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Use of Electrolytically Generated Hydrogen as a Purge Gas for the Isolation of Volatile Organic Compounds from Groundwater

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ABSTRACT

A device has been developed for use in determining parts per billion concentrations of volatile organic compounds in groundwater. This device is suitable for field use either as a self-contained, portable instrument or as an unattended monitor. The device consists of an immersible electrolysis cell in which hydrogen is generated. This hydrogen efficiently purges volatile organic compounds from water. Those volatile organic compounds are carried by the purge gas to a photoionization detector where their total concentration is measured. The significant advantages of this apparatus for use in the determination of volatile organic compounds include: 1) measurements are made in a hydrogen matrix which is free of interfering species present in water; 2) detection limits for volatile organic compounds are several orders of magnitude lower when compounds are purged from water than when they are measured in the headspace above water; 3) operation of this device does not require use of reagents or utilities other than electricity, which can be supplied by batteries; 4) the device can be readily configured such that it will fit in a small diameter sampling well; and 5) if used as a monitor in a sampling well, the only required connections with the surface would be signal and power lines. This device has a detection limit of less than 5 ppb for benzene. For 23 other organic compounds tested, response factors ranged from 0.1 to 1.5 times that for benzene. The device appears especially well-suited for use in monitoring the concentration of gasoline in groundwater in the vicinity of underground storage tanks.

INTRODUCTION

There is an increasing need for reliable and accurate methods for field or in-situ measurement of the concentration of volatile organic compounds such as gasoline and solvents in groundwater. Accurate and reliable inert gas purging-gas chromatographic methods are routinely used in the laboratory for determining volatile organic compounds in groundwater (1–10). In these methods, volatile compounds are purged from an aqueous sample with an inert gas such as helium and are then determined by gas chromatography.

To meet the need for a field monitor, a device was conceived in which the principles of well-established laboratory methods were transferred to a portable device. This concept contained the novel innovation of purging volatile organic compounds from water with electrolytically generated hydrogen rather than an inert gas such as helium. This innovation would eliminate the need for gas cylinders and associated gas transfer and regulation devices. The only utility required would be electricity supplied by a battery. Although other detectors could be used to determine the volatile materials purged from water, in the present work a photoionization detector was selected because it also requires only electricity, which again can be supplied by a battery.

EXPERIMENTAL

Electrolysis Cell. The cell for stripping volatile organic compounds from water using electrolytically generated hydrogen as the purge gas is depicted in Fig. 1. A diagram of the entire prototype apparatus is shown in Fig. 2. A modified 43-mm plastic Buchner funnel was used as the collector. A layer of twenty-mesh stainless steel screening material wrapped around the outside of the cell served as the anode. A twenty-mesh Nichrome screening material rolled into a spiral inside the cell served as the cathode. A fiberglass cloth, sold commercially for the repair of automobile bodies, was used as a spacer between the anode and cathode. Voltage was usually applied to the electrodes using a Hewlett-Packard power supply operating at either 30 or 60 V, but a series of batteries was used in some instances.

Detector. An HNU Model PI-52-02 photoionization detector was used as a monitor for the compounds tested. A standard 10.2 eV lamp was used during most studies. An 11.7-eV lamp was used in attempts to determine selected compounds. Output from the detector was recorded using a Fisher Series 5000 strip chart recorder.

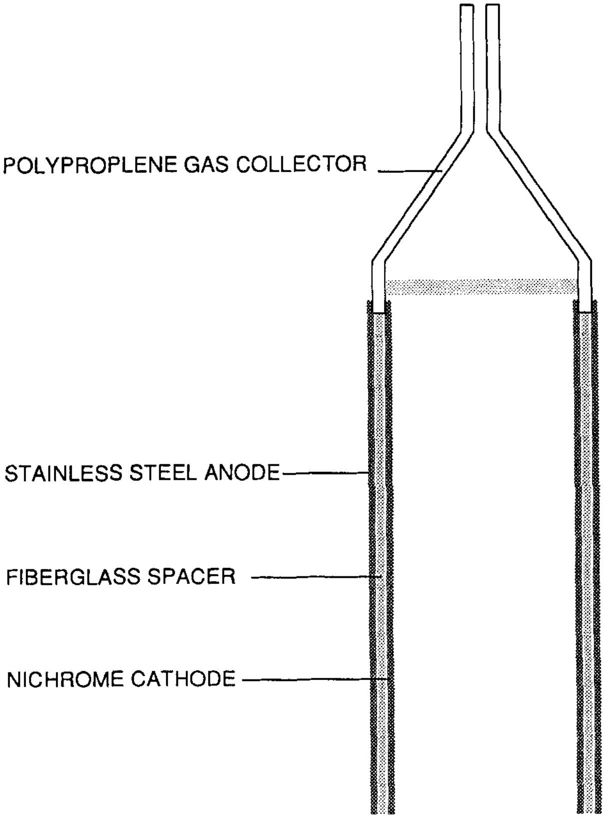

FIG. 1 Cell for the electrolytic generation of hydrogen.

