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# *IN SITU* MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS IN GROUNDWATER BY METHODS COUPLED TO THE CONE PENETROMETER

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## ABSTRACT

The objective of this investigation is to interface an *in situ*, on-line sparging system with a cone penetrometer to provide direct analysis of volatile organic compounds (VOCs) in groundwater by on-site analysis. Transfer line materials (15 m x 0.160-0.216 cm ID) composed of stainless steel, nickel, aluminum and Teflon®PFA, PTFE, and FEP were evaluated for their ability to quantitatively transfer chloroform, 1,1,1-trichloroethane, carbon tetrachloride, tetrachloroethylene, n-hexane, benzene, toluene, and o-xylene in the gas phase. The water content of the gas stream had an insignificant effect on the quantitative transfer of VOCs through Teflon® tubing but was critical to quantitative transfer of the compounds through metal tubing, particularly for nickel. Transfer efficiencies for all 7 analytes in moist gas streams through stainless steel tubing were greater than 95%. Toluene, tetrachloroethylene, and o-xylene were transferred with 93, 81 and 80% efficiency, respectively when drawn through Teflon®PFA tubing at 25°C. The sorption of these VOCs by Teflon® tubing was reversible and their transfer efficiencies improved to 94% when the tubing was flushed with 16 equivalent volumes of air. In general, the retention of the VOCs by Teflon® increased with decreasing aqueous solubility of the analyte. The efficiency at which VOCs were sparged from aqueous standards in Teflon®PFA, Type 304 stainless steel, and glass vessels were similar. These results have provided the technical basis for the design of an *in situ*, on-line sparging system in which (1) the sample is drawn into a stainless steel sparging vessel in the cone

penetrometer under a slight vacuum, (2) an optical level sensor controls sample collection and initiation of the purge cycle, (3) a stainless steel transfer line efficiently transports the VOCs to the surface, (3) the VOCs are preconcentrated at the surface on a mixed bed of porous and solid carbon sorbents, (4) the sample is desorbed on-site into an instrument for quantitative analysis, and (5) the transfer line and sparging vessel are backflushed with an inert gas to purge the system and drain the vessel for additional sample collections.

## INTRODUCTION

The coupling of sampling and analysis methods and technologies to a cone penetrometer is a minimally intrusive, efficient, and cost-effective means for obtaining information on the levels of contaminants in groundwater, soil, and soil gas. On-site analysis of samples collected by this methodology has been demonstrated to facilitate the characterization of sites by making real-time, interactive sampling decisions possible. Devices that isolate the contaminants from groundwater and soil within the cone penetrometer and are directly linked to analytical instrumentation at the surface would further increase the speed and accuracy of on-site analysis. The overall goal of our investigation is to develop methods and technology that can be interfaced with a cone penetrometer and field-deployable instrumentation, including gas chromatography/mass spectrometry, to directly transfer volatile organic compounds (VOCs) and semi-volatile organic compounds from subsurface material at depth to the analytical instrument in the field.

This manuscript describes (1) the evaluation of materials that will be used to construct an *in situ*, on-line sparging system, (2) the testing of a laboratory scale prototype, and (3) the design of a miniaturized version of a sparging system that can be interfaced with a cone penetrometer. The critical aspect of this approach is the quantitative sparging and transfer of VOCs from the groundwater to the preconcentration

device at the surface. The transfer efficiencies of several VOCs through tubings consisting of Type 304 and 316 stainless steel, nickel, aluminum, and Teflon®PFA, PTFE, and FEP were evaluated. Sparging vessels were constructed of Teflon®PFA and Type 304 stainless steel and their performance was compared with a glass sparging vessel. The results provided the technical basis for construction of a laboratory scale prototype and design of a miniaturized version for the cone penetrometer.

