Analysis of Volatile Aromatic Compounds in Gasoline-Contaminated Ground Water Samples by Static Headspace Sampling and High Speed Gas Chromatography

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Summary

A 15 second, high speed, gas chromatographic determination has been performed on the volatile aromatic compounds in gasoline-contaminated ground water following manual, static headspace sampling. Retention time reproducibility of the seven peaks studied ranged from 0.25 to 0.67 per cent (average relative standard deviation). Excellent linear correlations were obtained for plots of either peak height or peak area against the concentration of the compounds. Comparison was made between the results obtained from the analysis of three replicate samples of gasoline-contaminated ground water by the high speed GC, by two field-portable GCs, and by a laboratory-based GC. It is worthy of note that all the high speed GC analyses required for this study were accomplished in one day.

1 Introduction

An important application of gas chromatographic (GC) methods is the analysis of volatile organic compounds in water: a manual, static headspace method for the analysis of volatile aromatics in gasoline-contaminated ground water samples has been described by *Roe et al.* [1]. The use of high speed GC in conjunction with headspace sampling presents the possibility of obtaining within *ca.* 15 seconds the same separation which would normally take minutes on modern portable or laboratory-based GCs.

The possibility of high speed GC analysis was first demonstrated by *Desty* who, in 1965, performed a separation of 15 components in less than 2 seconds [2]. Since then, several reports have appeared dealing with both the theoretical and practical aspects of high speed GC [3–8]. Many of these have emphasized the importance of minimizing the extra-column band broadening caused by the injector, detector, and associated connectors.

Short (5–10 m), narrow (0.05–0.25 mm i.d.) capillary columns with thin (0.1 μm) films of stationary phase are most often used and it is of great importance that the injection device generates initial band widths no greater than 20 ms. Often a cryofocusing system is used to focus and to concentrate the sample prior to the GC separation.

A viable design, suggested by the innovative work of *Hopkins* and *Pretorius* [9], has been developed and described in a number of recent publications [10–15]. The system used in this study [12–14] employs a metal-coated capillary tube, cooled by chilled nitrogen gas, as a cold trap for cryogenic focusing of the solutes: the trap is then heated from −100 to 200 °C within *ca.* 20 ms by means of resistive heating by a high current pulse from a capacitor discharge power supply. The solutes are separated within a few seconds by a short capillary column and detected by a standard flame ionization detector (FID).

The detector output is collected and processed by high speed electronics and a personal computer with customized software. This study was conducted to compare the results obtained from the analysis of volatile organic compounds in gasoline-contaminated ground water using a high speed GC with results obtained using two field-portable GCs and a laboratory-based GC. For each analysis, the vapor headspace standards and replicate samples of gasoline-contaminated ground water were sampled by the same, manual, static headspace method.

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2 Experimental

2.1 Instrumentation

The high speed GC will be described only briefly, as its design and development have been described in several recent publications [12–14]. In this particular application, headspace vapor samples were introduced, by means of a gas-tight syringe into a manual, six-port valve (Valco, Houston, TX, USA) fitted with a 25 µL loop. A 50 cm, 0.25 mm i.d. piece of deactivated, fused silica tubing served as a transfer line between the injector and the cryogenic trap, a 15 cm × 0.25 mm i.d. (0.625 mm o.d.) piece of Monel® 400 tubing.

The trap, wound in a helix in order to accommodate any changes in length associated with heating and cooling, was enclosed in a Teflon® chamber which was cooled to *ca.* −100 °C by a continuous flow of nitrogen gas previously cooled by passage through a copper coil immersed in liquid nitrogen. The lower temperature of the cold trap could be conveniently controlled by adjusting the nitrogen gas pressure. The Monel® trap was heated by means of high current, variable voltage capacitor discharge power supply described elsewhere [11]. The trap temperature was monitored with a 36-gauge, type J thermocouple (Omega Engineering, Stanford, CT, USA).

