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Determination of C_6–C_{10} aromatic hydrocarbons in water by purge-and-trap capillary gas chromatography

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ABSTRACT

A method is described for the determination of the C_6–C_{10} aromatic hydrocarbons in water based on purge-and-trap capillary gas chromatography with flame ionization and mass spectrometric detection. Retention time data and 70 eV mass spectra were obtained for benzene and all 35 C_7–C_{10} aromatic hydrocarbons. With optimized chromatographic conditions and mass spectrometric detection, benzene and 33 of the 35 alkylbenzenes can be identified and measured in a 45-min run. Use of a flame ionization detector permits the simultaneous determination of benzene and 26 alkylbenzenes.

INTRODUCTION

In recent years numerous investigators have reported the presence of volatile hydrocarbons in groundwater, rivers, lakes and even coastal and estuarine ecosystems [1–15]. Contamination of aquatic environments results from a variety of causes. These include: (1) leakage of underground storage tanks, (2) leaching of landfills and other waste disposal sites, (3) discharge of industrial and municipal effluents and (4) occasional oil spills. Among the most toxic and water soluble constituents of crude oil and refined petroleum products are the aromatic hydrocarbons. When oil comes in contact with water the most soluble compounds enter the aqueous phase and are subsequently removed or transformed by a variety of physical and biological processes [16–18]. Because of differences in their physical properties and structures, the aromatic hydrocarbons may be transported and/or removed at

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different rates [3,19]. Consequently, the determination of a wide range of aromatics is of interest not only because these compounds are toxic, but also because they can serve as useful indicators of natural removal processes.

A number of techniques have been used to determine benzene and its alkylated derivatives in water. These include headspace analysis [5], purge-and-trap gas chromatography (GC) [11,20–24], microextraction [25,26] and closed loop stripping analysis [27,28]. Each technique has specific advantages and drawbacks [26,29,30], but purge-and-trap GC and its variants (*e.g.* Bianchi *et al.* [14] and Lucas *et al.* [31]) have enjoyed the widest use. Introduced originally in 1974 by Bellar and Lichtenberg [32] and currently recommended by the US Environmental Protection Agency, the purge-and-trap method is sensitive, precise, relatively simple and suitable for a wide range of volatile contaminants. However, it has rarely been applied to the determination of aromatic hydrocarbons other than benzene, toluene and the C_8 aromatics (BTEX). The principal objective of the present work was to develop a method based on purge-and-trap GC that permitted the measurement of most, if not all, of the C_6–C_{10} aromatic hydrocarbons in water. Extending the range of analytes to include the C_9 and C_{10} aromatics has substantially improved our ability to understand processes affecting the fate of petroleum hydrocarbons in groundwater. Because of the large number of isomeric C_9 and C_{10} aromatics (8 and 22, respectively) and similarities in the physicochemical properties of these isomers, it was possible to establish the importance of biological degradation in hydrocarbon removal [3,19]. Moreover, differences in apparent removal rates of isomeric hydrocarbons strongly suggest that the structures of the hydrocarbons control their rates of removal. Thus, the C_9 and C_{10} aromatics represent powerful molecular probes of biogeochemical processes affecting the fate of petroleum in aquatic environments. Here we present information on the identification, chromatographic separation and instrumental analysis of these compounds.

EXPERIMENTAL

Materials

Water used for preparation of standard solutions and for dilution of samples was purified by boiling with concurrent helium sparging. The volatile-free water (VFW) was stored in the erlenmeyer flask in which it was boiled. Purge-and-trap grade methanol (Burdick and Jackson) was used for preparation of standards without further purification.

Alkylbenzenes and alkanes were obtained from the following suppliers: Supelco, Alltech, Aldrich, Wiley Organics and the American Petroleum Institute. In all but one case (1,2-diethylbenzene; purity 95%), quoted purities exceeded 98%. The compounds were stored at −4°C in ampoules or in glass vials sealed with PTFE-lined lids. Prior to use in standard solutions, each compound was tested for purity by high-resolution gas chromatography–flame ionization detection (HRGC–FID).

Six alkylbenzenes were evaluated for suitability as recovery and internal quantitation standards: [$^2H_6$]benzene, [$^2H_{10}$]*o*-xylene, [$^2H_{10}$]*p*-xylene, [$^2H_{10}$]ethylbenzene, *n*-hexylbenzene and *n*-octylbenzene. [Perdeuterated species were obtained from Cambridge Isotope Laboratories (Woburn, MA, USA).] Comparison of the retention times of volatile hydrocarbons present in 12 oil-contaminated groundwater samples showed that [$^2H_{10}$]*o*-xylene and [$^2H_{10}$]ethylbenzene eluted in chromatographic regions free of interference. The higher alkylbenzenes we tested proved unsuitable because of their low stripping efficiencies in the purge-and-trap HRGC system under the conditions of analysis we employed. Perdeuterated *p*-xylene offered no advantage over [$^2H_{10}$]*o*-xylene or [$^2H_{10}$]ethylbenzene and [$^2H_6$]benzene was not always baseline-resolved from benzene, typically the dominant hydrocarbon in our samples. The C_8 aromatics elute in the middle of the elution range of alkylbenzenes considered here, whereas the other candidate elute either very early or late in the gas chromatogram. For these reasons, we selected [$^2H_{10}$]*o*-xylene and [$^2H_{10}$]ethylbenzene as recovery and internal (quantitation) standards, respectively.

