expected contaminant concentrations in the standpipe following the addition of spiking inorganic cations and VOCs to the mixing tank. The analyses were performed at the NASA Environmental Services Laboratory, operated by Lockheed/G. B. Tech. Cations were analyzed by EPA Method 6010 (inductively coupled plasma atomic emission spectroscopy) and VOCs were analyzed by EPA Method 8260b (purge-and-trap, capillary gas chromatography/mass spectrometry) [EPA, 1996b].

In addition to the analysis of confirmatory samples at an onsite laboratory, all vendor and reference test samples from both the USGS Standpipe and Tyndall were shipped to DataChem Laboratories (Cincinnati, OH) for analysis. Cation and VOC analysis were conducted at the DataChem using the same methods noted previously for the onsite NASA laboratory. A complete sample quality control package was generated by DataChem during the analysis sequence and submitted along with the results. These data quality control procedures are discussed in more detail in Appendix B.

Data Quality Control

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

Sample Management - All sampling activities were thoroughly documented by verification organization field technicians using chain-of-custody forms.

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

Pre-verification Test Analytical System Audit - Prior to the actual demonstration, a visit was made in August 2002 to both the USGS Standpipe and the Tyndall site for site survey and limited sample collection. A number of replicate samples were collected from a limited number of Tyndall wells and these samples were analyzed by DataChem for cation and VOC content. Results from this preliminary investigation revealed acceptable performance of the overall laboratory analysis scheme. Replicate sample results revealed adequate sample precision and ground-water sample contaminant concentrations were comparable to those available from historical data provided to the Verification Organization by Tyndall personnel.

Field Spikes - For an additional check on laboratory performance, a number of field spike samples of target cations and VOCs were prepared during the verification test. A more complete description of the field spikes and the laboratory results is given in Appendix B.

Tube Sampler Decontamination Rinsate Samples - In certain instances during the Tyndall tests, the tubing sampler was deployed in more than one well and decontamination procedures were carried prior to deployment of the sampler in the second well. A sample of rinse water that was cycled through the tube sampler after decontamination was collected and analyzed to insure the adequacy of the decontamination. Results of rinsate sample analyses are also given in Appendix B.

Analytical Methods - Quality control measures associated with DataChem implementation of EPA Method 6010a and EPA Method 8260b included the analysis of a preparation blank, a laboratory calibration standard, a matrix spike, and a matrix spike duplicate in each batch of 20 samples. Other QC measures included: 1) the fulfillment of 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 Method 6010a and 8260b quality control data for the various batches of samples analyzed is provided in Appendix B.

Verification Test Plan

The preceding information, as well as that which follows, is summarized from the Ground-water Sampling Technologies Verification Test Plan [Sandia, 2003], which was prepared by SNL and Battelle personnel with concurrence of all vendor participants prior to the field demonstration. The test plan includes a more lengthy description of the site, the roles and responsibilities of the test participants, as well as a discussion of the experimental design and data analysis procedures.

Standpipe and Direct-Push Well Sampling Details

The sampling matrix for the USGS Standpipe phase of the verification test is given in Table 2. The standpipe tests included a pre-test and eight trials that were conducted over the course of two days. The pre-test trial involved flushing and filling the pipe with tap water, followed by sample collection at selected standpipe ports. These samples were run at the onsite laboratory and results were used to confirm the cleanliness of the pipe. Trial 1 was a blank trial in which the standpipe was filled with tap water. Vendor and external port samples for both cations and VOCs were collected at a single depth of 35 feet. The standpipe then filled with a cation-spiked solution such that the final cation concentrations were in the range of 5000 to 10,000 μg/mL for Trials 2 and 3. Trial 2 was conducted with the vendor pump at a water depth of 17 feet and Trial 3 was done at a depth of 35 feet. The pipe was then drained and refilled with a spike level to raise the cation concentrations to the range of 12,000 to 15,000 μg/mL. Vendor and reference samples were again drawn from 17 feet water depth (Trial 4) and 35 feet (Trial 5).

Following draining and flushing of the standpipe, the pipe was refilled with VOC-spiked tap water such that the depth-to-water from the top of the pipe was approximately 50 feet, as measured by a calibrated pressure transducer at the bottom of the pipe. The approximate VOC concentration in the pipe mixture was 100 μg/mL. Trial 6 involved collection of samples from a position in the pipe that was 76 feet from the top of the pipe. In this trial, the height of the water column above the pump intake was about 26 feet and the total height the pump raised water was 76 feet. This trial was included to assess performance of the pump at water depths approaching the upper limit of the pump's useful deployment range in terms of water column lift potential. Following Trial 6, the standpipe was again drained and flushed and refilled to the top with spiked tap water. The target VOC concentration was again spiked at a nominal 100 μg/mL. Vendor pump and external port samples were collected at 17 feet (Trial 7) and 35 feet (Trial 8).

Sampling during each trial was conducted as follows: The vendor pump was deployed in the standpipe at the appropriate height and a 2-liter purge was carried out at flow rates typically in the range of 100 to 200 mL/min. Following the purge, four replicate 250-mL samples for cation analysis were collected in series from the vendor pump while external port samples were collected simultaneously (Trials 2-5). In the case of volatile organics sampling (Trials 6-8), four replicate zero-headspace samples were collected with the vendor pump in 40-mL VOA vials while external port samples were simultaneously collected in similar vials. All cation and VOC samples were collected into containers that were previously spiked with acid preservative. All samples were stored in ice-filled coolers in the field; then transferred to and stored in laboratory refrigerators until overnight air shipment to DataChem in ice-filled coolers.

In selected trials, the tube sampler was also deployed in the standpipe and paired tube sampler and external port samples were collected in the same manner as noted above. See Appendix A for a complete description of the tube sampler performance verification.

The Tyndall Air Force Base ground-water sampling matrix is shown in Table 3. Six wells were chosen based on an interest in deploying the vendor pump over a range of water depths and in ground-water containing a variety of VOC contaminants. All wells sampled were direct-push-installed 1-inch internal diameter wells constructed of PVC with stainless steel screen sections. Vendor and reference samplers were deployed by cable-tying the two pump strings together such that the inlets of the two samplers were in close proximity to each other before insertion into the well. This cable-tied sampler string was then lowered into the well such that the sampler inlets were positioned at the mid-point of the well screen.

Table 2. Standpipe Test Matrix

Trial	Analyte	Approx. Target Analyte Conc. (μg/L)	Standpipe Port Number	Depth (feet)	Vendor Samples	External Port Samples
Pre-test[a]	VOC/Inorganic	-	5, 12, 14	17, 35, 76	-	6
1[b]	VOC/Inorganic	-	12	35	4	4
2	Inorganic	5-10,000	14	17	4	4
3	Inorganic	5-10,000	12	35	4	4
4	Inorganic	12-15,000	14	17	4	4
5	Inorganic	12-15,000	12	35	4	4
6[c]	VOC	100	5	76	4	4
7	VOC	100	14	17	4	4
8	VOC	100	12	35	4	4
Total					32	38

Table 3. Tyndall Test Matrix

Well	Depth to center of screened interval (feet)	Number of Samples			
		Reference Sampler		Vendor Sampler	
		VOC	Inorganic	VOC	Inorganic
MW-2-P10	31	4	4	4	4
MW-5-P10	8	4	4	4	4
MW-8-P10	8	4	4	4	4
MW-9-P10	10	4	4	4	4
MWD-11-P10	17	4	4	4	4
T6-5-P10	13	4	4	4	4
Total		24	24	24	24

Sampling at Tyndall was conducted as follows: After deployment of the cable-tied reference and vendor samplers into the well, a low-flow purge was conducted while water quality parameters were monitored with flow-through cell water quality monitoring system (YSI, Model 6820). The in-line monitoring systems were performance-checked and/or calibrated immediately prior to use at each well. Water quality parameters (temperature, pH, conductivity, oxidative-reductive potential (ORP), dissolved oxygen and turbidity) were monitored until stability conditions were met. Typically, stability conditions were met after sampling of approximately one liter of water (5-10 minutes). Stability criteria used in this investigation are shown in Table 4. A complete description of the flow-through monitoring procedures and calibration methods is given in the Verification Test Plan.

Table 4. Water Quality Stability Criteria for Low-Flow Purging

Ground-water Constituent	Criteria
Dissolved Oxygen	± 0.2 mg/L
Oxidation Reduction Potential	± 20 mV
Turbidity	± 10%
Specific Conductance	± 3-5% of reading
Temperature	± 3% of reading (minimum of ± 0.2 °C)
pH	± 0.2 units, minimum

Note: The above stability criteria are based on sequential measurements every 3-5 minutes.
Reference: [City of San Diego, 2003]

At three of the wells, parallel and simultaneous water quality parameter measurements were made on both the reference and vendor sampling lines. These measurements were carried out in order to demonstrate that ground-water stability conditions were reached at the same time with the vendor and reference sampling methods. At the remaining three wells, water quality parameters were measured on the reference sampling line only.

Following the low-flow purge and the attainment of ground-water stability conditions, four replicate cation samples were simultaneously collected in series into 250-mL high-density polyethylene bottles from both the vendor and reference sampling lines. Next, four replicate VOC samples were collected into 40-ml VOA vials from the vendor and reference sampler.