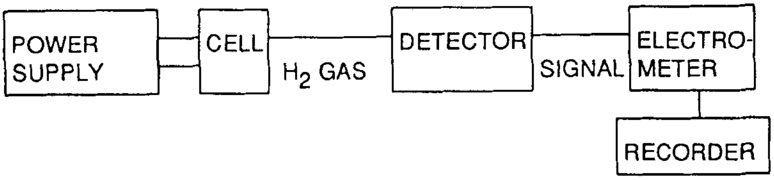

FIG. 2 Block diagram of the apparatus.

Chemicals. Commercially prepared standards (Supelco) having concentrations of either 100 or 500 μg/mL were used in most tests. For those compounds for which standards were not commercially available, concentrated standards were prepared by adding an appropriate amount of compound to methanol.

Water. Several different natural and prepared water samples were evaluated to determine the effect of inorganic constituents on the purging of volatile organic compounds. Tap water from Iowa State University (ISU), untreated well water from the Slater, Iowa, untreated well water from a limestone formation, and distilled water containing various levels of sodium chloride, sodium sulfate, and calcium carbonate were evaluated.

Test Procedure. The electrolysis cell was connected to the detector using $\frac{1}{8}$-in. PTFE tubing. The cell was immersed in 325 mL of water in a 400-mL beaker, and voltage was supplied to the electrodes from the power supply. The recorder was turned on and the signal was observed for a few minutes until it stabilized, which indicated that all air had been flushed from the system by the electrolytically generated hydrogen. A volume of a methanol solution of a test compound producing a concentration of 50 μg/L (ppb) in 325 mL water was then injected. Purging was then allowed to proceed for about 10 to 20 minutes until all of the analyte had been stripped from the sample and a stable baseline was reestablished. A sample containing 50 ppb of benzene was run during each series of tests, and the area contained under the peak for each test compound was compared with that for benzene in order to obtain a comparative response factor. The time required for the maximum signal to be obtained was compared with that for benzene to obtain relative stripping times.

RESULTS AND DISCUSSION

Development of the Electrolysis Cell. The basic elements of a cell for the generation of hydrogen gas are well known. Cells for the production of commercial quantities of hydrogen generally consist of nickel anodes and cathodes separated by a spacer fabricated from asbestos. Laboratory-scale devices often use platinum electrodes. In this work it proved impractical to use either platinum or nickel electrodes because commercial vendors quoted long times for the custom fabrication of platinum and nickel screens. Experiments were performed with several electrode materials, and results indicated that both stainless steel and Nichrome electrodes resulted in essentially the same rate of hydrogen generation as could be obtained using platinum. However, it was also observed that the use of Nichrome anodes resulted in dissolution of electrode materials and formation of flocculent precipitates that fouled the cell, and a similar dissolution and fouling occurred if stainless steel was used as the cathode material. The use of Nichrome cathodes and stainless steel anodes led to no serious dissolution or fouling problems.

The use of asbestos spacers was undesirable because of safety considerations. A spacer material was required that was stable and permeable to ions. A number of alternatives were investigated. Of these, only chamois leather and a fiberglass automobile body filler cloth were found to perform adequately. Most other fiberglass, plastic, and leather products tested partially dissolved after prolonged use.

Effect of Water Constituents on Electrolysis. A major concern was that hydrogen generation would vary with the ionic strength of the sample. Variations in the rate of hydrogen generation would lead to variations in the rate at which organic materials were purged from water. However, tests in the laboratory with solutions containing varied levels of sodium sulfate, calcium carbonate, and sodium chloride showed that essentially identical amounts of hydrogen were evolved regardless of the nature or the concentration electrolyte. In these tests a potential of 30 V was applied to the cell, and it was concluded that this potential dwarfed the effects from variations in ionic strength.

It was also found that ISU tap water, untreated water from Slater, Iowa, well water from a limestone formation, and a distilled water solution containing 2% sodium sulfate all yielded the same rate of hydrogen generation. However, significant amounts of unidentified volatile organic materials were stripped from both the ISU and Slater water samples, whereas the water from the limestone formation gave essentially no blank. Rather than pretreating solutions by stripping to remove interfering organic compounds before adding test compounds, water from the limestone formation was used in all tests.

Detection of Model Compounds. The compounds tested using this technique with a 10.2-eV photoionization detector are listed in Tables 1 and 2. Those listed in Table 1 were detected at 50 ppb concentrations, and those in Table 2 were not detected. Detection of a compound indicated that it was purged from water and was ionized in the detector. However, if a compound was not detected, that could either indicate that it was not purged from water, that it was purged from water but was not ionized, or both.

