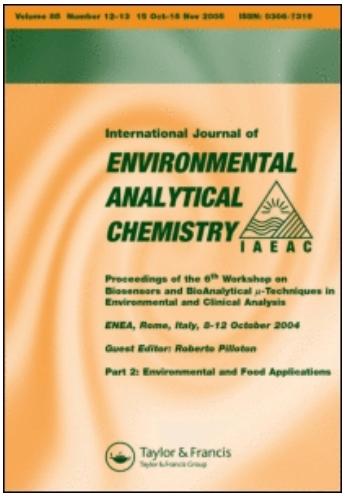

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Sample Handling and Analysis for 51 Volatile Organics by an Adapted Purge and Trap GC-MS Technique

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Sample Handling and Analysis for 51 Volatile Organics by an Adapted Purge and Trap GC–MS Technique

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An adapted, purge and trap GC–MS technique using heated, 100 mL aqueous samples was evaluated for the determination of organics in a water quality survey. The 51 volatile organics consisted of 7 aromatic, 40 halogenated aliphatic and aromatic, and 4 other compounds and included the purgeable priority pollutants listed by the U.S. E.P.A. Detection limits $<1\,\mu g/L$, analytical precision $<15\%$ RSD, recoveries $>70\%$, and precision $<20\%$ RSD for recoveries over all three concentrations were generally obtained for the 51 standards, each spiked at 1, 10, and $50\,\mu g/L$ into purified water. The few instances of abnormal recoveries, poor detection limits, and poor analytical precision were often related. Improved detection limits were obtained for several water soluble and a few halogenated compounds when the concentrator trap composition was changed, transfer line temperature was decreased, and the sparger vessel temperature was increased. For survey control samples, i.e. spiked purified water in bottles transported and stored for up to 1 month, recoveries were $90 \pm 15\%$ of those obtained for fresh calibration samples and the analytical precision for replicate control samples was $<20\%$ RSD for most of the organics. The importance of control samples in surveys was emphasized by the occurrence of some anomalous results.

KEY WORDS: Purge and trap GC–MS, water analysis, sample handling, volatile pollutants.

INTRODUCTION

The gas chromatographic–mass spectrometric (GC–MS) analysis of volatile organic contaminants in water has been well documented.[1-4] Several techniques, including the liquid liquid extraction,[5,6] static head space,[7,8] purge and trap,[9-11] and closed loop stripping[12,13] techniques have been used to isolate such organics for analysis. Since Bellar and Lichtenberg[9] introduced the purge and trap (P&T) technique, it has been widely used, particularly for the analysis of the priority pollutants specified by the U.S. Environmental Protection Agency.[1] This technique offers advantages over other techniques in that it allows facile isolation and concentration of target compounds while it reduces interferences and improves overall analytical detection limits. Also, it is compatible for direct use with GC–MS instruments and there are several commercially available P&T instruments which are reliable and simple to use.

There have been few attempts to extend the P&T technique to other volatile compounds or to those which are less volatile or more soluble in water than the U.S. E.P.A. purgeable organics.[1] Recently, a sensitive and reliable analytical technique was required for the determination of 51 organics in raw and treated water from municipalities near the Great Lakes.[14] An adapted P&T technique was evaluated for the determination of trace (μg/L) levels of these target organics some of which are not on the U.S.E.P.A. purgeable priority pollutants list. Also the effects of handling (transport and storage) on the levels of the organics in spiked water samples were investigated.

