JOURNAL OF MASS SPECTROMETRY, VOL. 32, 542–549 (1997)

Determination of Butyltin Compounds in Sediments by Means of Hydride Generation/Cold Trapping Gas Chromatography Coupled to Inductively Coupled Plasma Mass Spectrometric Detection†

E. Segovia García, J. I. García Alonso and A. Sanz-Medel*
Department of Physical and Analytical Chemistry, Faculty of Chemistry, C/Julián Clavería 8, 33006 Oviedo, Spain

A procedure for the determination of butyltin compounds in sediments is described. The method is based on the generation of volatile mono-, di- and tributyltin (MBT, DBT, TBT) hydrides from a 4% (v/v) acetic acid medium using $NaBH_4$. The hydrides formed are then trapped on a Chromosorb W HP SP2100 packed glass column immersed in liquid nitrogen. Sequential desorption of the hydrides is achieved by Nichrome wire heating of the column. The MBT, DBT and TBT hydrides are detected by mass spectrometry using an inductively coupled plasma source. Detection limits of 7, 4 and 4 pg (as Sn) for MBT, DBT and TBT, respectively, were obtained. The method was applied to the determination of organotin compounds (DBT and TBT) in the certified reference material CRM 462 with satisfactory results. © **1997 by John Wiley & Sons, Ltd.**

J. Mass Spectrom. **32**, 542–549 (1997)
No. of Figs: 8 No. of Tables: 5 No. of Refs: 27

KEYWORDS: speciation; butyltin compounds; cold trapping; inductively coupled plasma mass spectrometry; environmental analysis

INTRODUCTION

The environmental and toxicological effects of an element often depend on the form or chemical species of the element in the original sample. Organometallic compounds show a different toxicological behaviour to the inorganic compounds of the respective elements. In most cases, the organometallic species are orders of magnitude more hazardous,[1] with the exception of arsenic compounds. Organotin compounds, which are extensively used in marine anti-fouling paints, are extremely toxic to marine organisms and, as these compounds are continuously released into the marine environment, they accumulate in sediments, marine organisms and water.[2,3]

The simultaneous determination of the various organometallic forms of these elements in ultra-low concentrations is necessary in order to determine the extent of their toxicity. Recent trends have focused on interfacing chromatography with element-specific detectors, which can provide a means of selective determination of the various chemical species present.[4–12]

There has recently been much interest in the determination of organotin species in the environment and the methods employed have included the coupling of gas chromatography (GC)[4–8] and high-performance liquid chromatography (HPLC)[9–12] with different detectors. Also, hydride generation coupled to cryogenic trapping GC and atomic absorption spectrometry (HG/CT-GC/AAS) has recently been applied to organotin speciation.[13–18] Using the HG/CT-GC procedure, better sensitivity could be expected from the use of inductively coupled plasma mass spectrometry (ICP-MS) for selective detection of tin after atomization and ionization in the plasma ion source, but this detection technique has not been studied so far in combination with HG/CT-GC procedures.

ICP-MS offers some unique advantages over other atomic detection methods. It provides excellent sensitivity, a wide linear dynamic range and isotopic information. Methods based on isotope dilution analysis with species-specific enriched isotopes could be developed. Owing to its high detection power, on-line coupling of a chromatographic system with ICP-MS permits the determination of elemental species in natural aquatic systems without enrichment steps. In addition, the multi-element capability of the ICP mass spectrometer also allows the simultaneous detection of more than one element.[19–21] On the other hand, HPLC has

† This paper is one of the two recipients of the Journal of Mass Spectrometry Award given at the 8as Jornadas de Análisis Instrumental (JAI) during EXPOQUIMIA, Barcelona, 22–25 October 1996.

* *Correspondence to:* A. Sanz-Medel.

Contract grant sponsor: Dirección General de Investigación Científica y Técnica (DGICYT); *Contract grant number:* Project PB94-1331.

CCC 1076–5174/97/050542–08 $17.50

Received 29 October 1996
Accepted 22 January 1997

been the common separation technique for coupling to ICP-MS detection for organotin speciation,[22,23] but coupling interfaces for capillary GC/ICP-MS have also been described.[24,25]

In this paper, we describe the coupling of an HG/CT-GC interface to an ICP-MS instrument for the detection of butylated tin compounds whereby conventional packed columns are employed and can be directly applied to sediment extracts.

EXPERIMENTAL

Apparatus

The detection of organotin hydrides was performed using a Hewlett-Packard Model HP 4500 ICP-MS instrument. For the extraction experiments a Mixtasel centrifuge (Selecta, Barcelona, Spain) and a magnetic stirrer (Selecta) were used.

The HG/CT-GC system employed was based on that described by Donard[13] for AAS coupling and was modified for ICP-MS detection. Figure 1 shows a diagram of the HG/CT-GC/ICP-MS system. The sample is introduced into a 100 ml reagent flask where the hydride generation takes place. The sodium borohydride solution is transferred to the reaction flask by a peristaltic pump and a flow of helium is used to carry the hydrides formed to the glass chromatographic column (U-shaped, 48 cm × 5 mm i.d.) filled with a 28 cm bed of Chromosorb W HP (60–80 mesh) coated with 10% Supelco SP-2100 and immersed in liquid nitrogen. The main modification for ICP-MS detection included a three-way glass manually operated valve in order to prevent the hydrogen formed from reaching the plasma, and next to the valve, a make-up flow of argon is introduced tangentially to favour laminar flow and prevent condensation of the hydrides in the transfer tubing to the plasma. After the trapping stage, the liquid nitrogen Dewar vessel is removed and the column is heated by a Nichrome wire (15 Ω resistance) connected to a variable d.c. power supply (Model D-ADPS305, Dirland, France). Typically, 2.2 A were applied, which caused a temperature ramp from −196 to +200 °C in 4 min and constant temperature thereafter. Two solenoid switching valves are used to direct the carrier helium flow either to the reaction flask (purge and trapping step) or to the chromatographic column (desorption step).[13] All glass tubes and connections employed were cleaned in 10% HCl to reduce inorganic tin contamination.