Standard solutions used for instrument calibration were prepared as follows. A 1-dram (*ca.* 1.5 ml) borosilicate vial fitted with a PTFE mininert valve was positioned in a Dewar containing liquid nitrogen. Amounts of 50 μl of each component were transferred quantitatively into the vial with a 100-μl microsyringe. After this mixture had been prepared at liquid nitrogen temperatures, it was allowed to

warm to room temperature (valve closed). The mixture was then agitated to insure homogeneity, and a measured aliquot was transferred by microsyringe to a volumetric flask containing methanol. This stock solution was serially diluted to provide calibration standard solutions over an appropriate concentration range (2–260 ng μl^{-1} component^{-1}).

Sample preparation

Samples of contaminated groundwater were collected from water table wells using an all-PTFE bailer. Details of the sampling procedures are given elsewhere [33]. Groundwater was introduced to 40-ml amber glass bottles sealed with PTFE-faced silicone rubber liners. Before the bottle was sealed, each sample was poisoned with $HgCl_2$ and spiked with 2 μl of the recovery surrogate solution ([$^2H_{10}$]*o*-xylene in methanol). We prepared recovery surrogate solutions at several levels within a concentration range of 8.1–810 ng μl^{-1}. The concentration of [$^2H_{10}$]*o*-xylene used for introduction to a given sample was based on the expected concentration of volatile hydrocarbons in that sample. The bottles were sealed without headspace, taped secure and placed on ice in a cooler until return to the laboratory (where they were stored at 4°C). Similar procedures were used for collection and storage of produced water with the exception that these samples were taken directly from a spigot at the onshore water treatment plant (Carpenteria, CA, USA). Field banks, consisting of VFW spiked with various amounts of [$^2H_{10}$]*o*-xylene, were prepared and preserved according to the same protocol.

Just prior to analysis, water samples were permitted to warm to room temperature. When the concentration of volatiles was known to be extremely low (< *ca.* 5–15 $\mu g\ l^{-1}$ component^{-1}), an aliquot of the sample was poured (to overflowing) directly into a 5-ml gastight Luer-lok syringe fitted with a PTFE mininert valve in the open position. The syringe plunger was quickly inserted in order to seal the sample in the syringe without bubbles or headspace. The sample volume was then adjusted to 5 ml, expelling the excess to waste, and the mininert valve was closed. The internal standard solution (0.5 μl of [$^2H_{10}$]ethylbenzene in methanol; 44.5 ng μl^{-1}) was taken up in a 1.0-μl syringe. The mininert valve was then removed, the needle of the microsyringe was inserted into the 5-ml syringe, and the internal quantitation standard was introduced to the sample. The sample was immediately transferred to the purge vessel (see below) via the Luer-lok fitting.

As discussed below, the linear calibration range of the purge-and-trap HRGC–FID system described here is limited (<0.2 to 10 $\mu g\ l^{-1}$ in purge vessel). At the same time, the concentrations of aromatic hydrocarbons encountered in oil-contaminated waters often span more than four orders of magnitude [3–4]. Consequently, samples having individual hydrocarbon concentrations greater than *ca.* 10–15 $\mu g\ l^{-1}$ required dilution prior to being introduced into the purge vessel. First, an appropriate aliquot of the sample was measured in the 5-ml syringe and transferred to the purge vessel. Then VFW was loaded into the same syringe without headspace (as described above), and the volume was adjusted such that the total volume of the diluted sample (*i.e.* VFW + sample) equalled 5 ml. The VFW was immediately transferred to the purge vessel. The internal standard solution was introduced to either the VFW or the sample depending on which volume was greater. For extremely contaminated water (> *ca.* 300 $\mu g\ l^{-1}$ component^{-1}), microsyringes were used to transfer small aliquots (5–250 μl) of the sample to a syringe containing 5 ml VFW. As before, the internal standard solution was spiked into the 5-ml syringe before the diluted sample was introduced to the purge-and-trap concentrator.

Purge-and-trap gas chromatography

Analyses were performed on Tekmar LSC-2 and LSC-2000 purge-and-trap concentrators interfaced to Varian 3300 or 3500 high-resolution gas chromatographs equipped with hydrogen flame ionization detectors. In the case of the LSC-2, the heated transfer line (175°C) from the purge-and-trap device was 1/16 in. stainless-steel tubing. This was connected (within the GC oven) to a retention gap consisting of an uncoated length of deactivated fused-silica capillary (0.3 m × 0.25 mm I.D.) using a stainless-steel union. The uncoated fused-silica capillary was, in turn, connected to a 30 m × 0.25 mm I.D. fused-silica capillary column coated with a 1.0-μm film of DB-5 (J&W Scientific) using a stainless-steel zero dead volume union. By contrast, the LSC-2000 interfaces directly to the capillary column via an uncoated length of fused-silica capillary

tubing (0.5 m × 0.32 mm I.D.) originating at the multiport valve of the purge-and-trap device. Thus, only one zero dead volume union was required.

