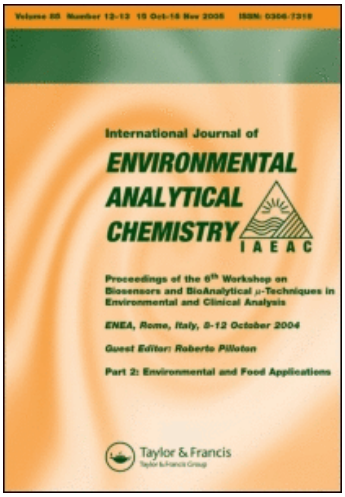

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Chlorinated Acetic Acids in Drinking Water by In-Situ Derivatization and Solid Phase Microextraction

B. Aikawa[a]; R. C. Burk[a]
[a] Centre for Analytical and Environmental Chemistry, Carleton University, Ottawa Ontario, Canada

To cite this Article Aikawa, B. and Burk, R. C.(1997) 'Determination of Chlorinated Acetic Acids in Drinking Water by In-Situ Derivatization and Solid Phase Microextraction', International Journal of Environmental Analytical Chemistry, 66: 3, 215 — 224
To link to this Article: DOI: 10.1080/03067319708028364
URL: http://dx.doi.org/10.1080/03067319708028364

Intern. J. Environ. Anal. Chem., Vol. 66, pp. 215–224
Reprints available directly from the publisher
Photocopying permitted by license only

DETERMINATION OF CHLORINATED ACETIC ACIDS IN DRINKING WATER BY IN-SITU DERIVATIZATION AND SOLID PHASE MICROEXTRACTION

B. AIKAWA and R. C. BURK*

Centre for Analytical and Environmental Chemistry, Carleton University, Ottawa, Ontario, Canada K1S 5B6

(Received 18 September 1996; In final form 6 November 1996)

A method is described for the determination of chlorinated acetic acids in water. The method employs *in situ* derivatization of the acids to their methyl esters using HCl and methanol, followed by solid phase microextraction and quantitation by GC/ECD. Optimized times of derivatization, adsorption and desorption have been determined. Formation of chloroform from decarboxylation of trichloroacetic acid is minimized by choice of reaction time, thereby maximizing formation of the trichloroacetic acid methyl ester. Detection limits are in the low μg/L range for the di- and trichloroacetic acids due to the efficient adsorption of their esters on the SPME fiber, and the large response of the ECD to these species. Recoveries are similar to those found using EPA method 552.

Keywords: Chlorinated acetic acids; drinking water; solid phase microextraction

INTRODUCTION

Drinking water from chlorinated supplies usually contains measurable amounts of chlorinated acetic acids, especially di- and tri-chloroacetic acids. The literature from the past five years contains descriptions of several methods for analysis of haloacetic acids in water samples. The most common of these involve extraction of the acids from water into an organic phase (typically an ether), followed by derivatization using diazomethane or BF_3-methanol and analysis using GC-ECD.[1,2] Addition of salts and acidification of the aqueous sample are known to increase the extraction efficiency.[3] In some cases, the acid also cata-

*Corresponding author.

lyzes the esterification of the acid to the methyl or ethyl ester in the presence of the appropriate alcohol. Some methods involve solid adsorbents. One such method[4] uses an ion exchange resin, followed by methylation using H_2SO_4/ethanol. EPA method 552.1 is similar, but specifies methanol instead of ethanol. EPA method 552 specifies a typical liquid-liquid extraction followed by diazomethane derivatization and GC analysis. The use of diazomethane is reason enough to look for a new method, but recoveries are also operator dependent, especially due to the methylation step.

A new technique for quantitation of organics in water samples has emerged in the last few years. Solid phase microextraction (SPME) makes use of a silica fibre coated with a very small amount of adsorbent in contact with the sample to be "extracted." The water sample is equilibrated with the solid phase and organic compounds are preferentially adsorbed. The fibre is then inserted into the hot injection port of a gas chromatograph (GC), where the analytes are thermally desorbed. Quantitation takes place as in a normal GC run. The method is advantageous for several reasons, namely; no organic solvents are required, sensitivity is high since large preconcentration factors are attainable for many organic species, only a small water sample is required, there is little chance for contamination or loss of analytes and the method is very rapid. Furthermore, the method can be selective, depending on the nature of the analyte and of the solid phase used, and precision is good, even at very low analyte concentrations.

