Applied Organometallic Chemistry (1989) 3 469–474
0268–2605/89/03602469/$03.50

SHORT PAPER

Butyltin speciation in sediments and biological samples by hydride generation gas chromatography quartz furnace atomic absorption spectrometry; a study of acid leaching procedures and hydride generation

V Desauziers, F Leguille, R Lavigne, M Astruc and R Pinel
Laboratoire de Chimie Analytique, Université de Pau et des Pays de l'Adour, Avenue de l'Université, 64000 Pau, France

Received 12 June 1989 Accepted 14 July 1989

The efficiency of the extraction of butyltin compounds from sediments and biological matter by acid leaching procedures has been evaluated on real samples using the hydride generation gas chromatography quartz furnace atomic absorption (GC AA) speciation method. The most efficient method uses cold pure acetic acid over a period of four hours. Hydride generation using sodium tetrahydroborate ($NaBH_4$) is dependent on matrix composition and care must be taken to adapt the amount of reactant to the organic content of the sample.

Keywords: Butyltin, analysis, extraction, sediments, hydride generation, matrix composition

INTRODUCTION

The development of reliable, rapid and inexpensive speciation methods for the determination of butyl- and butylmethyl-tin species in sediments and tissues is the cornerstone on which all tributyltin (TBT) research rests.[1] One of the most widely used methods for the speciation of organotin compounds in the aqueous environment combines hydride generation, cold trapping, gas chromatography and quartz furnace atomic absorption spectrometry.[2] The reasons for this success are that it is a low-cost and reasonably rapid method (up to six samples per hour) and it is simple and very sensitive if hydrogen (H_2) and oxygen (O_2) are added to the helium flux prior to introduction into the heated quartz furnace.

An assessment of the literature and of the results of some laboratory intercomparisons for TBT determination indicates that any discrepancy and scatter of the results may at least partly be generated by two factors: first, the choice of the extraction procedure of organotin from the substrate (sediment or tissue) and second, the volatilization of hydrides out of the complex solution thus obtained.

We have therefore compared some of the different leaching procedures described in the literature which are compatible with direct tin speciation by the hydride method. We have also studied the efficiency of hydride volatilization from leachates obtained from sediments and biological matter. The simplest general method to check the efficiency of such analytical techniques is to analyse a reference sample if one exists. However, there are no standard reference samples available for the speciation of organotins. We believe that spiking sediment or tissue is a very uncertain enterprise when dealing with speciation methods because of the necessary softness of the procedure in terms of its uncertain ability to model real environmental samples. We have therefore chosen to use 'naturally' polluted samples representative of various action situations for this study.

Leaching methods

The main literature procedures described for leaching organotins from sediments and tissues may be grouped in three classes:

(A) Acid leaching (or digestion) using hydrochloric, nitric or acetic acid.[3–5] The authors claim TBT recoveries from 60 to 180%.

(B) Alkaline leaching with sodium hydroxide[4–6] or Lumatom (a tetra-alkylammonium hydroxide in organic solvents).[7]

(C) Eventual extraction with an organic solvent after acid or alkaline leaching. The solvent sometimes contains a chelating agent.[8]

All these procedures are not necessarily compatible with the hydride speciation method. Class C extraction procedures are usually followed by concentration, derivatization (Grignard) and GC analysis. Alkaline leachates (B) are not directly suitable for hydride generation by sodium tetrahydroborate as this must take place in acidic solution.

Acid leaching (A) allows direct analysis of leachates by the hydride method. It is therefore this class of procedures that we have investigated further. Four methods have been tested using 0.1 mol dm^{-3} hydrochloric acid (HCl),[9] 2 mol dm^{-3} HCl,[6] 8 mol dm^{-3} HCl + methanol (CH_3OH),[10] and pure acetic acid (CH_3COOH).[5] They are numbered from I to IV respectively in the discussion below (Results and Discussion).

Hydride generation

When applied to natural waters, hydride generation by $NaBH_4$ from TBT is 100% effective as shown by an interlaboratory comparison involving the EEC Bureau of community Reference (BCR).[11] Things are not so simple when $NaBH_4$ is added to sediments or tissue leachates with a high organic content. We have investigated conditions for optimal tin hydride production with such extracts.

MATERIALS AND METHODS

Samples

Sediment samples of widely varying composition have been studied. These are classified as follows:

S_1	Arcachon Bay (France): a sandy sediment from a marina;
S_2	Boyardville Channel (France): a muddy sediment from the marina inlet;
S_3–S_7	Sado Estuary (Portugal): five different samples taken in five close locations (*ca* 100 m).

The sample site close to Setubal is very heavily polluted by organic matter, being located between shipyards and a sewer outfall. All of S_1–S_7 are surface samples; they were air-dried, crushed and sieved (63 μm). They were kept in sealed polyethylene bags at −20°C. The final sample was:

S_8	Rhine estuary (Netherlands).

A biological sample (B) was prepared from the flesh of 50 oysters (*Crassostrea gigas*) grown in tanks containing panels coated with TBT antifouling paints. The flesh was lyophilized; crushed and sieved (63 μm). Subsamples were kept in sealed polyethylene bags at −20°C.

