

# Development and Preliminary Evaluation of a Cone Penetrometer-Based Method for *In Situ* Determination of Volatile Organic Compounds in Groundwater

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**Abstract:** We report the development of an *in situ* method for quantitatively determining complex mixtures of volatile organic compounds (VOCs) at low levels in groundwater formations. The method is based on the use of a novel *in situ* groundwater collection and sample purging device that is integrated into a cone penetrometer testing (CPT) push rod. This device, the QVAC (quantitative volatiles analysis for cone penetrometry), is used for quantitatively measuring complex mixtures of VOCs in groundwater at regulatory levels. A breadboard prototype QVAC probe made of stainless steel was tested in the laboratory to identify the optimal design parameters for a CPT-scale version. A full-scale prototype QVAC probe was integrated within a CPT push rod, with the use of miniature valves and a conductivity-based level sen-

sor to accurately sample and purge a 5.0-ml groundwater sample. Following transfer of the VOCs through thermostated stainless-steel tubing to the sorbent trap at the surface, on-line thermal desorption/gas chromatography with mass spectrometric detection is performed. We report the design of the probe, optimization of the operational protocol, and the results of laboratory and initial field testing in which the precision, carryover, and calibration sensitivity were examined. © 1997 John Wiley & Sons, Inc, Field Analyt Chem Technol, 1:239–247, 1997.

**Keywords:** volatile organic compounds; cone penetrometer; *in situ* analysis

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## Introduction

Conventional sampling techniques for volatile organic compounds (VOCs) in the subsurface are cumbersome, even when applied during on-site analysis. The media (e.g., groundwater) are physically transported to the surface from the sampling device (e.g., a bailer) and transferred to airtight glass bottles, or the sample is purged with an inert gas on-site. The VOCs are trapped on solid sorbent cartridges. Typically, the containerized or adsorbed VOC sample is then transported to a laboratory and analyzed by purge-and-trap gas chromatography/mass spectrometry (GC/MS) or by direct thermal desorption GC/MS, respectively. These methods remain problematic, even when holding times and protocols for sample preservation are strictly observed. Contamination and loss of analytes can arise from sorption or desorption on the sampling material surfaces, biodegradation, and volatilization during transport to the analytical laboratory. This latter issue has been reported to lead to values

that are low by one order of magnitude or more, a degree of accuracy that is unacceptable.<sup>1</sup>

The capability of performing the sample collection and analytical measurement in an on-line *in situ* system would reduce these problems. In the investigation of hazardous waste sites, cone penetrometer testing (CPT) has matured into a minimally intrusive, efficient, and cost-effective method for defining subsurface stratigraphy, for differentiating aquifer (high permeability) and aquitard (low permeability) materials, and for obtaining subsurface soil and water samples for analysis of contaminants.<sup>2</sup> In addition, CPT has been used over the last decade for a broad range of sampling and analytical techniques for the chemical characterization of the subsurface.<sup>3</sup> *In situ* chemical samplers can be driven into the subsurface by CPT to collect soil gas,<sup>4,5</sup> groundwater,<sup>6–14</sup> or soil samples<sup>15</sup> at depth, thus providing a means of determining the vertical and horizontal extent of contamination. Furthermore, CPT has also been used as a means of delivering various *in situ* subsurface sensor probes, including laser-induced fluorescence spectroscopy for organics,<sup>16–25</sup> x-ray fluorescence<sup>26,27</sup> and laser-induced breakdown spectroscopies<sup>28,29</sup> for heavy metals, gamma ray spectroscopy for radionuclides,<sup>30</sup> and optical and electrochemical sensors for chlorinated organics<sup>31</sup> and explosives,<sup>32</sup> respectively. The data obtained by CPT are primarily used to maximize the cost effectiveness and efficiency of installing subsurface monitoring systems. No soil or groundwater is produced by drilling, thus eliminating disposal needs and minimizing exposure of personnel. The only disturbance at the site is a small-diameter hole that can be sealed efficiently by grouting with bentonite cement.

We are developing a method based on a subsurface sampling probe that is directly interfaced to the analytical instrument at the surface for the accurate determination of VOCs in groundwater. Our goal is to maintain the integrity of the sample and to improve the accuracy of results obtained during on-site analysis. The QVAC method (quantitative volatiles analysis for cone penetrometry) is designed to isolate the groundwater from the subsurface media within the CPT rod, to purge the sample at depth, to quantitatively transport the analytes to the surface from depth, to preconcentrate the analytes, and to present the preconcentrated analytes to the analytical instrument. In previous work, we described the results obtained from testing the probe and transfer line materials used in the QVAC system.<sup>33,34</sup> The development of the QVAC method, including the probe design, fabrication, laboratory testing, and initial field testing, is described herein.