Chronological Summary of Demonstration Activities

The verification test began on Monday, February 24 and was concluded on Friday, February 28. The first two days of the demonstration were devoted to testing at the USGS Standpipe and the following three days were devoted to testing at Tyndall. The demonstration technical team observed and recorded observations associated with the operation of the vendor technology during both standpipe and monitoring well trials to assist in the assessment of logistical requirements and technology ease-of-use. These observations also were used to document any pump performance anomalies as well as operator technical skills required for operation.

Deviations from the Verification Plan

In the following sections, a listing of the deviations from the test plan is summarized and an assessment of the resulting impact on the field test data set is discussed.

Change in reference sampler configuration-The configuration of the reference sampler included a length of 5/16-inch OD Teflon tubing that was connected to a 12-inch length of 1/8-inch ID tubing by means of a quick-connect stainless steel reducing union. Attempts to deploy this reference sampler configuration during the Tyndall field trials were unsuccessful as a result of insufficient clearance with the well inner diameter when the vendor and reference sampling lines were bundled together. To circumvent this problem, the tube sampler configuration was modified for the Tyndall field trials. The stainless steel quick-connector and 1/8-inch tubing were replaced with a stainless steel check valve that was threaded directly onto the down hole end of the 5/16-inch tubing. This configuration provided adequate clearance for the cable-tied vendor and reference lines to be inserted into the well. The affect of this configuration change on reference sampler performance is judged to be insignificant. See Appendix A for additional details on reference sampler design changes and performance.

Lost/dropped samples-One of the four replicate VOC sample vials from the standpipe reference sample port in Trial 7 was broken during shipment to the analytical laboratory. In this case the average external port value was based on three samples instead of the usual four. Dropping from four to three replicates in this case results in an insignificant impact on the overall results for this particular trial.

Loss of volatile target VOC species in field spike samples-The VOC target analyte list consisted of six compounds that were selected based on their likelihood of being encountered in typical groundwater sampling applications. The target compounds also were chosen such that a volatility range was represented. At the standpipe, a VOC-spiked solution was prepared in a mixing tank near the top of the standpipe and then drained into the standpipe with the total duration of this process being on the order of 10-15 minutes. Off-site lab analysis of the water samples collected from the standpipe from both the external port and the vendor bladder pump revealed that the two most volatile compounds, (vinyl chloride and ethyl benzene) were at non-detectable (<1 μg/L) levels, despite the fact that they were mixed at an original concentration of about 70 μg/L. These observed VOC losses were corroborated by the on-site, quick-turnaround analysis of samples that were collected immediately after VOC spiking in the mixing tank. Thus, significant volatile losses occurred in the 10-15 minutes that it took to mix the solutions and fill the standpipe. Although it would be desirable to have the data from these most volatile compounds, data are available from the other four target VOC compounds such that pump performance over a range of compound volatility can be determined.

Non-detectable VOC target analytes in a Tyndall monitoring wells-Well selection for the Tyndall phase of the field study was based upon well samples that were collected during an August 2002 pre-verification test sampling effort at Tyndall. During that visit, a number of wells were sampled and a subset of six wells was chosen based upon the VOC analytical results that were obtained. During the verification test, all vendor and reference samples from one well (MW-9-P10) were non-detectable for VOC compounds. Since results were available from five other wells at Tyndall, the impact of this non-detect is judged to be of minor consequence in overall performance assessment of the pump.

Section 4 — Geoprobe Model MB470 Mechanical Bladder Pump Performance Evaluation

Test Design Summary

The test design consisted of a series of sampling trials for cation- and VOC-spiked tap water at the standpipe, followed by an additional series of trials at six, 1-inch internal-diameter, direct-push wells at Tyndall Air Force Base. In all sampling instances, a co-located, simultaneous reference sample was matched to each sample collected with the vendor pump. The standpipe trials were designed to yield sampler performance parameters such as sampler precision and comparability with reference samples at a number of sampling depths and VOC concentration levels. The trials at Tyndall monitoring wells, in addition to providing additional performance data, also afforded the opportunity to observe the operation of the technology under actual conditions of use.

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 either μg/L or mg/L for the cation and VOC target compounds selected for use in this study. 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 are compiled into data notebooks and are available from the EPA Project Officer through special request.

Sampler Precision at Standpipe

The precision data for both Geoprobe and reference samples from the cation and VOC standpipe trials are given in Tables 5 and 6. (Trial 1 was a blank (tap-water) test and in the interest of brevity is not included in the tables. Results from this trial are discussed in a following paragraph. Relative standard deviation, as defined in Section 3, is the parameter used to represent precision for the Geoprobe and the reference samples. The results are listed by compound with test conditions (trial number, analyte concentration from external port and sampling depth) also shown in the tables. The column in each of the tables is the probability *p* associated with the F-ratio statistical test. The F-ratio test was used to assess whether the technology and reference precision estimates can be regarded as statistically different from one another. 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 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. For this test, the assumption is made that the vendor and reference precision estimates are statistically equivalent (e.g. from the same population). A value of *p* that is 0.05 under these assumptions indicates only a 5 percent likelihood that the two estimates are indeed from the same population. Conventional statistical interpretation is that a significant bias exists (e.g., the precision estimates are statistically different) when calculated p-values are less than 0.05.

Precision of the bladder pump and external port cation samples is comparable. Relative standard deviations are generally less than 2 percent for both pump and reference. With one exception, statistical testing indicates that precision estimates for the two methods are comparable (e.g., values of *p* associated with the F-ratio test are all greater than 0.05). A high RSD was observed for the external port sample for sodium on Trial 3; however, it appears that one of the four laboratory reported values is an outlier. If this outlier value is dropped, the port sample RSD becomes 1.0 percent and is statistically indistinguishable from that observed for the pump ($p = 0.28$).

The results for the VOC samples can be summarized as follows: Relative standard deviations for both the pump and port samples are less than 4 percent and the results of the F-Ratio tests reveal no method bias between the pump and port samples. The precision of the pump and reference samples for VOC samples is judged to be comparable.

Table 5. Model MB470 and Reference Precision Summary for Inorganic Species at the Standpipe

Compound	Trial No.	Conc. Level μg/L	Sampling Depth (Feet)	MB470 Precision (RSD %)	REF Precision (RSD %)	F-Ratio Test *p*
Calcium	2	9150	17	0.9	0.6	0.58
	3	9300	35	0.6	1.0	0.31
	4	14,700	17	0.6	0.6	0.95
	5	14,700	35	1.0	0.4	0.18
Iron	2	6680	17	0.8	0.7	1.00
	3	7400	35	2.0	2.8	0.43
	4	12,800	17	0.6	1.1	0.40
	5	12,000	35	1.2	0.8	0.48
Magnesium	2	5630	17	1.0	0.9	0.82
	3	6200	35	0.8	0.8	1.00
	4	11,500	17	0.5	0.5	0.98
	5	11,700	35	1.2	0.6	0. 33
Potassium	2	7400	17	1.3	1.3	1. 00
	3	6200	35	5.0	6.5	0.72
	4	14,200	17	0.9	0.7	0.63
	5	15,000	35	1.4	1.3	0.87
Sodium	2	102,400	17	0.3	1.1	0.06
	3	92,800	35	0.5	7.1	<0.01
	4	110,000	17	0.6	0.8	0.68
	5	114,300	35	0.9	0.4	0.25

Note: The concentration level shown is the mean value from the external port.

Table 6. Model MB470 and Reference Precision Summary for VOC Species at the Standpipe

Compound	Trial No.	Conc. Level μg/L	Sampling Depth (Feet)	MB470 Precision (RSD %)	REF Precision (RSD %)	F-Ratio Test *p*
Vinyl Chloride	6	ND	76	--	--	--
	7	ND	17	--	--	--
	8	ND	35	--	--	--
MTBE	6	69	76	1.7	2.5	0.54
	7	76	17	2.4	2.3	0.98
	8	79	35	1.0	1.2	0.80
cis-1,2-DCE	6	64	76	3.4	2.0	0.45
	7	71	17	1.2	1.8	0.47
	8	77	35	0.7	2.4	0.06
Benzene	6	71	76	1.8	1.1	0.50
	7	81	17	0.6	0.7	0.82
	8	85	35	0.2	0.3	0.32
TCE	6	67	76	3.2	0.0	--
	7	72	17	1.1	1.6	0.58
	8	78	35	0.7	0.6	1.00
Ethyl Benzene	6	ND	76	--	--	--
	7	ND	17	--	--	--
	8	ND	35	--	--	--

Note: The concentration level shown is the mean value from the external port.

Pump - Port Comparability at Standpipe

The Model MB470 pump and external port sample comparability data are shown in Tables 7 and 8 for cation- and VOC-spiked water respectively. Percent difference, as defined earlier in Section 3, is used to assess the comparability between vendor and reference technology. Percent difference values were computed for each of the target cation and VOC compounds in the standpipe trials. The difference data are given by compound for each of the variables in the trials (e.g. sampling depth and concentration).

For the cation trials, the difference values for the Geoprobe pump range from –12.6 to 3.6 percent. The –12.6 percent value is associated with iron in Trial 3 and appears to be caused by a single outlier value in one of the four replicate external port samples. All other difference values fall between –2.4 and 3.6 percent. The t-test results reveal three instances of method bias. When considering the comparability of the pump to a reference method, two measures of comparability, namely percent difference and the t-test result, should be considered together. As an example, consider an average percent difference of -2 percent that is determined to be a statistically significant difference in contrast to an average percent difference of –15 percent that is also determined to be a significant difference. In the former case the determination of a significant bias is much less a concern since the degree of difference between the two methods is very small. In the latter case, the degree of difference is considerably larger and the t-test result would add credence to the observed difference by indicating that some biasing factor is present when the two methods are compared. One of the four instances of significant bias for the cation samples is associated with the anomalous iron result in Trial 3. The other three are for calcium and magnesium in Trial 3 and iron in Trial 2; however, the determination of significant bias is associated with very small percent differences of –2.2 percent for calcium and iron and –2.4 percent for magnesium.