Although several purge-and-trap protocols were investigated, routine conditions of analysis were as follows: purge gas, nitrogen; purge flow, 40 ml min^{-1}; purge time, 11 min; dry purge time, 4 min; trap temperature (during purge), 22°C; (during desorption), 175°C; desorption time 4 min. Sample components were transferred from the trap to the column using helium carrier gas at a flow-rate of *ca.* 1.5 ml min^{-1} (linear velocity at 150°C = *ca.* 30 cm s^{-1}). The column was maintained at −50°C, the column was programmed to 40°C at 50°C min^{-1} (5-min hold), then to 150°C at 3°C min^{-1} folowed by a 25-min isothermal hold. This temperature program was developed after evaluating and optimizing the conditions of separation using complex oil-contaminated groundwater samples. The chromatographic conditions described here are similar to those reported by Johansen *et al.* [34] who analyzed gasoline samples on a glass capillary column coated with OV-101. Data were acquired and processed on a Nelson 2700 chromatography data system equipped with a Nelson 900 intelligent analog-to-digital interface operating at a sampling rate of 2 points s^{-1}.

The use of a narrow bore capillary column afforded the resolving power needed to separate the complex assemblages of alkylbenzenes we were primarily interested in. However, the low column flow-rates acted to reduce the efficiency of sample transfer from the trap for the most abundant components (principally benzene) in heavily contaminated samples. As described earlier, this affected only those samples having alkylbenzenes at concentra-

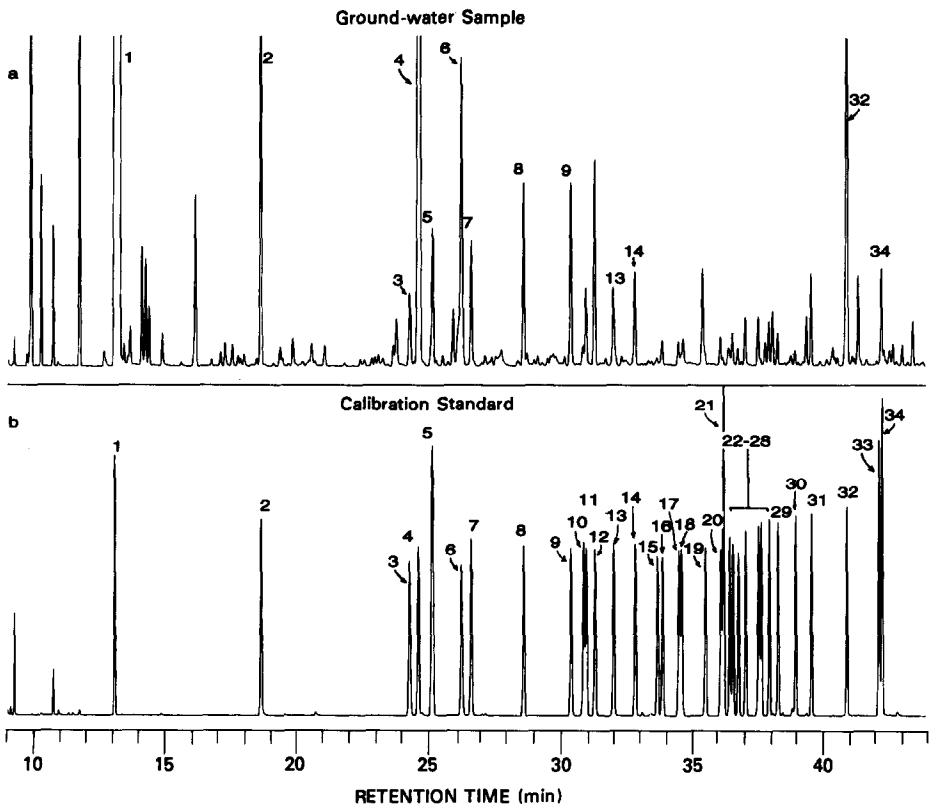

Fig. 1. High resolution gas chromatograms resulting from purge-and-trap HRGC–FID showing (a) volatile hydrocarbons in petroleum-contaminated groundwater, (b) calibration standard used for determination of benzene and C_7–C_{10} aromatic hydrocarbons. Identities of compounds in numbered peaks are given in Table I.

tions that spanned several orders of magnitude. This limitation was readily overcome by simply diluting the sample.

Gas chromatography–mass spectrometry

For purposes of qualitative analysis, the Tekmar LSC-2 was interfaced to a Finnigan 4510B HRGC–mass spectrometry (MS) apparatus in the same manner as described above. The end of the analytical column was inserted directly into the ion source. The HRGC–MS system was equipped with a Data General Nova 4C computer and SuperIncos data acquisition and processing software. The purge-and-trap concentrator and GC conditions were identical to those described in the preceding section. Mass spectral data were acquired in the full scan, electron impact mode (70 eV) with scanning from 50 to 150 amu at a rate of 1 scan s^{-1}.

