ELSEVIER

Journal of Chromatography A, 962 (2002) 197–206

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Analysis of organotin compounds by grignard derivatization and gas chromatography–ion trap tandem mass spectrometry

Shinji Tsunoi[a,*], Takashi Matoba[a], Hirotaka Shioji[a], Le Thi Huong Giang[a], Hiroya Harino[b], Minoru Tanaka[a]

[a]*Research Center for Environmental Preservation, Osaka University, Suita, Osaka 565-0871, Japan*
[b]*Osaka City Institute of Public Health and Environmental Sciences, Tennoji, Osaka 543-0026, Japan*

Received 1 March 2002; received in revised form 23 April 2002; accepted 25 April 2002

Abstract

The determination of organotin compounds in water using gas chromatography–tandem mass spectrometry (GC–MS–MS) is described. Several organotin derivatives were synthesized by the reaction of organotin chlorides with Grignard reagents such as methyl-, propyl- and pentylmagnesium halides. After the optimization of the GC–MS–MS conditions, several derivatizations with the Grignard reagents were compared by evaluating the molar responses and volatilities of the derivatives and derivatization yields. As a result, the derivatizing reagent of choice is pentylmagnesium bromide. Calibration curves for the mono-, di- and tributyltins and mono-, di- and triphenyltins with pentylmagnesium bromide were linear in the range of 0.5–100 pg of Sn. The instrumental detection limits of six organotins ranged from 0.20 to 0.35 pg of Sn. The recovery tests from water samples (500 ml) were performed by using sodium diethyldithiocarbamate (DDTC) as a complexing reagent. Except for monophenyltin, the absolute recoveries of organotins from pure water at 200 ng of Sn/l were satisfactory. The recoveries calibrated by surrogate compounds (perdeuterated organotin chlorides) ranged from 71 to 109%. The method detection limits ranged from 0.26 to 0.84 pg of Sn (500-ml sample). This method was applied to the recovery of organotins from river water and seawater. The calibrated recoveries were between 90 and 122%.

Keywords: Derivatization, GC; Grignard derivatization; Organotin compounds

1. Introduction

In the 1960s, tributyltin (TBT) and triphenyltin (TPT) had begun to be used as a biocide in antifouling paints. Since then, the growing use of TBT and TPT brought about the contamination of seawater through leaching of the organotins from the antifouling paints leading to the unexpected effects on nontarget marine organisms. At present, it is well-known that TBT and TPT are one of the endocrine disruptors (EDs) and have an influence on marine organisms even at the ng/l level [1]. TBT and TPT were found to undergo degradation accompanied by the loss of the organic groups to inorganic tin in the environment [2,3]. Furthermore, the high levels of TBT and its degradation products, monobutyltin

*Corresponding author. Tel.: +81-6-6879-8977; fax: +81-6-6879-8978.
E-mail address: tsunoi@epc.osaka-u.ac.jp (S. Tsunoi).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)00534-4

(MBT) and dibutyltin (DBT), were found in marine mammals [4].

The most commonly used techniques for the determination of organotin compounds are gas chromatography (GC) and liquid chromatography (LC) coupled with selective detection [5–8]. In spite of the requirement of derivatization, GC is an attractive method for the analysis of organotin compounds due to its high separation ability. After derivatizations with $NaBH_4$, RMgX, and $NaBEt_4$, the derivatized organotins were generally detected by selective techniques such as mass spectrometry (MS) [9–13], flame photometry [14–17], atomic absorption spectrometry [18], atomic emission spectrometry [19], and inductively coupled plasma-mass spectrometry [20–25]. Among them, GC–MS has been generally used due to its low detection limit, high selectivity and wide use. To detect the organotins at a ng/l level in water, the concentration of a large-volume sample has been performed with liquid–liquid and solid-phase extractions. Recently, the solid-phase microextraction (SPME) [11,15–17,25–27], large volume injection (LVI) of the sample into a GC [10,22], and the purge and trap method [13] have been also reported.

Tandem mass spectrometry (MS–MS), which has rapidly become popular since the appearance of ion trap instruments, is one of the most selective and sensitive analytical methods. Recently, the determination of three butyltins in human body fluids using SPME–GC–MS–MS was reported by Dunemann and coworkers [27]. They used $NaBEt_4$ as the derivatizing reagent. With the conventional GC–MS, several derivatizing reagents have been examined [9,28–30], however, with MS–MS, it has not yet been accomplished. We expected the more sensitive and selective determination of organotin compounds by using GC–MS–MS.