For the VOC trials, the difference values for the Geoprobe pump range from –5.0 percent for MTBE in Trial 7 to –0.3 percent for MTBE in Trial 8. Furthermore, it is not surprising all difference values are negative. In light of the volatile nature of the target analytes, losses from the pumping system; however, small they might be, are expected relative to the external port samples where the exposure of the water sample to air is of much shorter duration. Five instances of significant bias are observed for MTBE, benzene, and TCE. In light of the small magnitude of percent differences observed, these statistical indications of method bias hold only secondary importance.

Blank and High Water-Column Standpipe Trial Results

The analysis of pump and external reference port samples from the non-spiked tap water trial (Trial 1) at the standpipe revealed non-detectable levels for all of the target VOCs. Some of the target cation compounds (e.g., potassium and sodium) were detected as background constituents in the tap water used for the blank trial. The other target three target cations were not detected. These results indicate that the pipe was clean prior to the verification trials, and furthermore, that a new or decontaminated pump does not contaminate a clean sample of water.

Pump flow rates were measured in selected trials to illustrate typical pumping rates under varying depth and water-column heights. Summary flow rate data are shown in Table 9. The flow rates reported in the table were measured while operating the pump with the 12-Volt actuator at approximately 38 cycles per second. Flow rates ranged from a high of 145 mL/min for a 17-foot deployment and a depth to water of 3 feet to a low of 41 mL/min for a 76-foot deployment and an approximate depth to water of 50 feet. A brief test was also conducted operating the pump manually while at the 76ft sample depth. A flow rate of approximately 570 mL/min. was obtained during this short test. A longer pump stroke and faster cycle time were used to obtain this higher flow rate manually.

Table 7. Comparability of Model MB470 and Reference Cation Data from Standpipe Trials

Compound	Trial No.	Conc. Level[A] (μg/L)	Depth (Feet)	Difference (%)	T-Test[B] *P*
Calcium	2	9150	17	-0.5	0.36
	3	9300	35	-2.2	0.01
	4	14,700	17	-0.1	0.85
	5	14,700	35	0.4	0.43
Iron	2	6680	17	-2.2	0.01
	3	7400	35	-12.6	<0.01
	4	12,800	17	-0.5	0.45
	5	12,000	35	-0.1	0.88
Magnesium	2	5600	17	0.4	0.54
	3	6200	35	-2.4	0.01
	4	11,500	17	0.3	0.39
	5	11,700	35	0.2	0.83
Potassium	2	7400	17	0.7	0.49
	3	6200	35	3.6	0.41
	4	14,200	17	1.0	0.12
	5	15,000	35	-0.3	0.80
Sodium	2	102,400	17	0.9	0.19
	3	92,800	35	2.7	0.48
	4	110,000	17	0.6	0.26
	5	114,300	35	-0.5	0.36

Notes:

A The concentration level shown is the mean value from the reference sampler.

B The t-test was used to compare the mean recovery of the Model MB470 samples to the mean recovery of the reference samples for each compound in each trial. Small values of *p* (<0.05) are suggestive of statistically significant sampler difference. See text for further details.

Table 8. Comparability of Model MB470 and External Port VOC Data from Standpipe Trials

Compound	Trial No.	Conc. Level (μg/L)	Sampling Depth (Feet)	Difference (%)	T-Test *p*
Vinyl Chloride	6	ND	76	--	--
	7	ND	17	--	--
	8	ND	35	--	--
MTBE	6	69	76	-4.7	0.02
	7	76	17	-5.0	0.02
	8	79	35	-0.3	0.70
cis-1,2-DCE	6	64	76	-3.1	0.15
	7	71	17	-2.1	0.10
	8	77	35	-1.0	0.46
Benzene	6	71	76	-2.5	0.06
	7	81	17	-3.4	<0.01
	8	85	35	-1.4	<0.01
TCE	6	67	76	-2.6	0.14
	7	72	17	-1.4	0.21
	8	78	35	-3.2	<0.01
Ethyl Benzene	6	ND	76	--	--
	7	ND	17	--	--
	8	ND	35	--	--

Note: The concentration level shown is the mean reference value

Table 9. Pumping Rates for Various Sampler Depths

Trial No.	Sampler Depth^A (Feet)	Depth to Water^A (Feet)	Water Depth (Feet)	Flow Rate (mL/min)
2	17	2.9	14.1	145
3	35	4.0	31.0	102
6	76	49.5	26.5	41

Note: ^{A} Measured from top of standpipe

Water Quality Parameter Stability Monitoring at Tyndall

Water quality parameters were measured in parallel with the pump and the reference tube sampler in three of the six Tyndall wells selected for sampling. Parameters were measured with each sampling system using calibrated flow-through cells that were connected to the outputs of the pump and the reference tube sampler. Water quality parameters that were measured included: temperature, pH, conductivity, dissolved oxygen (DO), oxidation/reduction potential (ORP), and turbidity. Typically, DO and turbidity were the two parameters that were the most sensitive and last to stabilize according to the criteria given in Table 4. A typical times series plot of DO and turbidity for both sampling systems drawing from Tyndall Well Number MW-9-P10 is shown in Figure 3. This result is typical of those encountered at the other two wells. Water parameter stability was reached at essentially the same time with both sampling systems. These results show that the mechanical bladder pump does not alter the physical characteristics of the water sample when compared to a reference sampling technique.

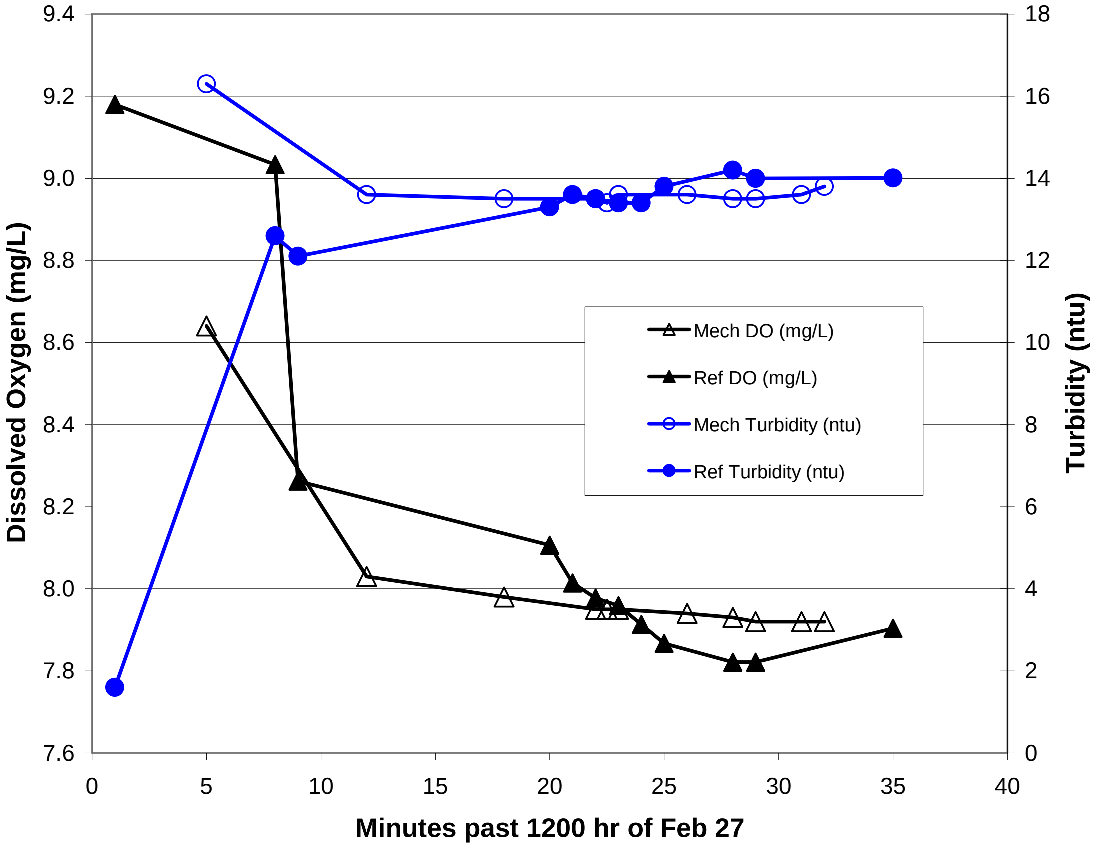

Figure 3. Simultaneous dissolved oxygen (DO) and turbidity measurements from Tyndall Well MW-9-P10 measured through the Model MB470 (Mech) and a reference tube sampler (Ref).