RESULTS AND DISCUSSION

Qualitative analysis

Our interest in volatile hydrocarbons originated with a study of groundwater contamination in a remote area of northern Minnesota (USA). At this site, crude oil accidentally released from an underground pipeline in 1979, migrated to the water table. Dissolution of the more soluble components of the oil resulted in volatile dissolved organic carbon concentrations of approximately 20 mg l^{-1} in the groundwater near the oil body [33]. A typical gas chromatogram of the volatile hydrocarbons in groundwater collected at the water table near the oil is shown in Fig. 1a. Preliminary purge-and-trap HRGC–MS analysis of this sample indicated the presence of a large number of aliphatic and aromatic hydrocarbons. The latter included benzene, a complex mixture of C_7–C_{11} monoaromatics and naphthalene [35]. Our initial efforts were, therefore, aimed at determining the retention characteristics of the alkylbenzenes and optimizing conditions for their purge-and-trap GC analysis.

Previous investigators have established the retention behavior of many of the C_6–C_{10} aromatic hydrocarbons on a varicty of stationary phases under isothermal and programmed temperature conditions (Johansen *et al.* [34]; Kumar *et al.* [36]; and references cited therein). These studies have demonstrated the difficulty of separating all isomeric C_6–C_{10} aromatics on a single high resolution capillary column. Kumar *et al.* [36] achieved the baseline separation of many of the alkylbenzenes on a 91-m capillary column coated with Carbowax 1540 using programmed temperature GC. They noted that the two principle problems associated with the GC analysis of the C_6–C_{10} aromatics are: (1) their separation from low-molecular-weight saturated hydrocarbons and (2) complete resolution of the aromatics from each other. Although non-polar phases provide excellent selectivity for the C_6–C_{10} aromatics [34,37–39], difficulties in separating them from saturated hydrocarbons can arise when petroleum products are analyzed. This obstacle is mitigated in the case of petroleum-contaminated waters for two reasons: (1) the high solubilities of the aromatic leads to their enrichment in the aqueous phase and (2) the saturated hydrocarbons are more rapidly biodegraded [33]. As illustrated in Fig. 1a, these phenomena result in elution of most of the C_7–C_{10} aromatics in regions that are effectively free of chromatographic interference from saturated hydrocarbons.

Retention data are provided in Table I for benzene, all 35 C_7–C_{10} aromatics, specific deuterated analogues (4) and selected alkanes (11) under two different temperature programs. Both of these programs provide good overall separations. For comparison, a typical gas chromatogram obtained using the faster program (RRT2) for a mixture of *most* of these pure compounds is shown in Fig. 1b. Benzene and all but seven of the alkylbenzenes can be (at least partially) resolved within 45 min under these conditions; 20 compounds (including the deuterated substances) are baseline-resolved (Table II).

Because of the incomplete chromatographic resolution of certain alkylbenzenes it was of interest to determine whether MS would permit more accurate qualitative and quantitative analysis of the partially resolved and co-eluting peaks. We, therefore, collected 70-eV electron impact mass spectra for benzene, each of the 35 C_7–C_{10} aromatics and 3 of the perdeuterated analogues. Only one pair of *co-eluting* alkylbenzenes (*m*-xylene/*p*-xylene) was found to have indistinguishable mass spectra. There are also two pairs of *partially* resolved alkylbenzenes whose mass spectra are virtually identical: (1) 1-methyl-3-ethylbenzene/1-methyl-4-ethylbenzene and (2) 1,4-methyl-2-ethylbenzene/1,3-dimethyl-4-ethylben-