The high speed, cryogenically controlled inlet was mounted into the side of a Model 301 gas chromatograph (HNU Systems, Newton Highlands, MA, USA) equipped with flame ionization detection and fitted with a 5 m × 0.25 mm i.d. capillary column coated with a 0.1 µm film of immobilized polydimethylsiloxane (Quadrex, New Haven, CT, USA); the column outlet was positioned at the base of the detector. All chromatograms were run isothermally at temperatures between 40 and 60 °C. Hydrogen was used as carrier gas at flow rates of 3 to 5 ml/min (average linear velocities between *ca.* 100 to 170 cm/s).

The prototype high speed electrometer used (HNU Systems) provided a response time of about 5 ms. The data were digitized by means of a 12-bit analog-to-digital converter (Data Translation, Marlboro, MA, USA) mounted in a 80286/287-based personal computer and collected at a frequency of 200 Hz using Labtech Notebook® software (Laboratory Technologies, Wilmington, MA, USA) modified for high speed GC instrumentation.

For purposes of comparison the data generated by replicate, high speed GC analysis of three samples of gasoline-contaminated ground water were compared with data obtained from three other GCs using the same manual headspace sampling technique. Two different portable GCs were used, the first a Model 311 (HNU Systems) equipped with a 10.2 eV. photoionization detector (PID) and fitted with a 25 m × 0.32 mm i.d. × 1.0 µm polydimethylsiloxane column, the second a Model 10S50 (Photovac, Huntington, NY, USA) equipped with PID detection and fitted with a 10 m × 0.53 mm i.d. × 2.0 µm CP-Sil-5-CP® column. The third, laboratory-based, GC was a Model 5890A (Hewlett-Packard, Avondale, PA, USA) equipped with a 10.2 eV PID detector (HNU Systems) in series with an FID (Hewlett-Packard), only the FID data from this instrument are reported here, and fitted with a 30 m × 0.55 mm i.d. × 3.0 µm polydimethylsiloxane column (J&W, Folsom, CA, USA).

2.2 Procedure

Aqueous standards, containing methyl t-butyl ether (MTBE) and a combination of benzene (B), toluene (T), ethylbenzene (E), and the three isomers of xylene (X), (often collectively abbreviated as BTEX), and the ground water samples taken from the site of a previously leaking underground gasoline storage tank were preserved with 60 mg/L mercury(II) chloride, previously found to be a very effective reagent for the preservation of aqueous solutions against microbial degradation [1].

The manual procedure for the preparation of the static headspace has also been described earlier [1]. For work with the high speed GC, 100 µL of the thermally equilibrated headspace was taken from each 40 mL glass vial by means of a 250 µL gas-tight, fixed needle micro syringe (Scientific Glass Engineering, Houston, TX USA) and injected so as to completely overfill the 25 µL loop of the six-port valve.

3 Results and Discussion

A representative chromatogram illustrating the separation of a dilute mixture of MTBE and BTEX by high speed GC is illustrated in **Figure 1**. The retention time of the last peak in the chromatogram, that of *o*-xylene was 15.2 s. Baseline separation was obtained between ethylbenzene (peak 5) and the coeluting *m*- and *p*-xylenes (peak 6), this illustrates the high column efficiency per unit time which can be obtained by high speed GC. Under these conditions, it was calculated that the number of effective theoretical plates for *m*-xylene was 5500; an improvement on the 2500 reported in an earlier publication [12].

The variation of the retention time of *o*-xylene with column temperature was investigated. Isothermal separation at 40 °C resulted in the separation illustrated above: affording a convenient retention time of *ca.* 15.2 s for *o*-xylene and excellent resolution of all the volatile aromatics of interest except *m*- and *p*-xylenes. At 60 °C the retention time of *o*-xylene was 8.0 s but MTBE was inadequately separated from the methanol used for preparation of the standards.