Comparison of Pump and Reference Samples at Tyndall Monitoring Wells

Geoprobe pump sample results for the target cations from six different Tyndall direct-push ground-water monitoring wells are shown alongside reference sampler data from the same wells in Table10. Four replicate samples were taken with the Geoprobe pump with the simultaneous collection of paired reference samples. For each of the five target cations, the pump average value, pump precision, reference average, reference precision, and the percent difference between pump and reference are shown in the table. The data in the table can be summarized as follows: precision, as reflected by the relative standard deviation, is high (low RSD values) for both pump and reference samplers, with RSD values ranging from 0.5 to 2.9 percent for the pump and 0.4 to 1.9 percent for the reference. Percent differences between the pump and reference range from a low of –12.7 to a high of 15.2 percent with a media value of -0.7 percent.

Table 10. Model MB470 and Reference Sampler Cation Results from Ground-water Monitoring Wells

Well Number	Cation	Pump AVG (μg/L)	Pump RSD (%)	Reference AVG (μg/L)	Reference RSD (%)	Percent Difference (%)
MW 2-P10	Ca	5650	1.0	6180	1.6	-8.5
	Fe	1120	0.6	970	0.9	15.2
	Mg	2210	0.6	2310	0.7	-4.4
	K	4300	0.5	4190	0.9	2.7
	Na	7020	0.9	7100	0.4	-1.1
MW-9-P10	Ca	74,250	0.7	74,750	0.7	-0.7
	Fe	ND	--	ND	--	--
	Mg	3930	1.3	3950	1.5	-0.6
	K	4880	1.0	4880	1.0	0.0
	Na	5110	0.7	5120	1.8	-0.3
MW-8-P10	Ca	16,520	0.3	15,620	0.4	5.7
	Fe	ND	--	ND	--	--
	Mg	1730	2.9	1730	2.9	0.0
	K	2510	0.4	2550	0.7	-1.8
	Na	4680	2.0	4930	1.9	-5.1
MW-5-P10	Ca	32,250	1.6	29,750	1.7	8.4
	Fe	ND	--	ND	--	--
	Mg	2580	1.4	2290	0.4	12.8
	K	2830	1.8	2830	1.8	0.0
	Na	5080	1.9	5080	1.0	0.0
T6-5-P10	Ca	77,040	1.1	81,100	0.8	-5.0
	Fe	ND	--	ND	--	--
	Mg	6380	0.8	6930	1.4	-7.9
	K	2580	1.9	2950	2.0	-12.7
	Na	4130	1.2	4280	1.2	-3.5
MWD-11-P10	Ca	15,340	2.5	14,850	1.3	3.3
	Fe	ND	--	ND	--	--
	Mg	2680	2.1	2730	0.9	-1.9
	K	5150	1.1	5550	1.0	-7.2
	Na	8530	0.6	9430	1.0	-9.5

Geoprobe pump and reference sample results for the VOC compounds detected in the five Tyndall monitoring wells are given in Table 11. Note that results are reported for only five wells since no VOCs were detected in one of the six wells sampled. All detected VOCs are reported for each sampling method and in many cases VOCs not on the target VOC list used at the standpipe are included. The well number is listed in the table and is followed by the VOC compounds detected at that particular well. Also shown in the table are the pump average value, pump precision (percent relative standard deviation), reference sampler average value, and reference sampler precision. The percent difference between the pump and the reference sample is given in the final column. VOC concentrations vary from low μg/L to low mg/L levels and the number of compounds detected in the ground-water varies from well to well. Relative standard deviation values are generally higher than those encountered during the VOC trials at the standpipe and are attributable to many additional factors that are encountered during field sampling. Two important factors are the degree of spatial and temporal homogeneity of the pump and reference ground-water samples.

Table 11. Pump and Reference Sampler VOC Results From Ground-water Monitoring Wells

Well Number	Compound	Pump AVG (μg/L)	Pump RSD (%)	Ref. AVG (μg/L)	Ref. RSD (%)	Percent Difference (%)
MW 2-P10	Benzene	528	5	493	9	7.1
	Toluene	5	10	7	7	-22.2
	m,p-Xylene	135	4	153	3	-11.5
	o-Xylene	24	2	34	1	-29.6
	1,3,5-Trimethylbenzene	5	3	5	4	-9.5
	1,2,4-Trimethylbenzene	17	3	20	3	-11.5
	Naphthalene	65	2	60	7	7.9
MW-8-P10	cis-1,2-DCE	188	3	253	5	-25.7
	Trichloroethene	94	3	97	2	-3.9
MW-5-P10	Trichloroethene	1475	10	2050	5	-28.1
T6-5-P10	Vinyl chloride	9	25	7	15	34.6
	Benzene	86	2	113	17	-23.3
	Ethyl benzene	42	2	34	18	25.2
	Isopropyl benzene	14	4	12	24	14.9
	Propyl benzene	16	6	13	24	24.0
	Naphthalene	110	13	120	10	-8.3
MWD-11-P10	m,p-Xylene	9	14	11	18	-20.5
	o-Xylene	8	10	10	18	-22.0
	1,2,4-Trimethylbenzene	6	9	7	26	-20.7

The study design specified the collection of co-located samples from each of the wells by the pump and the reference sampler. Furthermore, reasonable attempts were made to collect samples at the same time and only after water quality parameters had stabilized during a low-flow purging protocol. Temporal coincidence of the two sampling activities was difficult to achieve precisely because the sampling rate of the Geoprobe pump was lower than that of the reference system. Furthermore, it is nearly impossible to ascertain the stability of the VOC concentrations in formation ground-water with time or location. The data presented here implicitly assume temporal and spatial stability of the ground-water source; however, that assumption may not necessarily be valid. Consequently, the standpipe trials--with inherently more experimental control--are used to make definitive comparisons of pump versus reference performance and the Tyndall field data are included for more qualitative comparisons.

A comparison of compounds detected by pump and reference sampler indicates that the same VOCs were detected in both sets of samples. Precision data are lowest (highest RSD values) for selected compounds (e.g., ethyl benzene, vinyl chloride, propyl benzene) measured with the reference sampler. In contrast, the precision is in general much better for these same compounds when sampled with the mechanical bladder pump. The continuous-flow method of sampling used with the pump compared to the static sampling method used with the reference device is very likely a determinate factor here.

Percent difference values of the pump relative to the reference sampling device range from –29.6 to 34.6 percent with a median value of -8.3 percent. Thirteen of the 19 total detects at or above the laboratory method detection level (typically in the vicinity of 5 μg/L) were in the negative range and 13 of the 19 total VOC detects fall within the range of ± 25 percent.

Pump Deployment Logistics

The following observations were made during testing of the mechanical bladder pump at both the standpipe and ground-water monitoring wells.

- The weather during the Tyndall trials included windy and rainy conditions. The inclement weather did not adversely impact pump or support accessory performance at the well head.
- Only one person is required to operate the pump and controller. Training requirements are minimal with several hours of training required for a ground-water sampling technician to become proficient in routine field use of the equipment. The assistance of a second person can be advantageous, particularly when configuring the pump tubing for deployment into the well.
- The motor accessory for the pump was an early engineering prototype and was judged to be bulky to handle.
- External power is required when the pump is used with the motor drive accessory. The present version of the pump requires 12-volt DC power, which can be easily drawn from a vehicle battery.
- The pump can also be fitted with a manual, hand-crank accessory; however, prolonged hand pumping during low-flow purging and sampling operations can quickly become tiresome. Furthermore, hand-operation of the pump can result in a more erratic pumping rate that may adversely impact the low-flow purging protocol.
- The pump can be easily disassembled in the field for repair or decontamination.
- The tubing lengths associated with the pump need to be specifically fitted for a particular well deployment. Specifically, prior to installation into the well, the outer tubing must be cut at the appropriate length such that it can be held immobile by a clamping apparatus positioned at the well head.
- Deployment of the pump at the deeper (~75 feet) depths investigated in this study results in a significant reduction in flow rate at the pump outlet. Pumping efficiency is reduced both by the loss of rigidity in the long length of stiff inner tubing that is used to compress the bladder inside the pump body as well as from the high water column head pressure that must be overcome to move water up the inner tubing.

Pump Performance Summary

A summary of the Geoprobe Model MB470 Mechanical Bladder pump performance is given in Table 12. Summary categories include precision, accuracy, comparability with reference method, versatility, and logistical requirements. Cost and physical characteristics of the equipment are also summarized in the table.

The results of this verification test show that the Geoprobe mechanical bladder pump and associated mechanical actuator can be used to collect VOC-contaminated water samples that are statistically comparable to a reference method with regard to both precision and accuracy.

