Automated Headspace SPME-Retention Time Locked-Isotope Dilution GC/MS for the Analysis of Organotin Compounds in Water and Sediment Samples

ENVIRONMENTAL ANALYSIS

Christophe Devos, Frank David and Pat Sandra*
Research Institute for Chromatography, Kennedypark 20, B-8500, Kortrijk, Belgium,
*correspondence: pat.sandra@richrom.com

An automated method for the simultaneous determination of six important organotin compounds namely monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPhT), diphenyltin (DPhT) and triphenyltin (TPhT) in water and sediment samples is described. The method is based on derivatization with sodium tetraethylborate followed by automated headspace-SPME combined with GC/MS under retention time locked (RTL) conditions. Deuterated organotin analogues are used as internal standards. Limits of quantification (LOQs) are from 1.3 to 15 ng.L^{-1} (ppt) for water samples and from 1.0 to 6.3 µg.kg^{-1} (ppb) for sediment samples.

Introduction

Because of the recent awareness of the toxicological effects of many organometallic species, organometal speciation is presently a topic of intense research. Within the class of organometallics, organotin compounds are probably the most widely spread in the environment due to their use as biocides in polymers, in the agricultural industry, as antifouling paints, etc. [1-3]. Organotin compounds degrade in the environment into more polar metabolites and, consequently, a large diversity of organotin compounds can be detected in environmental samples. Alarming toxic effects on living organisms have been reported [4,5] and developing simple, highly sensitive and robust analytical methods for their determination in environmental samples is presently of utmost importance.

A fully automated organotin analyzer is presented. The method is applied to the determination of monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPhT), diphenyltin (DPhT) and triphenyltin (TPhT) in water and sediment samples. The method consists of in situ derivatization and automated headspace solid phase microextraction (SPME) combined with state-of-the-art retention time locked (RTL)-GC/MS. Home-synthesized deuterated organotin compounds are used as internal standards.

Experimental

Chemicals and reagents

Mono-(MPhT), di-(DPhT) and tri-(TPhT)phenyl tinchloride as well as mono-(MBT) and di-(DBT) butyltinchloride were purchased from Strem Chemicals (Newburyport, MA, USA). Tri-(TBT) and tetra-(TeBT)butyltinchloride were from Fluka Chemie AG (Buchs, Switzerland). Glacial acetic acid (99.99 %) and sodium acetate were obtained from Sigma-Aldrich (Bornem, Belgium) and a 0.2 M HOAc/NaOAc buffer with pH 5.3 was prepared. Ethanol (Suprasolv grade) was purchased from Merck (Darmstadt, Germany) and sodium tetraethylborate (NaBEt4) from Strem Chemicals. A 1 % (m/v) solution of NaBEt4 in Milli-Q water was freshly prepared daily. Deuterated organotin standards (as chlorides), MBT-d9, DBT-d18, TBT-d27, MPhT-d5, DPhT-d10 and TPhT-d15 were synthesized as described elsewhere [6]. For internal standardization, a solution of ca. 5 and 0.5 mg.L^{-1} in ethanol was used to spike sediment and water samples, respectively. Concentrations of organotin compounds are expressed as amount referring to the respective cation, except when mentioned otherwise.

Stock solutions of 100 mg.L^{-1} from the native organotin compounds and further dilutions were prepared in ethanol. Standard mixtures of butyltins and phenyltins were prepared separately as we observed that mixing the six organotin compounds together resulted in exchange of the butyl and/or phenyl groups, forming artifacts [6]. All standard solutions were stored in the dark at 4°C.

The freshwater reference sediment, BCR-646, was purchased from the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium).

Instrumentation

Analyses were performed on an Agilent 6890 GC – 5975 MSD (Agilent Technologies, Little Falls, DE, USA) combination equipped with retention time locking (RTL) software. A 0.75 mm i.d. SPME liner was installed in the split/splitless injector and the temperature was set at 250°C. The column was a 30 m x 0.25 mm i.d. x 0.25 µm df HP-5MS (Agilent Technologies). The oven was programmed from 50°C (1 min) at 10°C.min^{-1} to 300°C (4 min) and the carrier gas was helium (constant pressure 70 kPa, 41 cm.s^{-1} at 50°C). MS parameters were: transfer line 300°C, source temperature 230°C, MS quad temperature 150°C, 50 ms dwell time per ion and solvent delay 4 min. Automated headspace-SPME extraction and desorption were carried out with a Multi Purpose Sampler (MPS2) from Gerstel GmbH (Mülheim, Germany). The extraction time and temperature were 30 min and 80°C with a stirring rate of 500 rpm (1 min incubation time at 80°C). Desorption time was 1 min (splitless injection) followed by 2 min bake-out time. Fibers coated with 100 µm polydimethylsiloxane (Supelco, Bellefonte, PA, USA) were used.

