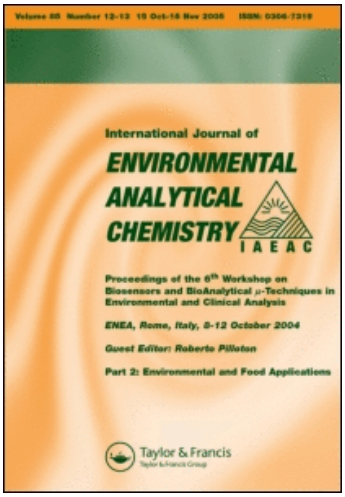

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Pyle, Steven M. and Marcus, Alvin B.(2000) 'Analysis of Volatiles and Semivolatiles by Direct Aqueous Injection', International Journal of Environmental Analytical Chemistry, 76: 1, 17 — 29
To link to this Article: DOI: 10.1080/03067310008034115
URL: http://dx.doi.org/10.1080/03067310008034115

Intern. J. Environ. Anal. Chem., Vol. 76(1), pp. 17-29
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ANALYSIS OF VOLATILES AND SEMIVOLATILES BY DIRECT AQUEOUS INJECTION

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(Received 21 January 1999; In final form 10 June 1999)

Direct aqueous injection analysis (DAI) with gas chromatographic separation and ion trap mass spectral detection was used to analyze aqueous samples for µg/L levels of 54 volatile and semivolatile compounds, and problematic non-purgeables and non-extractables. The method reduces sample handling, increases sample throughput, and avoids the use of solvents ordinarily required for solvent exchange and analyte pre-concentration which would otherwise require disposal as hazardous waste. Aqueous standards containing volatile and semivolatile organic compounds were directly injected in 0.1-µL volumes into a 0.22-mm id capillary column interfaced to an ion trap mass spectrometer. Peak shape was adequate for quantification, and method detection limits for replicate injections (n=7) ranged from 3 to 20 000 µg/L, averaging 100 µg/L. Precision (%RSD) was calculated at each level for each compound and averaged 12% at the highest level. Analysis of domestic tap water readily revealed the presence of three trihalomethanes (chloroform, dichlorobromomethane, and chlorodibromomethane) at the low-µg/L level. Analysis of an aqueous sample from a hazardous waste site monitored the presence of various volatile and semivolatile compounds at mg/L levels.

Keywords: Direct aqueous injection; volatile organic pollutants; tap water; GC-MS

INTRODUCTION

The development of simpler, faster, and less costly methodologies for the analysis of pollutants is part of the U. S. Environmental Protection Agency's (EPA), and specifically the Office of Research and Development's (ORD) continuing mission [1–3]. New methods are needed to provide data for exposure assessment and for decision making in safeguarding or restoring the environment. New analytical methods are developed to take advantage of new technologies, address new environmental concerns, or analyze for newly formulated industrial chemi-

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cals that have potential to become environmental pollutants. Therefore, method development is an ongoing process within ORD and is a vital element to maintain confidence in the EPA's ability to make effective decisions.

This manuscript deals with one such method, GC-MS analysis by direct aqueous injection (DAI). DAI was first explored by Grob et al [4] in 1983. Injecting 0.5 to 2 μL of water, they measured 5 volatile halogenated organics in drinking and ground water. A thick-filmed, apolar column and electron-capture detector (ECD) were used to gave low-ppb-range detection limits. ECD detection, due to its sensitivity and specificity, is particularly amenable to DAI analysis. Halogenated organic semivolatiles can be analyzed in this manner as well as halogenated volatiles [5,6]. A more recent advance in DAI have expanded to GC-MS analysis of alachlor and its degradation products [7] using a standard low polarity (5% diphenyl and 95% dimethyl polysiloxane) column. Common polar solvents, such as acetone, acrolein, butanone, and 1,4-dioxane have also been analyzed by DAI-GC-MS [8]. Using a distillation step to pre-concentrate the sample, DAI was successfully applied to treated waste water from a pharmaceutical factory.