TABLE I

RELATIVE RETENTION TIME DATA FOR VOLATILE ALIPHATIC AND AROMATIC HYDROCARBONS

Compound	RRT1[a]	RRT2[b]	Peak[c]
Aliphatic hydrocarbons			
2,3-Dimethylbutane	–[d]	0.3495	–
2-Methylpentane	0.3417	0.3527	–
3-Methylpentane	0.3449	0.3677	–
2,4-Dimethylpentane	0.3999	0.4284	–
2,3-Dimethylpentane	0.4756	0.4870	–
3-Methylhexane	0.4863	0.4977	–
2,2,4-Trimethylpentane	0.5078	0.5193	–
2,5-Dimethylhexane	0.5874	0.5990	–
2,3,4-Trimethylpentane	0.6258	0.6326	–
3-Methylheptane	0.6739	0.6838	–
2,2,5-Trimethylhexane	0.6931	0.7208	–
Aromatic hydrocarbons			
[$^2H_6$]Benzene	0.4620	–[d]	–
Benzene	0.4655	0.4787	1
Toluene	0.6609	0.6717	2
[$^2H_{10}$]Ethylbenzene	–[d]	0.8582	3
Ethylbenzene	0.8618	0.8691	4
[$^2H_{10}$]*p*-Xylene	0.8574	–[d]	–
m,p-Xylene	0.8797	0.8863	5
[$^2H_{10}$]*o*-Xylene	–[d]	0.9227	6
o-Xylene	0.9294	0.9352	7
Isopropylbenzene	1.0000	1.0000	8
n-Propylbenzene	1.0712	1.0595	9
1-Methyl-3-ethylbenzene	1.0906	1.0748	10
1-Methyl-4-ethylbenzene	1.0947	1.0781	11
1,3,5-Trimethylbenzene	1.1083	1.0866	12
1-Methyl-2-ethylbenzene	1.1399	1.1124	13
tert.-Butylbenzene	1.1758	1.1372	–
1,2,4-Trimethylbenzene	1.1776	–[d]	14
Isobutylbenzene	1.2179	1.1642	15
sec.-Butylbenzene	1.2276	1.1698	16
1-Methyl-3-isopropylbenzene	1.2580	1.1862	17
1,2,3-Trimethylbenzene	1.2637	1.1912	18
1-Methyl-4-isopropylbenzene	1.2672	–[d]	–
1-Methyl-2-isopropylbenzene	1.3113	1.2154	19
1,3-Diethylbenzene	1.3438	1.2311	20
1-Methyl-3-propylbenzene	1.3497	1.2340	21
1-Methyl-4-propylbenzene	1.3621	–[d]	–
1,4-Diethylbenzene	1.3649	1.2410	22
n-Butylbenzene	1.3653	–[d]	–
1,3-Dimethyl-5-ethylbenzene	1.3847	1.2510	23
1,2-Diethylbenzene	1.3721	1.2439	24
1-Methyl-2-propylbenzene	1.4031	1.2589	25
1,4-Dimethyl-2-ethylbenzene	1.4356	1.2724	26
1,3-Dimethyl-4-ethylbenzene	1.4422	1.2754	27
1,2-Dimethyl-4-ethylbenzene	1.4641	1.2842	28
1,3-Dimethyl-2-ethylbenzene	1.4877	1.2948	29
1,2-Dimethyl-3-ethylbenzene	1.5395	1.3145	30
1,2,4,5-Tetramethylbenzene	1.5730	–[d]	–
1,2,3,5-Tetramethylbenzene	1.5874	1.3324	31
1,2,3,4-Tetramethylbenzene	1.7094	1.3753	32
[$^2H_8$]Naphthalene	–[d]	–[d]	33
Naphthalene	–[d]	–[d]	34

[a] RRT1 = relative retention times using isopropylbenzene as reference peak. Chromatographic conditions as follows: – 50°C → 40°C at 50°C min^{-1}, 5 min isothermal hold, → 90°C at 3°C min^{-1} → 150°C at 1°C min^{-1}.

[b] RRT2 = relative retention times using isopropylbenzene as reference peak. Chromatographic conditions as follows: – 50°C → 40°C at 50°C min^{-1}, 5 min isothermal hold, → 150°C at 3°C min^{-1}, 40 min isothermal hold.

[c] Peak numbers refer to Fig. 1.

[d] Not determined.