Here, we report a method for the determination of six organotin compounds including three butyltins and three phenyltins using GC–MS–MS. Several derivatizations of the organotins were examined to make their sensitivities high. We also discuss the preparation of standard organotin solutions to avoid their adsorption onto the bottle surface. We used perdeuterated organotin chlorides as the surrogate compounds for an accurate analysis [10,31].

2. Experimental

2.1. Materials

Monobutyltin (MBT) trichloride and diphenyltin (DPT) dichloride were purchased from Aldrich (Milwaukee, WI, USA), monophenyltin (MPT) trichloride and triphenyltin (TPT) chloride from Strem Chemicals (Bischeim, France), dibutyltin (DBT) dichloride from TCI (Tokyo, Japan), tributyltin (TBT) chloride from Wako (Osaka, Japan), and the

Table 1
MS–MS conditions

Segment		Retention time (min)	Precursor ion (m/z)	Product ion (m/z)	CID voltage (V)
1	Bu_4Sn-d_{36} (I.S.)	12.73	318	254	0.75
2	TBT-d_{27}	13.53	323	253	0.80
3	TBT	14.03	305	249	0.80
4	DBT-d_{18}	14.82	323	253	0.75
	DBT	14.95	319	249	0.75
5	MBT-d_9	15.77	328	258	0.75
	MBT	15.83	319	249	0.75
6	MPT-d_5	18.33	344	274	0.75
	MPT	18.35	339	269	0.75
7	DPT-d_{10}	20.00	355	285	0.75
	DPT	20.07	345	275	0.75
8	TPT-d_{15}	21.73	366	202	1.3
	TPT	21.80	351	197	1.3
9	Ph_4Sn-d_{20} (I.S.)	23.47	366	202	1.3

Grignard reagents from TCI and Aldrich. Sodium diethyldithiocarbamate trihydrate (DDTC) and tropolone were obtained from Wako and TCI, respectively, deuterated organotin compounds (shown in Table 1) from Hayashi Pure Chemical Industry (Osaka, Japan), and the pesticide grade solvent and other chemicals from Wako. Water was processed with a Milli-Q VOC water purification system (Millipore, Bedford, MA, USA). Silica gel (BW-127ZH, 100–270 mesh) was a product of Fuji Silysia (Aichi, Japan).

2.2. Instrumentation and conditions

All analyses were performed with a Finnigan MAT GCQ (San Jose, CA, USA) ion trap mass spectrometer equipped with a Finnigan GC. The column was a DB-5MS (30 m×0.25 mm I.D., 0.25 μm d_f, J&W Scientific, Folsom, CA, USA). The carrier gas was high purity helium (99.9999%) with a constant linear velocity of 40 cm/s. The GC oven temperature was programmed as follows: 1 min at 50 °C, to 100 °C at 20 °C/min, to 290 °C at 10 °C/min, 5 min at 290 °C (total analysis time, 30 min). The ion source, injection and transfer-line temperatures were set at 200, 270 and 290 °C, respectively. All injections were in the splitless-mode with the split vent closed for 1 min. The mass spectrometer was operated in the electron ionization mode. The mass range was scanned from 50 to 600 u at 0.5 s/scan for the full scan mode. For MS–MS, the product ions were monitored by selected reaction monitoring (SRM). The MS–MS conditions are shown in Table 1. Chromatographic run was split into nine segments. In segments 4–8, the dual MS–MS mode was used for isolation and collision of the two precursor ions.

2.3. Synthesis of alkylated organotins

For identification and check of the volatility of the organotin derivatives, methyl, propyl and pentyl derivatives of each organotin were synthesized. The representative procedure is as follows: triphenyltin chloride (1.93 g TPT-Cl, 5 mmol) was added to hexane (200 ml). Pentylmagnesium bromide was added dropwise to the stirred solution at room temperature. The reaction was monitored by TLC (10% ethyl acetate–hexane: $R_f = 0.05$ for TPT-Cl, 0.60 for pentyl TPT). After the disappearance of TPT-Cl, the excess Grignard reagent was destroyed with 5 ml of 1 *M* H_2SO_4, and then 100 ml of water was added. The layers were separated, and the organic layer was washed with water (100 ml). The organic layer was dried over Na_2SO_4, filtered, and concentrated. Purification by column chromatography on silica gel (5% ethyl acetate–hexane) afforded pentyl TPT in 90% yield (1.90 g). The product was identified by GC–MS and ^{1}H- and ^{13}C-NMR.

