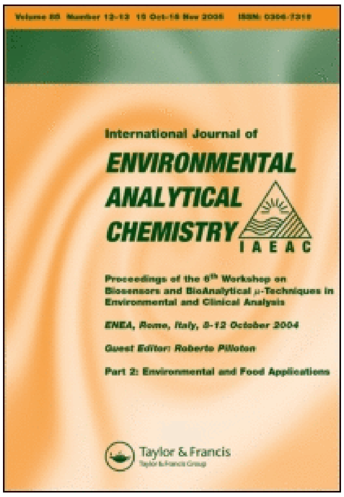

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ANALYSIS OF SEMI-VOLATILE AROMATIC CHLORINATED ACIDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION GC/MS

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An analytical procedure utilizing solid phase extraction with octadecylsilane bonded to silica (C_{18}) cartridges combined with gas chromatography/mass spectrometry (GC/MS) was developed to analyze semi-volatile chlorinated acids found in drinking water. A system has been designed which will enable the analysis of this class of compounds with minimum sample manipulation and detection limits in the low ng/L range. The overall accuracy and precision were comparable to other methods used for compliance purposes. Among the advantages of the developed methodology are its applicability for field sampling and at the same time, provides a simple and inexpensive mean for sample preservation.

KEY WORDS: Solid phase extraction, GC/MS, chlorinated acids, drinking water.

INTRODUCTION

There is evidence that proves the occurrence of chlorinated acidic compounds in treated surface and ground water.[1-3] Some of these organics are found in drinking water at levels considerably greater than those in the corresponding water supply.[2,3] The major source of chlorinated organics in water is the reaction of fulvic and humic acids with chlorine.[4,5] Fulvic and humic acids compose the larger fraction of organic substances in natural waters. It has been shown that the main mutagens in humus-rich chlorinated drinking water are acidic polar compounds.[6] Therefore, it is necessary to use an adequate method for monitoring these compounds.

For several classes of contaminants, well established analytical methodology is available. For example, volatile (bp < 150 °C), water insoluble compounds can be isolated by stripping them from the water with an inert gas that flows into a trapping column connected to a gas chromatograph (purge-and-trap).[7] Semi-volatile contaminants are generally extracted from water using an organic solvent, which may undergo further concentration, replacement, and/or derivatization before being analyzed by gas chromatographic methods. This procedure is usually time consuming, requires the use of large quantities of solvent and other suspected carcinogenic reagents, is subject to contamination (interferences and false positives), and/or loss of sample integrity, allows for possible formation of emulsions,

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and presents many difficulties for field applications[6] (such as the large size of the extractors, the need for a constant control of the stirring process, and the low flow rates required for good recovery). Only certain chlorinated acids can be determined with this method.

Several other complex analytical schemes have been used for the separation of the acidic fraction in drinking water (strong acids, weak acids, neutral, bases).[8,9] They are all based on solvent extraction followed by prefractionation and analysis using a wide variety of chromatographic methods. In most cases, GC/MS is needed for confirmation. The aim of these methods has been to provide a mean for "profiling" water samples without specific compound identification.

Solid supports, especially octadecyl (C-18) bonded to porous silica, have been used for solid phase extraction of organic components from water solutions. Applications of solid phase extraction to environmental waters have been more limited with more widespread use being for pesticides, aliphatic hydrocarbons, benzyl and alkyl benzenes, priority pollutants, polycyclic aromatic hydrocarbons, chlorinated phenols, polychlorinated phenols, polychlorinated biphenyls, chloroanilines, and tributyltin chloride.[10,11] Excellent recoveries have been reported for hydrophobic compounds and only in cases of more soluble compounds, such as phenol, did recoveries decrease to less than 50%.

Reported here are the results of a sensitive and specific analytical methodology for monitoring acidic chlorinated compounds in drinking water. The method is based on solid phase extraction. The water sample is passed through a small cartridge containing a solid phase sorbent that traps the organic compounds. The cartridge is then eluted with a small quantity of solvent, which undergo further concentration, and derivatization with diazomethane prior to analysis by GC/MS. This method is much more simple than the liquid–liquid extraction method and uses very little glassware. It does not use much solvent or take a lot of time. Fewer steps means less sample loss and fewer artifacts introduced. For the purpose of testing the method, six acidic chlorinated compounds were selected, as they comprise a range of important environmental pollutants such as chlorine disinfection by-products and acidic chlorinated herbicides.