## Experimental Section

### Reagents

Standard aqueous solutions were prepared in the laboratory and used in simulated sampling scenarios to test the *in situ* samplers and the analytical instrumentation. Stock standards (multicomponent calibration mixtures of VOCs in

methanol) were obtained from Supelco (Bellefonte, PA). Working standards at  $\mu\text{g/l}$  levels were prepared by dilution of the calibration mixture into reagent water (Barnstead NanoPure). Blank standards were prepared from reagent water. An internal standard (e.g., benzene, 50  $\mu\text{g/l}$ ) was added to all working standards, blanks, and test samples. Aqueous standards were analyzed within 8 h of preparation. All aqueous standards were stored in septum-sealed amber glass vials at 4 °C in the dark until analyzed. Test samples (e.g., groundwater) were stored in sealed glass bottles at 4 °C in the dark and analyzed within 72 h of collection. Standard and sample solutions used to test the QVAC in the laboratory were loaded by syringe or through the test fixture (vide infra) into the QVAC purging chamber.

### Instrumentation

**Purge-and-Trap Gas Chromatography.** Standard conditions for purge-and-trap analysis as described in U.S. Environmental Protection Agency (EPA) Method 5030A were followed where applicable.<sup>35</sup> A purge-and-trap concentrator (Model 3000; Tekmar, Cincinnati, OH) with helium as the purge gas (40 ml/min) was used. Analytes were concentrated on a VOCarb 3000 trap (3.18-mm OD  $\times$  15.3 cm) obtained from Supelco (Bellefonte, PA). Either a gas chromatograph (Model 5890, Series II; Hewlett-Packard, Palo Alto, CA) equipped with electron capture/flame ionization detectors (GC-ECD/FID) and a DB624 (0.53-mm ID  $\times$  75 m) capillary column or a gas chromatograph (Saturn IV; Varian, Palo Alto, CA) equipped with an ion-trap mass spectrometric detector (GC/MS) and DB624 capillary column (0.32-mm ID  $\times$  60 m) were used for sample analysis on the basis of EPA Method 624.<sup>36</sup> The GC-ECD/FID was also used to implement EPA Method 601 for field samples that had been collected onto solid sorbent cartridges (6.35-mm ID  $\times$  15.3 cm) packed with Carboxen (100-mg bed volume) and spiked with an internal standard (e.g., benzene).<sup>37</sup> During initial field testing, VOCs from the QVAC were collected onto solid sorbent tubes, and groundwater samples were collected by bailer. Both types of samples were then analyzed by EPA Method 8260 at an independent laboratory (ITS Environmental Labs, Burlington, VT). ITS also performed measurements of turbidity on water samples with the use of standard methods.

**QVAC Probe.** A breadboard laboratory-scale prototype was assembled by using off-the-shelf stainless steel fittings and tubing. The full-scale prototype probe for use in CPT was machined by using grade 304 stainless steel. The remaining major components of the QVAC probe were obtained commercially, including miniature electrically actuated three-way valves (Model 407; Angar Scientific Co., Inc., Cedar Knolls, NJ), a conductivity-based liquid level sensor (HR-1031 Series Conductivity Probe Control Amplifier; Pepperrl & Fuchs, Inc., Twinsburg, OH), polypropylene/polyethylene (PP/PE) inlet frit material (Polymeric Corp., Reading, PA), and thermostated gas-phase sample transfer lines (Parflex Division of Parker-Hannifin, Inc., Ra-

venna, OH). Metallic inlet frits were custom designed and manufactured by Bladon International (Oak Brook, IL).

## Results and Discussion

### Prototype Design

The objective of this project is to develop an on-line *in situ* system for purge-and-trap analysis of groundwater samples that contain VOCs and to demonstrate analytical performance that is equivalent to accepted regulatory criteria. The requirements of EPA Method 5030A for purge-and-trap analysis were applied to *in situ* CPT by designing a groundwater sampler that contains a purging chamber within a CPT push rod that is connected to a trap at the surface by a thermostated transfer line. Method 5030A for purge-and-trap analysis specifies the design of the purging chamber, solid sorbent trap, and trap desorption unit.<sup>35</sup> For the *in situ* design described herein for the QVAC, the trap and desorber are off-the-shelf items that conform to the EPA requirements. For the purging chamber, the QVAC conforms to the EPA design except that the construction materials were made of stainless steel, and the total volume of gaseous headspace between the water column and trap (Table 1) is more than fourfold larger as a consequence of the volume contained in the transfer line. However, EPA Method 5030A states that “alternate sample purge devices may be used, provided equivalent performance is demonstrated” (*vide infra*).<sup>35</sup>