Reagents and standards

Sodium borohydride (Probus, Barcelona, Spain) solution was prepared daily at 2% (w/v) and stabilized in 0.1% (w/v) NaOH (Merck, Darmstadt, Germany) by dissolving the reagent in ultrapure water. Glacial acetic acid was obtained from Merck. Methanol was of HPLC grade from Romil Chemicals (Cambridge, UK). Ultrapure water was obtained from a Milli-Q system (Millipore, Molsheim, France) and was used throughout. All other chemicals were of analytical grade.

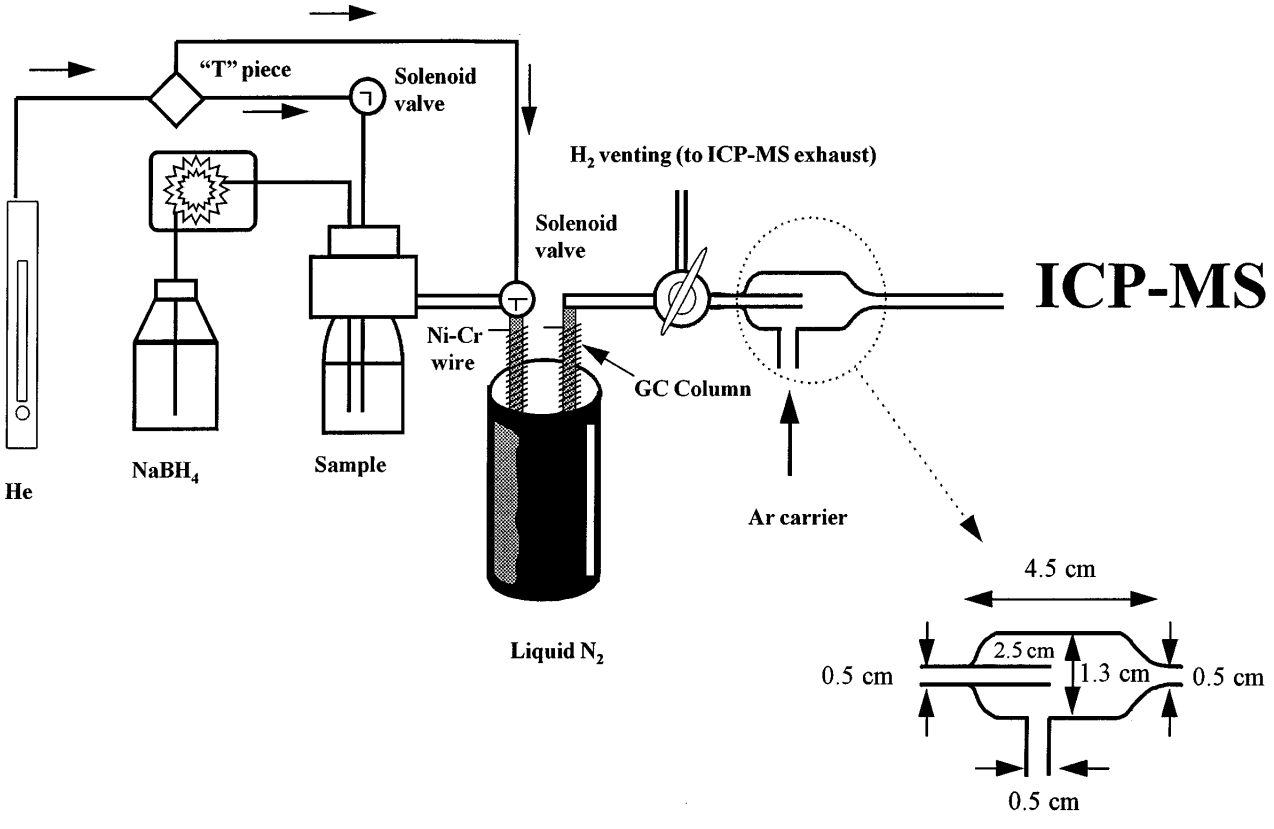

Figure 1. Instrumental set-up for HG/CT-GC coupled to ICP-MS.

The organotin compounds $BuSnCl_3$ (MBT), Bu_2SnCl_2 (DBT) and Bu_3SnCl (TBT) were obtained from Aldrich (Steinheim, Germany). Stock solutions of $BuSnCl_3$, Bu_2SnCl_2 and Bu_3SnCl ($\sim$1000 μg g^{-1} as Sn) were prepared in methanol. Mixed working solutions were prepared daily by dilution of the stock solutions with glacial acetic acid. A tin stock solution (1000 mg l^{-1}) as $SnCl_4$ in 5 M HCl was obtained from Merck. From this, working standards were prepared daily by dilution of the stock solution with 10% or 1% HCl.

The sediment reference material CRM 462 from the Institute for Reference Materials and Measurements (Geel, Belgium) was used.

Butyl tin extraction from sediments

The extraction of butyltin compounds from sediments was performed according to the procedure published by Martin *et al.*[26] Normally, the CRM 462 material was stored at 4 °C. Before analysis, it was kept at room temperature for 1 h, manually shaken for 5 min and allowed to settle for 10 min before sampling it. A 1 g amount of the sediment was taken from the bottle and mixed with $\sim$20 ml of glacial acetic acid in 30 ml glass vials. The sample was stirred for 12 h by means of a magnetic stirrer (1 cm bar). Subsequently, the solution was centrifuged for 20 min in a Mixtasel centrifuge and the supernatant was collected by means of a Pasteur pipette and transferred into a second glass vial.

