Bull. Environ. Contam. Toxicol. (1988) 40:244–248

Bulletin of Environmental Contamination and Toxicology

Analysis of Gasoline in Water Using a Stripping Preconcentration Procedure

Frederic Belkin and Michael A. Hable

US Army Environmental Hygiene Agency, Organic Environmental Chemistry Division, Aberdeen Proving Ground, Maryland 21010-5422

Gasoline, which is widely produced, transported and consumed in our society creates a high potential for environmental contamination to water supplies. The sources of the gasoline pollution are typically from leakage of old underground storage tanks, losses in transit and during product usage. Leakage of gasoline from underground tanks may require the drilling of monitoring wells and sampling a number of sites to determine the outline of the plume.

Monitoring for gasoline contamination in drinking water wells requires an analysis procedure capable of detecting parts per billion (ppb) levels of gasoline in water. A number of solvent extraction and stripping preconcentration procedures are reported in the literature (Nunez et al. 1984; Karasek et al. 1981). Traditional solvent extraction procedures for hydrocarbons in fuels are good for identification (Murray and Lockhart 1981; Roberts and Thomas 1986).

However, in solvent extraction procedures only an aliquot of the total concentrate is injected into and analyzed by gas chromatography. Low ppb detection limits may not be achieved with small water sample volumes. Stripping-thermal desorption procedures offer the highest possible concentration factor since the total volatile contaminant in a water sample is collected, desorbed, and analyzed.

This study was conducted to determine the applicability of using a stripping preconcentration procedure to measure low levels of gasoline in water.

MATERIALS AND METHODS

Test samples were prepared by fortifying laboratory tap water with known concentrations of unleaded gasoline obtained from a local service station. A 2 uL injection of a 44 ng/mL standard of 1-chlorohexane (Coleman et al. 1984) obtained from Pfaltz

Send reprint requests to Frederic Belkin at the above address.

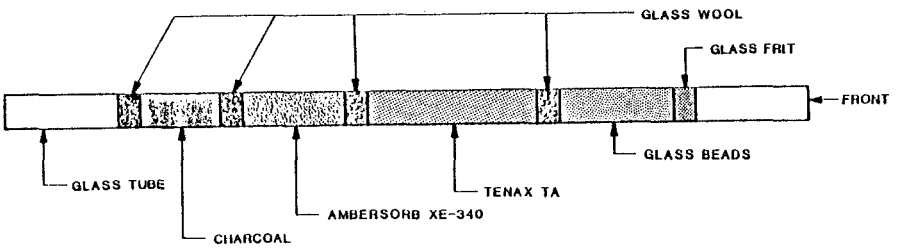

Figure 1. Multicomponent Collection Tube

and Bauer, Inc., was added to the fortified sample. All solutions containing 1-chlorohexane and gasoline were diluted with carbon disulfide (EM Science).

The fortified water sample (15-mL) was sparged (purged and trapped) from a 15 x 150 mm glass sparging vessel installed in the oven of a dynamic thermal stripper (Belkin and Esposito 1986). The air temperature of the oven was set at 50° C, and 20 min were allowed for the water temperature to equilibrate. The sparge gas used to strip the volatiles from the water and the "dry" gas used to prevent water condensation in the collection tube both had flow rates on 50 mL/min nitrogen. The block and tube heater temperatures were set at 130° C and 50° C, respectively. The volatile analytes from the water samples were collected on a 20.5 cm glass tube (7 mm o.d. x 4 mm i.d.) containing 250, 100, 150 and 50 mg of glass beads, Tenax®-TA, Ambersorb® XE340 and charcoal (Figure 1). To prevent water vapor from condensating in the collection tube after sparging was completed, "dry" nitrogen gas was continued to be passed thru the adsorption tube for 1 min. Using an Envirochem, Inc., Unacon Model 810A concentrator interfaced to a Hewlett Packard 5880A gas chromatograph, the collection tube was thermally desorbed at 250° C for 3 min and transferred to the concentrator. The dual trapping system in the concentrator includes large and small bore internal traps packed with the same adsorbents as the collection tube. The gas chromatograph was equipped with a fused-silica capillary column, 30m X 0.25 mm i.d., 1.0 µm film thickness of Durabond-1 (J&W Scientific Co., Inc.) and a flame ionization detector (FID). The helium flow rates thru the column and detector were 1.5 and 30 mL/min, respectively. The oven temperature was maintained at 40° C for 2 min, programmed at 25° to 95° C/min and held for 2 min, programmed at 8° C/min to a final temperature of 200° C.

®Tenax is a registered trademark of Enka N.V., the Netherlands
®Ambersorb XE-340 is a registered trademark of Rohm and Haas, Philadelphia, PA.