For the purposes of analyzing haloacetic acids however, SPME followed directly by GC is not a suitable approach. Without derivatization, these compounds are not analyzable by GC due to their acidities. GC Columns are available for analyzing underivatized fatty acids, but even the most acidic of these, acetic acid, has a $p_k a$ value of 4.75. By contrast, the $p_k a$ values for the mono- di- and trichloroacetic acids are 2.85, 1.48 and 0.70 respectively. The brominated acetic acids are even more acidic, and the chloro-bromo acids somewhere in between. Clearly, GC of these underivatized acids is not possible.

This report details a new method for these species, which employs a simple derivatization scheme (hydrochloric acid/methanol), followed by headspace SPME of the methyl esters formed.

EXPERIMENTAL

Derivatization and SPME

Chlorinated acetic acids in water samples were derivatized according to the following scheme. 2.6 mL water sample were measured into a 7 mL glass screw

cap vial. To this was added 2.7 mL methanol, 5 drops (approximately 0.1 mL) of concentrated HCl and a stir bar. The vial was capped with a teflon lined septum, and the vial was placed in a water bath at 100°C while stirring magnetically. The reaction was allowed to proceed for 10 minutes. The mixture was then cooled by holding the vial under cold running water, and the vial was equilibrated in room temperature air. The cooling and temperature equilibration took approximately three minutes. The mixture was then stirred magnetically for two minutes to effect equilibration of the esters between the liquid phase and the headspace in the vial. The septum was then pierced by the SPME sheath, and the fiber (30 μm thick polydimethylsiloxane coating, Supelco) was extended into the headspace for exactly 1 minute. The fiber was then retracted into the sheath, and the SPME assembly was withdrawn from the vial for immediate GC/ECD analysis. The entire procedure including the GC analysis thus took approximately 30 minutes.

The SPME fibers were found to be durable enough to last for approximately 200 analyses each before replacement was necessary. Since this method employed a highly acidic aqueous phase, the fibers were cleaned after each day of use by immersing in distilled water with stirring for 5 minutes, then desorbing any organic impurities by inserting into the GC injector at 250°C for 15 minutes.

Some samples were analyzed using EPA method 552. The protocol for the method was followed, except that the sample was not made basic and washed with solvent prior to extraction, since the samples used were relatively free of interferences.

Quantitation by GC/ECD

The GC used in these studies was a Varian 3600 equipped with an electron capture detector, and employing Varian GC-STAR integration software. The column was a 30 m long, 0.53 mm i.d., 0.25 μm film thickness DB-5 column (J&W Scientific). The carrier was helium (10 mL/min) and the makeup gas to the ECD was nitrogen (20 mL/min). The GC program was as follows: 40°C for 4 minutes, ramped to 72°C at 8°C/min, followed by ramping to 250°C at 40°C/min. (The esters of interest eluted during the first ramp; the second ramp to 250°C was used to elute any less volatile compounds that may have been extracted as well.) The injector was a Septum Programmable Injector (SPI) with an on-column glass insert. This insert was placed into the injector upside down from the recommended way, allowing the relatively thick SPME needle to be inserted. The injector was maintained at 250°C.

The SPME needle was inserted into the GC injector, the fiber was extended, and desorption was allowed to occur for 30 seconds, at which time the fiber was retracted and the needle was removed. Quantitations in real samples were based

on peak areas, by using the method of standard additions. Identifications of the esters were initially made by GC/MS (Varian Saturn II GC/ion trap). Subsequent work using the GC/ECD relied on retention times alone.

RESULTS AND DISCUSSION

The Fischer esterification method employed in this work is an acid catalyzed methylation using methanol. Sulphuric acid is often used as the catalyst. Initial studies showed that sulphuric did indeed produce the methyl esters of the three chlorinated acetic acids. However, the SPME fiber was irreversibly damaged even though the fiber was never immersed in the solution. The partitioning of sulphuric acid from the solution to the headspace and then into the fiber was apparently sufficient to oxidize the polymeric phase, rendering it useless. No damage to the fiber was observed using HCl. This was presumably because even though HCl has a higher vapor pressure, it is a much weaker oxidant than H_2SO_4. Thus, all results reported here involved HCl as the catalyst.