Quantification procedure for sediment analysis

The quantification was carried out by standard additions. A 100 μl aliquot of the extract was placed in a reaction flask containing 50 ml of water and 2 ml of glacial acetic acid. Increasing volumes of a mixed DBT and TBT standard solution were then added for the standard additions procedure. First, the solution was purged for 2 min with a helium flow, then 10 ml of 2% $NaBH_4$ were added and the hydride compounds were stripped from the flask by means of a 3 min helium flow and trapped in the glass column packed with Chromosorb W HP SP 2100 immersed in liquid nitrogen. The column was subsequently heated with an Ni–Cr wire connected to a power supply and the compounds were transferred to the detector with a helium flow.

Blanks and memory effects

In order to avoid and limit cross-contamination and to reduce blank values, the reaction flask was rinsed first with methanol–acetic acid (90:10) and later with water between samples. A blank solution was measured after every two samples or standard injections.

Measuring conditions

Tin was measured at *m/z* 116, 117, 118, 119, 120, 122 and 124 using the Time Resolved Analysis software supplied with the instrument with a 0.2 s integration time per mass. The peak areas for MBT, DBT and TBT on the chromatogram obtained were measured for each mass monitored. Each sample was analyzed in duplicate and a blank was analyzed between every duplicate. During the recording of the chromatograms a 60 s delay between desorption and acquisition was necessary owing to inorganic tin contamination from the reagents (sodium borohydride solution). The SnH_4 peak from the reagents was observed after $\sim$30 s and caused saturation of the ICP-MS detector, preventing any further data acquisition.

RESULTS AND DISCUSSION

Optimization studies

Plasma and mass spectrometer parameters. In order to distinguish the contribution of the detection parameters from those of the generation–separation procedure to the signal obtained in ICP-MS, optimization of the ion source and mass spectrometer was carried out with a continuous introduction system by both conventional nebulization and continuous hydride generation of inorganic tin.

For the hydride generation, a 10 ng ml^{-1} inorganic tin(IV) solution in 1% (v/v) HCl was continuously mixed with 1% (w/v) sodium borohydride solution by means of a peristaltic pump and transferred to a U-shaped gas–liquid separator. A flow of argon was used to carry the tin hydride to the plasma. For the conventional nebulization a 20 ng ml^{-1} tin standard solution in 0.1% (v/v) HCl was analyzed. In both cases the ion at *m/z* 120 was monitored. Optimum conditions for both sample introduction systems are given in Table 1. As can be observed, different values were obtained for the two sample introduction systems, which could be due to the presence of water in the nebulization procedure and hydrogen in the hydride generation.

Figure 2 shows the influence of the argon carrier flow rate. As can be observed, hydride generation provides a much higher signal for a concentration half of that for

Table 1. Optimum conditions for conventional nebulization and continuous hydride generation

Parameter	Conventional nebulization	Hydride generation
Sampling depth (mm)	6	5
Ar carrier gas flow rate (l min^{-1})	1.25	1.26
R.f. power (W)	1300	1200
Peristaltic pump (rev. s^{-1})	0.07	—
Extract 1 (V)	−300	−250
Extract 2 (V)	−200	−125
Einzel 1,3 (V)	−75	−150
Einzel 2 (V)	−18	−20
Omega bias (V)	−34	−34
Omega + (V)	4	4
Omega − (V)	−15	−15