Unlike other designs intended for fixed installation in a monitoring well,<sup>38</sup> we designed our probe to be compatible with direct push technology, such as the CPT or GeoProbe. From an engineering standpoint, when developing CPT-resident instrumentation, one is encumbered primarily by the narrow diameter of the CPT rods. For example, we designed the QVAC to fit into the most common size of rods used in CPT, namely, 25.4-mm ID  $\times$  44.5-mm OD. Therefore, we initially examined the ratio of the gaseous headspace above the sample in the purging chamber to determine if there were analytical advantages to extending the purging chamber in the vertical direction and, in so doing, began to address the equivalent performance goal. Headspace-to-sample volume ratios of 2:1, 1:1, and 1:2 were tested in the laboratory-scale prototype (constant sample volume of 5 ml). The purging efficiency and the extent of sample carryover (i.e., be-

tween consecutive spiked samples and blank samples) were chosen as key performance indicators. As a test system, we chose benzene solutions (1–50  $\mu\text{g/l}$ ) and GC-FID analysis based on EPA Method 601. The relatively high aqueous solubility of benzene (1780 mg/l at 20 °C) made it a good choice for examining purging efficiency and carryover. We found that the 2:1 ratio provided efficient purging of the test solution (5  $\mu\text{g/l}$ ; in <5 min) as well as minimal (<5%) sample carryover into subsequent reagent water (blank) samples (Figure 1). The other headspace-to-sample volume ratios examined showed similar behavior for carryover but a gradual decrease in efficiency proportional to decreasing headspace volume (results not shown). Because samples loaded into the chamber typically were left quiescent for 5 min, we attribute this effect to the decreased amount of benzene vapor as equilibrium was approached (in accordance with Henry's Law) that was present in the low-volume headspaces when purging commenced.

In addition to demonstrating equivalent analytical performance, the QVAC must withstand environmental conditions in CPT during subsurface pushes not intended for normal applications of EPA Method 5030A. These conditions include rough handling by truck operators, severe vertical and horizontal stresses during pushes, high humidity, high concentrations of solids (i.e., silts and fines) in most samples, and transfer of analytes through tubings that can approach 50 m. Therefore, with the use of the breadboard prototype, we initially examined materials for the QVAC, including the purging vessel, a thermostated sample gas transfer line, and groundwater inlet frit.<sup>34</sup> For the transfer line, we found that stainless steel (grade 304 or 316) was superior to various Teflon® polymers (PFA, PTFE, FEP) as well as aluminum and nickel. Stainless steel consistently transported a range of VOCs at ambient (25 °C) and elevated (110 °C) temperatures and various humidities (0–50%) quantitatively (<90%). We also found that the loss of VOCs to the Teflon® transfer lines was a function of the decreasing aqueous solubility of the VOCs, and that outgassing of contaminants from Teflon® increases with increasing temperature—this latter behavior would prohibit the effective use of an electron capture detector. Purging vessel materials made of glass, Teflon®, and stainless steel were found to have equivalent performance characteristics during purge-and-trap analysis (i.e., extent of sample carryover between runs). We examined level sensors based on flotation, ultrasound, optical motion sensing, and conductivity; the conductivity sensor was chosen for its accuracy, small size, low cost, and reliability. For the sample-collection frit, current methods for groundwater sampling in CPT (e.g., those based on the bailer) filter the sample through a 50/50 PP/PE filter (with a pore size range of  $\sim$ 100–150  $\mu\text{m}$ ); we therefore adopted this filter for further development.

Additional considerations in CPT operations specifically affect the design of the transfer line. Lines must be 50% longer than the depth to be studied in order to allow enough slack during rod storage and handling. For example, the 50-m transfer line that we developed and tested is limited to

TABLE 1. Comparison of purging chamber specifications between EPA Method 5030A and the QVAC technique.

