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Journal of Chromatography A, 775 (1997) 267–274

JOURNAL OF CHROMATOGRAPHY A

Purge-and-trap gas chromatography–mass spectrometry in the analysis of volatile organochlorine compounds in water

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Received 20 December 1996; revised 17 March 1997; accepted 18 March 1997

Abstract

A purge-and-trap concentrator combined with GC–MS or GC–MS–MS was evaluated for the determination of volatile organochlorine compounds in aqueous samples. A laboratory-made pulsed spray-and-trap technique has been developed for extraction. For optimization studies, a flow-rate of purge gas at 40 ml/min for 16 min, desorption temperature at 200°C for 3 min, and a cryo-trap at the injection port were used to produce the highest sensitivity for detection of volatile organochlorine compounds. Using sample extraction by purge-and-trap or laboratory-made pulsed spray-and-trap, the limits for detection of organochlorine compounds in aqueous solution, with selected-ion monitoring of GC–MS as well as neutral loss mode of GC–MS–MS, were estimated. The detection limits at the low ng/l levels are described. The application of the methods to the determination of organochlorine compounds in real samples was tested by analyzing a landfill leachate sample. Comparison with the normal purge-and-trap technique is made and the advantage of pulsed spray extraction operating with aqueous systems containing surfactants is also discussed. © 1997 Elsevier Science B.V.

Keywords: Sample handling; Water analysis; Environmental analysis; Purge-and-trap methods; Spray-and-trap methods; Organochlorine compounds; Volatile organic compounds

1. Introduction

Volatile organic compounds, especially organochlorines (VOCs) are an important chemical class of pollutants in water. Chlorination is generally used as a disinfecting step for drinking water. The concentration of organochlorines may increase after chlorination, particularly if natural precursors such as humic and fulvic acids or seaweed metabolic products are present. Most organochlorines are present only at trace levels in the water. They have been already detected in polluted surface waters as well as in ground water [1–5]. The analysis of volatile organochlorines has always been a major challenge to environmental chemists. Usually analytical techniques for the determination of trace amounts of volatile, relatively insoluble organic compounds in water require a pre-concentration step. Various pre-concentration techniques have been developed. Closed-loop stripping or static headspace was introduced by Grob [6]. The purge-and-trap (P&T) or dynamic headspace method has been widely described in literature [7–10]. The advantage of purge-and-trap is that it is sensitive and accurate enough to detect volatile organic compounds; unfortunately, during the analysis of many water samples, foam can cling to the apparatus and contaminate the trap. This may deactivate the trap and allow the introduction of

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PII S0021-9673(97)00306-3

thermal decomposition products from nonvolatile labile materials. Many techniques such as ultrasonic nebulization [11], spray-falling film [12], mammoth-type micropump [13], and spray extraction [14] have been proposed to solve this limitation. The spray-and-trap analytical method is unlike the purge-and-trap method, bubble stripping, however, the spray extraction offers a continuous analyte flux of constant concentration with surface aeration providing high efficiency for liquid to gas transfer. The overpressure for spray is the major problem to be considered in extraction. Matz [15] used a simple spray nozzle aeration ejector with a concurrent atomization process to perform spray extraction for water analysis in field application.

In this project, a short path (10 cm) purge-and-cryotrap technique combined with GC–MS or GC–MS–MS was evaluated for the determination of organochlorine compounds. The detection limits of eight volatile organochlorine compounds in spiked water were determined by using GC–MS and by GC–MS–MS. The applicability of the methods to the determination of organochlorine compounds in real samples was tested by analyzing tap water and landfill leachate samples. Laboratory-made pulsed spray techniques for the extraction of organochlorine compounds in water were studied. The formation of the partition equilibrium of chemicals between water and the gas phase was accelerated for some compounds by spraying the sample liquid and extracting the compounds from the aqueous system into the carrier gas. This spray technique is very useful for those surfactant-containing water samples analysis. The limitations and advantages of this technique are also discussed.