2.4. Standard solution of organotins

Standard stock solutions of individual organotin chlorides (1 μg/μl) were prepared in glass sample tubes by dissolving the organotin chlorides in acetone and stored at 4 °C. The mixed working solutions (100 pg/μl, 1 and 10 ng/μl as Sn in acetone) were prepared daily from the stock solutions. Surrogate solution (1 ng of Sn/μl) was also prepared by dissolving perdeuterated organotin chlorides in acetone and stored at 4 °C. Internal standard solution (100 pg of Sn/μl) was prepared by dissolving perdeuterated tetrabutyltin-d_{36} and tetraphenyltin-d_{20} in hexane and stored at 4 °C.

Concentration and detection limits of organotins given in this paper are expressed as an amount of Sn. Organotin chloride and their derivatives are indicated by the same abbreviations.

2.5. Grignard reagents

To avoid the contamination of organotin compounds [9,22], we prepared Grignard reagent in our laboratory.

2.6. Calibration curves

We used perdeuterated organotin chlorides as the surrogate compounds and tetrabutyltin-d_{36} and tetraphenyltin-d_{20} as the internal standards for an accurate analysis [10,31]. To toluene (1 ml) spiked with the standard solution of the organotins (5 or 10 μl) and the surrogate solution (10 μl), pentylmagnesium bromide was added and the mixture was then allowed to stand at 40 °C for 60 min. The excess

Grignard reagent was treated with 1 *M* H_2SO_4 (5 ml). After pure water (50 ml) was added to the mixture, the derivatized organotins were extracted with hexane (10 ml). The hexane solution was reduced in volume to 0.9 ml and the internal standard solution (0.1 ml) was added. One μl of this solution was then subjected to GC–MS.

The organotins were quantified by comparing the peak areas of the organotins with those of the internal standards (tetrabutyltin-d_{36} and tetraphenyltin-d_{20}).

2.7. Extraction from water samples

To 500 ml of water sample spiked with deuterated organotin (10 μl of acetone solution), sodium diethyldithiocarbamate (DDTC, 0.2 g) and sodium chloride (100 g) were dissolved, and the mixture was then extracted with toluene (50 ml). After the phase separation, the organic phase collected through a column of anhydrous sodium sulfate was evaporated to ca. 1 ml under reduced pressure. Pentylmagnesium bromide was added to the organic phase and then allowed to stand at 40 °C for 60 min. The reaction mixture was treated as described above.

3. Results and discussion

3.1. MS–MS conditions for pentylated organotins

We synthesized the methylated, propylated and pentylated organotin derivatives and purified them by column chromatography on silica gel. Confirmation of the alkylated organotins was performed by ^{1}H- and ^{13}C-NMR and GC–MS. To program the isolation of the parent ions for every compound, the overall run time was split into nine segments. For example, the optimum MS–MS conditions for the pentylated organotins are shown in Table 1, and the MS–MS spectra of pentyl TBT and TPT under the optimum collision-induced dissociation (CID) conditions, together with their MS spectra are shown in Fig. 1. With TBT, the CID of $m/z=305$ ($[Bu_2PeSn]^+$) showed two product ions, $m/z=249$ and 235, which correspond to the [precursor–Bu]$^+$ and [precursor–Pe]$^+$, respectively. On the other hand, with TPT, the CID of $m/z=351$ ($[Ph_3Sn]^+$) showed two product ions, $m/z=120$ and 197, which correspond to the [precursor–Ph_3]$^+$ and [precursor–Ph_2]$^+$, respectively.

3.2. Optimization of derivatizing reagents

A screening of the derivatizing reagents was performed by evaluating the volatilities and molar responses of the derivatives and the derivatization yields. At first, the recoveries of the derivatives in the concentration step were examined in which 10 ml of the hexane solution containing the synthesized alkylated organotins (methylated, propylated and pentylated organotins) was concentrated to 1 ml (Table 2). With methylation, DBT and MPT were significantly lost due to their high volatility. Compared with the other two derivatizations, pentylation showed a slightly better result than propylation. Recoveries of the six pentylated organotins were higher than 90%. Under the optimum MS–MS conditions, the molar responses of the propylated and pentylated organotins were compared. As can be seen in Table 3, the pentylated derivatives were more sensitive than the propylated ones except for DPT.