## EXPERIMENTAL SECTION

Transfer efficiencies for VOCs through 15 m lengths (0.160-0.216 cm ID) of the tubings were evaluated by using a dynamic dilution system in which a certified gas standard containing chloroform, 1,1,1-trichloroethane, carbon tetrachloride, tetrachloroethylene, n-hexane, benzene, toluene, and o-xylene is mixed with air that is saturated with water at 25°C. The concentration of the target analytes generated by the apparatus is determined by the analysis of samples collected on graphitized carbon black directly from the dilution manifold. The transfer line is then attached to the manifold, and five, 100 mL volumes of gas are drawn through the tubing at 25 mL $min^{-1}$ and collected on graphitized carbon black. The tubing is then purged with 2, 100 mL volumes of clean air. The transfer efficiency is operationally defined as the total mass transferred through the tubing in the 5 volumes of the diluted gas standard plus the 2, 100 mL volumes of purge air. A 200 mL volume of purge air should theoretically be able to exchange 98-100% of the air within the tubings that were evaluated. Transfer efficiencies were determined with the gas stream containing two different concentrations and mixtures of VOCs, (1) 0.07 ng $mL^{-1}$ of chloroform, carbon tetrachloride, and tetrachloroethylene and (2) 0.50-1 ng $mL^{-1}$ of chloroform, carbon tetrachloride, 1,1,1-trichloroethane, tetrachloroethylene, n-hexane, benzene, toluene, and o-xylene. Experiments were also performed in which the Teflon®PFA tubing was heated. The FID

response of 100 mL of air saturated with water that had been drawn through Teflon®tubing at 30, 60 and 110°C was measured.

Transfer efficiencies of the materials were further evaluated by purging in succession 3, 10 mL aliquots of a 10 ppb aqueous standard of the VOCs directly from a glass sparging vessel through Teflon®PFA and Type 316 stainless steel tubings at 40 mL $min^{-1}$ into a purge-and-trap concentrator. An additional sparging of the last aliquot was used to determine the amount of the VOCs remaining in the transfer line.

Teflon® and stainless steel were also evaluated as materials for sparging vessels. A metal sparger was made from a 75 mL Type 304 stainless steel gas sampling cylinder and Type 316 stainless steel fittings. A 40 mL Teflon® sparger was constructed from 2.667 cm OD Teflon®PFA pipe and fittings. Helium purge gas entered the base of the vessels through a 20.0 μm Type 316 stainless steel frit pressed into a short length of 0.635 cm OD tubing. Both vessels were designed and constructed to readily attach to a purge-and-trap concentrator. Aqueous standards were sparged for 11 min at 40 mL $min^{-1}$. Recoveries were determined and compared to those obtained with a glass sparging vessel.

A laboratory-scale prototype of the *in situ* sparging device was constructed of Type 316 stainless steel fittings and pipe (1.04 cm ID). The flow of water into the vessel was controlled by a solenoid valve which was electrically wired to an ultrasonic liquid level switch. When the desired volume of water had been transferred, helium purge gas entered the vessel at 40 mL $min^{-1}$ through 1.59 mm OD x 1.27 mm ID tubing . The sensitivity of the sparging efficiencies of aqueous standards of benzene to purge time and several different vessel headspace-to-sample volume ratios as recommended by EPA Methods 601 and 602 were evaluated.

## RESULTS AND DISCUSSION

Transfer efficiencies for chloroform, carbon tetrachloride, and tetrachloroethylene through metal tubing at concentrations of 0.07 ng $mL^{-1}$ were sensitive to the amount of water in the gas stream, especially for nickel tubing. All three analytes were totally absorbed from a dry gas stream by the nickel tubing. Transfer efficiencies for chloroform and carbon tetrachloride through nickel improved to 90 and 98%, respectively in moist air but were only 2% for tetrachloroethylene. The three analytes were transported in a moist air with >95% efficiency when drawn through the aluminum and stainless steel tubing. Water had no effect on the efficiency of VOC transfer through Teflon tubings. Transfer efficiencies for chloroform and carbon tetrachloride through Teflon®PTFE lined stainless steel, Teflon®PFA and Teflon®FEP tubings were greater than 92% but only 80-87% for tetrachloroethylene. Carbon tetrachloride and tetrachloroethylene were transported less efficiently through Teflon®PTFE tubing, that had a wall thickness of 0.158 cm, than through Teflon®PTFE lined stainless steel with a 1 μm thick film of PTFE deposited on its interior surface.

Transfer efficiencies for all the analytes at levels of 0.5-1 ng $mL^{-1}$ in moist air through Type 316 stainless steel at 25 and 110°C were nearly 100%. Toluene, tetrachloroethylene, and o-xylene were transported with 93, 81 and 80% efficiency, respectively, when drawn through Teflon® PFA tubing at 25°C. Transfer efficiencies for the the other analytes were 100%. Purging the tubing with 500 mL of clean air improved the efficiences of toluene, tetrachloroethylene, and o-xylene to greater than 94%.