Parameter	5030A	QVAC
Sample volume (ml)	5	5
Water column depth (cm)	>3	5
Headspace volume (ml)	<15	63
Bubble diameter (mm)	<3	<3
Purge gas inlet distance	<5 mm from base of water column	Enters at base of water column
Purge gas flow rate (ml/min)	40	40
Purge time (min)	11	11

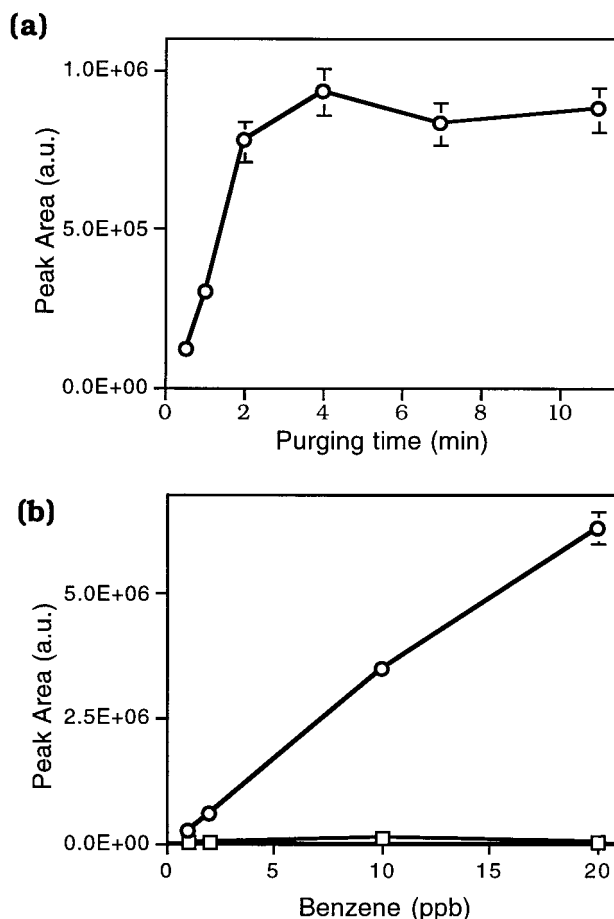


FIG. 1. Performance of 2:1 headspace-to-sample volume ratio with regards to (a) purging efficiency and (b) extent of sample relative percent carryover (squares) following a standard run (circles). GC-FID analysis of test samples (5-min purge cycle) containing 5  $\mu\text{g/l}$  benzene in reagent water ( $n = 5$ ).

a sampling depth of 35 m. A target maximum depth of 35 m was chosen to be capable of depth-profiling shallow aquifers in North America. The transfer lines must also be able to withstand a bend radius of 10 cm to provide slack in storage within the rod racks in the CPT truck. A bundle containing the VOC transfer line, heater, electrical lines for remote control, and helium purge gas line was fabricated to ease handling at the surface. Subsurface temperatures on the order of 15 °C necessitate the use of heat tracing to ensure efficient transport of the sample gas to the trap. Without heat tracing, condensation inside the lines during the purge cycle could be problematic. We found that a temperature of 50 °C conservatively accomplished the task of keeping the temperature of the transfer line above the dew point.<sup>33</sup> High-temperature-resistant insulated wiring was also used to prevent degradation of the insulation by the heating elements for the transfer line. The transfer-line assembly was designed to accommodate other wires, fiber-optic cables, and tubes that may be used simultaneously during a CPT push. A schematic diagram of the transfer-line assembly is shown in Figure 2.

#### Prototype Engineering

A schematic diagram of the CPT-scale QVAC probe is shown in Figure 3. The QVAC probe is machined as four separate pieces: (1) the sample section, (2) the insert sleeve, (3) the purge line insert, and (4) the inlet section. The sample section is the largest piece, containing the purge chamber (17.3 cm  $\times$  1.03 cm), purging line (1.59-mm OD), conductivity-level sensor, and connection to the thermostated transfer line (3.18 mm OD). A 60- $\mu\text{m}$  porous sintered nickel filter ( $\sim 3 \times 1$  mm) was welded to the end of the purging line to produce the small-diameter bubbles required by EPA Method 5030A (Table 1). The insert sleeve was machined separately for convenience, because it is eventually welded to the sample section. The main function of the sleeve is to house the purge line insert and receive the threaded inlet section. The purge line insert is the smallest piece, and it functions primarily to position the purge line at the base of the water column in the sample section. The inlet section has several functions, including alignment with the purge line insert, connection to the two miniature electrically ac-