2. Experimental

2.1. Materials

All chemicals and reagents in this study were of analytical or research grade, used without further purification. Standard solution of US Environmental Protection Agency (EPA) 551A Halogenated Volatile Mix including chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, bromodichloromethane, tetrachloroethylene, dibromochloromethane and 1,2-dibromo-3-chloropropane was purchased from Supelco (PA, USA). The internal standard *m*-chlorofluorobenzene was obtained from TCI (Tokyo, Japan). Stainless adsorbent tubes (6.0-mm O.D., 4.0-mm I.D., 10 cm) packed with 20 mg of Tenax TA (0.2 μm) and empty stainless tubes and packed materials were purchased from Scientific Instrument Services (NJ, USA). The landfill leachate samples were collected from a sewage farm at Taichung (Taiwan). 5-ml aliquots spiked with organochlorines and internal standard *m*-chlorofluorobenzene were used as the sample size and transferred into a 10-ml purge-and-trap tube. Tap water and landfill leachate samples were spiked with 10 ml of 100 μg/ml of internal standard and diluted to 100 ml. 5-ml aliquots were used as the sample size.

2.2. Apparatus

A thermal desorption system, Model TD-2 (Scientific Instrument Services) was attached to the injector port of a Hewlett-Packard (Palo Alto, CA, USA) 5890 Series II gas chromatographer equipped with HP 5989B MS Engine detector or JEOL JMS SX/SX 102A (Tokyo, Japan) four-sector tandem mass spectrometer. A 30-m×0.25-mm I.D., 0.14-μm film thickness DB-624 (J&W Scientific, USA) capillary column was used for chromatographic analysis. The GC was operated in the splitless mode and the injector port temperature at 300°C for normal operation. For the cryotrap system the temperature was set at −80°C. The GC–MS interface temperature was 250°C. Helium carrier gas was held at a rate of 1 ml/min by using electronic pressure control. The GC temperature programming was 35°C (held for 5 min) then increased at 10°C/min to 60°C and finally at 30°C/min to 220°C (held for 14 min). A Hewlett-Packard 5989B MS Engine equipped with EI was used for mass spectrometric data.

The operating principle of the laboratory-made spray-and-trap apparatus is shown in Fig. 1. The spray extractor consists of an extraction chamber where the spray process take place. It further consists of a on–off switch valve, solenoid valve, gauge, transfer system, trap tube and sample vessel. The spray extraction is a concurrent atomization process performed in a simple spray nozzle aeration ejector.

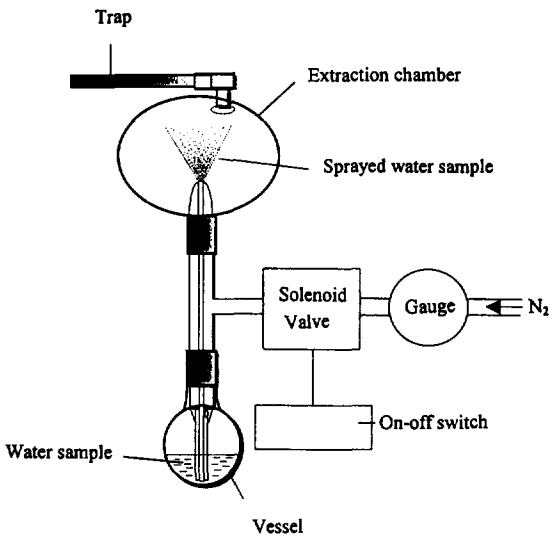

Fig. 1. Pulsed spray-and-trap system.

Turbulence is developed when nitrogen is fed into the water, causing a turbulent dispersion of gas in water. In order to produce an optimum size of droplets, the pressure of nitrogen was adjusted to about 13 p.s.i. (1 p.s.i.=6894.76 Pa). The connected trap cartridge impedes the flow of nitrogen and also cannot tolerate continuous high pressure. The spray efficiency is dependent on the flow-rate or nitrogen pressure. The on–off switch valve is used to control the time of inlet, the solenoid valve is opened for 0.5 s to allow nitrogen to enter the sample vessel. After spraying, the over-pressure in the sampling chamber is released by passing the sample through the trap cartridge while closing the nitrogen inlet valve for 1 s. Since the inlet valve opens immediately after release of excessive pressure for 1 s, a new water sample can enter the sample chamber.