EXPERIMENTAL

Reagents and Materials

Target chlorinated acidic compounds (2-chlorobenzoic acid, 2,4-dichlorobenzoic acid, 3,4-dichlorobenzoic acid, 2-(*p*-chlorophenoxy) propionic acid, 2,4-dichlorophenoxy acetic acid (2,4-D), and 2-(2,4,5-trichlorophenoxy) propionic acid) and the internal standard, *p*-chlorophenoxyacetic acid were obtained from commercial sources (Aldrich Chemical Co., Sigma and the U.S. Environmental Protection Agency). These compounds were selected on their known or possible occurrence in drinking water.[12] Solvents, such as: acetone, methanol, methylene chlorine, and ethyl ether were high purity, pesticide quality (Aldrich Chemical Co.). Sodium sulfate granular anhydrous (ACS grade), potassium hydroxide pellets

(ACS grade). concentrated sulfuric acid (ACS grade), Carbitol (diethylene glycol monoethyl ether), Diazald (N-methyl-N-nitroso-*p*-toluene-sulfonamide), and silicic acid were obtained from Aldrich Chemical Co. Solid phase extraction cartridges were obtained from Water Chromatography Division of Millipore (C18 Sep-Pak) (Milford, Massachusetts).

Stock standard solutions containing multiple analytes, and the internal standard were prepared from pure compounds or from certified standard solutions. Stock standard solutions were prepared in methanol. Aliquot of these solutions were used to spike organic free water. Organic free water was prepared by distilling water in the presence of potassium permanganate and potassium dichromate. Calibration solutions, at five concentrations, were prepared in methylene chloride. These solutions contained all analytes of interest at concentrations of 400, 240, 120, 60, and 20 ng/μL and a constant concentration of 60 ng/μL of the internal standard.

Instrumentation

The analyses were performed on a Hewlett-Packard 5995 gas chromatograph/mass spectrometer computer system. The GC column was an SPB-5 (Supelco), 30 m × 0.32 mm OD, 0.25 μm film thickness, packed with a 5% diphenyl, 94% dimethyl, 1% vinyl polysiloxane bonded phase. Helium was used as the carrier gas, the flow rate was set at 1 mL/min at 280 °C. The GC oven was fixed at 80 °C for 3 min and increased at 10 °C/min to a maximum of 280 °C. The transfer line, injector port, source and analyzer were maintained at 280, 250, 200, and 180 °C respectively. Capillary injection temperature was set to 50 °C, a 2 μL aliquot of the sample was injected. The mass spectrometer was used in the selective ion monitoring (SIM) mode, and only the ions characteristic of the target compounds and the internal standard were monitored. Single ion quantification was performed using the area of a single characteristic ion to calculate both response factor and amount for each of the target compounds. Response factors were found to be constant at this concentration range ($<10\%$ RSD). Average response factors were used in all subsequent calculations. The use of SIM provided a significant reduction in the detection levels as well as simplifying the chromatogram and reducing the integration time needed for quantitation.

Method

For the extraction of the water sample the following procedure was utilized. The water sample was poured into a 2 litre separatory funnel with the stopcock closed, 1 30 μL aliquot of a 60 ng/μL solution containing the internal standard was added, then the sample was acidified to pH of 2 with concentrated sulfuric acid and mixed until homogeneous. The cartridges were previously conditioned by elution of 5 mL of methylene chloride, followed by 5 mL of methanol, and 10 mL of organic free water. The cartridge was not allowed to drain dry after each flush and it was maintained under organic free water until used. The water sample (200 mL) was loaded allowing the separatory funnel to drain through the cartridge, a small vacuum was applied to maintain a flow of 14 mL/min through the cartridge. Recovery was unaffected by the sampling rate at a flow of 14 mL/min. At sampling rates higher than 14 mL/min and sample volumes higher than 500 mL some of the chlorinated acidic compounds were lost. After the sample has passed through, the vacuum was left on for 5 min to dry the cartridge. The cartridge was eluted sequentially with 5 mL of hexane followed by 10 mL of methylene chloride. Each of these two fractions are collected separately. A sodium sulfate drying column, placed between the exit of the cartridge and the top of a concentrator tube, was used to remove any water remaining in the eluant.