EXPERIMENTAL SECTION

Apparatus

All analyses were done on a UNACON 780B automatic concentrator–GC instrument (Envirochem Inc., Kemblesville, PA) connected by a heated transfer line to a Finnigan model 3200 MS. An INCOS MS 2000 data system with the NBS library was used to acquire and analyze the GC–MS data. The automatic concentrator was equipped with a 150 mL capacity sparger vessel with a side port which was sealed with a PTFE coated silicone disk and open top

screw cap. Two sequentially operated glass traps were used in the concentrator: a large bore (4 mm, i.d.) primary trap (trap 1) containing glass beads, Tenax, and Ambersorb 340; and a small bore (2 mm, i.d.) secondary trap (trap 2) with approximately one-tenth the capacity of the primary trap and originally containing glass beads, Tenax, SP2340, silica gel, Ambersorb 340, and charcoal. Initially the concentrator operating conditions were: transfer lines and valve compartment at 200°C; trap 1 desorbed at 300°C with helium gas flow of 50 mL/min for 5 min, trap 2 desorbed at 300°C with helium gas flow of 2.0 mL/min for 5 min onto a 50 m long, Superox 4 L capillary column (Alltech Associates, Inc.) held at 50°C; the column carrier gas (helium) flow of 2.0 mL/min was started and the column oven temperature was raised at a rate of 8°C/min to 200°C where it was held for 30 min. The MS settings were: electron multiplier at 1800 eV; scan rate (full spectrum) of 3.8 msec/mass unit; and mass range of 34 to 300 a.m.u. Prior to analyses, the MS system was calibrated with PFTBA (perfluorotributylamine).

Amber glass sample bottles (265 ± 1 ml capacity) were detergent washed, rinsed with both tap and distilled water and heated at 400°C for at least 4 hours. They were then cooled to about 50°C, spiked with an 0.5 ml aliquot of an aqueous solution containing 19.2 mg $Na_2S_2O_3 \cdot 5H_2O$ and sealed with PTFE coated silicone disks and open top screw caps.

Reagents

The standards (Table I) were obtained from several sources (Aldrich Chemical Co., Chem. Service Inc., Matheson Gas Products Inc.) and their purity, which in all instances was reported by the suppliers as greater than 97% was confirmed by GC/MS analysis. Purified water was prepared by irradiating distilled, deionized water for 5 hours at 254 nm in a 5 L-capacity vessel[15] and an aliquot of each batch was analysed. Appropriate amounts of the standards were injected into 25.0 ml of glass distilled methanol in Reactiflasks (Chromatographic Specialties Ltd.) sealed with Mininert valves (Chromatographic Specialities Ltd.) and to give standard methanolic solutions of known concentrations. Methanolic solutions containing gaseous and very volatile (b.p. < 32°C) compounds were prepared in a similar manner, except that the concentrations were confirmed from the

Table I Relative Retention Times (RRT), Ions Monitored, Detection Limits (DL), and Average Preparation Recoveries (PR)