Gas chromatograhy with mass spectral identification (GC-MS) has been an EPA stalwart technology for many years. Recent innovations in ion trap technology have increased GC-MS sensitivity and utility. Ion traps can now perform tandem mass spectrometry to make sample "clean-up" possible by preferentially trapping target analytes and expelling background or matrix ions from the manifold [9,10]. The added sensitivity has made direct analysis of samples without pre-concentration possible [11,12]. Typically, ion trap mass spectrometers can identify picogram quantities in the full scan mode. This translates to part-per-billion (μg/L) sensitivity with μL injection volumes.

Because of this increased sensitivity, ion trap mass spectrometers have been used increasingly for the analysis of environmental samples, especially aqueous samples. Specifically, ion traps have been used, with and without sample pre-concentration, to analyze for triazines in water and soil [13], semi-volatiles in water [14,15], petroleum products (benzene, toluene, ethyl benzene, and xylenes) in water [16], and volatile organics in water [17].

This study will define a proposed EPA method that can directly analyze both volatile and semivolatile compounds by direct aqueous injection (DAI) into a gas chromatograph with subsequent ion trap mass spectral detection. The method detection limits, concentration range, analytes, injection volume limitations, and target list have been determined. These method parameters will be submitted to the SW-846 Work Group for potential incorporation as an appendix into EPA Method 8270.

EXPERIMENTAL

GC/ITS instrumentation

Experimentation was carried out on a Finnigan (Sunnyvale, CA) Magnum ion trap mass spectrometer using Version 3 software. The separation column was an SGE, Inc. (Austin, TX) 12-m by 0.22-mm BPX-5 fused-silica capillary column coated with a 1.0-μm film of bonded 5% phenyl polysilphenylene siloxane liquid phase. The end of the analytical column was inserted directly into the vacuum manifold. These capillary column dimensions maintained helium flow into the manifold to the manufacturer recommended 1.5 mL/min at the initial pressure conditions. The ion trap detector was scanned from 42 to 300 amu at 0.6 scan/s (each scan was an average of 3 μscans) with the manifold temperature at 250 °C, a 58-s solvent delay, and a 100 mmu/100 amu mass defect. To facilitate the exclusion of m/z 18 from the manifold, the first tune segment RF storage potential was set to 240 digital-to-analog conversion units (DACs). The gas chromatograph was a Varian (Walnut Creek, CA) Model 3400 equipped with a septum programmable injector (SPI) and a CTC Model A200S autosampler. A Pentium™ personal computer controlled the autosampler, GC, and MS acquisition. After a 5-min hold, the GC was temperature programmed from 40 to 184 °C at 8 deg/min, followed by 25 deg/min to 300 °C with a final hold of 2.6 min (total run time 30 min). The initial linear velocity was 38 cm/s with a helium head pressure of 5 psig. The transfer line was held at 300 °C. The SPI injector was held at 100 °C for 30 min and upon completion of the run was ramped at 200 deg/min to 300 °C and held for 4 min.

Preparation of standard solutions

Standards of the target analytes were Supelco-certified : Appendix-IX-a Volatile Screening Mixes B, C, D, E (catalog numbers 4–8107 through 4–8110), Appendix IX Semivolatile Calibration Mix 3 (catalog number 4–7382), and Methyl t-Butyl Ether (catalog number 4–8483). These comprised 59 volatile compounds (see Table I) at 2 000 μg/mL in methanol. All purities were certified to be 97.6% pure or greater. The sealed amber ampules were opened when needed and immediately diluted and analyzed within 8 hours. The diluted aqueous standards were made directly in the 1.8-mL autosampler vial by addition of the appropriate volume (between 1 and 18 μL/vial) of methanolic stock solutions (or a secondary diluted stock solution) using a 10-μL syringe. Injection of 0. 1 μL of the aqueous samples preceded by a 2-μL air gap was performed in replicate (n=7) with a dis-

tilled water blank between each concentration level. Sample concentrations were 10, 50, 100, 500, 1 000, 5 000, and 10 000 μg/L in distilled water. A low injection volume was used to maximize column life while still giving adequate precision. Quantitation ion peak areas were determined by Magnum software and imported into a spreadsheet for further calculation. The method of external standardization was used for quantitation.