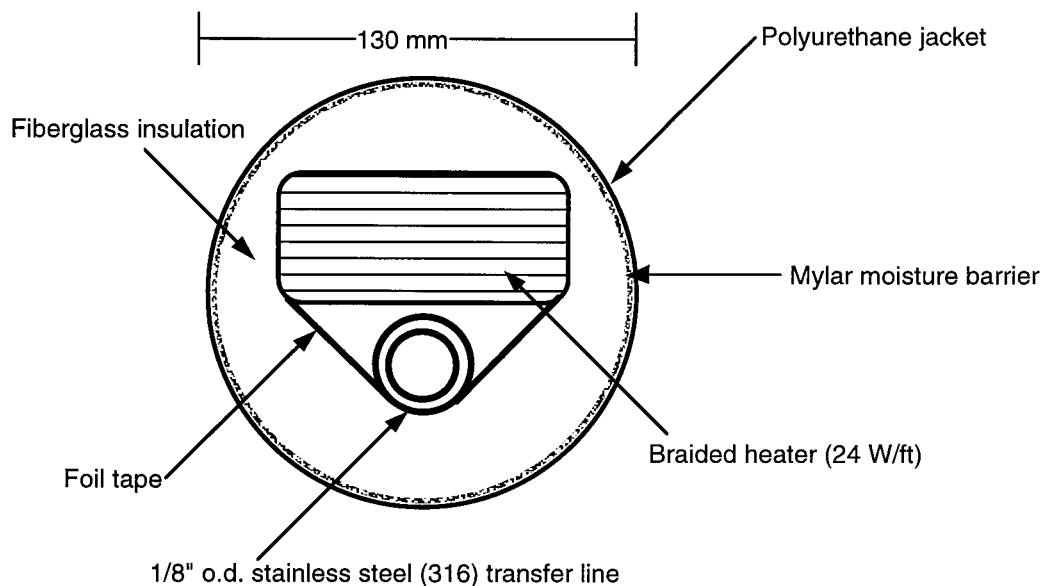


FIG. 2. Schematic drawing of the gas-phase sample transfer line (cross-sectional view) that connects the *in situ* purging chamber and the solid sorbent trap.

tuated three-way valves, inlet frit positioning, attachment of the groundwater inlet, and connection to the CPT rod. The probe is threaded on each end (male) to accept standard 44.5-mm-OD CPT rods. Vertical through holes were drilled through all sections to accommodate valve control wires and existing wiring that is used in the cone penetrometer tip for geophysical measurements. The probe is designed so that frit or valve replacement can be performed easily. The prototype QVAC probe has overall dimensions of 44.5 mm in diameter  $\times$  280 mm in length and weighs 3.5 kg.

The protocol for operating the QVAC is listed in Table 2. We estimate that the time required to collect, purge, and transfer each sample will be less than 25 min when using the current system. Purging time is specified in EPA Method 8260A at 11 min, and efficient transport of the purged VOCs at 40 ml/min to the trap at the surface through tubing with a total volume of 55 ml (3.18-mm OD, 0.51-mm wall thickness, and 15-m length) will take approximately 5 min. The greatest uncertainty lies in the estimation of sample collection time because this time depends on the hydrology of the site. We designed the QVAC for this step to occur within 5 min, depending on the porosity of the frit material, the hydrologic pressure, and the size and distribution of solid material. Note that the sample collection time for the QVAC is in stark contrast to conventional groundwater sampling techniques<sup>6,7</sup> that require larger (100 $\times$ ) volumes of sample. With a short time for sample turnaround, the reusable QVAC will have the capability to completely depth-profile an aquifer. More importantly, because of the low hydrologic pressure required to fill the purging chamber under typical conditions, the QVAC will also have the capability of sampling near the top of the water table, where light nonaqueous phase liquids

(LNAPLs) are found. Also, in contrast to other designs in which operations must be suspended while a sample chamber is lowered to the sampling point, the QVAC can be used without interruption during a single CPT push.

#### Prototype Laboratory Testing

In the present system, the analytical performance of the QVAC was compared with conventional EPA Method 8260A. For this work, samples of a standard VOC mixture were tested by using the QVAC without the heated transfer line to determine precision, carryover, and calibration sensitivity, as well as to optimize the operation of the QVAC. The effect of adding the transfer line on transfer efficiency, precision, carryover, and calibration range was then evaluated for various VOC samples. Rather than immerse the QVAC probe in varying depths of contaminated water, we affixed a small-volume water sample reservoir around the inlet frit (i.e., a leakproof glass/stainless-steel jacket), which could be pressurized to simulate various hydraulic pressures (i.e., depths below the water table). The test fixture for the probe could be slightly pressurized ( $< 5$  mm Hg) to force aqueous samples through the inlet frit, in this way simulating a subsurface hydraulic pressure. The effect of the frit composition and porosity on VOC recovery could also be examined in this way.