Next, we examined the derivatization yields of the propylation and pentylation reactions. The standard solutions of the organotin chlorides were subjected to the derivatization reactions. Based on the derivatization reactions, pentylation showed a much better yield than propylation (Table 4). We considered that the derivatization of choice was pentylation rather than propylation in view of the molar response and volatility of the derivatives.

3.3. Preparation of organotin chloride standard solutions

We first prepared the standard solutions (1, 10, 100 pg/μl) by dissolving the organotin chlorides in toluene in a glass sample tube. The toluene solution (0.5 or 1 ml) was used to construct the calibration curves. However, we could detect relatively small amounts of MBT and MPT from the 1 and 10 pg/μl solutions. It was anticipated that MBT and MPT were adsorbed onto the glass surface in toluene due to their high polarity. A 10-ng/μl standard solution (10 μl) was added to toluene (1 ml) and subjected to the derivatization (Table 5, run 1). We conducted the

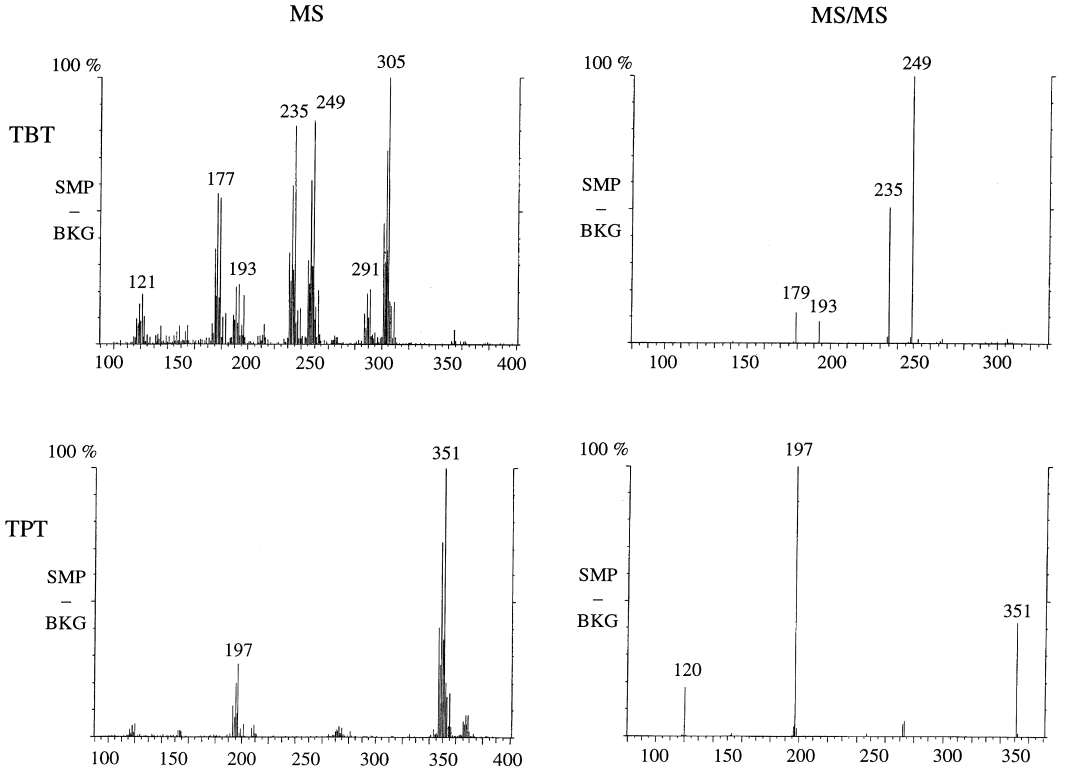

Fig. 1. MS and MS–MS spectra of pentyl TBT and TPT under optimun conditions.

Table 2
Recoveries of organotin derivatives during concentration

Organotin derivative	Recovery (%)					
	MBT	DBT	TBT	MPT	DPT	TPT
Methylated	–[a]	80.5	91.8	81.6	90.0	95.7
Propylated	88.3	88.8	92.4	82.5	94.9	94.8
Pentylated	96.4	91.8	91.6	100	100	101

Conditions: hexane solution (10 ng each/10 ml) was concentrated to 1 ml.
[a] Not determined.