The MTBE-contaminated well sample was analyzed by 0.5-μL aqueous injection into a split/splitless injector (split injection at 300 °C with 50:1 split ratio). The MTBE standard was used for establishing retention time but did not give a consistent quantifiable spectrum due to its co-elution with residual water.

RESULTS AND DISCUSSION

Analysis by direct aqueous injection uses no sample pretreatment, while also usually achieving part-per-billion (μg/L) sensitivity over a three-decade range. Additionally, volatiles and semivolatiles can be analyzed simultaneously, allowing for faster analyses.

Table I shows the results of the concentration versus detector response study for the 54 analytes along with their quantitation ions and retention time scan numbers. Replicate injections (n=7) were performed at each level to determine precision (expressed as percent relative standard deviation (% RSD)) and the method detection limits (MDLs). The MDL calculation is based on a statistical argument [1] and is defined as the minimum concentration of a substance greater than zero that can be measured with 99% confidence. The MDLs range from a low of 3 μg/L for ethyl benzene to 20 800 μg/L for 4-aminobiphenyl, with a median value of 103.5 μg/L. In general, the precision of the replicate analyses trends according to MDL, with greater certainty (lower % RSDs) at the higher concentrations for the more sensitive compounds. Of the possible 59 analytes, only 54 were quantifiable due to either poor water solubility or the GC elution temperature was too high for the column. The 5 non-quantifiable analytes at the end of the table are included for completeness.

Figure 1 shows the log/log plot of the average relative response of the 54 analytes (each response normalized to the highest concentration) versus concentration over the three-decade range. The solid line is the least-squares regression fit forced through zero. A linear model is maintained at the higher concentrations but at the lower end of the concentration range, the correlation becomes more logarithmic. Individual response curves also show this characteristic behavior. The nonlinearity at low concentrations will add to the uncertainty in this region.

TABLE I Analytical data for 59 volatile organic pollutants (in order of retention time)

no.	*compound*	*quan ion*	*Scan*	*MDL (μg/L)*	*% RSD*						
					10μg/L	*50μg/L*	*100μg/L*	*500μg/L*	*1mg/L*	*5mg/L*	*10mg/L*
1	Trichlorofluoromethane	101	106	8	25.3	38.5	32.0	37.8	6.9	12. 1	3.1
2	Acetone	43	119	4645						29.6	7.2
3	1,1-Dichloroethene	96	115	187			59.4	35.4	9.7	2.1	2.6
4	Iodomethane	141	140	111		70.9	45.0	49.6	20.7	29.6	59.9
5	Acrylonitrile	52+53	141	946				60.2	20.2	52.5	4.2
6	Dichloromethane	49	145	174			55.5	35.2	16.3	4.4	4.8
7	trans-1,2-Dichloroethene	96	172	268			85.3	93.8	13.6	48.5	71.4
8	1,1-Dichloroethane	63	190	17580						111.9	82.9
9	2-Butanone	43	213	1261					40.1	33.7	5.0
10	cis-1,2-Dichloroethene	96	227	821				52.2	11.5	32.2	29.2
11	Bromochloromethane	49	250	760				48.4	24.8	31.9	11.8
12	Trichloromethane	83	255	14	43.1	28.7	23.2	38.0	15.1	18.3	2.2
13	1,1,1-Trichloroethane	97	294	61		38.9	22.8	32.3	13.1	12.8	11.5
14	1,2-Dichloroethane	62	323	96			30.6	32.8	18.1	25.5	4.3
15	Tetrachloromethane	117	330	7	21.2	52.6	22.7	33.1	9.8	11.4	4.7
16	Benzene	78	332	12	39.0	24.6	23.0	30.7	14.4	16.8	3.8