Compound	RRT[a]	Ions (m/e)	DL (μg/L)	PR[c]	
				%	% RSD
1 dichlorodifluoromethane	0.28	85, 87	0.3	235	100
2 trichlorofluoromethane	0.30	101, 103	0.4	96	3
3 vinyl chloride	0.30	62, 64	0.1	137	67
4 chloromethane	0.30	50, 52	0.4	184	64
5 Freon 113	0.31	101, 151	0.4	106	17
6 chloroethane	0.31	64, 66	0.4	96	4
7 bromomethane	0.33	94, 96	0.3	143	71
8 1,1-dichloroethylene	0.34	61, 96	0.3	97	7
9 carbon disulfide	0.35	76, 78	0.3	102	15
10 3-chloropropene	0.38	41, 76	0.4	82	5
11 acrolein	0.42	55, 56	5.0	5	16
12 *t*-1,2-dichloroethylene	0.43	61, 96	0.4	85	6
13 1,1-dichloroethane	0.45	63, 98	0.2	94	9
14 carbon tetrachloride	0.45	117, 119	0.4	105	16
15 1,1,1-trichloroethane	0.46	61, 97	0.4	64	38
16 dichloromethane	0.51	49, 84	0.2	76	9
17 benzene	0.53	77, 78	0.1	84	13
18 trichloroethylene	0.61	95, 130	0.2	94	12
19 acrylonitrile	0.61	52, 53	5.0	3	28
20 chloroform	0.65	83, 85	0.2	74	5
21 tetrachloroethylene	0.67	129, 166	0.3	106	5
22 1,2-dichloropropane	0.69	63, 41	0.3	59	12
23 toluene	0.70	91, 92	0.1	95	9
24 1,2-dichloroethane	0.72	62, 98	0.2	28	16
25 1,4-dioxane	0.73	88, 58	150	—	—
26 2,3-dichloro-1-propene	0.75	75, 110	0.3	57	27
27 2-chloroethylvinylether	0.82	63, 43	80	—	—
28 ethylbenzene	0.83	91, 106	0.1	88	12
29 1,3-dichloropropene[b] (*cis*)	0.84	75, 110	0.4	41	52
(*trans*)	0.98				
30 1,4-xylene	0.85	91, 106	0.1	84	13
31 1,3-xylene	0.86	91, 106	0.1	80	5
32 bromodichloromethane	0.88	83, 129	0.3	38	3
33 1-bromo-2-chloroethane	0.90	63, 142	0.3	27	26
34 1,2-xylene	0.95	91, 106	0.1	80	31
35 chlorobenzene	1.00	112, 77	0.1	79	19
36 1,1,2-trichloroethane	1.06	97, 83	0.4	29	41
37 styrene	1.07	104, 78	0.2	64	28
38 1,2-dibromoethane	1.07	107, 109	0.4	21	51
39 dibromochloromethane	1.12	129, 208	0.3	28	30
40 bromobenzene	1.21	77, 156	0.3	45	12
41 dichloroacetonitrile	1.22	74, 82	80	—	—
42 1,1,2,3-tetra-[b] (*cis*)	1.28	143, 145	20	24	—
chloro-2-propene (*trans*)	1.57				
43 1,3-dichlorobenzene	1.30	146, 111	0.1	48	10
44 pentachloroethane	1.32	117, 167	0.4	33	17
45 hexachloroethane	1.33	201, 117	0.4	78	12
46 bromoform	1.33	173, 275	0.4	10	45
47 1,4-dichlorobenzene	1.34	146, 111	0.1	51	1
48 1,1,2,2-tetrachloroethane	1.39	83, 164	0.4	12	29
49 1,2-dichlorobenzene	1.40	146, 111	0.1	36	11
50 hexachlorobutadiene	1.41	225, 190	0.4	78	12
51 1,2,4-trichlorobenzene	1.59	180, 182	0.4	39	4

[a]Relative to deuterated chlorobenzene. [b]Mixture of isomers. [c]Average (%) and %RSD for values at 1, 10, and 50 μg/L.

difference in weight of the cold (about 4°C) Reactiflask before and after each addition of the standard by means of a cold (about 4°C) syringe. Aqueous composite standard solutions (aqueous calibration solutions and control samples) were prepared by injecting appropriate aliquots of methanolic standard solutions into sealed amber glass bottles filled with purified water.

Procedures

Prior to the start of an analysis, the sparger vial was purged with helium for 5 minutes by rotating the concentrator valve to "trap-out" mode. In this position, any volatile contaminants that were present in the sparger were purged without entering the trap. A 100 $\pm$0.5 ml aliquot of aqueous sample was transferred from a sealed amber glass bottle to the sparger by pressurizing the inverted bottle by means of a 17 gauge syringe needle connected to a source of compressed helium. PTFE tubing (2 mm i.d.) with a Luer Lock connector and 17 gauge syringe needle at each end was used to transfer the aqueous aliquot. Helium purge gas was passed for 30 minutes at a flow rate of 50 ml/min through the water sample in the vessel maintained at 35°C and into trap 1. Trap 1 was then heated to 300°C and the components were back flushed into trap 2 which was then heated to release (back flush) the volatile organics into the GC–MS system.