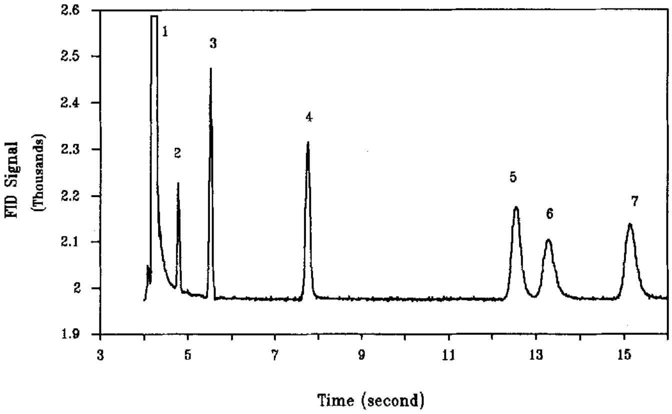

Figure 1

High speed GC separation of MTBE + BTEX standard: 1, methano (solvent); 2, methyl *t*-butyl ether; 3, benzene; 4, toluene; 5, ethylbenzene; 6, *m*- and *p*-xylenes (coeluting); 7, *o*-xylene.

Table 1 summarizes the overall precision of the analysis ($n = 27$) in terms of per cent average relative standard deviation (% ARSTD) of the retention times of the peaks: the reproducibilities varied from 0.25 to 0.67 % ARSTD.

Table 2 summarizes the results from five-point calibration performed on the dilute headspace samples taken from aqueous

Table 1

Reproducibility of retention times [s][a].

	Compound					
	MTBE	B	T	E	*m*- + *p*-X	*o*-X
Retention time	4.793	5.543	7.794	12.603	13.344	15.213
Standard deviation	0.012	0.015	0.028	0.059	0.089	0.079
Average relative standard deviation	0.25	0.27	0.36	0.47	0.67	0.52

[a] $n = 27$

Table 2

Summary of five-point calibration and method detection limit data obtained by high speed GC.

Based on Peak Height

	Compound					
	MTBE	B	T	E	*m*- + *p*-X	*o*-X
Correlation coefficient	0.9978	0.9946	0.9837	0.9709	0.9723	0.9627
Slope	2.12	19.34	12.91	7.86	6.10	4.09
Y Intercept	197	453	397	268	134	221
Method detection limit [µg/L (w/v)][a]	41	8.3	7.2	5.3	2.6	8.0

Based on Peak Area

	Compound					
	MTBE	B	T	E	*m*- + *p*-X	*o*-X
Correlation coefficient	0.9978	0.9948	0.9832	0.9673	0.9734	0.9734
Slope	0.132	1.45	1.57	1.81	1.64	1.15
Y Intercept	12.6	32.4	49.2	69.6	38.7	60.4
Method detection limit [µg/L (w/v)][a]	44	8.1	7.7	23	6.7	14

[a] as defined in reference 16

standard mixtures of MTBE and BTEX. The aqueous layer of these solutions contained, for example, 9.0, 45, 90, 450, and 900 µg benzene/L of water. (µg analyte/L water is equivalent to ppb *w/v*). Because of the excellent resolution of the peaks, similar correlation coefficients were obtained from either peak height or peak area measurements. Also incorporated in Table 2 are the "method detection limits" (MDL) [16] obtained for each compound, expressed in µg/L. A five-point calibration plot for benzene, resulted in a *Pearson's* linear correlation coefficient of 0.9946. The results indicated that under the conditions used, with a 25 µL volume of headspace vapor, the MDL of the analytes ranged from approximately 5 to 45 ppb (*w/v*): if a 1.0 mL injection volume were used it is reasonable, on the basis of other work [17], to extrapolate a minimum detection limit in the range of approximately 0.1 to 1.0 ppb. It is worthy of note that all the analyses performed by high speed GC were accomplished in one day.

One of the goals of this work was to analyze replicate samples of gasoline-contaminated ground water by the same manual static headspace method using several different gas chromatographs: the high speed GC, two field-portable instruments, and one laboratory-based GC. All instruments were fitted with capillary columns, according to previously developed methods [1].