The results of this testing are summarized in Table 3, where the QVAC is evaluated in three configurations: (i) the QVAC probe in place of the standard purge vessel, directly connected to the thermal desorption GC/MS system (with samples loaded into the purging chamber by syringe); (ii) the QVAC probe connected to the trap by a 15-m stain-

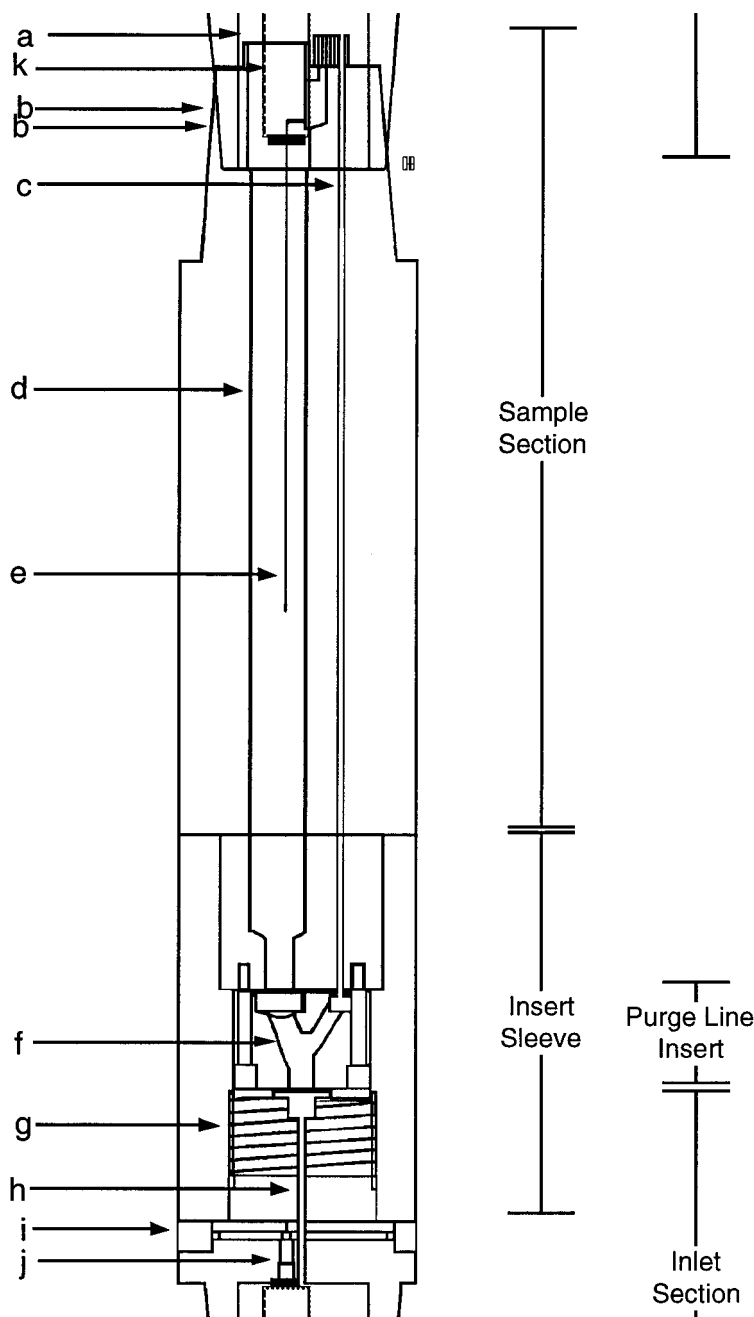


FIG. 3. Drawing of the QVAC to scale (1.0 in. = 1.5 in.) in cross section, where a = transfer-line connection, b = threading to CPT rods, c = purge gas line, d = sample chamber, e = level sensor, f = base of water column, g = inlet, h = conduit to inlet, i = inlet frit, j = valve manifold, and k = valve assembly.

less-steel (1.40-mm ID) transfer line maintained at a constant temperature of 50 °C (also with samples loaded into the purging chamber by syringe); and (iii) the QVAC probe in configuration (ii) but where samples are introduced through the inlet filtering frit near the base of the QVAC probe by

means of the pressurized sample reservoir. Results are presented for a set of 12 representative VOCs in the standard calibration mixture, as well as for benzene, to compare to the laboratory-scale testing (breadboard prototype) described above. Peak areas (for a selected quantitation ion for

TABLE 2. Steps in the operation of the QVAC method. V1 and V2 are separate two-position solenoid valves at the base of the QVAC.