Aqueous control blanks (purified water) and control samples (spiked water) for assessment of sample handling were prepared at Health and Welfare Canada laboratories in Ottawa. The bottles (always inverted) containing these control blanks and samples were packed in coolers containing cold Freeze-Paks and were shipped to Concord Scientific Corporation (Toronto) within 24 h of preparation. The coolers which also contained bottles used in a survey[14] were then transported by car or by air to and from the sampling sites. The coolers were delivered to the analytical facility (Mann Testing Laboratories Ltd.) where the bottles were stored at 4°C. Fifty-three control samples were shipped and stored in lots of 2 to 8 samples together with an equal number of shipped blanks. Randomly selected control samples and blanks from each lot were analyzed within 7 days after sampling.

Relative retention times (RRT) were obtained by comparison of

the compound's retention time with that of deuterated chlorobenzene (1.00), the internal standard used for all analyses. The sum of peak intensities for the characteristic ions listed in Table I was used for quantitation of each compound. Detection (quantitation) limits, analytical precision and linearity information were obtained from analyses of replicate aqueous composite standard solutions at concentrations of about 1, 10 and 50 μg/L. Technique detection limits were estimated from peak intensities for selected ions (Table I). Preparation recoveries and retention times were determined by comparison of analytical results for triplicate aqueous composite standards with those from appropriate methanolic standard solutions injected directly into the concentrator. At least one each of a purified water aliquot, two aqueous calibration solutions and a control sample were analysed on each analysis day. Handling recoveries were determined by comparison of analytical results for control samples with those for aqueous calibration solutions.

RESULTS AND DISCUSSION

The UNACON 780B concentrator was chosen for these studies since it had certain design features which were considered compatible with the use of GC–MS for reliable identification of trace levels of organics in water. An externally mounted sparger vessel allowed heating and sparging of large (max. ca. 100 mL), water sample aliquots. Thus, it was expected that the rate of collection and the amount of material collected for GC–MS analysis by use of this feature would be greater than with smaller, unheated sample aliquots. Also, the UNACON 780B trap system is designed so that trap 1 collects most organics but separates them from most of the water vapour. By proper choice of conditions, the collected target organics can then be readily transferred with reduced amounts of purged, interfering substances to trap 2. Transfer from this small bore trap is done at a rapid heating rate but at a relatively low helium flow rate (and volume) which is suitable for the capillary column. Most analytes are deposited at the head of the column and this aids the chromatographic resolution of the compounds. Although the column effluent is split (25:75) between a flame ionization detector (FID) and the MS to allow monitoring of system

performance by FID, this only reduces the amounts of materials entering the MS, and hence the technique detection limits, by 25%.

Analyses of prepurged, purified water showed that the background was less than the detection limits listed in Table I. However, carbon disulfide (max. 1.3 μg/L), dichloromethane (max. 3.9 μg/L), chloroform (max. 3.7 μg/L), and styrene (max. 2.6 μg/L) were detected above 1 μg/L in some of the 19 control blanks from the handling test. In addition, 1,1,1-trichloroethane (max. 0.6 μg/L), benzene (max. 0.4 μg/L), trichloroethylene (max. 0.7 μg/L), toluene (max. 1.0 μg/L), 1,4-dichlorobenzene (max. 0.2 μg/L), 1,2-dichlorethane (max. 0.3 μg/L), and the xylenes (max. 0.4 μg/L) were detected in some control blanks. Similar results were obtained for purified water samples shipped directly to the analytical laboratory. The appropriate values from analyses of control blanks were used to adjust the analytical results for control samples shipped in the same cooler.