After reducing the volume of the methylene chloride extract to 1.0 mL, the sample was methylated using diazomethane.[13] The esterified sample was transferred to a vial, sealed and stored in a dark cool place until analysis.

Procedural blanks were analyzed to assess possible contaminant input from the sample workup. Reagent, organic free, water is treated in identical manner as actual samples. This method of monitoring is considered to be most suitable since blank extracts are subjected to the same potential experimental artifacts under the same relative conditions as the samples. Based upon the analysis of blanks, it appears that the major contribution from artifacts is the adsorbent cartridge, and these seem to vary from batch to batch. Chemical characterization carried out by GC/MS showed that the major contaminants present are primarily residual phthalate esters. These contaminants can be distinguished and they do not interfere with the recognition and quantification of the compound of interest.

RESULTS AND DISCUSSION

The analysis of certain chlorinated acid herbicides in hazardous wastes,[14] ground water,[15] and in ground and finished drinking water,[16] has been demonstrated by several well-established methods developed by EPA. These methods are based on solvent extraction, followed by derivatization and analysis by gas chromatography with electron capture detection. However, only certain chlorinated acids can be determined with these methods, which is time consuming, uses large volumes of highly toxic and suspected carcinogenic reagents and solvents and also needs a confirmatory GC column. Even though the use of capillary columns provides the resolution, the use of electron capture detection may lack the required specificity. In addition the electron capture detector does not offer a large dynamic concentration range, is not rugged, and it is subject to several interferences such as the presence of O_2 that raises background level and thus increases the detection level. Performance requirements for these methods will be used for comparison.

To test the applicability of solid phase extraction combined with gas chromatography/mass spectrometry to analyze semi-volatile chlorinated acids a representative mixture of acidic chlorinated compounds were analyzed. These compounds were selected taking into account its occurrence in water as chlorination by-products or because of its wide use as herbicides.[12] These are thought to represent semi-volatile acidic chlorinated compounds that might be present in

Table 1 Recovery of target compounds from water samples using C_{18} bonded phase cartridges

Compound	*Reagent water*[a]		*Reagent water*[b]		*Reagent water*[c]	
	Mean	*Std. dev.*	*Mean*	*Std. dev.*	*Mean*	*Std. dev.*
2-Chlorobenzoic acid	94.6	10				
2,4-Dichlorobenzoic acid	99.1	13				
3,4-Dichlorobenzoic acid	104.7	11				
2-(*p*-Chlorophenoxy) propionic acid	113.4	6.8				
2,4-D	66.8	18	75	4	96	14
Silvex	100.8	13	88	5	116	22
	Drinking water[a]		Drinking water[d]			
	Mean	*Std. dev.*	*Mean*	*Std. dev.*		
2-Chlorobenzoic acid	102.5	17				
2,4-Dichlorobenzoic acid	67.7	9				
3,4-Dichlorobenzoic acid	67.8	9				
2-(*p*-Chlorophenoxy) propionic acid	192.5	24				
2,4-D	30.7	9.8	71	5		
Silvex	100.8	13	80	5		

[a] This work.
[b] Reference 14.
[c] Reference 15. Average among all spiking levels.
[d] Reference 14. Average among two spiking levels.

drinking water. Optimization studies of the eluants were performed in order to quantitate all chlorinated acidic compounds. The conditions mentioned in the experimental section represent those where the best recoveries were obtained.

To demonstrate laboratory accuracy and precision, seven samples of a laboratory, fortified blank, containing each analyte of concern at a concentration of 2 μg/L were analyzed following the procedure described before. Accuracy was calculated as the mean percentage of the value; and precision, as the relative standard deviation of the measurement. The results are shown in Table 1. Even though there is not enough evidence in the literature as to determine what accuracy and precision should be expected, mean accuracy between 90–115% of the true value and a relative standard deviation $<15\%$ were obtained except for 2,4-D. To determine the extent of possible matrix effects, drinking water samples were split and spiked with the target compounds. Results for this test are also shown in Table 1. Significant differences were observed in the recovery of target compounds from real water samples as compared to organic free water. These differences cannot be totally explained at this moment; however, they might be due to the fact that water samples were considerably high in dissolved solid (water samples were from ground water source with a high calcium and magnesium carbonate content). Differences in the recoveries of chlorinated acids from hard artificial ground water compared to reagent water have been also observed.[15]