Sample preparation and derivatization

Water samples. Aqueous test samples were prepared by adding an appropriate amount of organotin standard solutions to a mixture of 5 ml Milli-Q water and 5 ml buffer solution in a closed-cap headspace vial of 20 ml. For real-life water samples, the same procedure was applied but 1 ml ethanol was added to prevent adsorption of the organotin compounds to the glass wall or to the small particles present in those samples. Subsequently, appropriate amounts of the six internal standards are added, resulting in a concentration of approximately 250 ng.L^{-1}. Derivatization is performed by adding 300 µL of a 1 % NaBEt4 solution. The sample vials are vigorously shaken and placed in an ultrasonic bath for 10 min. The vials are then placed in the MPS-2 autosampler for headspace-SPME extraction.

Sediment samples. The organotin compounds are leached out according to the procedure described by De Smaele et al. [7]. 1 ml glacial acetic acid (99.99 %) and 1 ml ethanol were added to 0.5 g of wet sediment sample and the sample is placed in an ultrasonic bath for 3 h. Appropriate amounts of deuterated internal standards were added together with, in case of spiking experiments or standard addition calibration, native organotin standards. Internal standard concentrations in the order of 100 µg.kg^{-1} (ppb) were used. Afterwards, 8 ml of buffer solution was added and derivatization was performed with 500 µL of the 1 % NaBEt4 solution as described for the water samples. The dry mass of the sediment sample was measured off-line by weighing after thermal treatment at 105°C for 12 h.

Results and discussion

The GC method was retention time locked (RTL) with tetrabutyltin (tr=16 min) according to the procedures described [8,9]. The locked retention times for the different target organotin compounds with their deuterated analogues are listed in Table 1. Combining GC/MS in scan mode with the RTL screener software provides easy peak location and identification of the target organotin compounds based on their mass spectra and retention times. From the mass spectra of pure compounds, specific ions for ion monitoring detection were chosen in order to construct the GC/MS method. The selected ions and ion monitoring windows for all organotin compounds, deuterated and native, are given in Table 1.

Headspace SPME analysis was applied because it offered not only the fastest equilibration times and highest sensitivities, but above all because it was much more robust for enrichment from difficult matrices such as sediment samples compared to liquid SPME. Extraction at 80°C during 30 min was applied as standard operating procedure.

Figure 1 shows the twofold TIC chromatogram of a 100 ng.L^{-1} (ppt) spiked water sample obtained when measuring in the simultaneous scan/SIM mode with the Agilent 5975 MSD. A much higher sensitivity (20 to 30 times) is reached when working in SIM mode.

Water was spiked with 250 ng.L^{-1} of the deuterated internal standards and with the native organotin compounds in the range 10-1000 ng.L^{-1} (9 point calibration) and analyzed as described. Regression coefficients were between 0.997 and 0.999. The limit of detection (LOD is 3 x signal/noise) for each of the six organotin compounds was determined and they are presented in Table 2. The limit of quantification is put higher than usual (LOQ is 10 x signal/noise) because background concentrations in an analytical laboratory environment have been taken into consideration. Relative recoveries (spike versus internal standards) for all organotin solutes ranged from 98 to 117%.

Blank sediment samples were spiked in a 1-1000 µg.kg^{-1} range (5 point calibration) with a fixed concentration of the deuterated internal standards (100 µg.kg^{-1}) giving regression coeffi-

cients between 0.998 and 0.999. The LOD and LOQ values for sediment are given in Table 2.

Figure 2 shows a twofold chromatogram, analyzed simultaneously in scan and SIM, of the BCR 646 reference material certified for all six organotin compounds. Phenyltins are substantially less present in the sample than the butyltin compounds. Table 3 presents the obtained concentrations for the organotin compounds with the certified values depicted in column 1. When comparing both TIC signals A and B, the major advantage, i.e. higher sensitivity, of measuring organotin compounds in SIM mode is obvious. For sediment samples, an even more huge and unstable background in scan mode is obtained, compared to water samples (Figure 1). The same freshwater reference sediment was analyzed in the scan mode only (chromatogram C) and, remarkably, the simultaneous scan/SIM mode shows almost no loss in sensitivity compared to working only in scan mode.

In 2005, the described method has been accredited in a routine laboratory under the norm NBN EN ISO 17025. The method was tested thoroughly for its long-term robustness during a case-study at the harbor of Antwerp where sediment samples in different areas were taken and subsequently screened for TBT contamination. Concentrations ranged from 15 µg.kg^{-1} in the port of Antwerp up to 43 mg.kg^{-1} near a ship repair unit [10].