The choice of trapping materials influenced the recovery and chromatography of the target organics. Good recovery of 1,1,1-trichloroethane was obtained with the original design of trap 2 containing, in sequence, glass beads, Tenax, SP2340, silica gel, Ambersorb 340 and charcoal. However, at elevated temperatures the SP2340 released silicone compounds which interfered with the analyses. When the trap was replaced with one which did not contain SP2340, the 1,1,1-trichloroethane recovery gradually decreased. The analytical evidence suggested a conversion to 1,1- and 1,2-dichloroethylene. Results from investigation of this phenomenon by omitting one trapping material at a time indicated that silica gel was responsible for the conversion. (However, new traps obtained after these investigations did not cause significant problems with the determination of halogenated organics.) The omission of silica gel from trap 2 resulted in a broadening of GC peaks for polar and very volatile compounds. Tests done after trap 2 was changed, i.e. without silica gel and SP2340, showed significant decrease in recoveries in certain compounds. Recoveries determined before and after (Table I) the change in traps were 69% and 39% for bromodichloromethane, 77% and 47% for 1,4-dichlorobenzene, and 52% and 25% for 1,2-dichloroethane at 10 μg/L. In consideration of potential variations in characteristics of the analytical system (e.g. traps), aqueous calibration solutions were analyzed every day by the same procedures as for samples.

The relative retention times, technique detection (quantitation) limits, and masses of characteristic ions used in quantitation of 51 selected organics listed in Table I were obtained after the change in trap 2 (without silica gel and SP2340). The average of preparation recoveries at 1, 10, and 50 μg/L are also listed in Table I. Preparation recoveries represent the comparison of analytical results for aqueous calibration solutions prepared in bottles with those for methanolic standard solutions injected directly onto trap 1 of the concentrator. Dichloroacetonitrile, 1,4-dioxane, and 2-chloroethylvinyl ether were not detectable at the highest concentration (50 μg/L) used in evaluation of the P&T technique. Acrolein and acrylonitrile also showed detection limits ≥ 1 μg/L and poor preparation recoveries. These five compounds are relatively soluble in water and hence, perhaps, also less likely to be retained by the traps than the other selected organics. A poor detection limit (20 μg/L) was also found for 1,1,2,3-tetrachloro-2-propene. Degradation of this and other polyhalogenated aliphatics in the analytical system may have occurred, since there was evidence that hexachloroethane was partly converted to tetrachloroethylene. Heated transfer lines in the concentrator, when coupled with water vapour from sparging, could provide conditions suitable for catalytic conversion. Poor recoveries of halogenated compounds, such as pentachloroethane, dibromoethane, bromoform, chlorodibromomethane, and bromodichloromethane may have been partly due to such conversion. It is interesting to note that, for RRT >0.7, recoveries of halogenated compounds generally ranged from 20 to 50% whereas recoveries were generally $>50\%$ for aromatic hydrocarbons. However, the recoveries of gaseous compounds such as dichlorodifluoromethane (b.p., -30°C), chloromethane (b.p., -24°C), vinyl chloride (b.p., -14°C), and bromomethane (b.p., 3°C) showed a reverse trend. Although they were detectable at 1 μg/L in aqueous calibration solution, abnormally high recoveries were found when the analytical results (P&T) were compared with those obtained by direct injection of methanolic standard solutions onto trap 1. It was assumed that breakthrough of these compounds from trap 1, probably aided by the presence of methanol, had occurred for the direct injection since the phenomenon was more obvious with increasing concentration. Preparation recoveries were generally $>70\%$ for compounds with RRT <0.72. For comparison, purging efficiencies $>75\%$ were gener-

ally obtained in other studies[10-13] with similar selections of organics.