TABLE II

IDENTIFICATION OF ALKYLBENZENES BASED ON RETENTION TIMES AND MASS SPECTRAL CHARACTERISTICS

Compound	Resolution[a]	Potential GC–MS quantitation ions[b]	Other significant ions[c]
Benzene	b	**78**	77(25)
Toluene	b	**91**	92(62)
[$^2H_{10}$]Ethylbenzene	b	**98**	116(31)
Ethylbenzene	b	**91**	106(34), 77(11)
[$^2H_{10}$]*p*-Xylene	b	**98**	116(52), 114(16)
p-Xylene	c [d]	**91**	106(53), 105(25), 77(17)
m-Xylene	c [d]	**91**	106(53), 105(25), 77(17)
[$^2H_{10}$]*o*-Xylene	b	**98**	116(49), 114(13)
o-Xylene	b	**91**	106(50), 105(21), 77(15)
Isopropylbenzene	b	**105**	120(30), 77(18)
n-Propylbenzene	b	**91**	120(25)
1-Methyl-3-ethylbenzene	p [d]	**105**	120(33), 91(9), 77(10)
1-Methyl-4-ethylbenzene	p [d]	**105**	120(31), 91(9), 77(9)
1,3,5-Trimethylbenzene	b	**105**	120(55), 91(9), 77(12)
1-Methyl-2-ethylbenzene	b	**105**	120(32), 91(10), 77(10)
tert.-Butylbenzene	c [e]	**119**, 134(27)	120(10), 105(1), 91(58)
1,2,4-Trimethylbenzene	c [e]	**105**, 120(52)	119(13), 91(8)
Isobutylbenzene	p [e]	**91**, 92(57)	134(29), 105(1)
sec.-Butylbenzene	p [e]	**105**	134(20), 92(2), 91(13), 77(10)
1-Methyl-3-isopropylbenzene	b	**119**	134(27), 91(21), 77(6)
1,2,3-Trimethylbenzene	p [e]	**105**, 120(49)	119(11), 91(8), 77(10)
1-Methyl-4-isopropylbenzene	p [e]	**119**, 134(27)	105(5), 91(18), 77(6)
1-Methyl-2-isopropylbenzene	b	**119**	134(29), 91(19)
1,3-Diethylbenzene	p [e]	119(98)	134(48), **105**, 91(21)
1-Methyl-3-propylbenzene	p [e]	**105**	134(26), 119(4), 91(8), 77(9)
1-Methyl-4-propylbenzene	c [e]	**105**	134(22), 119(1), 91(6), 92(2)
1,4-Diethylbenzene	c [e]	**119**, 105(82)	134(47), 92(2), 91(26)
n-Butylbenzene	c [e]	**91**, 92(56)	134(29), 119(3), 105(8)
1,2-Diethylbenzene	b	**105**	134(50), 119(86), 91(28)
1,3-Dimethyl-5-ethylbenzene	b	**119**	134(33), 91(14), 77(6)
1-Methyl-2-propylbenzene	b	**105**	134(24), 91(14), 77(6)
1,4-Dimethyl-2-ethylbenzene	p [d]	**119**	134(33), 105(15), 91(13)
1,3-Dimethyl-4-ethylbenzene	p [d]	**119**	134(28), 105(4), 91(12)
1,2-Dimethyl-4-ethylbenzene	b	**119**	134(30), 105(8), 91(13)
1,3-Dimethyl-2-ethylbenzene	b	**119**	134(29), 105(5), 91(12)
1,2-Dimethyl-3-ethylbenzene	b	**119**	134(32), 105(10), 91(14)
1,2,4,5-Tetramethylbenzene	b	**119**	134(54), 105(3), 91(13)
1,2,3,5-Tetramethylbenzene	b	**119**	134(49), 105(3), 91(12)
1,2,3,4-Tetramethylbenzene	b	**119**	134(47), 105(3), 91(14)

[a] Chromatographic resolution based on chromatographic conditions given in Table I (RRT2): b = baseline resolved, c = coelution, p = partial coelution.

[b] Masses underlined are specific to the compound present in the coeluting peak. Negligible or no interference from other alkylbenzenes. Base peak is in **bold**.

[c] Numbers in parentheses indicate abundance (%) relative to base peak.

[d] Mass spectra of coeluting peaks are essentially identical.

[e] Mass spectra are readily distinguishable.

zene. All other non-baseline-resolved alkylbenzenes can be readily differentiated by HRGC–MS for purposes of qualitative analysis. In some of these latter cases, the co-eluting components yield ions that are sufficiently unique to make quantitation by selected ion monitoring possible. In other instances,

the mass spectra differ only in the relative abundances of common ions, and some deconvolution would be necessary. Table II summarizes these findings.

Together these data indicate that purge-and-trap HRGC–MS should permit the qualitative and quantitative analysis of benzene and 33 of the 35 alkylbenzenes of interest here. Assuming there are no interferences from substances other than aromatic hydrocarbons, purge-and-trap HRGC–FID should, in principle, be applicable to the determination of 28 of the 35 C_7–C_{10} aromatic hydrocarbons. In practice, however, separation of the 1,2,3-trimethylbenzene/1-methyl-4-isopropylbenzene doublet was not sufficient to permit accurate determination of the individual components. Use of more selective stationary phases either in series (*e.g.* Mathews *et al.* [40]) or in parallel could provide further improvements in the separation of the difficult multicomponent peaks.

Quantitative analysis

Based on the retention data described above, we developed a 35-component calibration standard solution (*cf.* Fig. 1b). A multipoint calibration was performed on the LSC-2000/Varian 3500 system using eight serial dilutions of the calibration standard ranging in concentration from 2 to 250 ng μl^{-1}. Purge-and-trap HRGC–FID analyses were carried out on 5-ml aliquots of VFW amended with 0.5 μl of each dilution of the calibration standard solution (duplicate analyses at each level). Calibration of the system was performed for all targeted compounds because the stripping efficiencies of the C_6–C_{10} aromatics decrease with decreasing vapor pressure.

Table III lists results developed from linear regression analysis of the data obtained during the multipoint calibration experiment. Results are shown for benzene and six representative alkylbenzenes. The tabulation is for data that span the full concentration range (eight levels) as well as subsets of the complete data set. In the latter cases, levels have been excluded from the regression in a cumulative fashion starting with the highest concentration and progressing to increasingly lower concentrations. This procedure provides an objective means of evaluating the practical linear calibration range using trends in the correlation coefficient and response factors (*i.e.* the slope) for each regression analysis.