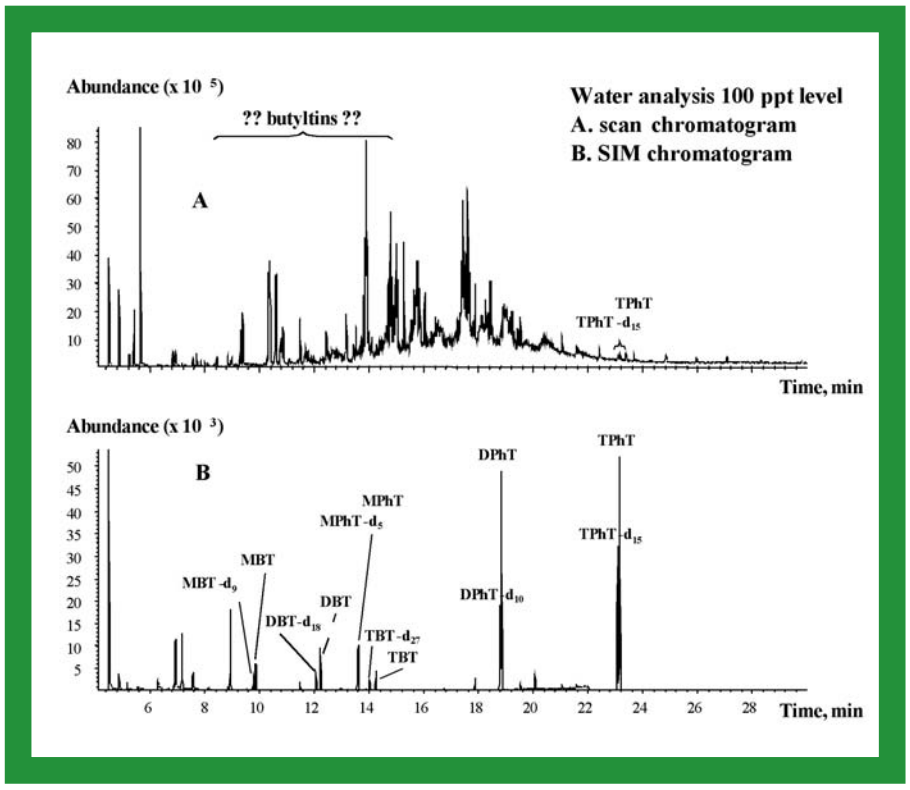

Figure 1 Twofold TIC chromatogram of a spiked water sample (+/- 100 ng.L^{-1} level) analyzed in the simultaneous scan(A)/SIM(B) mode.