The lack of detection for acetonitrile, ethyl acetate, methyl ethyl ketone, propylamine, pyridine, tetrahydrofuran, and methanol was anticipated. Because of their high affinity for water, these were not removed by purging.

The low relative response factors shown in Table 1 for bromoform and bromomethane, and the lack of response shown in Table 2 for bromodi-

TABLE 1

Relative Response Factors and Purge Times for Compounds Present in Water at 50 ppb Isolated Using Electrolytically Generated Hydrogen and Detected Using a 10.2-eV Photoionization Detector

Compound	Boiling point (°C)	Relative response factor (benzene = 1)	Relative purge time (benzene = 1)
Bromoform	150	0.3	0.8
Bromomethane	4	0.1	0.8
Chlorobenzene	132	0.6	0.9
Chloroethyl vinyl ether	109	0.7	0.8
Cyclohexane	81	0.9	0.8
Dibromochloromethane	120	0.2	0.9
1,2-Dichlorobenzene	179	1.2	0.8
1,3-Dichlorobenzene	172	1.0	0.8
1,1-Dichloroethene	30	3.0	1.0
cis-1,2-Dichloroethene	60	0.9	0.9
trans-1,2-Dichloroethene	48	2.1	0.9
1,2-Dichloroethene (80% *trans*, 20% *cis*)	—	1.7	1.0
1,2-Dichloropropene	75	0.6	0.7
1,3-Dichloropropene	106	0.6	0.9
Gasoline	—	1.5	0.9
n-Heptane	98	1.3	0.8
Isooctane	98	1.2	0.8
Tetrachloroethene	121	0.7	0.9
Thiophene	84	1.0	1.0
Toluene	111	1.1	1.1
Trichloroethene	87	1.0	0.9
Vinyl chloride	−14	1.2	0.7
Xylene	137	1.1	1.8

TABLE 2

Compounds Present in Water at 50 ppb Not Detected When Isolated Using Electrolytically Generated Hydrogen and Using a 10.2- or 11.7-eV Photoionization Detector

Compound	Boiling point (°C)	Compound	Boiling point (°C)
Acetonitrile	82	Propylamine	48
Bromodichloromethane	87	Pyridine	115
Carbon tetrachloride	77	1,1,2,2-Tetrachloroethane	147
1,2-Dichloroethane	83	Tetrahydrofuran	67
Ethyl acetate	77	1,1,1-Trichloroethane	75
Methyl ethyl ketone	80	1,1,2-Trichloroethane	110

chloromethane, carbon tetrachloride, tetrachloroethane, and trichloroethanes, resulted because the 10.2-eV source used has insufficient energy to efficiently ionize most aliphatic compounds having four or less carbon atoms and their halogenated homologues. These compounds were, in fact, efficiently purged from water by electrolytically generated hydrogen, but were inefficiently ionized by the detector.

In an attempt to determine those compounds in Table 2, a higher energy 11.7-eV source having an almost universal response for organic compounds was used. The 11.7-eV source proved to be far less sensitive than the 10.2-eV source, and gave no response at 50 ppb concentrations. At much higher concentrations (i.e., ppm levels) an 11.7-eV source was suitable for the detection of saturated halogenated organic compounds, but no need was perceived for determinations at such high levels.

Effect of Experimental Variables on the Detection of Volatile Organic Compounds. Experimental curves obtained for benzene and four chlorinated hydrocarbons are depicted in Fig. 3. Small differences in the shapes of these curves arise because of differences in the rate of diffusion of the compounds into the cell and the rate at which they are purged from water by hydrogen. More pronounced effects were observed in the curve for benzene when the thickness of the fiberglass spacer was varied. When a single layer of fiberglass was used, peaks due to benzene became sharper and the total time for stripping decreased slightly. When multiple layers of fiberglass were used as a spacer, the benzene peak became flatter and stripping times increased.

After several hundred determinations were performed, it appeared that calcium carbonate and iron hydroxide were deposited on the fiberglass spacer, which reduced the rate of diffusion through the cell and slightly flattened the response vs time curves. In the present work, the deposition of salts on the spacer had no serious effect on the performance of the device, but if a device were used as an unattended, in-situ monitor in water containing high levels of calcium carbonate or iron, a more porous spacer or periodic cleaning might be required.

Long-Term Stripping of Benzene from Water. An experiment was performed to determine if electrolytically generated hydrogen could be used for an extended period to strip benzene from water. In this experiment, the cell was immersed in 16 L water containing 62 ppb benzene, and purging was performed for 9 hours. A maximum response was observed after 1 hour, and all benzene had been depleted from the container after 9 hours.