Table 3
Relative sensitivity of organotin derivatives with MS–MS

Organotin derivative	Relative sensitivity (%)					
	MBT	DBT	TBT	MPT	DPT	TPT
Propylated	59.3	91.1	80.9	97.8	110	97.5
Pentylated	100	100	100	100	100	100

Table 4
Relative overall yield

Grignard reagent	Relative yield (%)					
	MBT	DBT	TBT	MPT	DPT	TPT
C_3H_7MgBr	84.7	82.6	95.4	59.2	86.9	87.7
$C_5H_{11}MgBr$	100	100	100	100	100	100

Conditions: standard solution (100 ng each/10 μl) was derivatized with Grignard reagents (C_3H_7MgBr: 2 *M* in THF (1 ml), $C_5H_{11}MgBr$: 1 *M* in THF (1 ml), in toluene (1 ml).

following experiment to examine the degree of adsorption; a 10-ng/μl standard solution was quickly diluted to 0.1 ng/μl with toluene in a glass tube and then 1 ml of the solution was subjected to derivatization (run 2). As compared with run 1, low yields of the derivatives in run 2 were observed for all six organotins, especially in MBT and MPT. To suppress the adsorption on the glass wall, several bottles were examined (Table 5). Silylation of the glass with 1,1,1,3,3,3-hexamethyldisilazane suppressed the adsorption to some extent (run 3). With the use of PFA (copolymer of tetrafluoroethylene and perfluoro(alkyl vinyl ether)) bottles, the recoveries of three butyltins were apparently low (run 4). LDPE (low density polyethylene) bottles could almost suppress the adsorption (run 5), but were not suitable for long-term storage due to the apparent leak of toluene. Next, we examined polar solvents for preparation of organotin standard solutions. Then, by using acetone, the adsorption of the organotins onto the bottle surface was completely suppressed even in a glass sample tube. For the derivatization with Grignard reagent, the standard solution is generally prepared by dissolution in an aprotic solvent to avoid its reaction with Grignard reagent. Though the Grignard reagent is consumed by the reaction with acetone, 20 μl of acetone (0.269 mmol) is significantly less than the amount of Grignard reagent used in this study (1 mmol).

3.4. Qualitative analysis

With pentylmagnesium bromide, the quantitative calibration and detection limits were examined using an organotin standard solution prepared in acetone. As described above, the standard solution (5 or 10 μl of acetone) and surrogate solution (10 μl of acetone) were transferred to toluene (1 ml), and then pentylmagnesium bromide was added to the solution. As a result, all six organotins showed good linearity having *R*-values ranging from 0.9941 to 0.9996 in the range of 0.5–100 pg/μl. The detection limits obtained from the standard deviation at 0.5 pg were in the range of 0.20–0.35 pg (Table 6).

Table 5
Effect of the bottle material on the adsorption of the organotins

Run	Bottle material	Standard solution used		Amount of organotins added (ng)	Relative yield (%)					
		Concentration (ng/μl)	Amount (μl)		MBT	DBT	TBT	MPT	DPT	TPT
1	Glass	10	10[e]	100	100	100	100	100	100	100
2	Glass	0.1[d]	1000	100	38.7	79.9	74.9	41.9	83.6	91.3
3	Silylated glass[a]	0.1[d]	1000	100	66.4	79.9	87.3	81.9	76.0	90.2
4	PFA[b]	0.1[d]	1000	100	82.4	81.3	79.3	106	89.3	94.3
5	LDPE[c]	0.1[d]	1000	100	91.0	92.2	92.6	93.9	94.0	95.4

[a] Silylated with 1,1,1,3,3,3-hexamethyldisilazane.
[b] Copolymer of tetrafluoroethylene and perfluoro(alkyl vinyl ether).
[c] Low density polyethylene.
[d] Prepared by diluting standard solution (10 ng/μl) with toluene in the bottle, and then transferred to a reaction flask.
[e] Added to toluene (1 ml) in the reaction flask.

Table 6
Quantitative calibration and detection limit

	MBT	DBT	TBT	MPT	DPT	TPT
Correlation coefficient, R	0.9966	0.9966	0.9941	0.9996	0.9984	0.9963
Detection limit[a], pg	0.29	0.29	0.35	0.35	0.20	0.21

Concentration range: 0.5–100 pg/μl.
[a] Calculated as standard deviation×t, where t=1.895 from one-sided t-distribution at 95% confidence level (n=8, at 0.5 pg).