Calibration of the ECD for the methyl esters

The ECD was calibrated for its response to the three methyl esters. These esters were first synthesized in gram quantities in our laboratory using the H_2SO_4/methanol system. Their structures were verified by GC/MS and by ^{1}H-NMR. The esters were then dissolved and diluted individually in hexane and repeatedly injected (n = 3) to determine the linear dynamic range and limit of detection for each. The results are presented in Table I. As expected, the sensitivity of the ECD is greater for the more chlorinated species.

Optimization of method parameters

The first parameter to be evaluated was the esterification reaction time. Figure 1 presents plots of peak area versus reaction time (at 100°C) for the di- and

TABLE I Linear dynamic range and limit of detection of each ester on GC/ECD. Limit of detection is based on a S/N ratio of 3.

Ester	*Upper Limit of Linear Dynamic Range (ng)*	*Limit of Detection (pg)*
monochloro	320	15
dichloro	16	5
trichloro	1.6	0.1

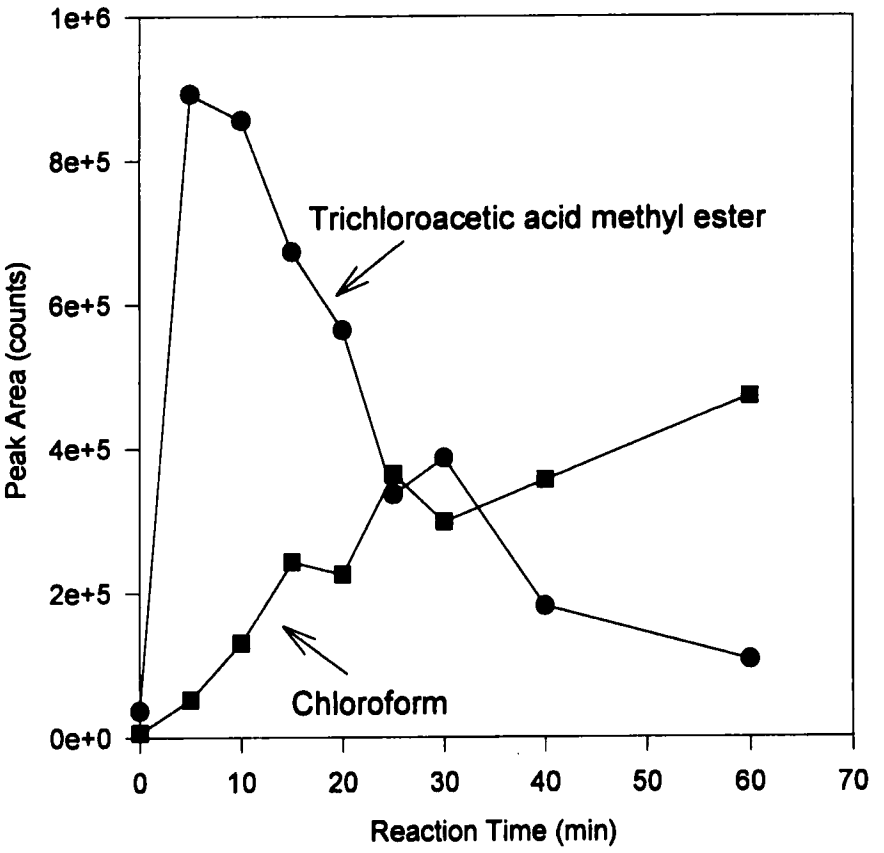

FIGURE 1 Peak areas of trichloroacetic acid methyl ester and chloroform versus reaction time.

trichloroacetic acid methyl esters formed. It is apparent that the dichloroacetic acid has reacted completely, or at least attained equilibrium, within approximately fifteen minutes. However, the peak area for the trichloroacetic acid methyl ester increased until approximately five minutes, then decreased thereafter until almost no ester was detectable. This is explained by the decarboxylation of trichloroacetic acid to chloroform, as has been observed, and made use of, by other researchers.[5,6,7] Thus, the methylation competes with decarboxylation for the trichloroacetic acid as follows:

$$Cl_1CCOOH + CH_3 \Leftrightarrow Cl_3CCOOCH_3 + H_2O \quad (1)$$

$$Cl_3CCOOH \Rightarrow Cl_3CH + CO_2 \quad (2)$$

Reaction (1) is catalyzed by acidic conditions, and is reversible. We have shown, for instance, that the ester is readily hydrolyzed back to the acid in aqueous solution. Reaction (2) requires heat for evolution of chloroform to occur. According to some references, temperatures as low as 40°C are sufficient to produce some chloroform.[8] For the present purposes, it is obviously important to maximize the production of the ester, while avoiding the production of chloroform. This was accomplished by holding the reaction mixture at 100°C only long enough to produce the ester, but not so long as to produce a significant amount of chloroform. The peak area observed for chloroform is also plotted on figure 1, and it was observed that a 10 minute reaction time resulted in high production of ester and low production of chloroform. Since this time was also sufficient for efficient production of the dichloroacetic acid methyl ester, all subsequent reactions were carried out for 10 minutes as well.