Knowledge of the reproducibility of % recoveries is important in quantitative analyses of water samples by the P&T technique. In these studies, relative standard deviation (RSD) values $<15\%$ were generally obtained for preparation recoveries at each of 1, 10, and 50 μg/L. The few RSD values which ranged from 15 to 20% RSD, and high %RSD values in general, were usually associated with unusually low or high % recoveries and determinations near the detection limits. Values above 20% RSD were only found for chloromethane (1 μg/L, 27%), acrolein (10 μg/L, 23%), acrylonitrile (10 μg/L, 32%), 1,2-dibromoethane (1 μg/L, 25%), and pentachloroethane (1 μg/L, 22%). The reproducibility of % recovery values over the 1 to 50 μg/L concentration range was also estimated as shown in Table I. No analyses were done for *trans*-1,3-dichloropropene or *trans*-1,1,2,3-tetrachloro-2-propene and due to poor detection limits, no precision values for the concentration range could be obtained for 2-chloroethyl vinyl ether, *cis*-1,1,2,3-tetrachloro-2-propene, 1,4-dioxane, and dichloroacetonitrile. The precision of recovery values obtained at 1, 10, and 50 μg/L was poor (64–100% RSD) for the four gaseous compounds which had abnormally high recovery values (Table I). Values of $<19\%$ RSD were found for 31 compounds and values ranged from 26% to 45% for an additional 10 compounds. About one-half of the compounds showed analytical precision of better than 15% RSD both for triplicate recovery determinations at each concentration and when recovery values obtained at all three concentrations were compared. However, the results for the remaining compounds showed poor precision (i.e. poor linearity of % recovery–concentration relationship) and indicated a need for care in the quantitative analysis of water by this P&T technique. The concentration of a compound in the aqueous calibration solution should be of the same order of magnitude and if possible the same as that of the compound in a water sample.

The analytical procedures were changed to attempt reduction of some of the foregoing problems. Silican gel was added to trap 2 to aid collection of the very volatile compounds. The temperature of the valve oven compartment, block heater, and transfer lines were reduced to 100°C from 200°C to minimize chemical conversion. To improve purging efficiency, the sparger bath temperature was in-

creased from 35°C to 45°C. A new Superox GC column was installed. Subsequent results from analyses of aqueous calibration solutions at 0.4 μg/L indicated a reduction in degradation of chlorinated aliphatics such as 1,1,1-trichloroethane. Improvement in detection limits were generally found and noticeable improvements were noted for compounds with previous (Table I) detection limits >1 μg/L. Improved detection limits were 1 μg/L for acrolein, acrylonitrile, dichloroacetonitrile, and tetrachloropropene and 10 μg/L for 1,4-dioxane and 2-chloroethyl vinyl ether. Although the precision of triplicate determinations was generally <15% RSD, preparation recoveries for many compounds at 0.4 μg/L were not within ±25% of recoveries at 1 μg/L. This again emphasized the need for frequent, multilevel calibration of the analytical system.

To challenge the analyst, different combinations of the target organics were spiked into purified water to give known concentrations (nominal range, 5 to 50 μg/L) of each compound in the control samples. The analyst was not informed of the nature and concentrations of the spiked materials. Each compound was present in at least one of the 19 control samples selected for analysis. Acrylonitrile and 1,3-xylene were only present in a single sample. Replicate samples were considered to be those which had identical composition based on the identity and amount of compounds used in their preparation. Results for three sets (A, B, C) of triplicate and two sets (D, E) of duplicate samples were available for determination of the precision and average of the handling recoveries.

The precision of recovery values for individual compounds in each replicate set was usually <15% RSD and <20% RSD with the exceptions noted in Table II. Average recoveries for compounds in sets A, B, and D ranged from 76 to 105%, i.e. 90±15%, with the exception of the four values listed in Table II. However, average recoveries for about one half of the target compounds in sets C and E were either lower than 76% or higher than 105% with values generally ranging from 56 to 115%. Exceptions were trichlorofluoromethane (386% at 7.0 μg/L) and 1,1-dichloroethylene (124% at 7.9 μg/L) in set C and vinyl chloride (50% at 33.8 μg/L), chloroethane (42% at 32.9 μg/L), 2-chloroethyl vinyl ether (0% at 47.4 μg/L), and 1,4-dichlorobenzene (35% at 10.6 μg/L) in set E. It is likely that the unusually high % recovery for trichlorofluoromethane was largely due to interference from coeluting Freon 113 and the use of m/e 101