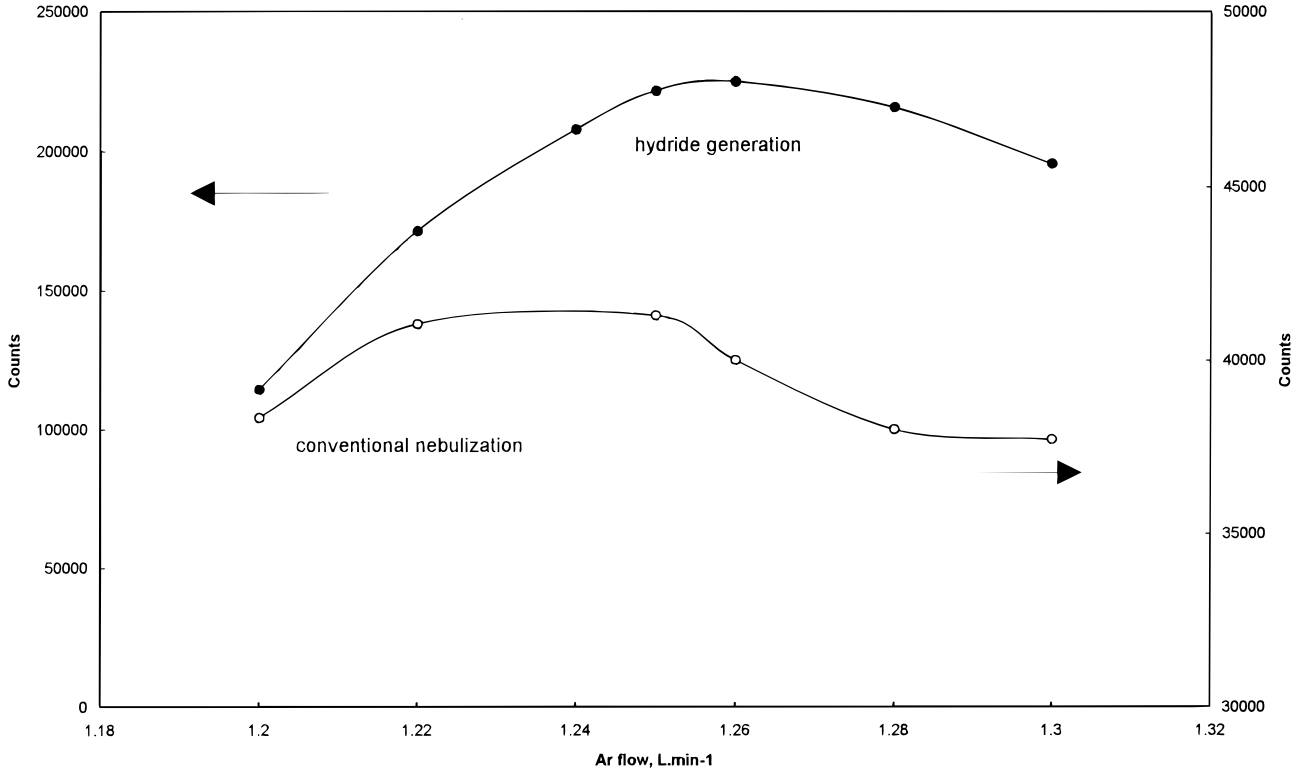

Figure 2. Comparison of argon flow rate optimization for hydride generation and conventional nebulization.

nebulization. Figure 3 shows the influence of the power applied to the plasma. As can be seen, lower plasma powers are needed for hydride generation as no water is introduced into the plasma. Figure 4 shows the influence of sampling depth (distance between load coil and sampler cone). Sampling the ions closer to the plasma seems to be better for hydride generation.

Coupling HG/CT-GC to ICP-MS. Once the plasma and mass spectrometer parameters had been optimized for

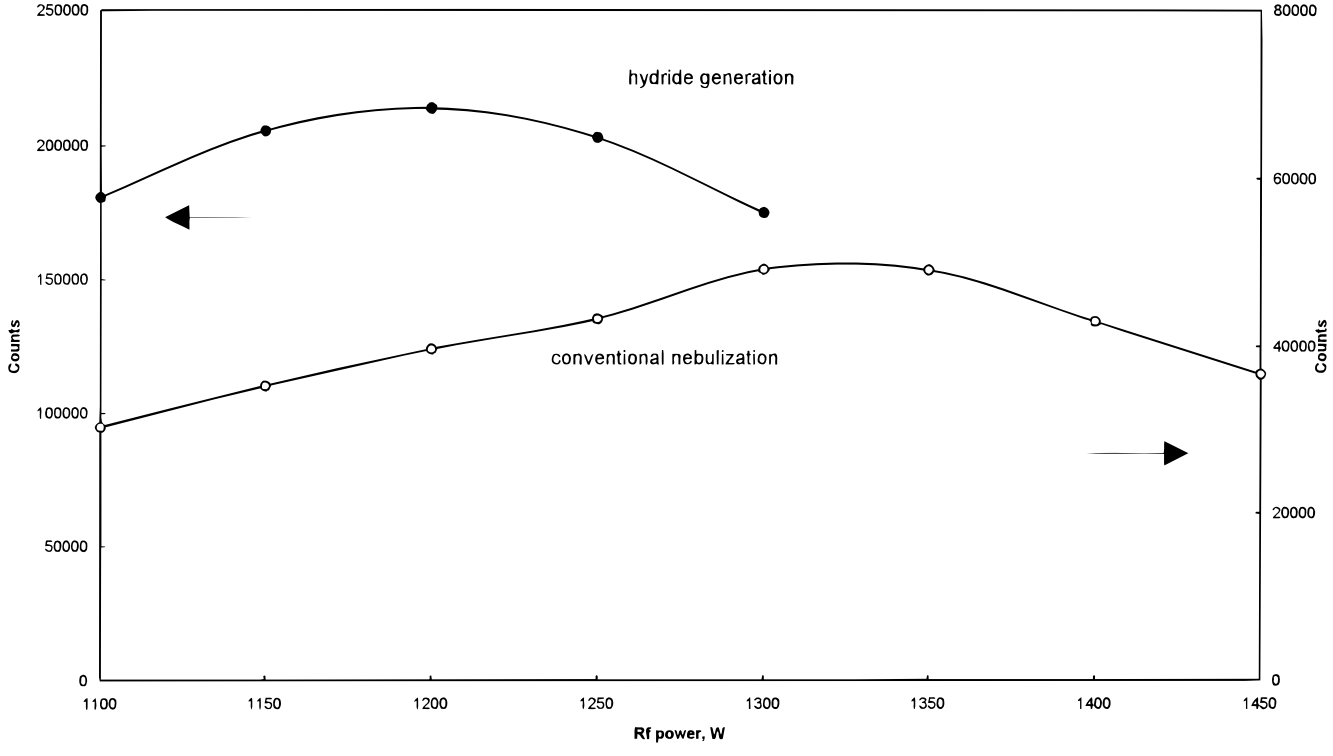

Figure 3. Comparison of r.f. power optimization for hydride generation and conventional nebulization.