Table 12. Model MB470 Bladder Pump Performance Summary

Performance Parameter	Performance Summary
Precision	**Inorganic cations**: For 6 target cations at concentrations ranging from 5 to 115 mg/L, and at 17-foot and 35-foot standpipe sampling depths: Relative standard deviation range: 0.3 to 5.0% Median relative standard deviation: 0.9% **VOC Compounds**: For 4 target VOCs at an approximate 70 µg/L concentration level and 17-, 35- and 76-foot standpipe sampling depths: Relative standard deviation range: 0.2 to 3.4% Median relative standard deviation: 1.2%
Comparability with Standpipe External Port Samples	**Inorganic Cation Standpipe Trials**: For cation target compounds at concentrations ranging from 5 to 115 mg/L, and at 17-foot and 35-foot sampling depths: Percent difference range: -12.6 to 3.6 Median percent difference: 0.0 **VOC Standpipe Trials**: For VOC target compounds at an approximate concentration level of 70 µg/L and at 17-foot, 35-foot and 76-foot sampling depths: Percent difference range: -5.0 to -0.3 Median percent difference: -2.5
Comparability with Tyndall Reference Sampler	**Inorganic Cation Field Trials**: For cation target compounds at concentrations ranging from 4 to 7 mg/L and at sampling depths ranging from 8 to 31 feet below the surface: Percent difference range: -12.7 to 15.2 Median percent difference: -0.7 **VOC Field Trials**: For VOC target compounds at concentrations ranging from 5 to 1500 µg/L and at sampling depths ranging from 8 to 31 feet below the surface: Percent difference range: -29.6 to 34.6 Median percent difference: -8.3
Sampler versatility	The Model MB940 demonstrated consistent performance across the tested range of compound volatility and sampler depth. The pump was successfully used with a low-flow sampling protocol and flow-through cell monitoring of water quality parameters Reduced pump flow rates at depths in excess of 50 feet may be incompatible with certain sampling protocols.
Logistical requirements	Pump can be operated by one person with several hours of training. The pump, when equipped with motor-driven actuator, requires a 12-Volt DC power source.
Completeness	System was successfully used to collect all of the samples prescribed in the test plan.
Purchase cost	Pump cost: $430 Accessories: Mechanical actuator - $240; Motor-driven actuator - not available Tubing costs: HDPE/FEP $100 (50-foot roll); HDPE/LDPE $54 (50-foot roll)
Size and weight	Model MB470: 0.47-inch diameter x 25.5-inch length, 0.45 lbs. Motor Drive Accessory: Unit still under development Hand Crank Accessory: 12 x 5 x 27 inches, 11.4 lbs

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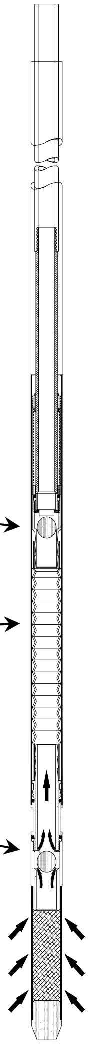
Section 5 – Mechanical Bladder Pump Technology Update

Note to reader: The following additional information and data on pump performance has been provided by the vendor. The data reported here were not a part of the ETV verification test design. The data are provided for the reader's information; however, these data have not been verified and are not considered a part of the verification study.

The following schematic diagram provides a brief explanation of how the mechanical bladder pump works. During the intake stroke the corrugated bladder is expanded vertically as the inner tube is raised. During the sample stroke the bladder is compressed vertically as the inner tube is lowered and the spring expands. Water is purged to the surface simply by raising and lowering the inner tube repeatedly.

Intake Stroke:



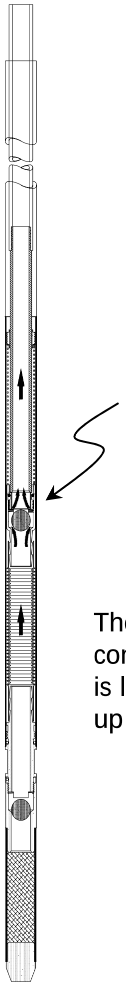
At the surface the outer tube is held stable and the inner tube is pulled up ...

As the inner tube is raised the upper check ball seats and prevents water from flowing back down into the bladder ...

The bladder expands filling with water ...

As the bladder expands the lower check ball opens and water flows in from the well through the intake screen into the bladder.

Sample Stroke:



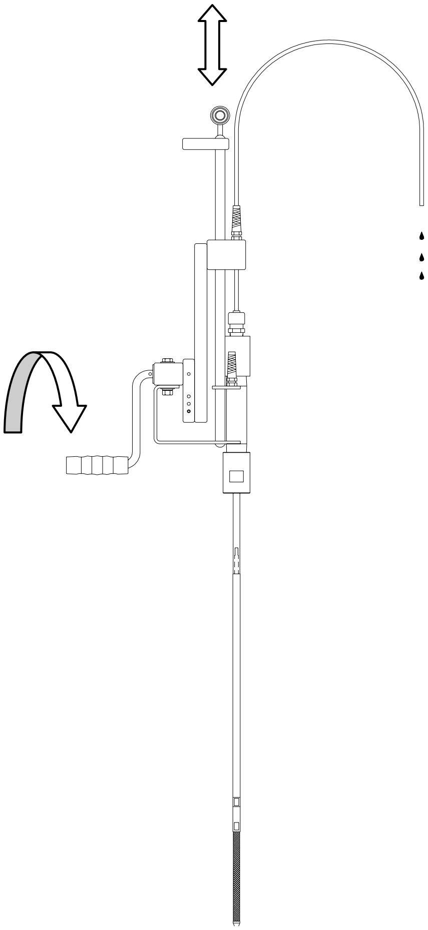
At the surface the outer tube is held stable and the inner tube is lowered ...

As the inner tube is lowered the upper check ball opens and water is pushed up the inner tube to the surface ...

The corrugated bladder compresses as the inner tube is lowered and water is pushed up & out of the bladder.

As the bladder is compressed the lower check ball is closed preventing water from flowing out of the intake valve.

Following the field activity for the Verification study Geoprobe Systems conducted a series of field tests to develop flow curves for the MB470 pump. The flow curves were developed using two different methods to actuate the pump. A manually powered mechanical actuator (model MB600, see Figure 4) can be used to operate the pump using either circular strokes or vertical strokes. The circular stroke spreads out the work load making for easier operation over a longer period. The vertical stroke provides more efficient operation when higher flow rates are required. The length of the pump stroke was set at four inches (~100mm) for both the circular and vertical stroke tests.



The mechanical actuator is operated manually to actuate the mechanical bladder pump down hole. This actuator permits the use of either a circular stroke or vertical stroke to operate the pump. The circular stroke spreads out the work load while the vertical stroke provides for higher flow rates when needed, such as for development.

Figure 4. The MB6000 mechanical actuator.

For the first series of tests the pump intake was set at 70 feet below grade in a closed standpipe. The water level was lowered in increments of 10 feet and the flow rate was measured at each interval. For the last interval the water level was lowered 8 feet (to 68ft) so that only two feet of water was above the pump intake. Water was added to the standpipe as pumping was conducted to maintain the water at the desired level. The pump was operated at different speeds (cycles per second) at each depth interval to see how flow rate changed with speed. Results for the tests using a circular stroke with the actuator (Figure 5) show much as expected the flow rate decreases as the water level is lowered. The maximum flow rate of about 350ml/min is obtained with the static water level at 10ft and pump speed at 150 cycles per minute. Again as expected the minimum flow rate (~50ml/min) occurs when the water level is at 68ft and the pump speed is at 100 cycles per minute

When a vertical stroke is used to operate the pump under the same set of conditions the flow rate at each water level and pump speed is noticeably higher (Figure 6). The vertical stroke results in more efficient opening and seating of the check balls during the pump cycle so that the volume of fluid pumped per stroke is improved as compared to use of the circular stroke.

For the second series of tests the pump was lowered on 10-foot increments and the water level was maintained 5 feet above the intake during each test in the standpipe. Using the actuator with circular stroke the maximum flow rate achieved is almost 850ml/min with the pump intake at 10 feet, water level at 5 feet, and pump speed of 150 cycles per minute (Figure 7). When a vertical stroke is used to actuate the pump under the same conditions the maximum flow rate approaches 950ml/min (Figure 8). While even the maximum flow rates obtained here are relatively modest, keep in mind that the pump is less than 0.5 inches (only 12mm) in diameter and about two feet (~60cm) long. The flow rates that can be obtained are very useful for the low-flow minimal-draw down sampling protocol recommended by the U.S. EPA and many state regulatory agencies for water quality sampling.

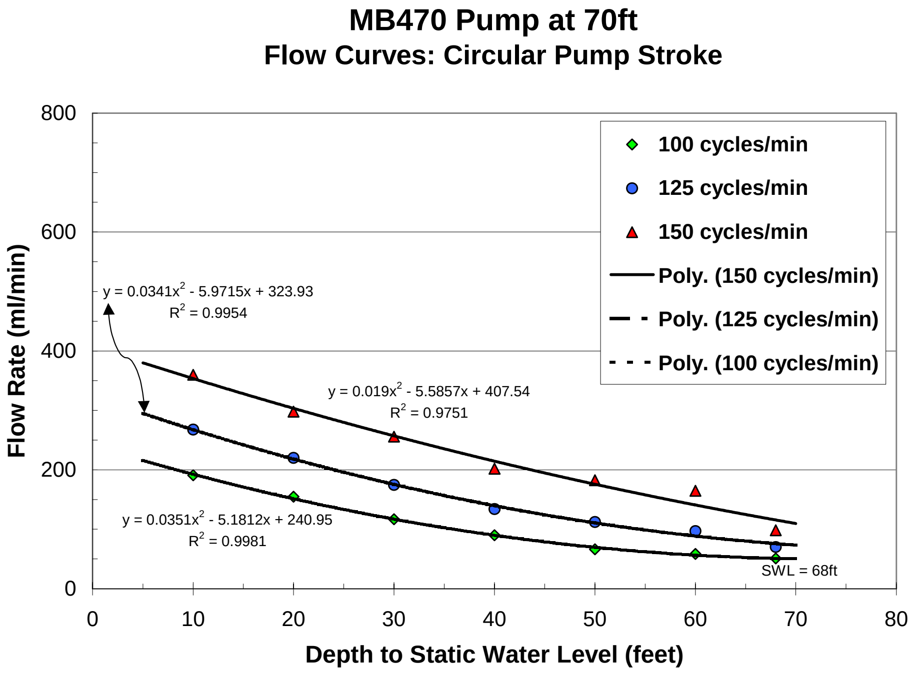


Figure 5. Flow data for MB470 pump with a circular pump stroke.