3.5. Extraction from pure water

A complexing reagent is generally required for the extraction of monoorganotins due to their high polarity. First, a recovery test from pure water was carried out in the presence of tropolone. However, the recovery with tropolone was significantly low, especially for the di- and mono-organotins (data not shown). To improve the recovery, we used sodium diethyldithiocarbamate (DDTC) alternatively utilized

Table 7
Recoveries of organotins from pure water

DDTC (g)	NaCl (g)	Absolute recovery,%					
		MBT	DBT	TBT	MPT	DPT	TPT
0	0	0	0	109	0	0	104
0.2	0	113	113	126	151	129	118
0.2	100	115	110	120	149	127	114

Extraction conditions: pure water, 500 ml; toluene, 50 ml; spiked OTs, 100 ng each.

Table 8
Method detection limits

	MBT	DBT	TBT	MPT	DPT	TPT
Detection limit,[a] ng/l	0.84[b]	0.42	0.55[b]	0.64	0.26	0.60

[a] Calculated as standard deviation×t, where t=1.895 from one-sided t-distribution at 95% confidence level (n=8, at 0.5 pg each).
[b] Calculated as B+standard deviation×t, where B=positive blank and t=1.895 from one-sided t-distribution at 95% confidence level (n=8, at 0.5 pg each).

Table 9
Recoveries of organotins from environmental water

		MBT	DBT	TBT	MPT	DPT	TPT
River water[a]	Absolute recovery,% [c]	67.7	94.1	103	90.1	117	105
	(RSD, n=4)	(36)	(8.0)	(7.9)	(44)	(10)	(7.9)
	Calibrated recovery,% [d]	90.1	106	108	122	94.9	116
	(RSD, n=4)	(16)	(10)	(2.8)	(24)	(13)	(4.1)
Seawater[b]	Absolute recovery,% [c]	80.1	96.6	101	85.2	108	100
	(RSD, n=4)	(40)	(7.5)	(6.5)	(29)	(11)	(8.3)
	Calibrated recovery,% [d]	91.0	99.5	105	88.6	106	103
	(RSD, n=4)	(12)	(8.8)	(5.2)	(16)	(9.2)	(5.9)

Extraction conditions: pure water, 500 ml; DDTC, 0.2 g; toluene, 50 ml; spiked OTs, 100 ng each.
[a] Taken from Ina river.
[b] Taken from Port of Osaka.
[c] Mean recovery calculated by the peak area ratio to I.S.
[d] Mean recovery calculated by the peak area ratio to corresponding surrogates (except that MPT was calibrated by MBT-d_9 due to instability of MPT-d_5 in the solution, see Refs. [32,33]).