The ionization energy of EI mode was 70 eV. The neutral loss experiments were performed with a JEOL JMS SX/SX 102A high-resolution double focusing four-sector tandem mass spectrometer. The mass spectrometer was operated at a full accelerating voltage of 10 keV. Spectra were obtained with a magnet scan rate of 10 s per decade. In neutral loss experiments, helium was used as the collision gas to attenuate the intensity of the ion beam from the source by 30%. MS–MS data were recorded using a linked scan at a constant ratio of $(B/E)^2 \cdot (E_0 - E)$ to record neutral loss mass spectra from reactions occurring in the first field-free region of the instrument where E_0 is the electric field voltage allowing the passage of precursor ion. The resolution of the mass spectrometer was about 3000.

3. Results and discussion

The analytical selected-ion-monitoring (SIM) conditions for the organochlorines studied, performed by MS are shown in Table 1. Optimization of the purge step working conditions is studied with respect to extraction efficiency for compounds used to spike a 5-ml water sample. A flow-rate of purge gas at 40 ml/min for 16 min and desorption temperature 200°C for 3 min were used to produce the highest sensitivity for detection of volatile organochlorine compounds.

Table 1
The analytical GC–MS (SIM) conditions of organochlorine compounds

No.	Compound	Molecular mass	Retention time (min)	Selected ion (*m/z*)	Confirmed ions (*m/z*)
1	Chloroform	118	7.82	83	85
2	1,1,1-Trichloroethane	132	8.10	97	61, 99
3	Carbon tetrachloride	152	8.31	117	119
4	Trichloroethylene	130	9.16	130	95, 132
5	Bromodichloromethane	162	9.57	83	85
6	Tetrachloroethylene	164	10.56	166	129, 164
7	Dibromochloromethane	206	10.69	127	129
I.S.	*m*-Chlorofluorobenzene	130	10.89	130	95
8	1,2-Dibromo-3-chloropropane	234	13.10	157	75,155

3.1. Comparison of extraction with and without the GC cryo-trap method

The temperature of the oven or the injector is a very important parameter which must be considered primarily for volatile analysis by gas chromatography. Typical total ion chromatograms, obtained when analyzing a standard aqueous solution containing 50 μg/l of each of the selected volatile organochlorines and 10 μg/l of internal standard by purge-and-trap with and without GC cryo-trap method, are obtained. The responses of compounds such as trichloroethylene bromodichloromethane, tetrachloroethylene, dibromochloromethane, 1,2-dibromo-3-chloropropane are higher than that obtained for low boiling point compounds chloroform, 1,1,1-trichloroethane, carbon tetrachloride. Compared with normal purge-and-trap, the response of all compounds is increased with the cryo-trap method. The peak shape is improved greatly, it is narrower and sharper, especially for the low boiling point compounds such as chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, bromodichloromethane. The retention times in the mass chromatogram of those compounds is also longer. For the compounds tetrachloroethylene, dibromochloromethane, *m*-chlorofluorobenzene and 1,2-dibromo-3-chloropropane, the retention times are not changed by using the cryo-trap method. This is very useful for trace volatile compound analysis with the cryo-trap method due to improvement in the peak shape and response of the compounds. Therefore, the GC cryo-trap device was carried in our study for analysis of volatile organochlorines in water.

3.2. Limit of detection

The response factors for analytes were studied which varied from 0.024 to 0.173 with standard deviation from 4.3% to 8.9% (Table 2). This can be explained by the fact that the dipole–dipole interaction of more polar compounds with water molecules reduces their effective vapor pressure and improves their solubility in water. The quantification signal was obtained by integrating the ion current over the scans during elution of the analyte to obtain the GC peak. The limit of detection (LOD) was calculated as the amount of sample necessary to give a signal-to-noise (*S/N*) ratio of 3. The LOD results for all analytes obtained with the purge-and-trap thermal desorption GC–MS with the selected-ion monitoring technique are summarized in Table 3. The relative standard deviation of the integrated GC peak areas varied from 3% to 9%. The detection limits for the determination of all organochlorine compounds except 1,1,1-trichloroethane (10 ng/l) and carbon tetrachloride (30 ng/l) can be down to the ng/l range in water (dibromochloromethane 1 ng/l, trichloroethylene and 1,2-dibromo-3-chloropropane 3 ng/l). From Table 2, the strongest response obtained with the analysis instrument, among the organochlorine compounds, is dibromochloromethane.