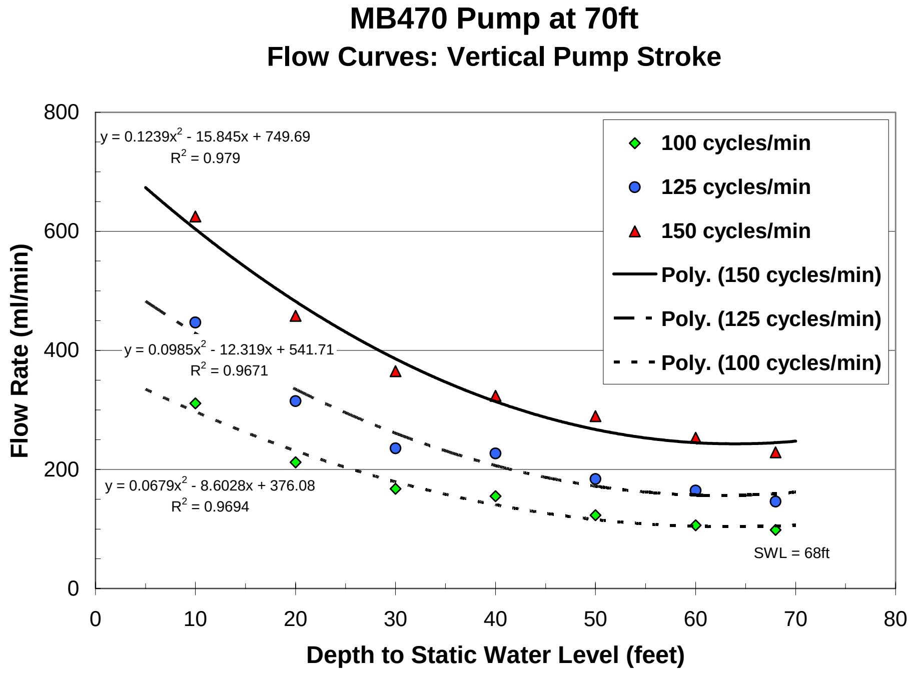


Figure 6. Flow data for the MB470 with a vertical pump stroke.

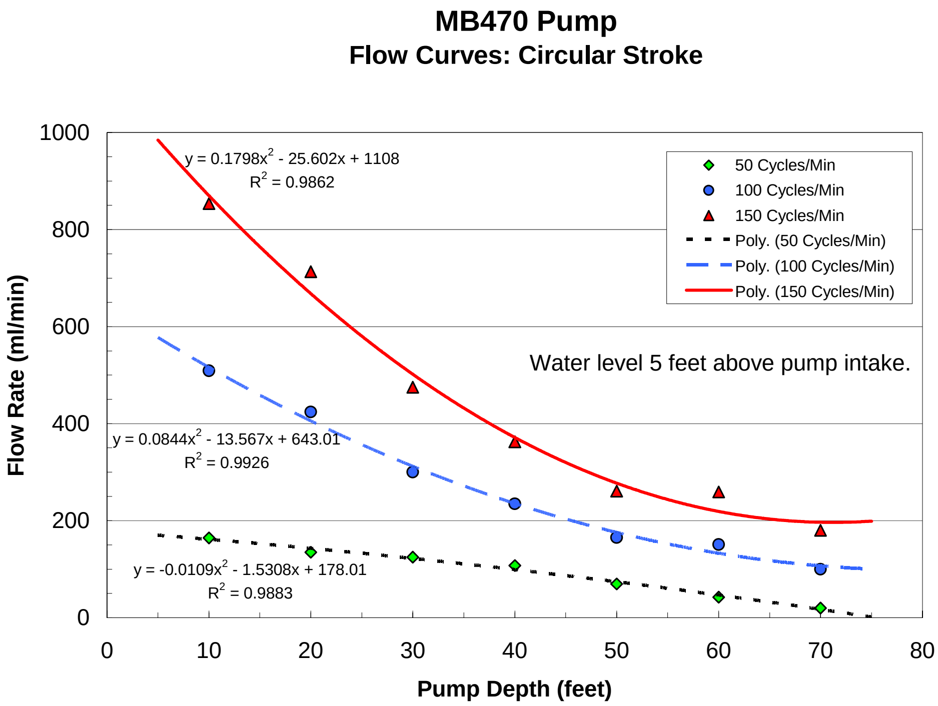


Figure 7. Flow data for the MB470 pump with a 5-foot water column above the pump intake and a circular stroke.

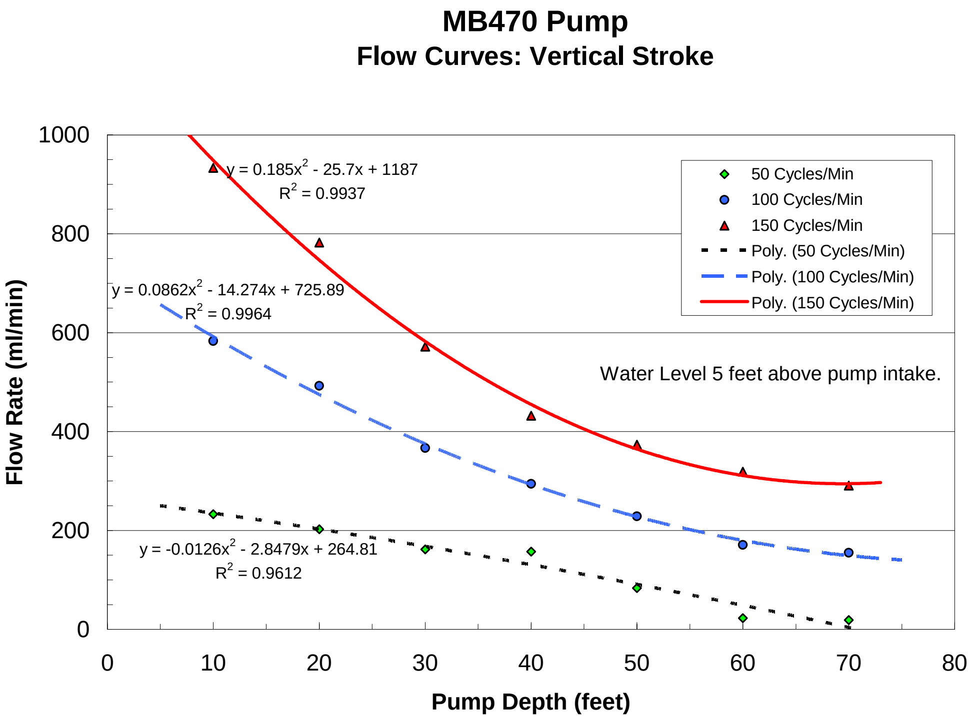


Figure 8. Flow data for the MB470 pump with a 5-foot water column above the pump intake and a vertical stroke.

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Appendix A – Reference Sampler Method and Performance

Introduction

This appendix contains information on the reference sampler that was used alongside the vendor's pump during the Tyndall field trials. One of the challenges of this verification test was the inclusion of a reference sampler with a small cross sectional profile such that it could be co-located with the vendor pump in the 1-inch internal-diameter wells used in the study. Included in this summary is a brief description of the reference method as well as a summary of the performance of the reference sampler as determined during the standpipe portion of the test.

Method Summary

The reference method, hereafter referred to as the tube sampler, was used to collect a co-located sample alongside the vendor technology from the USGS Standpipe and the narrow-diameter wells at Tyndall AFB during the verification test. The sampler is simple in concept and is designed to provide a sample with minimal volatile organic compound losses during sample handling. The sample is collected by inserting a length of inert tubing into the standpipe or well alongside the vendor technology such that the two inlets are co-located at the desired point along the well screen. A sample is then collected by purging a fixed volume of sample through the tube with a peristaltic pump. Following this purge, the flow is stopped and a vacuum is applied at the top of sampling tube. The tube is then withdrawn from the well and sample is dispensed from the bottom of the tube. Only the bottom two-thirds of the water column in the tube is used for sample. The top third of the water column in the tube is discarded as this water is expected to lose some volatiles through the air/water interface at the top of the tube. A diagram of the sampler as deployed during the Tyndall tests is shown in Figure A-1.