The minimum detection limit (MDL) was determined using the procedure described by Glaser *et al.*[17] This is based on the determination of the concentration value that corresponds to three times the standard deviation of replicate

Table 2 Method detection limit for target compounds

Compound	*Concentration (ng/L)*	*MDL (ng/L)*[a]	*MDL (ng/L)*[b]
2-Chlorobenzoic acid	600	26	
2,4-Dichlorobenzoic acid	780	26	
3,4-Dichlorobenzoic acid	660	44	
2-(*p*-Chlorophenoxy) propionic acid	120	74	200
2,4-D	1080	230	1200
Silvex	780	100	170

[a] This work.
[b] Reference 14.

instrumental measurements for the analyte in organic free water. At this concentration, seven samples of organic free water containing the analytes are processed through the entire analytical method. The standard deviation of these seven replicate measurements was calculated and the MDL is computed as:

$$\mathrm{MDL} = t_{(n-1,1-\alpha=0.99)} \times \mathrm{Sc}$$

where $t_{(n-1,1-\alpha=0.99)}$ is the Student's *t* value for a one-tailed test at the 99% confidence level with $n-1$ degrees of freedom. Sc is the standard deviation of the seven replicate analyses. The results for the MDL determination are shown in Table 2; detection levels were obtained at the low ng/L range. When compared to the MDL for acidic chlorinated herbicides using gas chromatography with electron capture detection, ours are lower by approximately a factor of two of the values reported and a factor of 20 of the practical quantitation levels. These detection levels should be appropriate for the monitoring of acidic chlorinated compounds in drinking water as stated in the upcoming regulation.[18] Even though there is not enough information in the literature, from the information presented in Tables 1 and 2 this method compares favorably to the accepted methodology for the analysis of acidic chlorinated herbicides in ground water and hazardous wastes.

To study the effect other water contaminants may have in the recovery of acidic chlorinated compounds, organic free water containing the target compounds was spiked with a mixture of base neutral priority pollutants, phenols and pesticides, Table 3. The water sample was subjected to the same analytical procedure, the results are shown in Figures 1–3. Preliminary evaluation of the analytical procedure using only methylene chloride as the eluting solvent showed coelution between acenaphthene and 2-(*p*-chlorophenoxy) propionic acid, methyl ester and between Silvex and gamma-BHC (Figure 1). The quantitation of coeluting peaks can be successfully accomplished when there is no interference in the mass of the ion used for quantitation. Such is the case for Silvex and gamma-BHC. However, there might be an interference in the methylene chloride extract between acenaphthene and 2-(*p*-chlorophenoxy) propionic acid, methyl ester if the m/z 155 ion is used for quantitation since this ion is a prominent one in the spectra of both compounds. However, when the cartridge is eluted first with hexane, less polar

Table 3 Compound spiked into reagent water samples

Compound No.	*Compound*
1	Chlorotoluene
2	1,4-Dichlorobenzene
3	1,2,3-Trichlorobenzene
4	Naphthalene
5	1,3,5-Trichlorobenzene
6	Chlorobenzoic acid, methyl ester
7	2,4-Dichlorophenol
8	1,2,4,5-Tetrachlorobenzene
9	Internal standard, methyl ester
10	1,2,3,4-Tetrachlorobenzene
11	2,4-Dichlorobenzoic acid, methyl ester
12	3,4-Dichlorobenzoic acid, methyl ester
13	Acenapththene
14	2-(*p*-Chlorophenoxy) propionic acid, methyl ester
15	Fluorene
16	4-Chlorophenyl phenyl ether
17	2,4-D, methyl ester
18	4-Bromophenyl phenyl ether
19	α-BHC
20	Pentachlorophenol
21	β-BHC
22	Silvex, methyl ester
23	δ-BHC
24	Anthracene
25	Heptachlor
26	Aldrin
27	Heptachlor epoxide
28	Fluoranthene
29	2,4,6-Trichloroaniline
30	DDE
31	4,4'-DDD
32	DDT
33	Bis(2-ethyl hexyl) phthalate

compounds are eluted in this fraction while chlorinated acids remain in the cartridge. These are then eluted with methylene chloride. Figure 3 shows the chromatogram of the methylene chloride fraction, it can be seen that the interferences were removed. Figure 2 shows the chromatogram for the hexane fraction, less polar compounds were recovered in this fraction. No chlorinated acidic compounds were detected in this fraction. This fact will allow us to analyze for basic and neutral compounds, pesticides and semi-volatile chlorinated acids simultaneously. Thus minimizing the time spent in sampling, sample preparation, and analysis.