Tests to evaluate the effect of heating the Teflon®PFA tubing to improve transfer efficiencies indicated that a complex mixture of compounds with boiling points less than approximately 60°C were emitted from the tubing. FID response factors of hexane and chloroform were used to evaluate the magnitude of the individual contaminants that off gassed from the tubing in this boiling point range. Levels of VOCs in 100 mL of purge air increased from about 1 to 5 ng of hexane and 5 to 50 ng of chloroform when the temperature of the tubing was increased from 30 to 110°C. The complex mixture of

contaminants released from the tubing at 110°C saturated the ECD detector over the entire elution range of the analytes on a DB-624 capillary column indicating that the contaminants were probably halogenated.

Tests in which 3, 10 mL aliquots of a 10 ppb aqueous standard were purged in succession from a glass sparging vessel through the Type 316 stainless steel and Teflon®PFA transfer lines indicated that some of the VOCs were sorbed by Teflon® and confirmed the results obtained with the dynamic dilution apparatus. Recoveries were 96, 95 and 94% for toluene, o-xylene and tetrachloroethylene, respectively, from Teflon and 99, 98 and 99%, respectively, from stainless steel.

The efficiencies of sparging aqueous standards of the analytes in vessels constructed of glass, Teflon® and stainless steel vessels were similar. Based upon the results of the transfer line experiments, some uptake of tetrachloroethylene onto the Teflon® vessel was expected. However, the VOCs are exposed to a Teflon surface in the sparging vessel that is 7 times less in area than the interior surface of the Teflon®PFA transfer line. Also, a larger volume of gas is used to sparge the sample in the vessel (440 mL) than was used to calculate recoveries in the transfer line experiments (200 mL).

Results from these experiments indicated that toluene, o-xylene and tetrachloroethylene partition into Teflon® polymers. These VOCs and n-hexane are the least water soluble of the analytes that were tested. n-Hexane which is the least water soluble of this group was not retained, however it is also the least polar. Consequently, predictions of the sorption of VOCs by Teflon® cannot be based solely on their aqueous solubility. The uptake is reversible and the amount of air necessary to purge the VOCs from Teflon® depends upon the surface area and thickness of the polymer. Unlike the relatively, nonspecific sorption of the analytes by Teflon®, active sites on metal surfaces appear to be responsible for sorption of VOCs. The sites apparently have a greater affinity for water because sorption of the VOCs can be reduced by adding water to the gas stream.

These results provided the technical basis for designing a laboratory scale prototype of the *in situ* sparging device. The sparging efficiency of laboratory prototype vessels with headspace to sample volume ratios of 2:1 and 1:1 were identical. Tests with an ultrasonic water level sensor indicated that the inflow of water and purge gas to the vessel could be conveniently controlled by wiring the sensor to two solenoid valves.

Results from the evaluation of the materials and testing of the laboratory scale prototype provided the information needed to design a miniaturized version of the sparging vessel for the cone penetrometer. The design incorporates the following features, (1) a narrow stainless steel vessel with a 1:1 headspace to sample volume ratio in which the purge gas enters the base of the vessel through a stainless steel frit to optimize sparging efficiency by maximizing the contact between the purge gas and water, (2) the ability to draw the sample into the vessel under a slight vacuum to facilitate sample collection, (3) control of the collection of a known volume of the sample and initiation of the purge cycle by an optical water level sensor electrically wired to two solenoid valves, (4) a heated, stainless steel transfer line to efficiently transport the VOCs to the surface, (5) preconcentration of the VOCs at the surface on a mixed bed of porous and solid carbon sorbents, (6) on-site desorption of the VOCs into an instrument for quantitative analysis, and (7) a backflush cycle in which the transfer line is purged and sparging vessel is drained in preparation for additional sample collections.

## CONCLUSIONS

Type 304 and 316 stainless steel is superior to the Teflon® polymers as materials for an on-line, *in situ* sparging system for the cone penetrometer. Transfer efficiencies of several VOCs through stainless steel were nearly 100%. In general, the transfer efficiencies of the VOCs through Teflon® decreased with decreasing aqueous solubility of the analyte. The sorption of VOCs by Teflon® is reversible. However, the volume of gas required to completely recover the analytes greatly exceed the internal volume of the

tubing and will decrease the speed of sample collection and complicate the preconcentration of VOCs at the surface.

A miniaturized version of an *in situ* , on-line sparging system has been designed in which collection of the sample and initiation of the purge cycle is controlled by providing electrical contact between an optical level sensor and two solenoid valves. The sample enters a stainless steel vessel under slight vacuum and is purged with an inert gas that enters the base of the vessel through a stainless steel frit. The VOCs are transported to the surface through a heated, stainless steel transfer line.

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