The time allowed for adsorption of the esters onto the fiber was set to one minute. This value was chosen, since it was demonstrated that the peak area of dichloroacetic acid methyl ester was constant as long as the adsorption time was at least 20 seconds. The value of one minute was therefore expected to be adequate, even for the slower diffusing trichloroacetic acid methyl ester. The desorption time in the GC injector (30 seconds) was similarly chosen, since it was found that times greater than 10 seconds did not result in greater peak areas for the dichloroacetic acid methyl ester.

Testing the method using synthetic samples

The method was first tested using water samples made in the laboratory by dissolving known amounts of chlorinated acetic acids in distilled, de-ionized water. Figure 2 presents plots of mass of ester desorbed from the fiber versus concentration of the three chlorinated acids in the water sample. The mass of each ester desorbed was calculated from SPME peak area data, and the appropriate ECD calibration curve. Limits of detection (3σ of blank) and quantitation (5σ of blank) for each acid are presented in Table II.

TABLE II Method limits of detection and quantitation for each acid.

Acid	*LOD (μg/L)*	*LOQ (μg/L)*
monochloroacetic	400	600
dichloroacetic	5	13
trichloroacetic	1.6	2.7

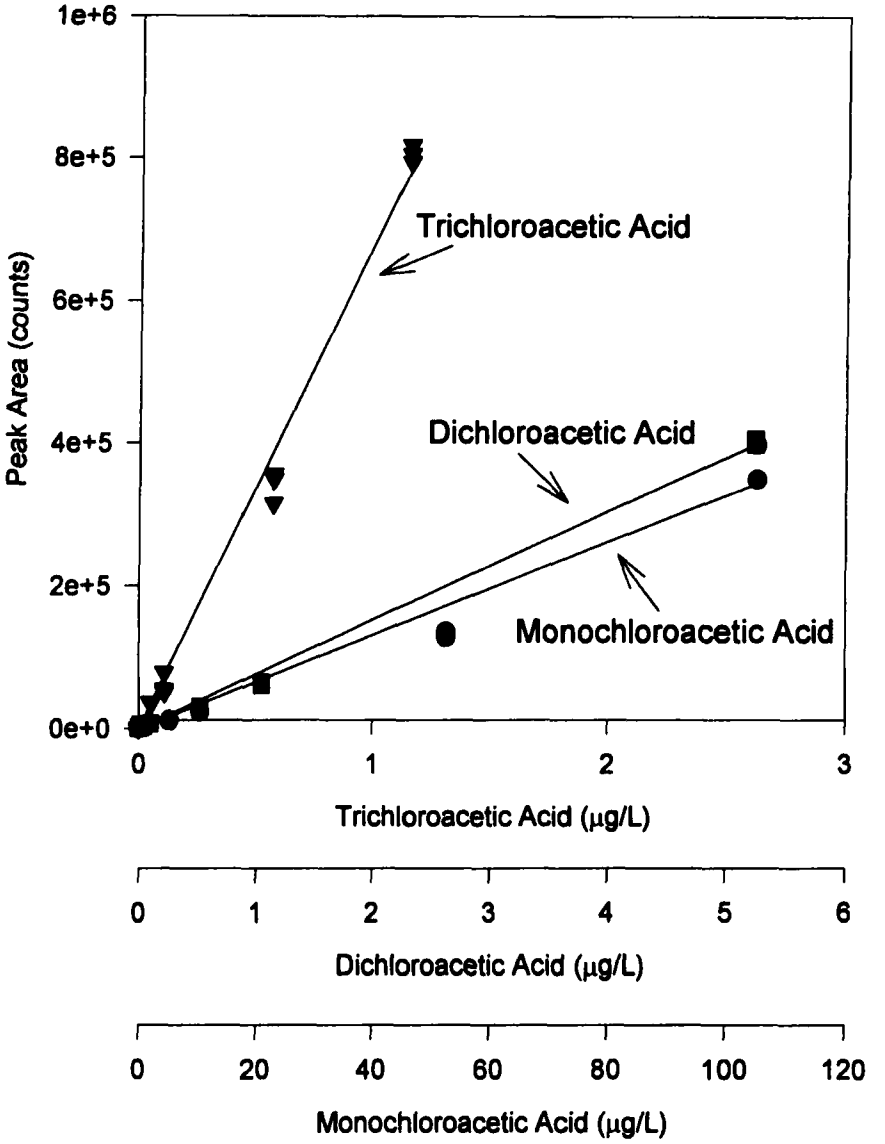

FIGURE 2 Method calibration curves for the three chlorinated acetic acids. Note that the species being detected are the methyl esters of these acids.

Note the different concentration scales for each acid in Figure 2. The more highly chlorinated the acid, the higher is the signal for a given concentration. This is a combination of more sensitive detection by the ECD of more chlorinated species, and of better partitioning of the more chlorinated species into the

fiber. The latter can be illustrated by the overall partition coefficients for the three species, i.e. (mass of ester on fiber)/(concentration of chlorinated acetic acid in solution). This quantity is the slope of the appropriate line in Figure 2 divided by the slope of the appropriate ECD calibration curve. These data are presented in Table III. It is apparent that not only is the order of ECD responses tri > di > mono, but also the amount of partitioning of each ester into the fiber is tri > di > mono. The low ECD response and low partition coefficient of monochloroacetic acid methyl ester combine to give the rather low sensitivity for this species.