no.	*compound*	*quan ion*	*Scan*	*MDL (µg/L)*	*% RSD*						
					10µg/L	*50µg/L*	*100µg/L*	*500µg/L*	*1mg/L*	*5mg/L*	*10mg/L*
17	Trichloroethene	130+132	434	8	25.1	32.1	25.3	32.6	13.0	15.7	5.1
18	1,2-Dichloropropane	62+63	446	123			39.1	32.3	15.4	21.2	4.4
19	Dibromomethane	174	454	855				54.4	32.3	21.5	5.0
20	Bromodichloromethane	83	470	16	50.1	26.4	17.2	35.1	13.8	21.9	3.1
21	4-Methyl-2-pentanone	43	542	999				63.6	23.2	34.6	4.9
22	cis-1,3-Dichloropropene	75	547	15	46.6	35.1	29.2	34.2	15.7	19.0	0.7
23	Methylbenzene	91	615	4	13.6	26.5	19.3	32.5	10.3	18.4	6.7
24	trans-1,3-Dichloropropene	75	631	16	52.2	23.5	20.9	32.5	15.8	17.8	1.8
25	1,1,2-Trichloroethane	83	663	18	58.0	30.8	13.8	33.1	11.9	22.2	2.3
26	2-Hexanone	43	685	507					16.1	34.5	5.3
27	Perchloroethene	164+166	722	11	33.8	46.6	13.1	24.3	8.4	8.4	9.6
28	Dibromochloromethane	127+129	729	11	33.8	20.3	26.5	35.4	14.2	21.5	3.0
29	1,2-Dibromoethane	107+109	759	13	42.9	20.3	17.7	34.1	16.5	22.2	2.4
30	N-Nitroso-n-methylethylamine*	88	799	10261							32.6
31	Chlorobenzene	112	847	5	14.5	30.6	17.6	32.0	12.1	18.8	6.1
32	1,1,1,2-Tetrachloroethane	131+133	868	25	32.0	16.1	13.7	31.7	10.0	18.3	4.1
33	Ethylbenzene	91	880	3	10.4	22.5	18.3	29.7	8.8	24.8	8.2

no.	*compound*	*quan ion*	*Scan*	*MDL (µg/L)*	*% RSD*						
					10µg/L	*50µg/L*	*100µg/L*	*500µg/L*	*1mg/L*	*5mg/L*	*10mg/L*
34	p-Xylene	91	907	4	13.7	20.7	18.8	28.9	8.7	24.8	8.1
35	o-Xylene	106	965	5	15.7	18.1	16.6	30.9	10.4	24.5	8.4
36	Styrene	104	967	8	24.8	31.1	25.3	32.1	12.4	22.1	6.3
37	Bromoform	173	989	174	86.9		55.3	97.1	31.7	17.3	13.5
38	1,1,2,2-Tetrachloroethene	83	1057	38		23.9	21.5	34.7	13.9	19.2	2.6
39	trans-1,4-Dichloro-2-butene	53+88	1069	463				29.5	9.9	20.8	3.6
40	1,2,3-Trichloropropane	75	1071	7	21.8	49.3	25.3	37.5	15.2	22.3	3.7
41	Aniline*	93	1197	1489					47.4	45.4	7.8
42	o-Dichlorobenzene	146	1284	6	18.7	24.5	22.3	28.2	8.8	24.9	9.1
43	p-Dichlorobenzene	146	1325	10	32.4	16.1	19.3	28.8	9.5	22.2	8.1
44	N-Nitroso-di-n-propylamine*	70	1401	2036					64.8	41.8	8.6
45	N-Nitrosomorpholine*	86	1420	7160						45.6	12.6
46	1,2-Dibromo-3-chloropropane	155+157	1465	160			50.9	43.5	30.5	21.9	10.2
47	4-Chloroaniline*	127	1698	6081						38.7	8.0
48	1,2,3-Trichlorobenzene	180+182	1709	7	23.2	26.1	28.8	24.0	9.5	23.4	11.2
49	N-Nitroso-di-n-butylamine*	84	1790	5639						35.9	5.5
50	2-Nitroaniline*	138	2086	7904						50.3	5.8