Comparison of Stripping with Headspace Analysis. Commercial instruments are available in which a photoionization detector is used to determine total hydrocarbons in the air (headspace) above groundwater

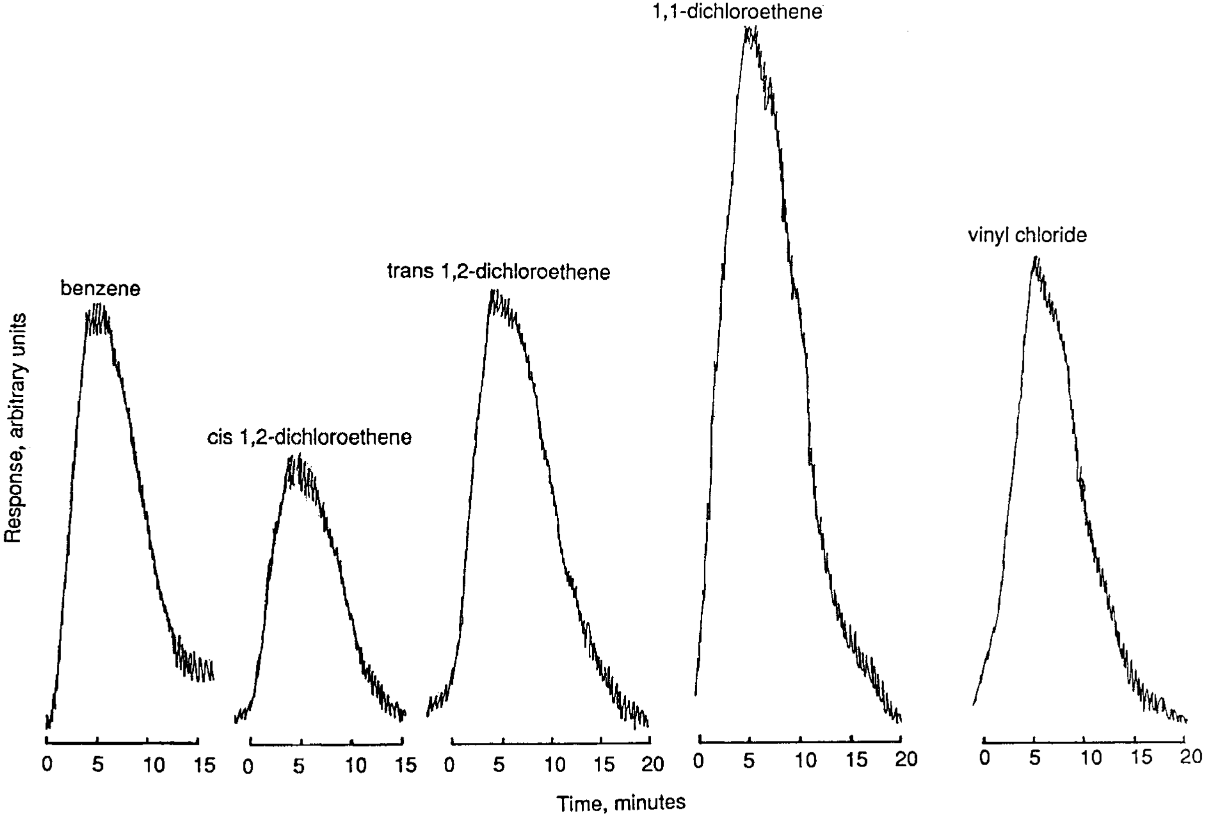

FIG. 3 Response to 50 ppb each of benzene, *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, 1,1-dichloroethene, and vinyl chloride purged from water with electrolytically generated hydrogen and detected using a photoionization detector with a 10.2-eV source.

as an indication of hydrocarbon contamination. In the present work, samples of air above a container containing 50, 100, and 1000 ppb benzene were drawn into a syringe and injected directly into the photoionization detector. No response above the background noise level of 3 arbitrary units was observed. In contrast, purging a solution containing 50 ppb benzene with hydrogen consistently gave a response of 40 arbitrary units with the same background noise level of 3 units.

It is, of course, not surprising that purging would result in much higher levels of benzene in the vapor phase than are present in the headspace above water. However, current regulations require remediation when water contains more than 50 ppb benzene. Headspace analysis with this photoionization detector appears incapable of detecting benzene at concentrations of 1000 ppb, whereas purging with electrolytically generated hydrogen provides a means for detecting levels as low as 5 ppb.

CONCLUSIONS

The present work has demonstrated that the innovative concept of using electrolytically generated hydrogen as a purge gas results in near quantitative isolation of compounds from water into the vapor phase, and resulted in a prototype device which could be employed, with few modifications, as a monitor to determine if harmful amounts of gasoline have leaked from underground storage tanks. Purging with hydrogen from a gas cylinder or helium would provide the same enhanced detection limit, but a battery-powered device producing hydrogen by electrolysis would be more convenient for field use, far more portable, and could readily be used in deep sampling wells.

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