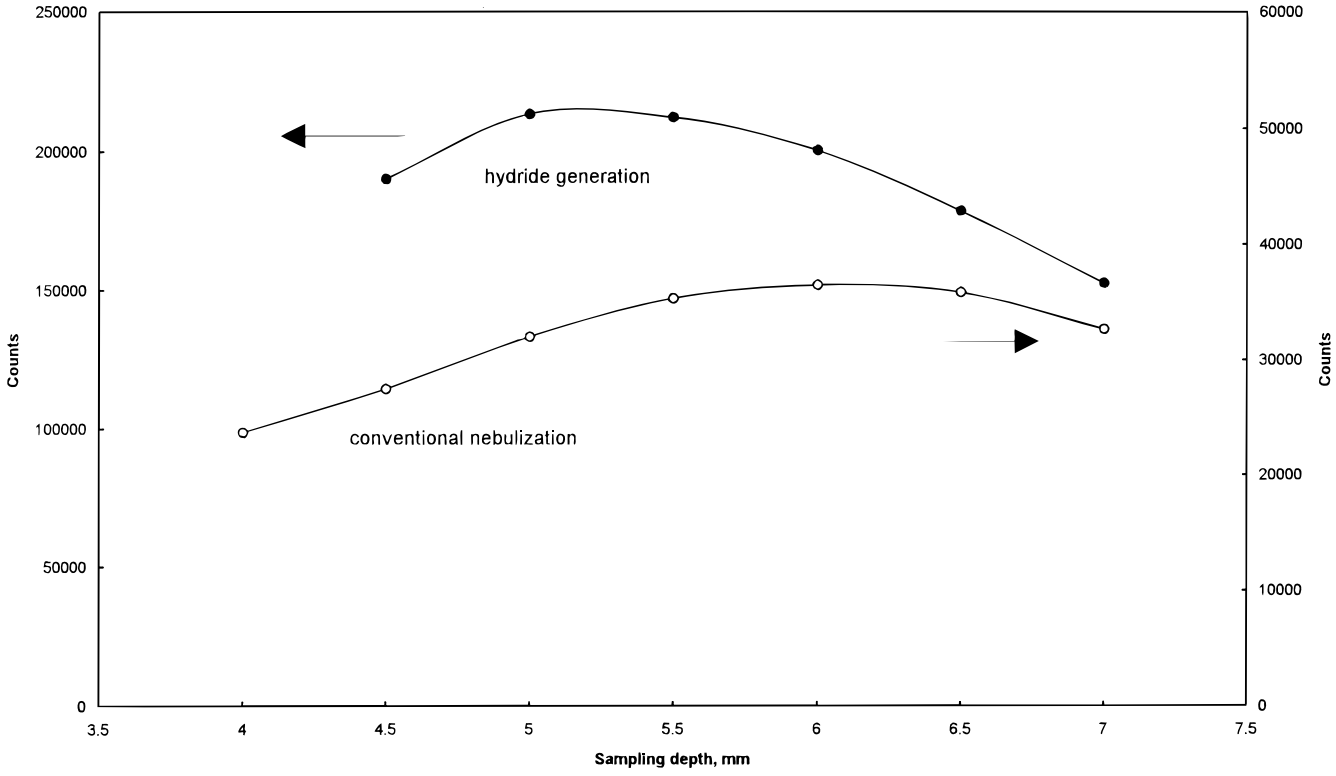

Figure 4. Comparison of sampling depth optimization for hydride generation and conventional nebulization.

hydride generation, the described HG/CT-GC interface was studied. Parameters which influence the generation, trapping and desorption of butyltin hydrides are sodium borohydride concentration and volume, purge time and helium purge flow, helium carrier flow, argon carrier flow and column heating ramp. Optimum values for these parameters are given in Table 2. The helium carrier flow rate had an important effect on the signal obtained for each organotin compound, but the influence was dramatic for TBT. Figure 5 shows the chromatograms obtained at two of the different helium flow rates tested (220 and 280 ml min^{-1}). As can be seen, the signal for MBT was not much affected by the carrier flow rate but the signals from DBT and TBT were strongly flow dependent. Also, better resolution of the chromatographic peaks was obtained at higher helium flows.

The effect of the argon carrier flow rate was studied with the complete system and is shown in Fig. 6. It was observed that optimum conditions were obtained at lower argon carrier flow rates than that shown in Table 1 and depended on the butyltin species monitored. The compromise value showed in Table 2 is the optimum for DBT and TBT. For MBT a higher carrier flow rate would have been selected as shown in Fig. 6.

In order to improve the shape of the TBT peak, the temperature of the column was optimized by changing the current flowing through the heated Ni–Cr wire. The temperature of the column was measured by using a thermocouple which had been previously calibrated. The chromatograms were recorded from 1.6 to 3.2 A and it was observed that at high column temperatures the peaks became distorted, the profiles of the peaks worsened and also DBT and TBT overlapped. At 2.2 A (around 200 °C final temperature) a good compromise between resolution and sensitivity was obtained.

Table 2. Optimum conditions for the coupling of HG/CT-GC to ICP-MS

$NaBH_4$	2% (v/v), 10 ml
He purge (I)	2 min, 180 ml min^{-1}
He purge (II)	3 min, 180 ml min^{-1}
He carrier flow rate	280 ml min^{-1}
Ar make-up flow rate	1.20 l min^{-1}
Sampling depth (from load coil)	5.5 mm
Column heating ramp	−196 to +200 °C

Table 3. Analytical characteristics

Parameter	MBT	DBT	TBT
Sensitivity (integral counts ng^{-1})	8×10^5	1×10^7	7×10^6
Blank value (integral counts)	2×10^4	3×10^5	2×10^5
Correlation coefficient	0.9992	0.9996	0.9997
Precision (%)	10	10	10
Limit of detection (3 σ) (pg)	7	4	4

Analytical characteristics

Figure 7 shows the final separation obtained for an injection of 2 ng of MBT and 1 ng of DBT and TBT, monitored at mass 120. The calibration graph was found to be linear for all butyltin species at least in the