Table 2
Response factor of organochlorines using different extraction and detection methods

Compound	Response factor (R.S.D.)		
	Purge-and-trap GC–MS (R.S.D.[a])	Spray-and-trap GC–MS (R.S.D.)	Purge-and-trap GC–MS–MS (R.S.D.)
Chloroform	0.117 (4.3)	0.023 (6.2)	0.224 (5.4)
1,1,1-Trichloroethane	0.024 (5.6)	0.003 (9.7)	0.115 (8.3)
Carbon tetrachloride	0.033 (4.6)	0.002 (8.3)	0.132 (7.1)
Trichloroethylene	0.145 (4.3)	0.060 (4.8)	0.222 (6.8)
Bromodichloromethane	0.164 (5.3)	0.124 (7.1)	0.121 (7.7)
Tetrachloroethylene	0.100 (7.4)	0.049 (5.1)	0.239 (3.6)
Dibromochloromethane	0.173 (6.8)	0.238 (6.5)	0.087 (8.5)
1,2-Dibromo-3-chloropropane	0.113 (8.9)	0.312 (7.2)	0.032 (6.0)

[a] R.S.D.: relative standard deviation (%).

Table 3
Comparison of different methods for detection of organochlorine compounds

Compound	LOD (μg/l)		
	Purge-and-trap GC–MS	Spray-and-trap GC–MS	Purge-and-trap GC–MS–MS
Chloroform	0.008	0.030	1.3
1,1,1-Trichloroethane	0.010	0.250	3.4
Carbon tetrachloride	0.030	0.340	2.3
Trichloroethylene	0.003	0.020	0.6
Bromodichloromethane	0.007	0.005	1.4
Tetrachloroethylene	0.004	0.090	3.5
Dibromochloromethane	0.001	0.004	2.1
1,2-Dibromo-3-chloropropane	0.003	0.002	2.5

3.3. Analysis of tap water and landfill leachate by the purge-and-trap method

The applicability of the method to the determination of organochlorine compounds in real samples was tested by analyzing tap water and landfill leachate samples. None of the studied organochlorine compounds were detected in the tap water sample. Only chloroform was found, about 19.4 μg/l, in the landfill leachate sample by quantification with the addition of internal standard (Fig. 2). Table 4 shows the quantified landfill leachate sample with the standard addition method. In this technique, the samples are spiked with 50 μg/l of the target compounds and 10 μg/l of the internal standard. The relative standard deviations for all target compounds are below 8.0%. The purge-and-trap thermal desorption system has proven to be a useful technique for the analysis of trace organochlorine compounds. The flexibility of the technique means that it can be used for the analysis of trace target compounds in fresh water and landfill leachate supplies.

3.4. GC–MS–MS analysis

The fundamentals and difficulties associated with trace organic analysis and the application of tandem mass spectrometric techniques to the determination of trace organic compounds in complex matrix have been explained in detail by Johnson and Yost [16]. The widespread application of tandem mass spectrometry to trace analysis, as reflected in the number of papers published, is due to its high sensitivity and high selectivity. The major goal of this study is to take advantage of the highly selective neutral loss scan of MS–MS to determine the trace level components of organochlorine compounds in aqueous samples. Neutral loss of mass number 35 u is selected for monitoring the chlorine-containing compounds. The analysis of aqueous samples containing 50 g/l target compounds and 10 g/l internal standard

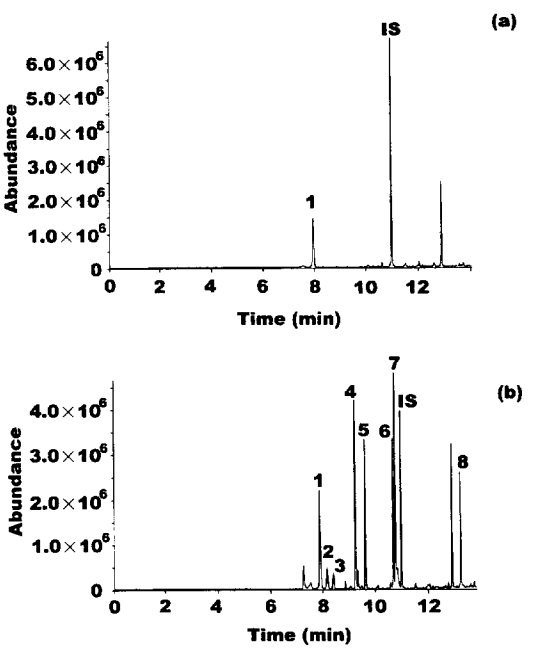

Fig. 2. Analysis of a landfill leachate sample using purge-and-trap GC–MS. (a) Spiked, 10 μg/l internal standard (b) spiked, 50 μg/l organochlorines and 10 μg/l internal standard.