Figure 2 illustrates the chromatogram obtained by high speed GC analysis of the static headspace vapors above gasoline-contaminated ground water sampled on 2/23/91 from the site of an

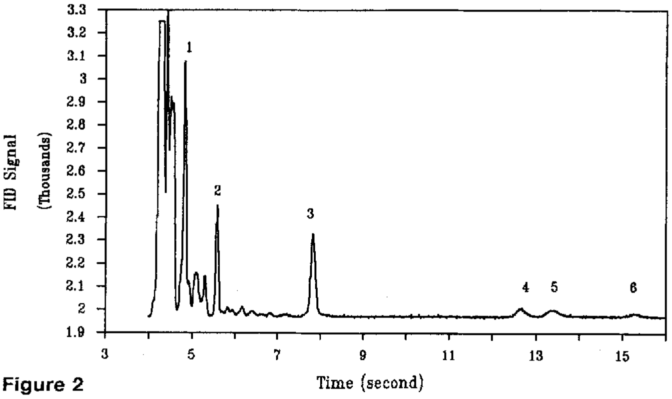

Figure 2

High speed chromatogram of the static headspace above a sample of gasoline-contaminated ground water: 1, methyl *t*-butyl ether (2370 µg/L); 2, benzene (97 µg/L); 3, toluene (109 µg/L); 4, ethylbenzene (2 µg/L); 5, coeluting *m*- and *p*-xylenes (12 µg/L); 6, *o*-xylene (<0.3 µg/L).

Table 3

Comparison of results obtained with four different gas chromatographs from three samples of gasoline-contaminated ground water [μg/L (*w/v*)].

	Compound					
	MTBE	B	T	E	*m*- + *p*-X	*o*-X
Chromatograph	Monitoring well #3, shallow depth					
Fast GC, peak height	35,900	1,380	12,200	1,570	5,720	2,790
Fast GC, peak area	41,700	1,490	14,200	1,580	5,740	2,710
Photovac 10S50	36,000	1,700	12,000	960	3,300	1,200
HNU 311	–[a]	1,550	21,600	1,960	7,380	3,190
Hewlett-Packard 5890	46,400	895	15,300	1,720	6,230	3,080
	Monitoring Well #3, Deep Depth					
Fast GC peak height	22,700	60	864	625	2,320	753
Fast GC peak area	23,500	58	1,215	593	2,280	740
Photovac 10S50	26,000	380	2,300	770	1,900	930
HNU 311	–[a]	163	875	654	2,500	772
Hewlett-Packard 5890	30,100	–[a]	910	682	2,400	878
	Monitoring Well #4					
Fast GC peak height	2,370	97	109	2	12	<0.3
Fast GC peak area	3,260	102	111	<0.5	13	<0.3
Photovac 10S50	6,400	310	470	73	91	39
HNU 311	6,790	221	287	28	28	18
Hewlett-Packard 5890	5,810	236	310	44	60	11

[a] coelution with other peaks; quantitation not possible

underground gasoline storage tank, in the State of Connecticut, which was known to have leaked. **Table 3** summarizes the results obtained when the data from the four very different GCs were compared: the number of samples was insufficient to perform statistical analysis of the data. While the degree of agreement provided by the methods leads to a preliminary conclusion that high speed GC is a suitable method for the analysis of volatile organic compounds in water, the variability of the results indicates that further studies are necessary before this can be considered to be a validated technique.

In agreement with results published elsewhere [13, 17], the amount of water vapor present in the vapor used for static headspace sampling was found to produce no observable effect either on the injection systems or the chromatographic performance of the high speed GC. Future options being considered for the high speed GC involve an automated static headspace injection system and a high speed backflushing device to remove the late eluting components and aid in flushing the injection system. These options would assure even faster, repetitive capability for the high speed GC.

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