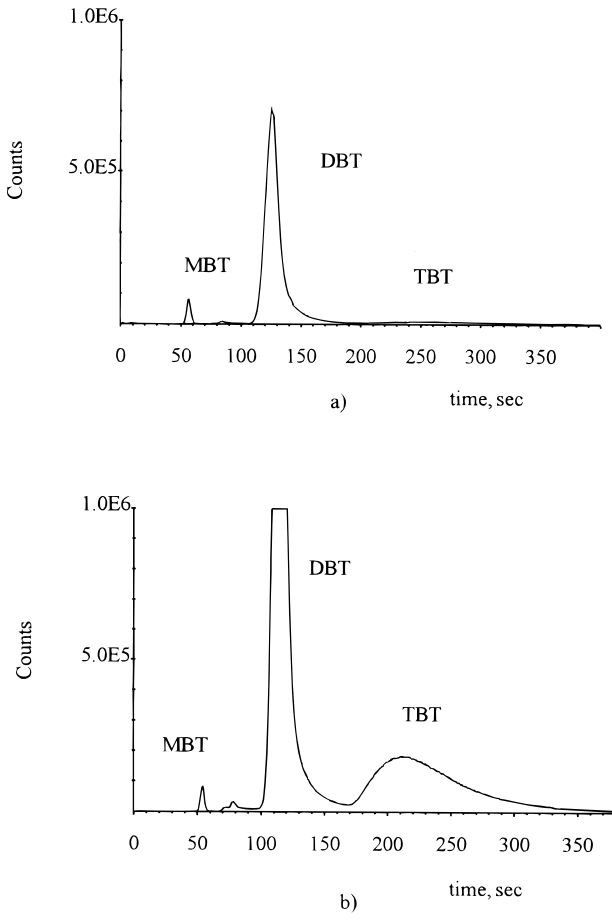

Figure 5. Influence of helium carrier flow rate on the chromatograms obtained for MBT, DBT and TBT. (a) 220; (b) 280 ml min^{-1}.

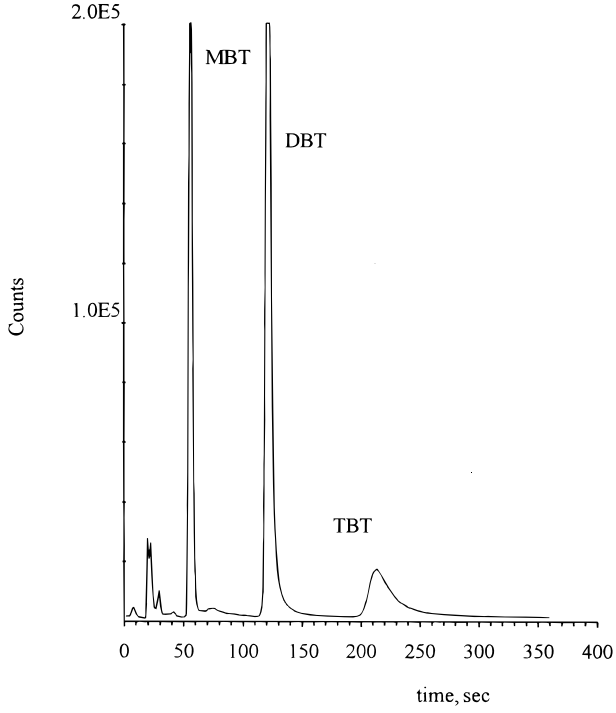

Figure 7. Chromatogram of a standard sample of MBT, DBT and TBT (2, 1 and 1 ng injected, respectively).

ranges 0.02–10 ng (MBT), 0.005–10 ng (DBT) and 0.01–10 ng (TBT) (higher amounts were not tested). The results obtained for the sensitivity, blank value, correlation coefficient, precision and estimated method detection limits are presented in Table 3. As can be observed, the sensitivity, expressed as integral counts per nano-