no.	*compound*	*quan ion*	*Scan*	*MDL (µg/L)*	*% RSD*						
					10µg/L	*50µg/L*	*100µg/L*	*500µg/L*	*1mg/L*	*5mg/L*	*10mg/L*
51	Dibenzofuran*	168	2281	13	42.2	22.1	41.2	36.0	47.1	8.9	5.9
52	2-Naphthylamine*	143	2336	8064						51.3	7.3
53	Diphenylamine*	168+169	2405	5376						34.2	6.0
54	1,3,5-Trinitrobenzene*	74	ND								
55	4-Aminobiphenyl*	169	2527	20758							66.0
56	Methapyrilene*	58	ND								
57	p-Dimethylaminoazobezene*	225	ND								
58	2-Acetylaminofluorene*	181	ND								
59	7,12-Dimethylbenz(a)anthracene*	256	ND								

ND=not determined; see Results and Discussion. *denotes semivolatile component.

Trace level analyses are difficult because of the increased signal uncertainty (measured as area counts) at low levels. Figure 2 shows seven replicate reconstructed ion chromatograms (m/z=96) of three isomers of dichloroethene at the 500-μg/L level. The first isomer, 1,1-dichloroethene, shows a reproducible (and higher) signal in each of the replicates while the trans-1,2-dichloroethene and cis-1,2-dichloroethene show more variation in the signal. The greater the signal variation, the higher the corresponding MDLs (see Table I). The reason for different intensities to the same isomer is unknown.

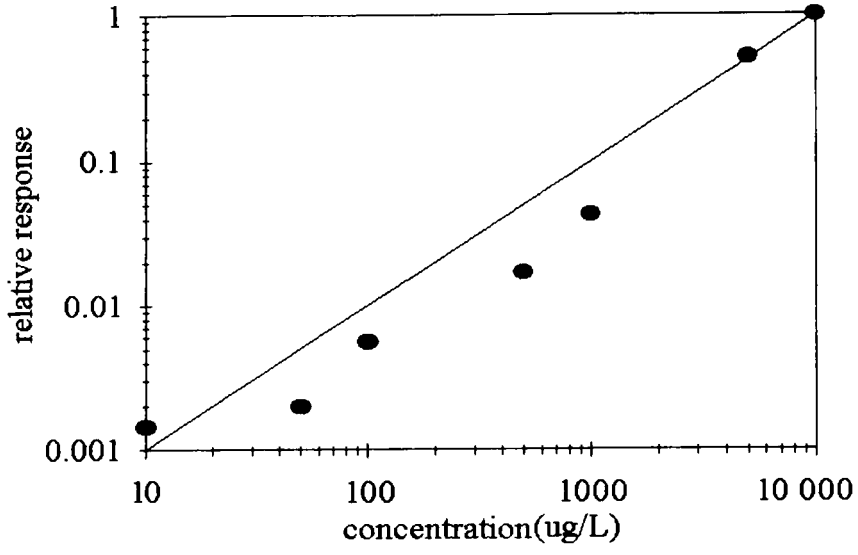

FIGURE 1 Log/Log plot of relative response versus concentration for 54 analytes

The results of a trace level analysis of tap water are shown in Figure 3 and Table II. The presence of the trihalomethanes are indicated by the peaks at the correct time and mass-to-charge ratio (m/z) at the low part-per-billion (μg/L) level. Recently, low levels (< 100 μg/L total) of trihalomethanes in drinking water supplies have been implicated in an increased incidence of miscarriage [18,19] fetal neural tube defects [20], and spontaneous abortions [21]. Trace level analyses are problematic since the analyte signals are obscured by the baseline noise. Therefore, at these levels, the analytes must be run in the target mode. The analyst must know where to look (retention time) and what to look for (quantitation ion). The identification of bromoform in the tap water sample is questionable since the signal is so weak (2 μg/L). It is included in the figure and table for completeness.