For comparison with an established analytical method, samples of water fortified with 40 μg/L of each of di- and trichloroacetic acid were analyzed five times using each of the EPA method and the SPME method. Using the EPA method, the recoveries were 83 ± 9% for dichloroacetic acid and 125 ± 8% for trichloroacetic acid. For the SPME method, the recoveries were 79 ± 5% and 108 ± 5% respectively.

Analysis of Drinking Water Samples

To test the method on real samples, water samples were collected from several points in the City of Ottawa drinking water distribution system, since it is well established that the concentrations of chlorinated by-products vary with distance from the water treatment plant.[9] Samples representing residence times in the system of 0 (i.e. at each of the two treatment plants), 1 and 8 days were taken, transported to the laboratory and analyzed on the same day. To take account of any matrix effects, all samples were analyzed by the method of standard additions. Additional concentrations of 10, 20 and 30 μg/L of di- and trichloroacetic acids were added to each water sample, and the method as outlined above was followed. No standard additions of monochloroacetic acid were to any sample, since previous surveys of Ottawa water had found concentrations of this species well below our detection limit.[9]

TABLE III ECD and method responses, and calculated partition coefficients.

Acid	*Method Response (peak area/(μg acid/L))*	*ECD response to ester (peak area/μg)*	*Partition Coefficient (μg ester on fiber/(μg acid/L))*
Monochloroacetic	3.37×10^{3}	1.0×10^{8}	3.4×10^{-5}
Dichloroacetic	7.71×10^{4}	1.7×10^{9}	4.5×10^{-5}
Trichloroacetic	6.85×10^{5}	5.5×10^{9}	1.2×10^{-4}

Figure 3 presents a typical standard addition curve for di- and trichloroacetic acids in water from the treatment plant. These plots were linear, with $r^2 > 0.99$. Furthermore, the slopes of these plots matched those obtained from extraction of samples made from distilled water. This indicates little or no interference from components of the drinking water. A summary of analytical data is presented in Table IV, along with the approximate residence time of the water in the distribution system at the four sampling points used. The concentrations of the two species are of the magnitudes expected for these water samples, based on previous surveys.[9] The measured values are at or below the provisional guidelines set by the World Health Organization. Both are low near the treatment plant. The concentration of dichloroacetic acid increases through the distribution system, whereas that of the trichloroacetic acid is approximately constant. The latter may be due to competing phenomena—one tending to increase the concentration, and the formation of chloroform decreasing it, as outlined above.