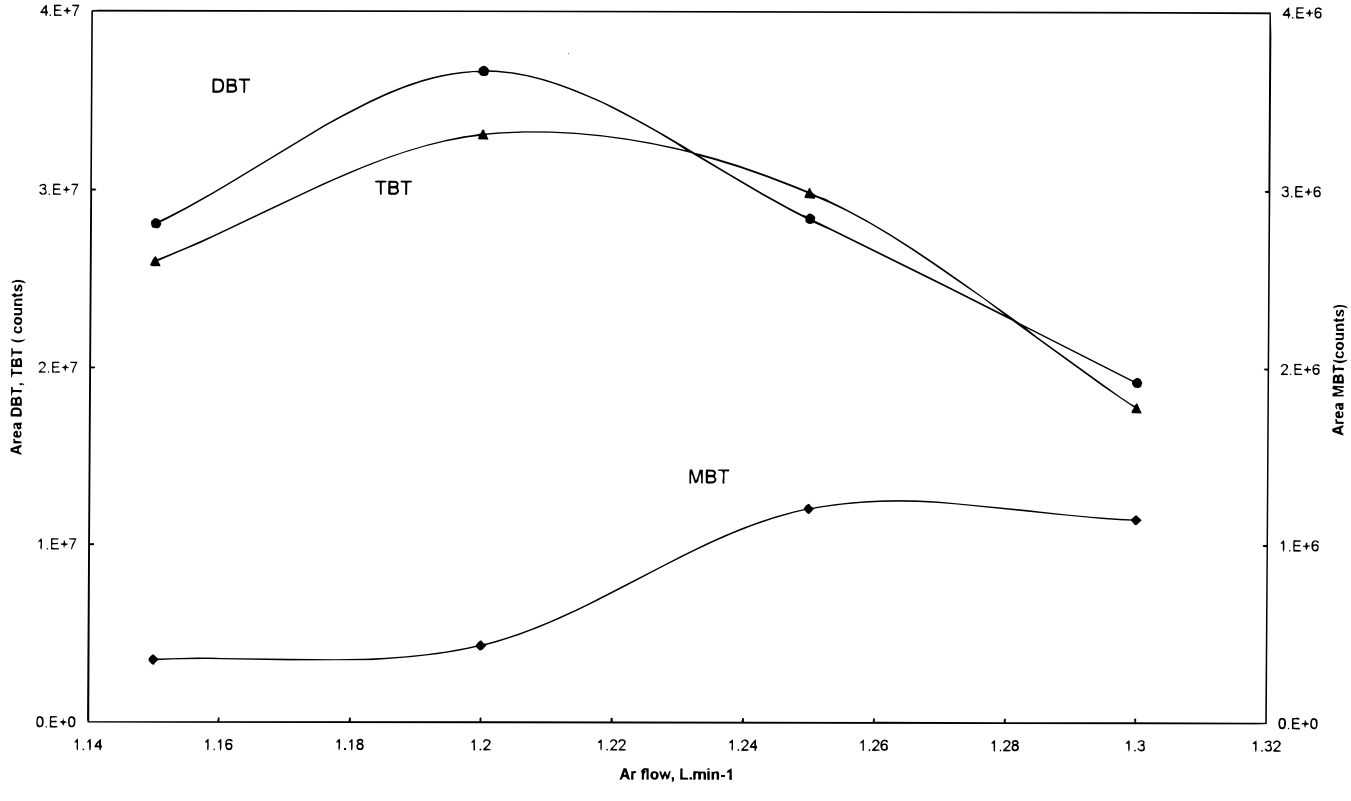

Figure 6. Influence of the argon make-up flow rate on the peak area obtained for each organotin compound.

gram of tin, is similar for DBT and TBT but much lower for MBT. This is opposite to what was observed for AAS detection,[15,16] which could be due to the lack of complete atomization for TBT hydride in the H_2–O_2 flame. Limits of detection in the low-picogram range were obtained for all three species using the 3 σ criterion for ten blank determinations.

Typical precision values in the peak area mode were around 10% for all species. However, this will be greatly improved by the use of isotopic ratios (peak-area ratios for different masses). Table 4 shows that typical isotope ratio precisions were ~1–2% ($n = 10$ at different concentration levels). This would facilitate the use of isotope dilution analysis using species-specific enriched isotopes. From Table 4 it can be observed also that significant differences in the isotopic ratios for MBT, DBT and TBT were found and this was observed also on different days and in different runs. The explanation for these differences is under study but they will not affect the quantification by standard additions.

Analysis of CRM 462 reference material

The developed method was applied to organotin speciation in CRM 462, which is certified for DBT and TBT

Table 4. Peak-area ratios (R) for MBT, DBT, TBT and their relative standard deviations ($n = 10$)

	MBT		DBT		TBT	
Isotopic ratio (m/z)	R	RSD (%)	R	RSD (%)	R	RSD (%)
116/120	0.3644	2.1	0.4305	1.0	0.4008	1.1
117/120	0.2034	2.5	0.2284	1.8	0.2187	0.7
118/120	0.6726	1.8	0.7301	0.7	0.7055	1.1
119/120	0.2522	2.0	0.2608	1.8	0.2584	1.3
122/120	0.1588	1.4	0.1458	2.3	0.1505	1.5
124/120	0.2162	1.6	0.1856	2.0	0.1966	1.7

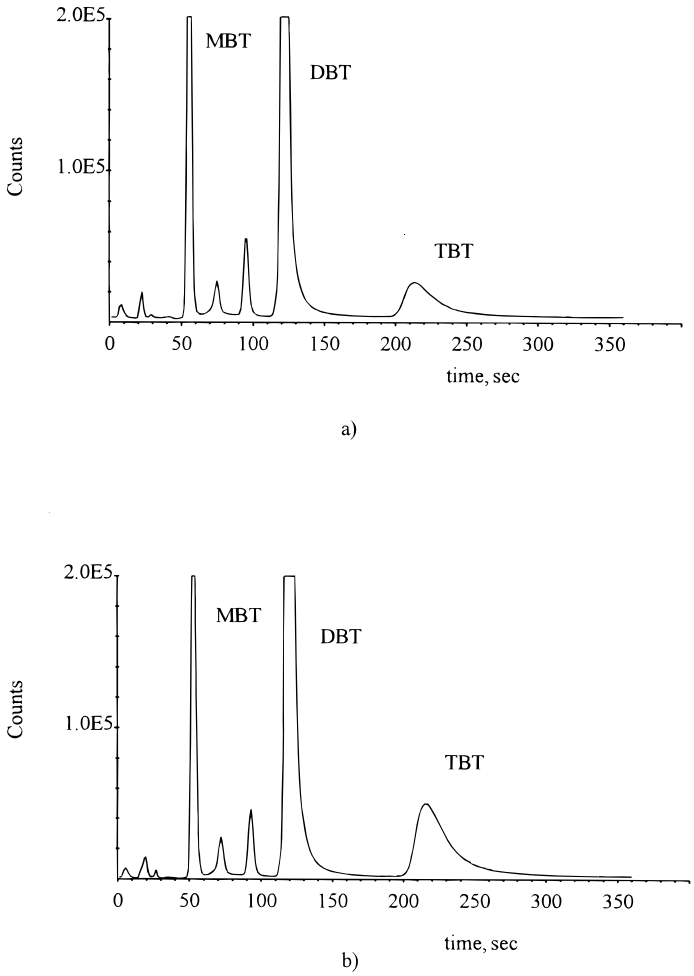

Figure 8. Chromatograms of (a) the CRM 462 sediment extract and (b) the CRM 462 sediment extract with standard additions of 0.6 ng of DBT and 0.4 ng of TBT.