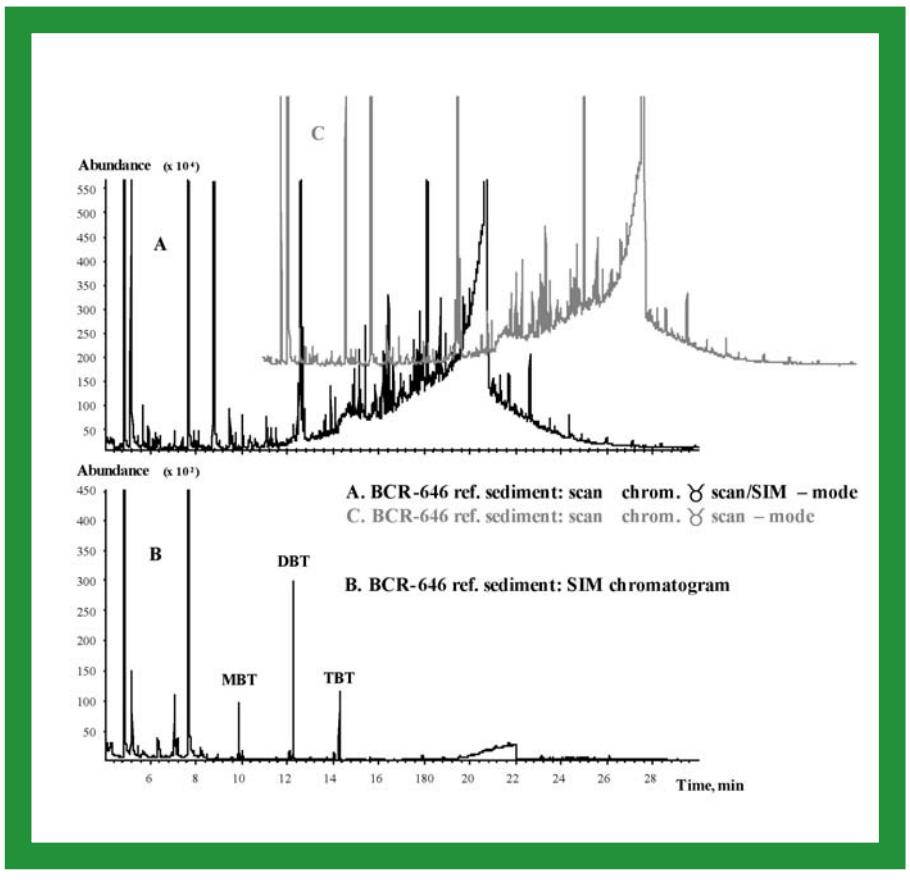

Figure 2 Twofold TIC chromatogram of the BCR 646 freshwater sediment sample measured in the simultaneous scan(A)/SIM(B) mode. Chromatogram C: Analysis of the BCR-646 sample in scan mode only.

Table 1. Locked retention times, windows for ion monitoring and selected ions (bold are quantification ions) for the target organotin compounds and their deuterated analogues.

Organotin compound	Locked retention time time (min)	SIM windows (min)	Selected ions
MBT(d9)	9.82	8.50-11.40	242, 244
MBT	9.91	8.50-11.40	233, 235
DBT(d18)	12.09	11.40-13.00	277, 279
DBT	12.26	11.40-13.00	261, 263
MPhT(d5)	13.60	13.00-13.80	316, 318
MPhT	13.63	13.00-13.80	289, 291
TBT(d27)	14.05	13.80-17.00	258, 260
TBT	14.28	13.80-17.00	227, 255
DPhT(d10)	18.83	17.00-22.00	311, 313
DPhT	18.89	17.00-22.00	301, 303
TPhT(d15)	23.09	22.00-25.00	364, 366
TPhT	23.17	22.00-25.00	349, 351

Table 2. LODs and LOQs in water and sediment samples

Organotin compound	Water samples LOD ng.L^{-1} (ppt)	LOQ ng.L^{-1} (ppt)	Sediment samples LOD µg.kg^{-1} (ppb)	LOQ µg.kg^{-1} (ppb)
MBT	0.8	15	0.3	1.0
DBT	0.6	15	0.3	1.0
TBT	0.4	1.3	0.4	1.3
MPhT	0.8	2.6	1.4	4.6
DPhT	0.5	15	0.7	2.3
TPhT	1.1	3.6	1.9	6.3

Table 3: Measured concentrations for the BCR 646 freshwater sediment compared with the certified concentrations. Repeatability test (n=6) on the BCR 646 reference material.

Organotin compound	Certificate concentrations (Cx ± uncertainty, k=2)	Concentration (Cx ± 2s) (µg.kg-1 as cation)	RSD (%) n=6
MBT	480 ± 80	522 ± 62	6.0
DBT	770 ± 90	746 ± 72	4.9
TBT	610 ± 120	497 ± 20	2.0
MPhT	29 ± 11	45 ± 11	12.6
DPhT	36 ± 8	34 ± 9	13.0
TPhT	69 ± 18	46 ± 13	14.0

References

[1] T.V. Hoang, A. Michel, A. Guyot, Polymer Degradation and Stability 4 (1982) 213.

[2] H. Rudel, Ecotoxicology and Environmental Safety 56 (2003) 180.

[3] H.H. Van Den Broeck, G.B.M. Hermes, C.E. Goewie, Analyst 113 (1988) 1237.

[4] T.-C. Hung, W.-K. Hsu, P.-J. Mang, A. Chuang, Environ. pollut. 112 (2001) 145.

[5] T. Horiguchi, Z. Li, S. Uno, M. Shimizu, H. Shiraishi, M. Morita, J.A.J. Thompson, C.D. Levings, Mar. Environ. Res. 57 (2004) 75.

[6] C. Devos, M. Vliegen, L. Moens, P. Sandra, unpublished results.

[7] T. De Smaele, L. Moens, P. Sandra, R. Dams, MIKROCHIM. ACTA 130 (1999) 241.

[8] V. Giarrocco, B. Quimby, M. Klee, Agilent Tech. Publ. 5966-2469E, www.agilent.com.

[9] F. David, P. Sandra, P.L. Wylie, Agilent Tech. Publ. 5988-9256EN, www.agilent.com.

[10] C. Devos, M. Vliegen, B. Willaert, F. David, L. Moens, P. Sandra, J. Chromatogr. A, 1079 (2005) 408.