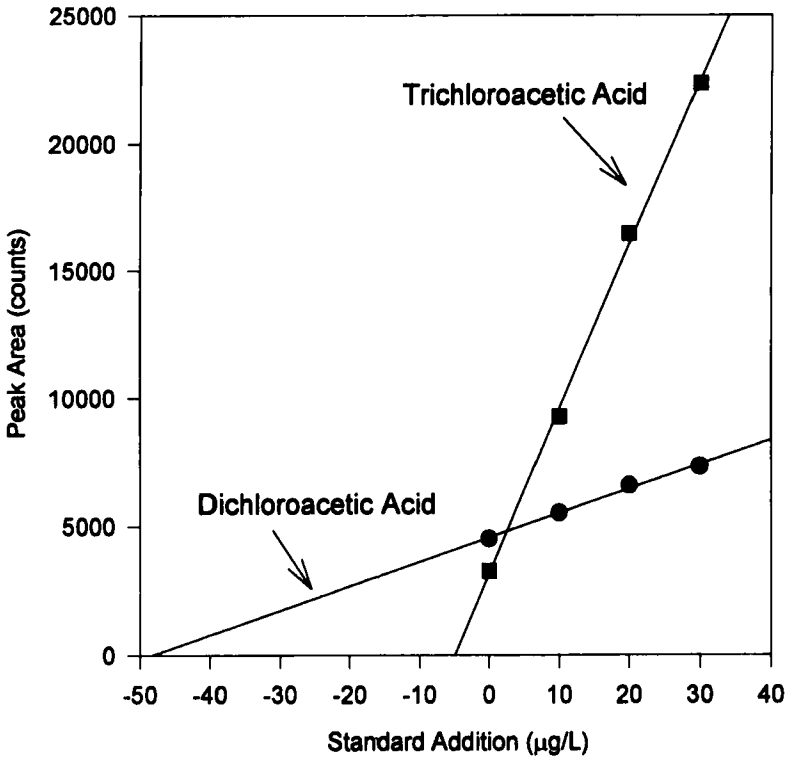

FIGURE 3 Standard addition curves for di- and trichloroacetic acid in water.

TABLE IV Summary of analytical results for drinking water samples

Sampling Point	*Water residence time, days*	*Dichloroacetic Acid, μg/L*	*Trichloroacetic Acid, μg/L*
Lemieux Island treatment	0	9	5
Britannia treatment plant	0	15	10
Carleton University	1	25	10
Carleton University	1	33	10
Carleton University	1	66	8
Carleton University	1	16	6
Carleton University	1	48	5
Manotick, Ontario	8	59	9

CONCLUSIONS

A rapid and sensitive method for the determination of chlorinated acetic acids has been described. The method relies on the formation of the methyl esters of the acids, followed by their determination by headspace SPME. The method in inexpensive, since the only reagents required are methanol and hydrochloric acid, and the only equipment required is the SPME fiber and holder assembly and the GC. The formation of chloroform from trichloroacetic acid is minimized if the esterification reaction time is optimized. The detection limits for the di- and trichloroacetic acids are in the low μg/L range. Whereas we used fibers with a 30 μm thick adsorbent, others are available with a 100 μm thick adsorbent. The detection limit for the monochloroacetic acid could thus be improved by the use of a thicker film SPME fiber, since the quantity of analyte presented to the GC detector is proportional to the volume of the adsorbent phase on the fiber.

References

[1] A. G. Mohan, T. A. Cleveland and C. D. Hertz, *Proc. Water Qual. Technol. Conf*, (pt. 1), pp. 135–148 (1990).
[2] R. C. Barth and P. Snyder, *J. Am. Water Works Ass.* **84**, 94–98 (1992).
[3] R. J. Peters, C. Erkelens, E. W. B. de Leer and L. de Galan, *Water. Res.* **25**, 473–477 (1991).
[4] E. E. Hargesheimer and T. Satchwill, *Aqua (London)*, **38**, 345–351 (1989).
[5] V. Senft. *J. Chromatogr.* **337**, 126–130 (1985).
[6] J. M. Christensen, K. Rasmussen and B. Køppen, *J. Chromatogr.* **442**, 317–323 (1988).
[7] K. Cammann and K. Hübner, *J. Chromatogr.* **648**, 294–298 (1993).
[8] G. L. Lebel and D. T. Williams, *Intern. J. Environ. Anal. Chem.*, **60**, 213–220 (1995).
[9] D. T. Williams, G. L. Lebel and F. M. Benoit, Health Canada Report 95-EHD-197 (1995).