The stability of the samples adsorbed to the cartridge was assessed by analyzing one cartridge at a week interval after collection. After sampling the cartridges had simply been kept wrapped in aluminum foil in a refrigerator at 4 °C.

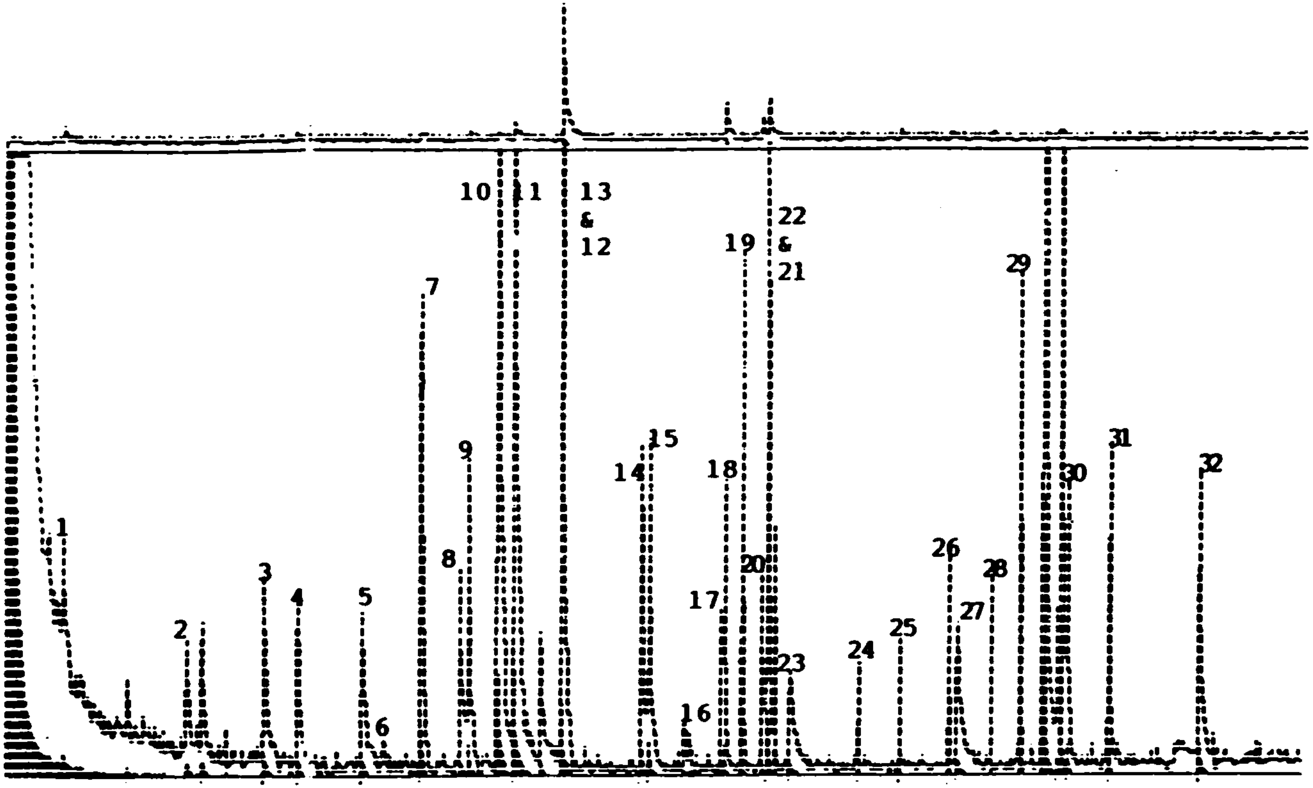

Figure 1 Total ion current chromatogram for the methylene chloride extract of a spiked reagent water sample containing chlorinated acids and common water pollutants. For chromatographic conditions refer to the text. For compound numbering scheme refer to Table 3. The top chromatographic tracing corresponds to the m/z 139 ion.