Table 5. Concentrations of DBT and TBT found in the certified reference material CRM 462

Compound	Obtained (ng g^{-1})	Certified (ng g^{-1})
DBT	122.0	
	118.7	
	130.1	
	mean ± SD 124 ± 6	128 ± 16
TBT	78.8	
	80.4	
	74.0	
	mean ± SD 78 ± 3	70.5 ± 13

content. The extraction and quantification procedures described previously were used. As is well known, hydride generation is affected by interference effects from organic constituents.[27] For this reason, the method of standard additions was chosen. A chromatogram corresponding to a 100 μl of extract from CRM 462 and standard additions (0.6 ng of DBT and 0.4 ng of TBT) to the CRM are shown in Fig. 8. It can be seen that the presence of MBT, DBT and TBT is clearly observed, which indicates the detection power of the technique. Also, two unknown tin-containing compounds at retention times between those of MBT and DBT were detected. The final results for a triplicate determination of DBT and TBT in the sediment are summarized in Table 5. There is good agreement between the certified and experimental values.

CONCLUSIONS

The coupling of an HG/CT-GC system to an ICP-MS detector for butyltin speciation provided picogram-level detection limits for sample volumes up to 2 ml of acetic acid extracts (only 100 μl were used in the present study). This results in concentration detection limits in the pg ml^{-1} range, which is suitable for the direct analysis of most environmental samples. The conditions for the organotin detection and coupling were optimized and the method was validated by applying it to a certified reference material (CRM 462).

Acknowledgements

We thank Hewlett-Packard for the loan of the HP 4500 ICP-MS instrument and the Dirección General de Investigación Científica y Técnica (DGICYT, Spain) for financial support (Project PB94-1331).

REFERENCES

1. J. P. Craig, *Organometallic Compounds in the Environment*. Longman, London (1986).
2. R. J. Maguire, *Environ. Sci. Technol.* **18**, 291 (1994).
3. R. J. Hugget, M. A. Unger, P. F. Seligman and A. O. Valkirs, *Environ. Sci. Technol.* **26**, 232 (1992).
4. M. Ceulemans and F. C. Adams, *J. Anal. At. Spectrom.* **11**, 201 (1996).
5. J. S. Lobinska, M. Ceulemans, R. Lobinski and F. C. Adams, *Anal. Chim. Acta* **278**, 99 (1993).
6. D. Dyne, B. S. Chana, N. J. Smith and J. Cocker, *Anal. Chim. Acta* **246**, 351 (1991).
7. H. Suyani, J. Creed and J. Caruso, *J. Anal. At. Spectrom.* **4**, 777 (1989).
8. J. M. Ombada and E. Barry, *J. Chromatogr.* **598**, 97 (1992).
9. L. Ebdon, S. J. Hill and P. Jones, *Talanta* **38**, 607 (1991).
10. M. Astruc, A. Astruc and R. Pinel, *Mikrochim. Acta* **109**, 83 (1992).
11. J. A. Stab, M. J. M. Rozing, B. van Hutten, W. P. Cofino and U. A. Th. Brinkman, *J. Chromatogr.* **609**, 195 (1992).
12. G. Schulze and Ch. Lehman, *Anal. Chim. Acta* **288**, 215 (1994).
13. O. F. X. Donard, in *Sonderdruck aus Colloquium Atomspektrometrische Spuren Analytik* (*5*), pp. 395–417. Bodenseewerk Perkin-Elmer, Überlingen (1989).
14. O. F. X. Donard, S. Rapsomanikis and J. H. Weber, *Anal. Chem.* **58**, 772 (1986).
15. L. Randall, O. F. X. Donard and J. H. Weber, *Anal. Chim. Acta* **184**, 197 (1986).
16. L. Schebek, M. O. Andreae and H. J. Tobschall, *Environ. Sci. Technol.* **25**, 871 (1991).
17. S. Rapsomanikis and R. M. Harrison, *Appl. Organomet. Chem.* **2**, 151 (1988).
18. F. Pannier, A. Astruc and M. Astruc, *Anal. Chim. Acta* **287**, 17 (1994).
19. K. G. Heumann, L. Rottmann and J. Vogl, *J. Anal. At. Spectrom.* **9**, 1351 (1994).
20. M. J. Tomlinson, L. Lin and J. A. Caruso, *Analyst* **120**, 583 (1995).
21. L. Rottmann and K. G. Heumann, *Fresenius' J. Anal. Chem.* **350**, 221 (1994).
22. J. W. McLaren, K. W. M. Sin, J. W. Lam, S. N. Willie, P. S. Maxwell, A. Palepu, M. Koether and S. S. Berman, *Fresenius' J. Anal. Chem.* **337**, 721 (1990).
23. J. I. García Alonso, A. Sanz-Medel and L. Ebdon, *Anal. Chim. Acta* **283**, 261 (1993).
24. A. Prange and E. Jantzen, *J. Anal. At. Spectrom.* **10**, 105 (1995).
25. T. De Smaele, L. Moens, R. Dams and P. Sandra, *Fresenius' J. Anal. Chem.* **355**, 778 (1996).
26. F. M. Martin, C.-M. Tseng, C. Belin, Ph. Quevauviller and O. F. X. Donard, *Anal. Chim. Acta* **286**, 343 (1994).
27. F. M. Martin and O. F. X. Donard, *J. Anal. At. Spectrom.* **9**, 1143 (1994).