Step	Function	Valve status	Purge gas	Timing (min)
Clean	Optional step used to force nitrogen from the surface to clean the frit.	V1 on/V2 off	Off	(Optional)
Fill A	Begin to collect groundwater sample through frit into purging chamber.	V1 on/V2 on	Off	0:00
Fill B	Conductivity-level sensor triggers closing of V1 when water column reaches a height of 5 cm.	V1 off/V2 on	Off	5:00 (estimated)
Purge	Complete purge gas (He) introduction from surface at 40 ml/min.	V1 off/V2 on	On	16:00
Transfer	Gas-phase VOCs transported to trap in analytical vehicle at surface.	V1 off/V2 on	On	20:00
Drain	Sample in the purge chamber drains through valve assembly into rod below.	V1 off/V2 off	Off	22:00
Rinse A	Optional step used to rinse purge chamber in situ with water from surface.	V1 on/V2 off	Off	(Optional)
Rinse B	Optional step used to drain the chamber rinsate.	V1 off/V2 off	Off	(Optional)

each compound) were normalized to an internal standard, and calibrations were made at 1, 10, 100, and 1000  $\mu\text{g/l}$  for each analyte. The range of variation in the reproducibility as measured by the *rsd* ( $n = 5$ ) increased slightly when the transfer line was added, and for the fixture. The degree of carryover was measured by running a blank following a 100-ppb sample. We observed that relative percent carryover (i.e., normalized blank signal following the 1000-ppb standard) was negligible for samples loaded by syringe into the purging chamber in configurations (i) and (ii), and that it rose to 1.5% when the sample was drawn through the inlet frit. We intend to examine other frit materials to minimize this behavior, although we expect that this low level of carryover will be considered tolerable if those efforts fail.

Table 4 lists the results that we obtained when testing the complete system (iii) for a set of 12 representative VOC standards. Precision was less than 10%, with 1,1-dichloroethene and tetrachloromethane (i.e., carbon tetrachloride) exhibiting the most variation. The efficiency of transport

through the 15-m stainless-steel transfer line ranged from 89.4 to 104%. Carryover was the final parameter examined, ranging from 0.08 to 1.36% for the 12 compounds, with tribromomethane skewing the range (average = 0.48%). No clear trends corresponding to the physical properties of the various VOCs were evident for carryover behavior.

#### Prototype Field Testing

The QVAC was field tested with the CPT on three separate occasions. The primary goal of these preliminary tests was to obtain data on operational performance of the hardware, for example, physical condition following CPT pushes and the ability to obtain water samples. During the first two field tests, PTFE, PP, and PE porous inlet filters were used. These polymeric filters are used on conventional subsurface groundwater samplers (e.g., bailers). The polymeric filters did not provide adequate flow of sample into the collection chamber—in some cases, the requisite 5.0-ml samples could not be collected after more than 30 min of exposure of the inlet to the aquifer.

The third test took place adjacent to the D Area Oil Seepage Basin at the U.S. Department of Energy's Savannah River Site. A geophysical profile was obtained by CPT, and the sampling depths were selected to correspond to permeable sandy horizons. An unconfined aquifer was present at a depth of approximately 2.6–8.5 m, with permeable sands interpreted to occur between 4.9 and 6.7 m. The soils were more silty and less permeable immediately above and below this interval. A total of 11 groundwater samples (5.0 ml each) were collected at two different locations, with depths ranging from 5.2 to 7.6 m. These depths were limited by site conditions and test objectives, not by the QVAC hardware. During the third test, we replaced the polymeric inlet frits with Bladon metallic frits. At a depth of 5.2 m, five consecutive samples were collected; the average collection time was 155 s, and the standard deviation was 3.19 s (2.06% *rsd*). The Bladon inlet proved to be far superior to the other inlet frits that we tested previously, with the average sample collection time equal to 178 s and a standard

TABLE 3. Comparison of analytical performance in laboratory testing of the CPT-scale QVAC. Syringe introduction was used for (i) direct interfacing the trap and (ii) separated by the 15-m transfer line (TL). In (iii), the sample was introduced directly using the test fixture. Precision measured at 100 ppb for (i) and (ii) ( $n = 5$ ) and (iii) ( $n = 2$ ). Relative percent carryover is measured for a blank following a 100-ppb standard. Sensitivity is normalized to an internal standard peak area. The value for benzene is shown above the range for the 12 components of the VOC standard mixture (listed in Table 4).