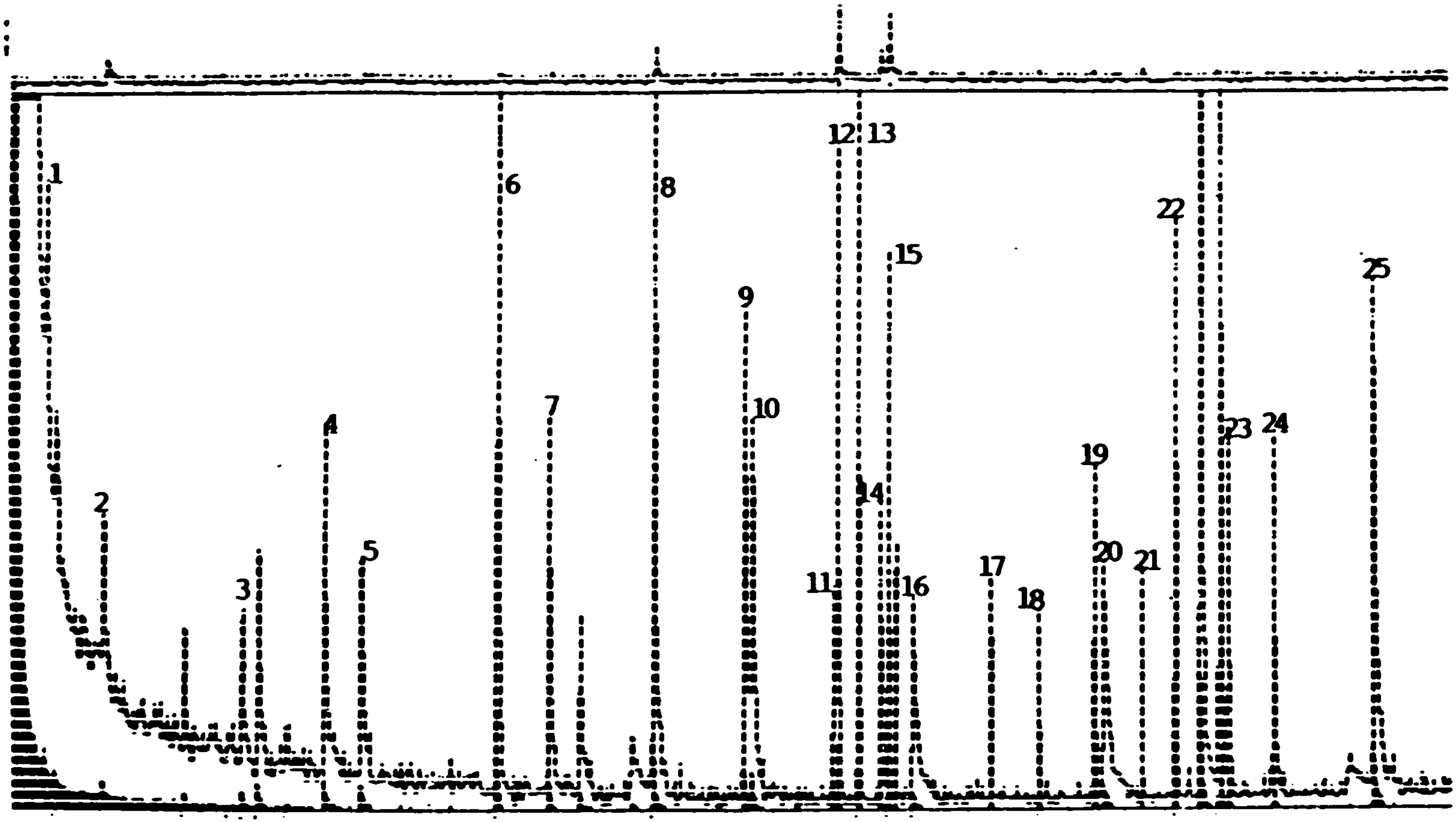

Figure 2 Total ion current chromatogram for the hexane fraction extract of a spiked reagent water sample containing chlorinated acids and common water pollutants. For chromatographic conditions refer to the text. For compound numbering scheme refer to Table 3. The top chromatographic tracing corresponds to the m/z 139 ion.