Table 4
Organochlorine compounds detection in landfill leachate by using spray-and-trap GC–MS with spiked concentration addition methods

Compound	Before spike (μg/l)	Spike concentration (μg/l)	After spike (μg/l)	R.S.D. (%)
Chloroform	19.4	50	72.1	6.2
1,1,1-Trichloroethane	ND[a]	50	49.4	8.0
Carbon tetrachloride	ND	50	48.1	5.3
Trichloroethylene	ND	50	50.3	4.2
Bromodichloromethane	ND	50	49.6	5.2
Tetrachloroethylene	ND	50	53.4	7.3
Dibromochloromethane	ND	50	48.3	4.1
1,2-Dibromo-3-chloropropane	ND	50	51.2	2.5

[a] ND: below limit of detection.

with purge-and-trap GC–MS–MS neutral loss scan is exhibited in Fig. 3. The detection response depends on many complex parameters including collisionally-induced dissociation of ions in the field-free region of MS–MS, the potential for neutral chlorine loss and for the transmission of analyzed compound ions, etc. Tetrachloroethylene gave the highest response. The calibration curves for all analyzed compounds exhibit linearity in the concentration range from 5 μg/l to 100 μg/l. The limit of detection of trichloroethylene is 0.6 μg/l. The other compounds cannot be determined below μg/l levels in water by using this method (Table 3). These results can explain why the highly selective neutral loss scan will lose some sensitivity in MS–MS analysis. However, due to its high selectivity, it is very useful for monitoring trace compounds exhibiting a common functionality, especially in a complex matrix sample. In the application of this technique to real sample landfill leachate analysis, chloroform was detected at the level of about 18.2 μg/l. There is no difference compared to that obtained with GC–MS analysis.

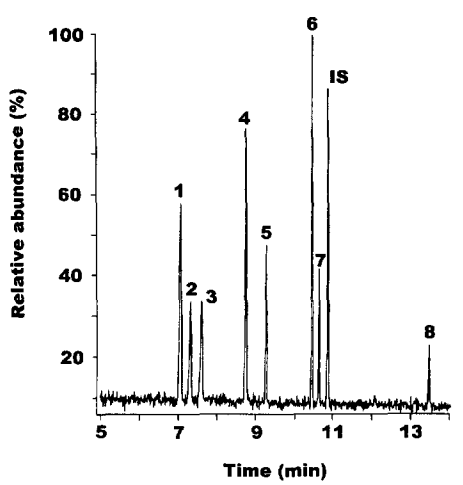

Fig. 3. Gas chromatogram of purge-and-trap GC–MS–MS neutral loss scan of a water sample containing 50 μg/l organochlorines and 10 μg/l internal standard.

3.5. Spray-and-trap

To make the isolation of organic compounds from an aqueous phase by stripping as highly efficient as possible, it is necessary to maximise the contact surface between the liquid phase and the stream of gas which passes through the liquid and transports the organic compounds to the pre-concentration unit. In purge-and-trap analyzes of real samples containing surfactants, the foam produced diminishes the efficiency of extraction. The spray-and-trap method was developed to solve this problem. The one advantage of this technique is that it can achieve very large interfacial areas between water and air. The efficiency of extraction depends on the aqueous sample spray. The droplets can be sprayed faster depending on the pressure applied to the spray nozzle. To control the flow-rate of sparge gas is the determining step for extraction. In the sampler and trap tube of conventional purge-and-trap, the flow-rate cannot be altered to much. Therefore, different kinds of spray methods were designed in laboratories [15,16]. In our study, in order to solve the pressure problem of sparge gas, a laboratory-made pulse spray system was used with an on–off switch to