Table II Compounds with RSD >20% for control samples

Compound	Set[a]	μg/L	% RSD	% Recovery
chloromethane	E	33.8	21	68
Freon 113	B	13.7	22	91
carbon disulfide	E	10.5	25	66
dichloromethane	A	15.2	30	82
toluene	C	5.3	27	98
1,2-dichloroethane	A	11.7	32	127[b]
1,3-dichloropropene	A	15.5	43	10[b]
	B	15.5	31	24[b]
	D	10.8	38	28
1,4-xylene	B	15.0	27	98
	C	5.3	24	92
dibromochloromethane	A	15.1	24	91
1,4-dichlorobenzene	E	10.6	123	35
bromoform	A	15.3	6	116[b]

[a]Control sample sets (see text).
[b]Sole instances of average recoveries <76% and >105% in sets A, B, and C.

for quantitation (Table I). The wide range in recoveries for sets C and E was surprising since handling times for samples in these sets ranged from 8 to 15 days whereas handling times for sets A, B, and D ranged from 21 to 29 days. Thus, prolonged handling did not have a significant effect on recoveries in sets A, B, and D.

The unusual composition of sets C and E, as compared to sets A, B, and D, may have been the cause of anomalies in their analyses and hence the cause of unusual recovery values. Sets C and E contained the first 10 (very volatile), the last 5 (relatively involatile), and several other compounds listed in Table I which were not generally present in the other three sets. Also, set C contained more (38) compounds than the other sets (A, 16; B, 22; D, 20; E, 22) and the range of spike concentrations was wider for sets C and E (ca. 5 to 45 μg/L) than for sets A, B, and D (ca. 10 to 15 μg/L). In summary, although recoveries of $90 \pm 15\%$ were usually obtained after 1 month of handling, recoveries outside this range were obtained for some compounds and under certain circumstances. The anomalous results suggest that control samples are important for evaluating the analytical results and care should be taken in the handling and analyses of water samples from surveys.

Results (Table III) for duplicate samples from a raw water supply on the Great Lakes demonstrate the sensitivity and reproducibility of the analytical technique. The precision of duplicate results ranged from $\pm 6\%$ to $\pm 16\%$ for the four compounds detected at $>1.0\,\mu g/L$. Chromatographic quality is depicted in Figure 1 by the reconstructed ion chromatogram from the analysis of one of the water samples.

Table III Target compounds detected at $>0.1\,\mu g/L$ in duplicate raw water samples

Compound[a]	Concentration ($\mu g/L$)	
	Sample 1[b]	Sample 2
15 1,1,1-trichloroethane	—	0.3
16 dichloromethane	2.3	3.1
18 trichloroethylene	0.2	—
20 chloroform	6.4	4.6
23 toluene	0.8	0.1
28 ethylbenzene	—	0.1
32 bromodichloromethane	4.0	3.3
37 styrene	0.5	0.2
39 dibromochloromethane	1.6	1.8
47 1,4-dichlorobenzene	—	0.2

[a]See Table I.
[b]See Figure 1.

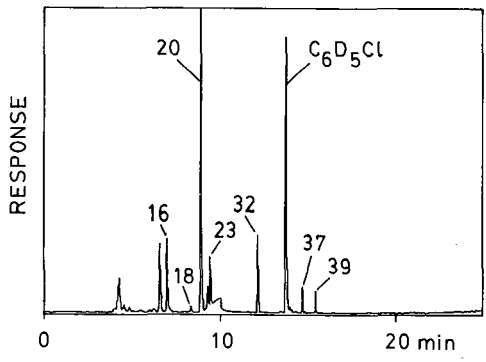

Figure 1 Reconstructed ion chromatogram from analysis of a raw water sample (Table III). The internal standard peak (C_6D_5Cl) and peaks corresponding to target organics (Table I) detected at $\geqq 0.1\,\mu g/L$ are identified.

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