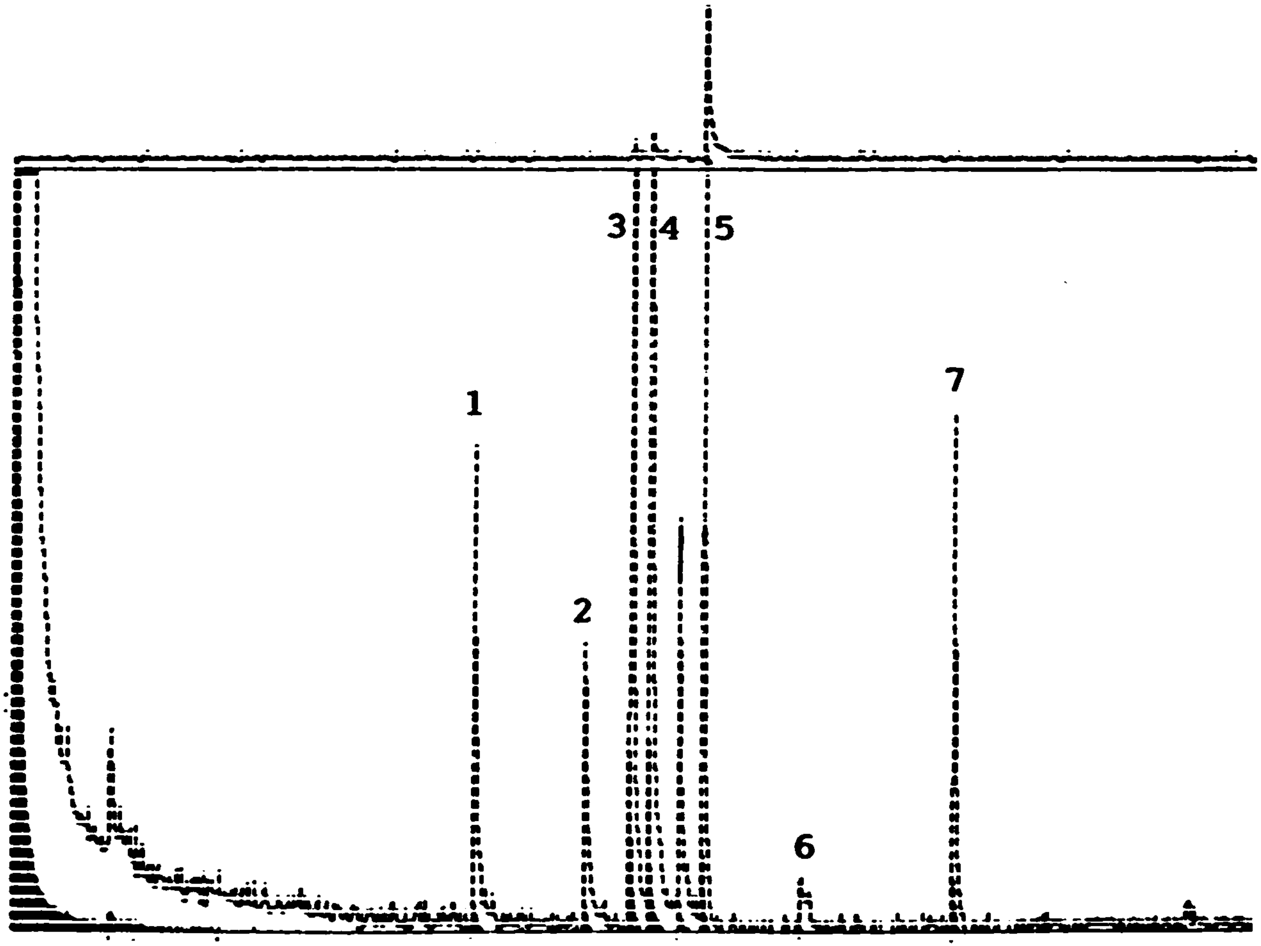

Figure 3 Total ion current chromatogram for the methylene chloride fraction extract after a hexane wash for a spiked reagent water sample containing chlorinated acids and common water pollutants. For chromatographic conditions refer to the text. For compound numbering scheme refer to Table 3. The top chromatographic tracing corresponds to the m/z 139 ion.