control the time of spray. The pulse of the spray was set at 0.5 s and switched off for 1 s to release the over-pressure in the sampling vessel. The total ion chromatogram of one of the test mixtures extracted from the aqueous solution is shown in Fig. 4. In the mixture, in spite of the concentration of internal standard (10 μg/l), all the compounds have the same concentration (50 μg/l). The GC peak areas show the response of the system to the analyzed compounds. The calibration curves for all analyzed compounds are constructed linearly in the concentration range 0.1 μg/l to 100 μg/l. The correlation coefficients are over 0.999. A higher response factor was obtained with the higher boiling point components such as 1,2-dibromo-3-chloropropane than with the low boiling point compounds. The response factors for dibromochloromethane and 1,2-dibromo-3-chloropropane are better by a factor of approximately 1.5~3.0 than those obtained with the conventional purge-and-trap method (Table 2). For other compounds, the high flow-rate or over-pressure of sparge gas probably reduced the adsorption of the trap tube. This response is a little less sensitive than the results obtained for those compounds with the spray-and-trap system. The detection limits for all analyzed compounds are shown in Table 3. The best result is 0.002 μg/l for 1,2-dibromo-3-chloropropane. Method validation by spiking was also conducted. The results demonstrate the reliability of the method (Table 4). In order to observe the effects of surfactants on the quantitative experimental data, a solution containing 50 μg/l of analytes and 10 μg/l of internal standard has been spray extracted with surface active agents. The solution was prepared by spiking 3 ml of detergent (Snoop liquid leak detector, Nupro, OH, USA) into the aqueous sample and diluting to 100 ml. A 5-ml portion of the aqueous sample was used for the extraction. The solution containing detergent caused some reductions in the concentration detected (Fig. 4). However, this result shows that the spray-and-trap sampling method is very convenient for the sensitive detection of trace amounts of dissolved organic matter in water samples containing surfactants.

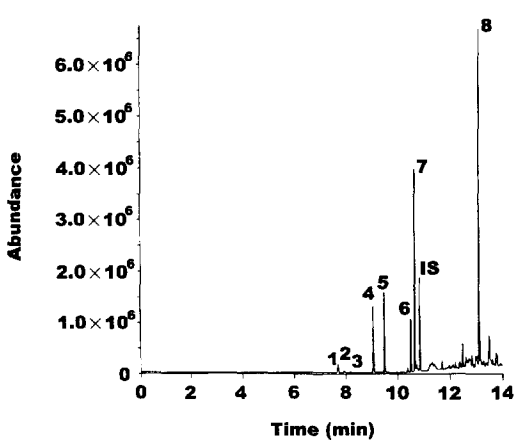

Fig. 4. Gas chromatogram of spray-and-trap GC–MS of a water sample containing 50 μg/l organochlorines and 10 μg/l internal standard.

4. Conclusions

Purge-and-trap as well as spray-and-trap methods combined with GC–MS or GC–MS–MS were evaluated for the determination of organochlorine compounds in water. Conditions of purge-and-trap will affect the sensitivity of detection. For optimization studies, a flow-rate of purge gas at 40 ml/min for 16 min, desorption temperature at 200°C for 3 min, and cryo-trap at injection port were used to produce the highest sensitivity for detection of volatile organochlorine compounds. Comparisons were made by using SIM of GC–MS with various ionization methods. The EI-SIM method was found to be the best mode for the determination of organochlorine compounds at trace levels. Based on these results, the limits for detection of dibromochloromethane and carbon tetrachloride were determined to be 0.001 μg/l and 0.030 μg/l, respectively with sample introduction by purge-and-trap extraction. At neutral loss mode of MS–MS, the limit for detection of trichloroethylene and 1,1,1-trichloroethane were determined to be 0.6 μg/l and 3.4 μg/l respectively, with sample introduction by purge-and-trap extraction. The application of the purge-and-trap system to the determination of organochlorine compounds in real samples was tested by analyzing a landfill leachate sample. Chloroform was detected at the level of 19.4 μg/l.

Laboratory-made pulsed spray extraction of organochlorine compounds in water was also studied. The detection limits for 1,2-dibromo-3-chlo-

ropropane and carbon tetrachloride were 0.002 μg/l and 0.34 μg/l respectively with SIM detection mode in GC–MS. Water samples containing surfactants can also be sampled using the spray-and-trap method. In comparison with the conventional purge-and-trap technique, the pulsed spray extraction has the advantage of being capable of monitoring aqueous systems containing surfactants.

Acknowledgments

The authors thank the National Science Council of the R.O.C. for financial support under grant No. 85-2113-M-005-013.

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