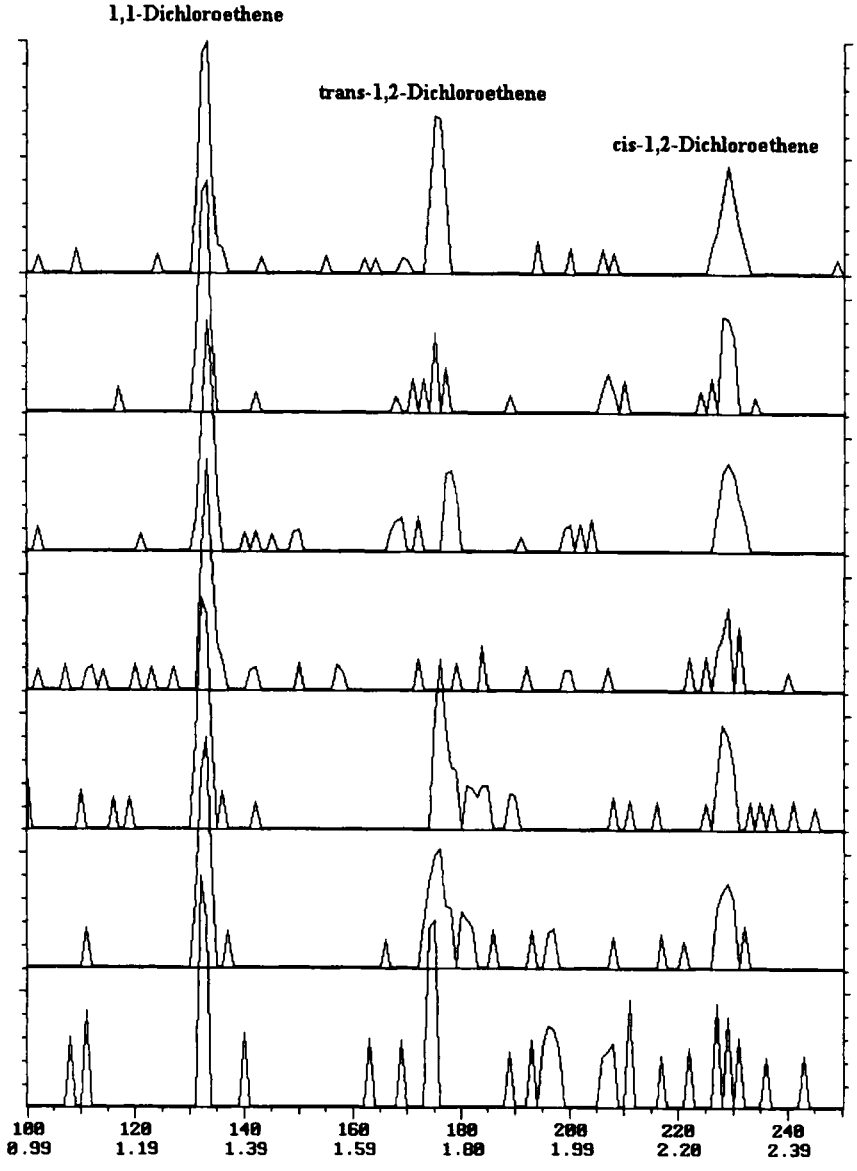

FIGURE 2 Replicate (n=7) reconstructed ion chromatograms (m/z=96) of 3 dichloroethene isomers, each at the 500-µg/L level