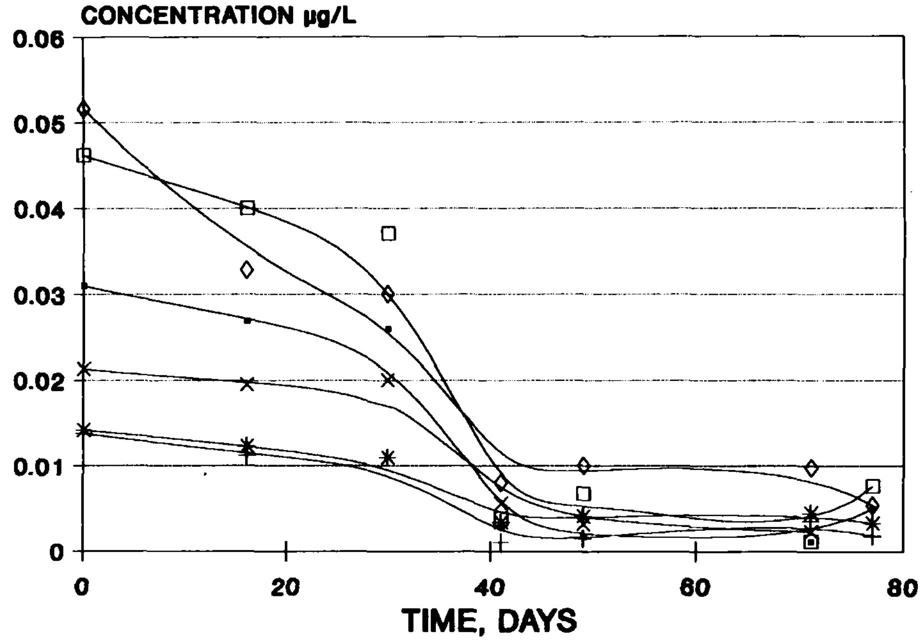

Figure 4 Effect of sample storage. Sample concentration as a function of time. Figure legend: -●- 2-Chlorobenzoic; -+- 2,4-Dichlorobenzoic; -✱- 3,4-Dichlorobenzoic; -⊟- 2-(*p*-Chlorophenoxy); -×- 2,4-D; -◇- Silvex.

The results are shown in Figure 4 The samples were at a concentration below the MDL concentration (2-chlorobenzoic acid, 0.035 μg/L; 2,4-dichlorobenzoic aid, 0.015 μg/L; 3,4-dichlorobenzoic acid, 0.015 μg/L; 2-(*p*-chlorophenoxy) propionic acid, 0.050 μg/L; 2,4-dichlorophenoxy acetic acid (2.4-D), 0.025 μg/L; and 2-(2,4,5-trichlorophenoxy) propionic acid (Silvex), 0.050 μg/L). The results indicate that the sample can be kept for approximately 35 days without significantly affecting the analytical result. The stability seems to be compound dependent, that was the case of Silvex for which a reduction of approximately 40% in the concentration is observed after the first week of storage, for the other compounds this reduction was not as drastic. However, in general our sampling method proved to be not only an effective sample preconcentration method but also an efficient sample preservation method. Furthermore the method is well suited for field applications.

CONCLUSION

Semi-volatile chlorinated aromatic acidic compounds can be extracted from drinking water samples by passing the sample through a cartridge containing C_{18} as adsorbent. The chlorinated acidic compounds were eluted from the cartridge with a small quantity of methylene chloride, concentrated further by evaporation of some of the solvent using a stream of pure nitrogen, and converted to their methyl ester using diazomethane as derivatizing agent. The compounds were separated by injecting an aliquot of the concentrated extract into a fused silica capillary column of a GC/MS system. The overall accuracy and precision are comparable to other methods used for compliance purposes. The detection limit was in the low ng/L range. Possible interferences that can overlap target compounds were removed by washing the extraction cartridge with hexane prior to eluting the target compounds with methylene chloride. The sample preparation method proved to be an effective method for sample preservation. Degradation of the sample components was not observed for periods extending to several weeks.

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