Sampler Parts Specification

25-foot section of FEP Teflon tubing (5/16-inch ID, 3/8-inch OD, 1/32-inch wall thickness)
1-foot section of FEP Teflon tubing (1/8-inch ID, 3/16-inch OD, 1/32-inch wall thickness)
Stainless steel quick connect fittings: female 1-4-inch ID (Fisher Cat. No. 15-340-6) and male 1/8-inch ID (Fisher Cat. No. 15-340-10)
10 to 20-foot section of Tygon tubing (3/8-inch ID, 1/32-inch wall thickness)
3-foot section of Masterflex tubing for peristaltic pump (Cole Parmer Cat. No. U-96500-17 or equivalent)
Peristaltic pump motor and pump head (Cole Parmer Cat. Nos. A07520-40 and A07518-00 or equivalent)
Hand vacuum pump (Fisher Cat. No. 13-874-614A)
40-mL VOA vials and labels
Clamp (for holding tubing in place when installed in well)
AC power source
Stainless steel check valve (5/16-inch ID)

Note: Two sampler design variations were used in this verification test. At the standpipe, a 12-inch length of 1/8-inch ID tubing was connected to the 5/16-inch tubing via a stainless steel quick connect fitting. This section of narrow tube was used to reduce the loss of water sample prior to the dispensing of samples into the VOA vials when the tubing string was withdrawn from the standpipe. At the Tyndall field site, due to clearance limitations, the design with the quick-connect fitting could not be deployed in the narrow-bore wells alongside the vendor's pump so an alternative design was used. The narrow tubing and quick-connect fitting were replaced with a stainless steel check-valve fitting (See Figure A-1) that was threaded directly onto the lower end of the 5/16-inch OD tubing. This design gave sufficient clearance for the reference and vendor sampling systems to be co-located in the narrow-bore wells. The check valve prevented any loss of sample from the reference tubing when it was withdrawn from the well. Following withdrawal of the tubing from the well, a paper clip was used to dislodge the check-ball and release water into the sampling vials.

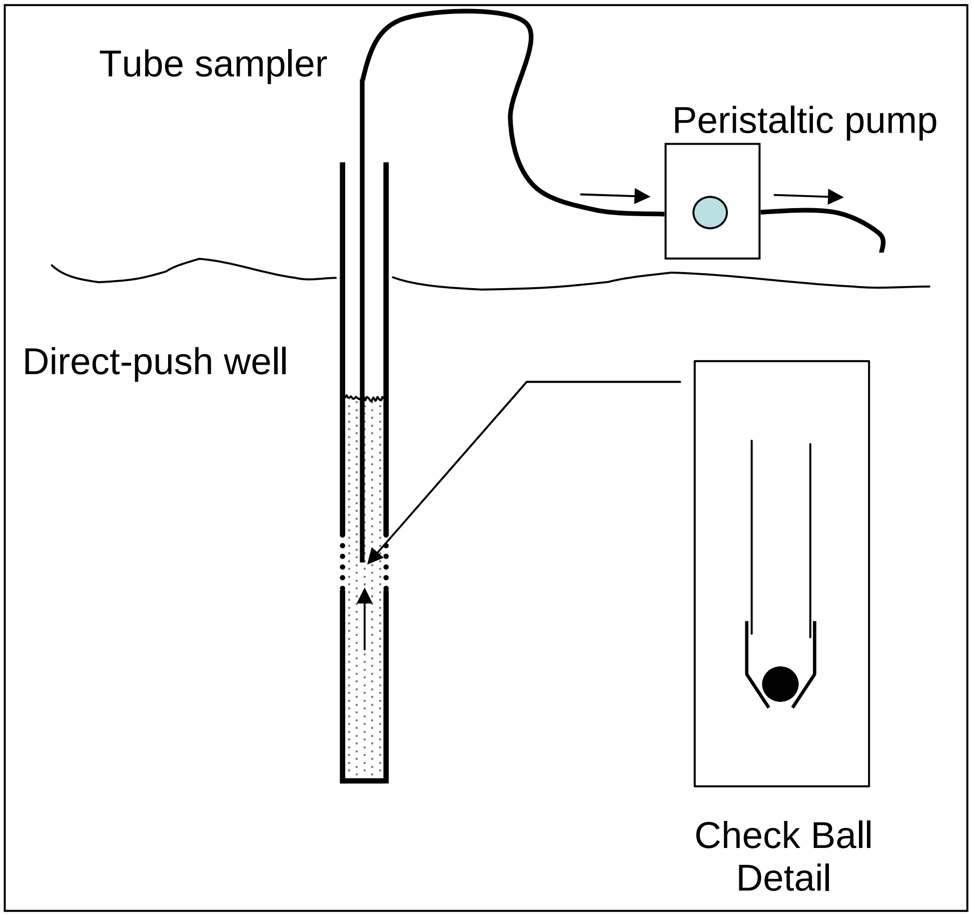

Figure A- 1. Schematic diagram of the reference tube sampler. Inset figure shows detail of the check ball fitting at the down-well end of the tube.

Detailed Sampling Procedure

1. Prepare and label four 40-mL VOA vials for sample collection. (Include preservative acid spike.)
2. Assemble tubing in the following order from down-hole end to top: 1/8-inch Teflon tubing, quick connectors, 5/16-inch Teflon tubing, 3/8-inch Tygon tubing [length cut to allow positioning of tubing inlet at desired point along well screen], pump tubing.
3. Mark the exposed tubing such that the alignment of the mark with the top of the well will position the inlet at the desired point along the well screen.
4. Gently install the tubing in the well. [A careful, slow installation will minimize the increase in well water turbidity.] Use a clamp to hold the tubing in place at the well head.
5. Insert the pump tubing into the peristaltic pump head, turn on pump and flush 1 liter of water through the tubing at a flow rate of approximately 200 mL/min.
6. At end of purge, stop pump, attach hand-held vacuum pump at outlet end of tubing and apply vacuum to maintain the water column in the tubing.
7. Remove the tubing from the peristaltic pump head.
8. Withdraw tubing from well, keeping the end with the vacuum pump attached at least 10 feet above the inlet end of the tubing. A stepladder may be necessary to accomplish this.
9. Hold inlet end (1-8-inch tubing) over 40-mL vial and slowly dispense sample into the 40-mL vial by using the vacuum release lever on the hand pump.

10. Dispense the sample into the four VOA vials in a continuous fashion. (A third person should be available to take the VOA vials and cap them immediately after filling.)
11. Following collection, verify correct labeling on VOA vials
12. Disassemble and decontaminate the lengths of Teflon tubing and quick connectors if they are intended for use in another well.

Note: For the alternate sampler design used at Tyndall, Step 2 and Step 9 are changed as follows:

2. Thread the stainless steel check valve on the end of the 5/16-inch OD tubing. The top end of the 5/16-inch tubing is connected to the Tygon tubing and the Tygon is in turn connected to the short length of peristaltic pump tubing.
9. Hold end of 5/16-inch tubing over 40-mL vial and using the end of a paper clip, release sample from the tubing by pushing the check ball upward. The vacuum pump lever should continuously be released during this sample dispensing procedure.

Tube Sampler Performance

In order to ascertain the tube sampler's performance characteristics, it was deployed in selected tests during the standpipe trials. Tube samples were collected from the standpipe at the same time as external port samples for target cation and VOCs. Each test included four paired tube sampler and external port samples such that tube sampler precision and accuracy relative to the port samples could be determined. The precision and accuracy results for the tube sampler for the target cations are given in Tables A-1 and A-2 respectively.

Table A- 1. Tube Sampler and External Reference Port Precision for Cations

Compound	Trial No.	Conc. Level μg/L	Sampling Depth (feet)	Tube Sampler Precision (RSD %)	REF Precision (RSD %)	F-Ratio Test p
Calcium	2	9500	17	0.6	0.5	0.82
	4	15,200	17	0.9	1.5	0.42
Iron	2	6400	17	1.3	2.2	0.39
	4	13,000	17	0.9	1.8	0.26
Magnesium	2	5800	17	0.3	0.7	0.25
	4	11,700	17	0.9	1.8	0.32
Potassium	2	5900	17	0.4	3.8	0.39
	4	14,800	17	1.3	2.3	0.36
Sodium	2	89,800	17	0.1	4.0	0.47
	4	115,500	17	1.2	1.8	0.49

Table A- 2. Tube Sampler and External Reference Port Comparability for Cations

Compound	Trial No.	Conc. Level (µg/L)	Sampling Depth (feet)	Difference (%)	t-Test *p*
Calcium	2	9500	17	-1.8	<0.01
	4	15,200	17	0.5	0.58
Iron	2	6400	17	-1.6	0.27
	4	13,000	17	-0.4	0.73
Magnesium	2	5800	17	0.7	0.11
	4	11,700	17	-0.1	0.92
Potassium	2	5900	17	3.4	0.40
	4	14,800	17	0.0	0.98
Sodium	2	89,800	17	3.1	0.44
	4	115,500	17	-0.4	0.71

Tube sampler precision for cations is as good as or better than that observed with the external port samples. The percent relative standard deviations for the tube sampler ranged from 0.1 to 1.3 percent whereas the range was 0.5 to 4.0 percent for the external port samples. Statistical testing shows precision differences between tube sampler and external port samples were not significant in all test cases. The comparability of the tube sampler with the external port sample data is quite good with percent difference values ranging from -1.8 to 3.4 percent for all target cations. Results of the paired t-test also shown in Table A-2 indicate one statistically different result (Trial 2, Calcium); however, the -1.8 percent difference noted is small.

Similar results for precision and accuracy are shown in Tables A-3 and A-4 for target VOC compounds that were detected during the standpipe trials. Tube sampler precision for the VOCs is comparable to that observed for the port samples. The percent relative standard deviations for the tube sampler ranged from 0.6 to 1.9 percent whereas the range was 0.7 to 1.6 percent for the external port samples. Statistical testing further shows that observed precision differences between tube sampler and external port samples were not significant. The comparability of the tube sampler with the external port sample data is good with percent difference values ranging from -1.3 to 0.8 percent for all detected VOCs. Results of the paired t-test, also shown in Table A-4, reveal that none of the observed differences were statistically significant at the 0.05 level.