All calibration curves for the complete concentration range (All Data) exhibit a convex upward trend. The correlation coefficients and slopes tend to increase (and then plateau) as increasing numbers of levels (at the highest concentrations) are excluded from analysis. For example, higher correlation coefficients and slopes are obtained when all but the three highest levels (All Data-3) are used as compared to the case where all eight levels (All Data) are included in the regressions. The results show

TABLE III

STATISTICAL RESULTS OF MULTIPOINT CALIBRATION

Compound	Dataset[a]									
	All Data		All Data-1		All Data-2		All Data-3		All Data-4	
	r^2	Slope[b]	r^2	Slope	r^2	Slope	r^2	Slope	r^2	Slope
Benzene	0.790	1.98	0.879	3.96	0.964	5.74	0.994	7.86	0.995	7.26
Toluene	0.841	2.53	0.922	4.76	0.925	6.55	0.989	7.79	0.967	7.47
Ethylbenzene	0.889	3.11	0.962	5.48	0.963	6.94	0.996	7.38	0.993	6.63
o-Xylene	0.864	2.80	0.946	5.14	0.997	6.79	0.997	7.36	0.995	6.94
1-Methyl-3-ethylbenzene	0.929	5.51	0.974	8.82	0.996	6.92	0.998	7.51	0.998	6.99
1-Methyl-2-propylbenzene	0.853	2.59	0.941	4.84	0.994	6.47	0.996	7.23	0.987	6.68
1,2,3,4-Tetramethylbenzene	0.854	2.34	0.935	4.33	0.989	5.81	0.994	6.84	0.983	6.04

[a] All data = includes all eight levels; All Data-1 = all levels but highest; All Data-2 = all levels but two highest; All Data-3 = all levels but 3 highest; All Data-4 = all levels but 4 highest.

[b] Slope = [peak area (cts)/concentration (ng ml^{-1})] · 10^{-5}.

TABLE IV

LIMITS OF DETECTION (LOD) AND QUANTITATION (LOQ) FOR PURGE-AND-TRAP CAPILLARY GC WITH FID ($\mu g\ l^{-1}$)

LOD and LOQ determined as mean + 3 S.D. and mean + 10 S.D., respectively based on $n = 5$ (Keith *et al.* [43]).

Compound	LOD	LOQ
Benzene	0.019	0.043
Toluene	0.043	0.058
Ethylbenzene	0.022	0.037
m,p-Xylene	0.072	0.155
[$^2H_{10}$]*o*-Xylene	0.022	0.054
o-Xylene	0.027	0.066
Isopropylbenzene	0.011	0.029
n-Propylbenzene	0.006	0.014
1-Methyl-3-ethylbenzene	0.041	0.109
1-Methyl-4-ethylbenzene	0.015	0.035
1,3,5-Trimethylbenzene	0.023	0.060
1-Methyl-2-ethylbenzene	0.016	0.042
tert.-Butylbenzene + 1,2,4-Trimethylbenzene	0.169	0.442
Isobutylbenzene	0.022	0.060
sec.-Butylbenzene	0.003	0.005
1-Methyl-3-isopropylbenzene	0.016	0.041
1,2,3-Trimethylbenzene + 1-Methyl-4-isopropylbenzene	0.008	0.016
1-Methyl-2-isopropylbenzene	0.003	0.007
1,3-Diethylbenzene	0.020	0.048
1-Methyl-3-propylbenzene	0.020	0.046
1-Methyl-4-propylbenzene + 1,4-Diethylbenzene + *n*-Butylbenzene	0.020	0.049
1,2-Diethylbenzene	0.035	0.080
1,3-Dimethyl-5-ethylbenzene	0.023	0.058
1-Methyl-2-propylbenzene	0.035	0.092
1,4-Dimethyl-2-ethylbenzene	0.028	0.073
1,3-Dimethyl-4-ethylbenzene	0.020	0.054
1,2-Dimethyl-4-ethylbenzene	0.011	0.026
1,3-Dimethyl-2-ethylbenzene	0.080	0.191
1,2-Dimethyl-3-ethylbenzene	0.120	0.299
1,2,3,5-Tetramethylbenzene	0.027	0.067
1,2,3,4-Tetramethylbenzene	0.025	0.066

that the effective linear calibration range is approximately <0.2 to 10 $\mu g\ l^{-1}$ (purge vessel concentration). This narrow range does not reflect a limitation of the flame ionization detector, but rather the purge-and-trap GC system as a whole.

We also analyzed VFW repetitively in order to estimate limits of detection and quantitation for all the compounds in our calibration mixture. A summary of these results is given in Table IV. In general, the data show that the C_6–C_{10} aromatics can be detected at concentrations above approximately 30 $ng\ l^{-1}$. These detection limits are similar to, albeit slightly higher than, data reported by Ho [22] obtained with a photoionization detector. On the other hand, they are significantly lower than those observed by a number of other investigators using variants of the purge-and-trap method [15,23,41, 42].