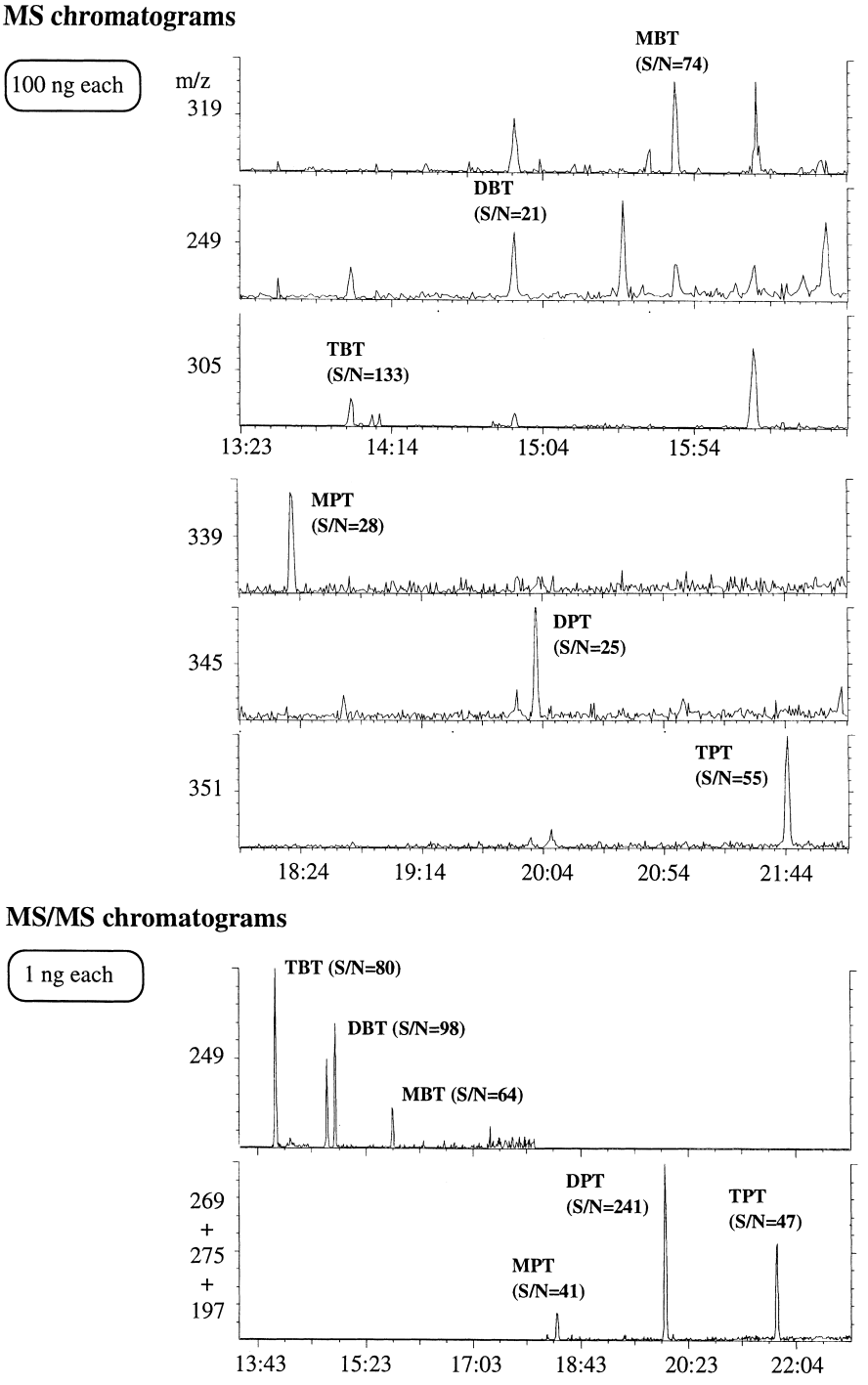

Fig. 2. MS and MS–MS chromatograms of six organotins spiked in river water.

as a complexing reagent [9]. Because it is known that DDTC is decomposed to an amine and CS_2 under acidic conditions, the extraction was performed under neutral conditions.

The results of the recoveries are shown in Table 7. Even in the absence of DDTC, TBT and TPT were quantitatively recovered. No signals for the other four organotins were observed. The addition of DDTC drastically improved the recoveries of the four organotins and the recoveries of all the organotins were satisfactory. The addition of NaCl was indispensable for the fast clear-phase separation. The method detection limits obtained from standard deviation at 0.5 pg (500-ml sample) were in the range of 0.26–0.84 pg (Table 8).

3.6. Recovery from environmental water

The recovery tests from river water and seawater samples (500 ml) were performed at 200 ng/l. Except for MBT and MPT, the absolute recoveries were in the range of 94.1–117% (Table 9). The reproducibilities of this method were found to be RSD 6.5–11% for four replicates. The reproducibilities of the monoorganotins were improved by calibrating with the surrogate compounds.

River water samples spiked with 1 and 100 ng of organotins were analyzed by MS–MS and MS methods, respectively. Fig. 2 shows the chromatograms obtained by the two methods. The S/N ratios obtained from the MS chromatograms at 100 ng were comparable to those obtained from the MS–MS chromatograms at 1 ng. Without any clean up of the sample, less interferences were observed in the MS–MS chromatograms of the river water sample. The S/N ratios in the MS–MS chromatogram of the river water were very similar to those of pure water. This is clearly ascribed to the high selectivity of the MS–MS analysis.

4. Conclusion

We have demonstrated the MS–MS analysis of six organotins. The optimum derivatization for MS–MS was pentylation in view of the molar response and volatility of the derivatives. We have shown that the standard solution of organotin chloride should be prepared in a polar solvent of acetone even for the Grignard derivatization in order to avoid the adsorption of organotin chloride on the glass wall. The present MS–MS method has several advantages over conventional GC–MS. The response in GC–MS is more susceptible to background level than that in GC–MS–MS. In the case of GC–MS state used in this study, the limit of detection with MS–MS is about two orders of magnitude lower than that with MS. Less interferences were observed in the MS–MS analysis of environmental water sample due to its high selectivity. MS–MS using perdeuterated organotin chlorides as surrogate compounds can provide a precise and accurate measurement. Thus, the MS–MS analysis was proved to be effective for its application to environmental water samples. However, further improvement is required for the extraction of the monoorganotin compounds from water samples.