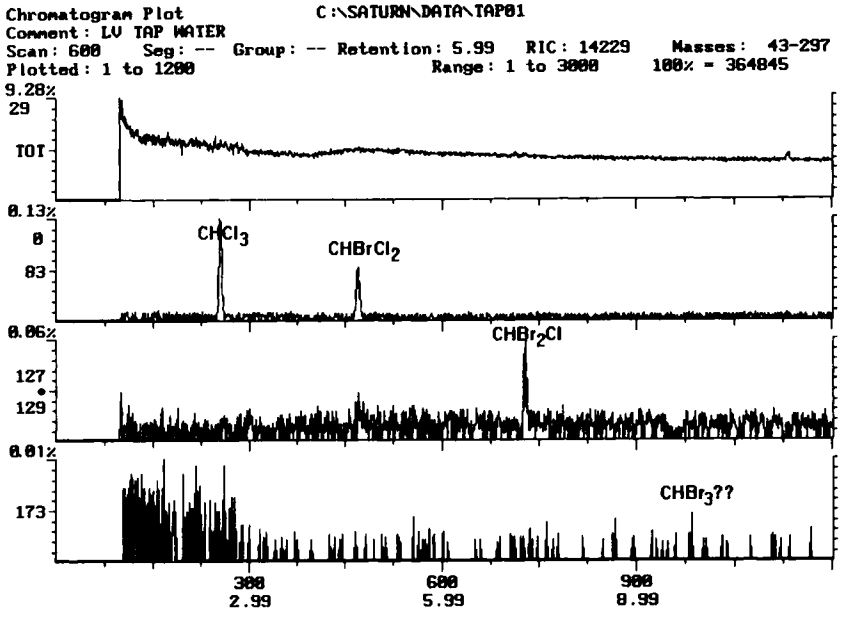

FIGURE 3 Trihalomethanes in tap water

TABLE II Trihalomethanes in tap water

no.	*compound*	*area response*	*% RSD*	*conc (μg/L)*
12	Trichloromethane	2667	6.6	104
20	Bromodichloromethane	1679	5.5	78
28	Dibromochloromethane	1190	11.5	42
37	Bromoform	17	102.5	2

Figure 4 shows the analysis of an aqueous sample from a well located on a hazardous waste site contaminated with methyl t-butyl ether (MTBE), a gasoline oxygenate. The analysis showed part-per-million (mg/L) levels of benzene, toluene, xylenes (C_8H_{10}), and various other alkylated benzenes (C_9H_{12}) as well as MTBE. Because of the relatively high levels, several non-target list identifications could be made.

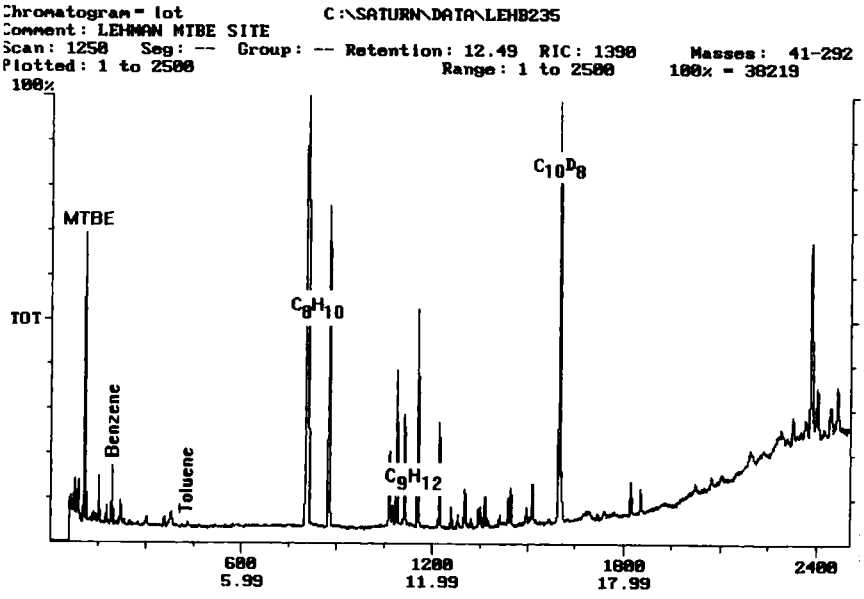

FIGURE 4 MTBE-contaminated hazardous waste site sample by DAI

SUMMARY

1) Quantitation data was collected for 54 out of 59 volatile and semivolatile analytes in aqueous standards.

2) Direct aqueous injection was shown to be easily applied and gave consistent results.

3) Direct aqueous injection was successfully applied to real-world samples for quantitative and qualitative analysis.

NOTICE

This research was funded by the U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), which partially funded and collaborated in the research described here. It has been subjected to the Agency's peer review and has been approved as an EPA publication. Neither the EPA nor ORD endorses or recommends any trade name or commercial product

mentioned in this article; they are mentioned solely for the purpose of description or clarification.

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