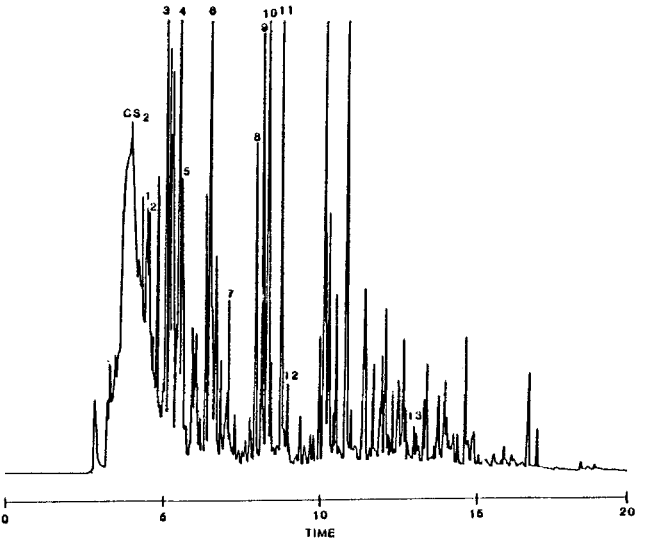

Figure 2. Chromatogram of 100ppb Gasoline Sparged from Water. Selected Peaks are Identified in Table 2

Calculations were made by comparing the ratio of total area found for the external gasoline standard to the area found for the gasoline peaks in the sample. 1-Chlorohexane was used as an internal standard, to evaluate the efficiency of each individual stripping procedure.

RESULTS AND DISCUSSION

A summary of the analysis of gasoline in water from 10 to 500 ppb (w/v) is detailed in Table 1. The recoveries for gasoline varied from 95 to 104% with the coefficient of variation between 9.4 and 10.6%. The precision and accuracy for selected components of gasoline stripped from water are shown in Table 2.

The variability of analytical results from stripping the gasoline from water is similar to the precision found in repetitive analysis of the gasoline standards.

Most stripping procedures involving thermal desorption use Tenax as the collection medium (Kuo et al. 1977; Drozd et al. 1986). However Tenax has a low retentivity for low molecular weight hydrocarbons (Krost et al 1982; Sydor and Pietrzyk 1978). For gasoline in water (500 ppb), comparison of the Tenax collection tube versus the multicomponent tube showed that the Tenax adsorbent had a poor collection efficiency for hydrocarbons eluting from the column before toluene. The multicomponent tube (glass beads/Tenax-TA/Ambersorb XE-340/charcoal) was effective in the collection and desorption of the wide range of compounds found in gasoline.

Table 1. Precision and accuracy for gasoline in water

Theoretical Concentration Level* (ppb)	Recovery (%)	Coefficient of Variation (%)
500	95.4	10.6
100	104.0	9.4
10	100.0	9.7

* Six analysis at each level

Table 2. Precision and accuracy for selected compounds in gasoline at a concentration of 100 ppb in water

Compound No.	Compound Name	Recovery (%)	Coefficient of Variation (%)
1	3-Methylpentane	128	32
2	n-Hexane	77	30
3	Benzene	106	13
4	Isooctane	104	12
5	n-Heptane	121	33
6	Toluene	100	4.6
7	n-Octane	101	7.0
8	1-Chlorohexane*	116	10.4
9	Ethyl benzene	100	5.0
10	p+m-Xylene	100	4.4
11	o-Xylene	99	4.3
12	n-Nonane	99	5.6
13	n-Undecane	100	10.4

*1-Chlorohexane is a standard added to the water sample.

The stripping procedure involves using a small water sample (15 mL). The method is relatively rapid since three samples can be sparged at one time. The thermal desorption - gas chromatography time was less than 30 min. A typical chromatogram is shown in Figure 2. Greater resolution in the chromatography may be obtained by using conditions that prolong the analysis time such as slower temperature programming or a longer capillary column. In this study a balance was made between acceptable resolution and analysis time.

Acknowledgments.

The opinions or assertions contained herein are the private views of the authors and are not be construed as reflecting the views of the Department of the Army or the Department of Defense.

REFERENCES

Belkin F, Esposito GG (1986) Dynamic thermal stripping procedures for the analysis of fuel oil no. 2 and kerosene in water. Chrom Sci 24:216-219.

Coleman WE, Munch JW, Streicher RP, Ringhand HP, Kopfler FC (1984) The identification and measurement of components in gasoline, kerosene, and no. 2 fuel oil that partition into the aqueous phase after mixing. Arch Environ Contam Toxicol 13:171-178.

Drozd J, Vodakova Z, Novak J, (1986) Repetitive stripping and trapping applied to the determination of trace hydrocarbons in aqueous samples, J Chromatogr 354:47-57.

Karasek FW, Clement RE, Sweetman JA (1981) Preconcentration for trace analysis of organic compounds. Anal Chem 53:1050A-1057A.

Krost KJ, Pellizzari ED, Walburn SG, Hubbard SA (1982) Collection and analysis of hazardous organic emissions, Anal Chem 54:810-817.

Kuo PPK, Chian ESK, DeWalle FB, Kim JH (1977) Gas stripping, sorption and thermal desorption procedures for preconcentrating volatile polar water-soluble organics from water samples for analysis by gas chromatography. Anal Chem 49:1023-1029.

Murray DAJ, Lockhart WL (1981) Microextraction and gas chromatography analysis of selected petroleum hydrocarbons in water and fish tissue. J Chromatogr 212:305-11.

Nunez AJ, Gonzalez LF., Janak J (1984) Preconcentration of headspace volatiles for trace organic analysis by gas chromatography. J Chromatogr 300:127-162.

Roberts AJ, Thomas TC, (1986) Characterization and evaluation of JP-4, jet A and mixtures of these fuels in environmental water samples. Envir Toxicol and Chem 5:3-11.

Sydor R, Pietrzyk DJ (1978) Comparison of porous copolymers and related adsorbents for the stripping of low molecular weight compounds from a flowing air stream. Anal Chem 50:1842-1847.

Received May 14, 1987; accepted May 22, 1987.