References

[1] P.E. Gibbs, G.W. Bryan, P.L. Pascoe, G.R. Burt, J. Mar. Biol. Ass. U.K. 67 (1987) 507.
[2] R.J. Maguire, J.H. Carey, E.J. Hale, J. Agric. Food Chem. 31 (1983) 1060.
[3] R.F. Lee, A.O. Valkirs, P.F. Seligman, Environ. Sci. Technol. 23 (1989) 1515.
[4] S. Tanabe, Mar. Pollut. Bull. 39 (1999) 62.
[5] K.M. Attar, Appl. Organomet. Chem. 10 (1996) 317.
[6] M. Abalos, J.-M. Bayona, R. Compano, M. Granados, C. Leal, M.-D. Prat, J. Chromatogr. A 788 (1997) 1.
[7] L. Ebdon, S.J. Hill, C. Rivas, Trends Anal. Chem. 17 (1998) 277.
[8] M. Takeuchi, K. Mizuishi, T. Hobo, Anal. Sci. 16 (2000) 349.
[9] J.A. Stäb, W.P. Cofino, B. van Hattum, U.A.T. Brinkman, Fresenius J. Anal. Chem. 347 (1993) 247.
[10] C.G. Arnold, M. Berg, S.R. Müller, U. Dommann, R.P. Schwarzenbach, Anal. Chem. 70 (1998) 3094.
[11] N. Cardellicchio, S. Giandomenico, A. Decataldo, A. Di Leo, Fresenius J. Anal. Chem. 369 (2001) 510.
[12] K. Mizuishi, M. Takeuchi, T. Hobo, J. Chromatogr. A 800 (1998) 267.
[13] R. Eiden, H.F. Schöler, M. Gaastner, J. Chromatogr. A 809 (1998) 151.
[14] H. Harino, M. Fukushima, M. Tanaka, Anal. Chim. Acta 264 (1992) 91.
[15] G. Lespes, V. Desauziers, C. Montigny, M. Potin-Gautier, J. Chromatogr. A 826 (1998) 67.
[16] S. Aguerre, C. Bancon-Montigny, G. Lespes, M. Potin-Gautier, Analyst 125 (2000) 263.

[17] G.B. Jiang, J.Y. Liu, Anal. Sci. 16 (2000) 585.
[18] D.S. Forsyth, D. Weber, K. Dalglish, Talanta 40 (1993) 299.
[19] R. Lobiński, W.M.R. Dirkx, M. Ceulemans, F.C. Adams, Anal. Chem. 64 (1992) 159.
[20] L. Moens, T. De Smaele, R. Dams, P.V.D. Broeck, P. Sandra, Anal. Chem. 69 (1997) 1604.
[21] T. De Smaele, L. Moens, R. Dams, P. Sandra, J.V. der Eycken, J. Vandyck, J. Chromatogr. A 793 (1998) 99.
[22] H. Tao, R.B. Rajendran, C.R. Quetel, T. Nakazato, M. Tominaga, A. Miyazaki, Anal. Chem. 71 (1999) 4208.
[23] J. Vercauteren, A. De Meester, T. De Smaele, F. Vanhaecke, L. Moens, R. Dams, P. Sandra, J. Anal. At. Spectrom. 15 (2000) 651.
[24] A.M. Leach, M. Heisterkamp, F.C. Adams, G.M. Hiefyje, J. Anal. At. Spectrom. 15 (2000) 151.
[25] J. Vercauteren, C. Pérès, C. Devos, P. Sandra, F. Vanhaecke, L. Moens, Anal. Chem. 73 (2001) 1509.
[26] E. Millan, J. Pawliszyn, J. Chromatogr. A 873 (2000) 63.
[27] L. Dunemann, H. Hajimiragha, J. Begerow, Fresenius J. Anal. Chem. 363 (1999) 466.
[28] J. Ashby, P.J. Craig, Sci. Total Environ. 78 (1989) 219.
[29] R. Morabito, P. Massanisso, P. Quevauviller, Trends Anal. Chem. 19 (2000) 113.
[30] M.B. da la Calle-Guntiñas, R. Scerbo, S. Chiavarini, P. Quevauviller, R. Morabito, Appl. Organometal. Chem. 11 (1997) 693.
[31] P.W. Looser, M. Berg, K. Fent, J. Mühlemann, R.P. Schwarzenbach, Anal. Chem. 72 (2000) 5136.
[32] J.A. Stäb, U.A.T. Brinkman, W.P. Cofino, Appl. Organometal. Chem. 8 (1994) 577.
[33] T. Iwamura, K. Kadokami, D. Jin-ya, K. Tanada, Bunseki Kagaku 49 (2000) 523.