Method performance

In order to develop estimates of method precision, we performed analyses of contaminated groundwater samples collected with a PTFE bailer. Groundwater was sampled from water table wells in the vicinity of a crude oil spill. All wells were located downgradient of the spill area, and no visible free oil phase was present. Data for three representative wells are presented in Table V. Replicates

TABLE V

RESULTS OF ANALYSES OF REPLICATE SAMPLES OF OIL-CONTAMINATED GROUNDWATER AND PRODUCED WATER

Sample	n	Component	Concentration ($\mu g\ l^{-1}$)		R.S.D. (%)
			Mean	S.D.	
Groundwater samples[a]					
522A	7	Benzene	2080	198	9.5
		Toluene	353	51	14.4
		$\sum C_8$-aromatics	1060	71	6.7
		$\sum C_9$-aromatics	470	40	8.5
		$\sum C_{10}$-aromatics	218	19	8.5
		Bz + $\sum$ABs	4190	293	7.0
534B	3	Benzene	618	19	3.1
		Toluene	94.2	9.5	10.0
		$\sum C_8$-aromatics	313	5.1	1.6
		$\sum C_9$-aromatics	235	11.5	4.9
		$\sum C_{10}$-aromatics	150	4.9	3.3
		Bz + $\sum$ABs	1410	21	1.5
530B	5	Benzene	15.2	1.6	10.5
		Toluene	0.48	0.23	47.6
		$\sum C_8$-aromatics	0.73	0.04	5.4
		$\sum C_9$-aromatics	2.21	0.18	8.3
		$\sum C_{10}$-aromatics	61.0	4.08	6.7
		Bz + $\sum$ABs	79.7	5.79	7.3
Produced water[b]					
Wemco #3	4	Benzene	1210	15.6	1.3
		Toluene	1390	22.7	1.6
		$\sum C_8$-aromatics	945	30.5	3.2
		$\sum C_9$-aromatics	319	18.6	5.8
		$\sum C_{10}$-aromatics	361	46.5	12.9
		Bz + $\sum$ABs	4225	103	2.4

[a] Samples collected in 1987 from groundwater contamination site near Bemidji, MN, USA (Eganhouse *et al.* [33]).
[b] Sample collected in 1988 from onshore teatment plant, Carpenteria, CA, USA.

were taken as separate subsamples (n = 3–7) from a single deployment of the bailer at wells representing varying degrees of contamination (benzene + $\sum C_7$–C_{10} aromatics = 0.08 to 4.2 mg l^{-1}). It is assumed that the water collected within the bailer is homogeneous with respect to dissolved constituents. However, for purposes of comparison, we also performed replicate analyses of a produced water sample collected from an onshore oil production treatment plant. In this case, the *same* sample was repeatedly analyzed (n = 4) over a one day period to estimate method precision. Alkylbenzenes were determined by purge-and-trap HRGC–FID according to procedures described in the Experimental section.

The method precision for individual (benzene, toluene) and homologue group analytes ranges from *ca.* 1.3–48% relative standard deviation (R.S.D.), but most values fall below 10%. The high R.S.D. values for toluene in the groundwater sample from well 530B (48%) is attributable to an anomalous result obtained for one of the five replicate subsamples (toluene concentration = 0.88 $\mu g\ l^{-1}$). The R.S.D. values for individual alkylbenzenes (data not tabulated here) were generally less than 10% with the lowest values being observed for the more highly contaminated samples. These results are consistent with data developed by other investigators using purge-and-trap HRGC methodology [15,23,41].

TABLE VI

RECOVERY OF [$^2H_{10}$]*o*-XYLENE FROM CONTAMINATED GROUNDWATER SAMPLES

Spiked concentration ($\mu g\ l^{-1}$)	*n*	Recovery		
		Mean (%)	1 S.D.	R.S.D. (%)
51.4	28	85.4	16.5	19.3
5.14	17	108.8	21.8	20.1
0.51	19	103.8	20.5	19.7

Finally, as part of our field studies near Bemidji in 1987 we measured the recovery of [$^2H_{10}$]*o*-xylene from 64 field-spiked groundwater samples. These included petroleum-contaminated water samples containing widely varying concentrations of aromatic hydrocarbons and pristine groundwater collected from a control well. Three spiking levels were used within a concentration range of 0.51 to 51.4 $\mu g\ l^{-1}$. The results, given in Table VI, show that mean recoveries ranged from *ca.* 85–109%. The same degree of variation (about 20% R.S.D.) was observed regardless of the spike solution concentration. These recoveries are similar to data reported by other investigators [22,23,41]. However, when compared with results obtained from the analysis of replicate samples of ground water (Table V), the precision associated with recovery of [$^2H_{10}$]*o*-xylene in the field-spiked samples was significantly poorer. This difference is most likely attributable to errors associated with the field spiking procedures and possible matrix effects. Until improved procedures for spiking field samples are developed, recovery correction of the data would appear to be unwarranted.

CONCLUSIONS

A method for determining C_6–C_{10} aromatic hydrocarbons in contaminated water samples has been developed based on purge-and-trap GC with FID and MS. When HRGC–MS is used, benzene and 33 of the 35 C_7–C_{10} aromatics can be identified and measured within a chromatographic run time of approximately 45 min. When FID is employed, benzene and 26 alkylbenzenes can be determined with a detection limit of approximately 30 $ng\ l^{-1}$. The precision of the method is generally less than 10%, and recovery of surrogates spiked in contaminated field samples ranges from 85–108%.

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