Test configuration	Precision (% <i>rsd</i> )	Carryover (%)	Sensitivity (counts/ppb)
(i) QVAC probe only	4.0 1.0–6.0	0.21 0.19–0.72	2.8 0.62–7.4
(ii) QVAC probe–TL	3.0 0.50–9.8	0.19 0.19–0.64	7.0 0.49–7.0
(iii) QVAC–TL–fixture	18 1.5–27	0.48 0.08–1.4	2.9 0.43–2.9

TABLE 4. Analytical performance comparison for individual VOCs in the test mixture. QVAC configuration as in Table 3 (iii). Carryover samples were introduced through the test fixture; other conditions as in Table 3.

Test Analyte	Efficiency (%)	Precision (%)	Carryover (%)
1,1-dichloroethene	104	9.4	0.36
Dichloromethane	100	4.3	0.50
1,2-dichloroethene	95	3.5	0.43
1,1-dichloroethane	95	0.50	0.40
Trichloromethane	91	2.3	0.50
1,1,1-trichloroethane	94	7.4	0.40
Tetrachloromethane	94	9.8	0.38
Benzene	98	3.0	0.37
Trichloroethene	93	1.5	0.38
Bromodichloromethane	97	4.2	0.62
Tetrachloroethene	89	4.6	0.08
Bromoform	95	8.5	1.4

deviation of 75.1 s ( $n = 11$ ). The collection period ranged from 106 to 342 s and was a function of the stratigraphy in that longer times ( $>300$  s) were observed in siltier formations. The turbidity of the groundwater at this location was measured at 35 nephelometric turbidity units (NTU); for comparison, water collected with a bailer sampler that used a PP/PE frit had a measured turbidity of 6.0 NTU. Nine of the 11 samples were collected during a single CPT push, thereby demonstrating the ability to profile an aquifer formation. However, for the nine samples collected at the first site, chemical analysis in an off-site laboratory showed no evidence of subsurface contamination.

At a second (nearby) location, samples were obtained with the QVAC at a depth of 5.8 m ( $n = 2$ ); collection times were 242 and 271 s. A conventional bailer sample was also collected at this depth, and the analytical results for both sample types are presented in Table 5. Direct comparison of the two sampling techniques can be misleading because the depth interval that is sampled with a bailer is approximately 20 cm, whereas the inlet frit on the QVAC probe is 1 cm in height. Nevertheless, the data for the QVAC method showed good precision (average of  $<10\%$  rsd for all but the highly

volatile vinyl chloride), and the values generally agree with the bailer sample with the notable exception of *cis*-1,2-dichloroethene, where a much higher concentration (150%) was found with the QVAC method. Current work is planned for further evaluation of the QVAC at sites of differing hydrology to define the analytical utility of this methodology. We also intend to evaluate VOC sensors for situations that do not require the amount and quality of information that EPA Method 8260A produces.

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TABLE 5. Comparison of field-test results obtained for the QVAC method and a conventional bailer sampler. Samples were collected at a depth of 5.8 m in adjacent ( $<1$ -m-distant) CPT boreholes. QVAC samples were purged for 20 min at 60 ml/min to ensure quantitative transport through the 50-m transfer line. Vapor pressure data are at 20 C in kilopascals. Trip blank concentrations (i.e., blank sorbent cartridges from the off-site laboratory that were not used in sampling) for the five analytes were less than  $2 \mu\text{g/l}$  for each sample type (nd = not detected).

Analyte ( $\mu\text{g/l}$ )	Vapor pressure (kPa)	QVAC samples ( $n = 2$ )					Bailer ( $n = 1$ ) ( $\mu\text{g/l}$ )	% $\Delta$
		Rep 1 ( $\mu\text{g/l}$ )	Rep 2 ( $\mu\text{g/l}$ )	Avg. ( $\mu\text{g/l}$ )	s	rsd		
Vinyl chloride	344	91	16	53	53	99%	$<120$	nd
trans-1,2-dichloroethene	34.7	4.3	4.7	4.5	0.24	5.4%	$<36$	nd
cis-1,2-dichloroethene	27.5	$1.8E + 03$	$2.2E + 03$	$2.0E + 03$	$2.7E + 02$	13%	$8.1E + 02$	150%
Trichloroethene	7.86	$3.9E + 02$	$4.1E + 02$	$4.0E + 02$	13	3.2%	$3.1E + 02$	29%
Tetrachloroethene	1.80	8.6	10	9.4	1.1	12%	18	—48%



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