Table A- 3. Tube Sampler and External Reference Port Precision for VOCs

Compound	Trial No.	Conc. Level (µg/L)	Sampling Depth (feet)	Tube Sampler Precision (RSD %)	REF Precision (RSD %)	F-Ratio Test *p*
MTBE	7	76	17	1.3	1.0	0.37
cis-1,2-DCE	7	74	17	1.9	1.6	0.27
Benzene	7	81	17	0.6	0.7	0.06
TCE	7	73	17	0.8	0.8	0.12

Table A- 4 Tube Sampler and External Reference Port Comparability for VOCs

Compound	Trial No.	Conc. Level μg/L	Sampling Depth (feet)	Difference (%)	t-Test p
MTBE	7	76	17	0.8	0.36
cis-1,2-DCE	7	74	17	-0.9	0.52
Benzene	7	81	17	-1.3	0.06
TCE	7	73	17	-1.1	0.12

Tube Sampler Performance Summary

The results of the testing at the standpipe reveal that the tube sampler performs acceptably both with regard to precision and accuracy for target cations and VOCs when used as a co-located reference sampler in the narrow-diameter wells during the Tyndall ground-water sampling portion of this verification test.

Appendix B – Analytical Method and Quality Summary

Introduction

DataChem Laboratories in Cincinnati, OH conducted the analysis of all samples collected during this study. For cation analysis, EPA Standard Methods 3010A (Acid Digestion of Aqueous Samples and Extracts For Total Metals by FLAA or ICP Spectrometry) and 6010B (ICP Atomic Emission Spectrometry) were used for analysis. For VOC analysis, EPA Standard Method 8260B (Volatile Organic Compounds by Gas Chromatography/Mass Spectroscopy) was used. Various data quality measures were incorporated into both the field sampling and the laboratory analysis components of this study. This appendix summarizes those data quality measures.

Data Quality Measures

Performance measures used to track overall laboratory data quality for inorganic cation and VOC samples are given in Tables B-1 and B-2. These measures are used to verify acceptable instrument performance and the adequacy of the final analytical results. Cation and VOC lab performance measures are essentially the same and included field spikes, method or preparation blanks, lab calibration standards as well as matrix spikes and matrix spike duplicates. The VOC method also included the addition of surrogate VOC spikes in each sample. This appendix provides only a general summary of the data quality control measures in order to provide an overall indication of the quality level of the laboratory data. All quality control data are available in a data notebook compiled for with this test and which is available from the EPA Project Officer via special request.

Table B-1. Cation Analysis Quality Control Measures

Quality Control Check	**Description**	**Frequency**
Field Spikes	Replicate 100 ppm spike samples made up in distilled water	One set per site, Minimum of 4 replicates per set
Prep. Blanks	Laboratory blank	Every 20th sample
Lab Calibration Standard	Laboratory spike sample	Every 20th sample
Matrix Spike	Lab spike into a field sample	First sample in batch
Matrix spike duplicate	Repeat analysis of matrix spike	First sample in batch

Table B-2. VOC Analysis Quality Control Measures

Quality Control Check	Description	Frequency
Field Spikes	Replicate 100 ppb spike samples made up in distilled water	One set per site, Minimum of 4 replicates per set
Prep. Blanks	Laboratory blank	Every 20th sample
Lab Calibration Standard	Laboratory spike sample	Every 20th sample
Matrix Spike	Lab spike into a field sample	First sample in batch
Matrix Spike Duplicate	Repeat analysis of matrix spike	First sample in batch
Surrogate Standards	Spike of three unique VOCs	Every sample

Data Quality Examples

The following sections present examples of system performance throughout the course of the study. In the interest of brevity, all quality control data is not shown in this appendix. A complete tabulation of all quality control data is included in a hardcopy data notebook, available for viewing through special request to the EPA Project Officer.

Preparation Blanks

Preparation blanks for each batch cation samples were reported as not detected (<1 ppm) for each of the target analytes. Preparation blanks for each VOC analysis batch were also reported as not detected (<10 ppb) for each of the target analytes.

Laboratory Calibration Standard Results

Cation Analysis - The inorganic method criteria for the laboratory calibration standards specify a recovery of ±10 percent or within documented laboratory-specific acceptance ranges for the particular sample matrix being analyzed. Normal LCS percent recovery ranges for the six target analytes were as follows: Calcium 68-143, Iron 81-115, Magnesium 71-127, Potassium 67-126 and Sodium 55-146. Recovery data are best for Ca, Fe, and Mg and more variable for K and Na. None of the reported cation results were flagged by the laboratory as being out of normal LCS recovery range for six the target analytes. An example of the batch-to-batch LCS performance for Stennis cation analysis is given in Figure B-1. None of the LCS recovery data were flagged by the laboratory as being outside recovery ranges encountered during normal operation of the instrument.

VOC Analysis - LCS percent recovery ranges encountered by the laboratory under normal instrument operating conditions are as follows: 1,1-dichloroethene 59-129; hexane 48-143; benzene 76-127; trichloroethene 69-121; toluene 69-123; chlorobenzene 74-122. None of the LCS recovery data were flagged by the laboratory as being outside the recovery ranges encountered during normal operation of the instrument.

Matrix Spike and Matrix Spike Duplicate Results

Cation Analysis - One sample batch was reported outside the normal recovery range for the MS and MSD quality control checks (Standpipe, Trial No. 2, Calcium); however, the spike was done in a tap water sample that had low calcium background. According to method guidelines, the calcium concentration in the sample should be 10-fold higher than the method detection limit, thus the results from this matrix check should be viewed accordingly. All other MS and MSD quality checks met laboratory acceptance criteria. The recovery ranges are similar to those given for LCS checks; however, for the sake of brevity they are not reproduced here. Complete information is available in the Data notebook from the verification test available by special request from the EPA Project Officer.

VOC Analysis - The MS and MSD results from all batches of VOC samples met laboratory acceptance criteria. The recovery ranges are similar to those given for LCS checks; however, for the sake of brevity they are not reproduced here. Complete information is available in a data notebook compiled for the verification test and available by special request from the EPA Project Officer.

Surrogate Standards

Each VOC sample was spiked with a mixture of dibromofluoromethane, toluene-d8, and bromofluorobenzene. Recovery levels for these spiked compounds are calculated for each sample as an additional quality control measure. All recoveries for these three surrogate standards were within the normal recovery range encountered by the laboratory under normal instrument operating conditions.

Field Spikes

Cation Analysis - Field spikes containing the target cation compounds were prepared during the standpipe and Tyndall portions of the verification test. Laboratory analysis results are shown in Tables B-3. Recoveries range from 93 to 118 percent and the relative standard deviations are all less than or equal to 5 percent. The results show acceptable sample cation recovery from the field spikes.

Table B-3. Target Cation Field Spike Results

Location/Target Cation	Average (μg/L)	Recovery (%)	Precision (%RSD)
Standpipe			
Calcium	10,250	103	5
Iron	11,000	110	0
Magnesium	10,250	103	5
Potassium	9300	93	2
Sodium	9575	95	2
Tyndall			
Calcium	10,000	100	0
Iron	10,667	107	5
Magnesium	9883	99	1
Potassium	9850	99	1
Sodium	11,833	118	3

VOC analysis - Field spikes containing the target VOC compounds were also prepared during the standpipe and Tyndall portions of the verification test and results are shown in Table B-4. During the standpipe trials, an initial attempt at spike preparation was made by injecting a spike solution though the septa of VOA vials that were pre-filled with distilled water. Evidence of leakage through the septa was observed, so these samples were discarded. Alternatively, four replicate samples were drawn from the standpipe mixing tank just prior to filling the standpipe in order to derive a measure of overall sampling and analytical precision. Since the concentration level of the VOCs in the mixing tank was not known precisely, spike recovery for the standpipe samples could not be determined. Spikes at Tyndall were prepared in a different manner by filling VOA vials with distilled water, injecting 2 μl of chilled VOC spiking solution and then quickly topping off the VOA vials with distilled water and capping them.

The spike sample results from the standpipe show very rapid losses of vinyl chloride and ethyl benzene from the mixing tank. This loss was also observed in all of the vendor and reference samples. As a result, spike analysis results for these two compounds invalidate the use of these two compounds in the standpipe test matrix. Precision of the other four compounds ranges from 0 to 5 percent RSD and is acceptable. Tyndall recoveries range from 82 to 125 percent with the highest observed for vinyl chloride, further evidence of the difficulty associated with sampling and analysis of this volatile compound. Overall, the VOC recoveries are judged to be acceptable and within the anticipated range.

Table B-4 Target VOC Field Spike Results

Location/Target Cation	Average (μg/L)	Recovery (%)	Precision (%RSD)
Standpipe			
Vinyl Chloride	ND	--	--
MTBE	80	--	1
cis-1,2-DCE	76	--	2
Benzene	84	--	2
TCE	76	--	3
Ethyl Benzene	ND	--	--
Tyndall			
Vinyl Chloride	125	125	7
MTBE	89	89	7
cis-1,2-DCE	81	81	9
Benzene	87	87	8
TCE	82	82	8
Ethyl Benzene	82	82	11

Overall Summary of Quality Control Measures

The results of various quality control measures applied both in the field and in the laboratory and summarized in this appendix indicate that the quality of the data produced during this verification test is acceptable and at the level anticipated for an analytical laboratory that is proficient in carrying out the EPA standard methods for determination of cations by inductively coupled plasma atomic emission spectroscopy and VOCs by purge-and-trap followed by capillary-column gas chromatography/mass spectrometry.