Reagents

Hydrochloric acid and methanol were Normapure reagents (Prolabo). Acetic acid was Merck '*pro analysi*'. The sodium tetrahydroborate solution was 5% (w/v) $NaBH_4$ (Fluka) and 1% (w/v) NaOH (Suprapure Merck) in Milli Q-Mille RO water.

Sampling leaching procedure

Sediment samples (0.1–1 g) or 1 g tissue samples were placed in a 25 cm^3 Pyrex flask with a ground glass stopper together with 20 cm^3 of one of the acid leaching reagents. Magnetic stirring was applied during four hours. The suspension was then centrifuged (4000 rpm, 10 min). Aliquots of the supernatant were then withdrawn with micropipettes for analysis.

Analytical method

Subsamples (0.1–1 cm^3) of leachates were introduced in the 150 cm^3 Pyrex hydride generation flask (0.5 cm^3 of acetic acid was added if the leachate did not contain this reagent) and diluted to 100 cm^3 with pure water. After a 1 min purge of the flask by helium, the sodium tetrahydroborate ($NaBH_4$) solution was injected by a peristaltic pump (2.25 cm^3 min^{-1}). Tin hydrides, thus generated, flushed from the solution by the helium, were carried to a Pyrex U-shaped tube

(30 cm × 0.5 cm) packed with 1.25 g of Chromosorb GAWHP 80–100 mesh, cooled in liquid nitrogen. This collecting step was discontinued 1 min after the end of $NaBH_4$ addition. Then the cooling nitrogen was removed and progressive electrical heating of the column selectively evaporated organotin hydrides, which were carried to the open-ended atomic absorption quartz furnace (10 cm × 1.6 cm) by helium flux. The quartz furnace was electrically heated to 950°C; hydrogen (H_2) and oxygen (O_2) were added to the gax flux just before introduction into the quartz furnace. Heating of the GC column must be long enough to completely eliminate water (temperature gradient up to 200°C for about 3 minutes). An IL 151 atomic absorption spectrometer was used in this study.

Care must be taken in this procedure against excess pressure in the reaction flask due to increasing head pressure loss in the trap, thereby inducing explosions.

The chromatograms were recorded on a Servotrace recorder and only peak heights were used for analytical purposes. The following results are the average of two independent determinations, each obtained by a standard addition procedure practised on the extracts (not on the solid samples).

RESULTS AND DISCUSSION

Four leaching procedures (I to IV) have been applied to sediments S_1 and S_2 and oyster tissue B. The results (Table 1) did not provide evidence for the presence of methyltin or butylmethyltin compounds. This was expected as the method was operated at low sensitivity owing to the large amounts of butyltin compounds that were present. Other investigations[12,13] on these samples and others from the same areas evidenced methylated species at much lower concentrations.

It is clear from Table 1 that the leaching procedures studied have very different efficiencies. Procedure I using 0.1 mol dm^{-3} hydrochloric acid is by far the less efficient for organic or inorganic tin. Methods II (2 mol dm^{-3} HCl) and III (8 mol dm^{-3} HCl + CH_3OH) are the most efficient for leaching of inorganic tin (TRIT; i.e. total recoverable inorganic tin) and have quite good efficiencies for $BuSn^{3+}$ and Bu_2Sn^{2+}. The very high level of inorganic tin extraction from sediments is not an advantage as tailing of the very large SnH_4 peak may complicate the determination of methylated species or even that of $BuSnH_3$. Moreover, non-toxic organic tin is of secondary interest only.

Pure acetic acid (method IV) is by far the best extractant for TBT, the most interesting compound in environmental tin speciation. It seems also very efficient for $BuSn^{3+}$ and Bu_2Sn^{2+}, especially for the tissue sample B.

The question that remains is whether TBT extraction by method IV is quantitative. For sediment samples a positive answer is contained in a previous paper,[14] where we compared TBT determinations in a Porto Vecchio (Corsica, France) sample (mud and organic

Table 1 Comparison of leaching procedures

Sample[a]	Leaching procedure[a]	Concentrations (mg kg^{-1} as Sn)					
		$BuSn^{3+}$	Bu_2Sn^{2+}	Bu_3Sn^+	TOT[b]	TRIT[c]	TET[d]
S_1	I	0.043	0.081	0.134	0.258	0.141	0.399
	II	0.230	0.286	0.247	0.763	2.84	3.60
	III	0.117	0.271	0.549	0.937	3.56	4.50
	IV	0.108	0.235	0.810	1.15	0.638	1.79
S_2	I	1.05	7.60	5.02	13.7	1.55	15.2
	II	6.50	7.00	1.28	14.8	22.2	37.0
	III	7.15	6.05	9.52	22.7	22.1	44.8
	IV	6.81	4.93	11.8	7.45	7.45	31.0
B	I	0.65	1.00	ND	1.65	0.85	2.50
	II	1.95	2.45	ND	4.40	2.60	7.00
	III	2.75	1.10	ND	3.85	2.90	6.75
	IV	2.90	4.15	0.430	7.48	1.00	8.48

[a]Samples S_1, S_2 and B as well as leaching procedures I to IV are desribed in the text. [b]TOT, total organic tin, i.e. the sum of individual butyltin concentrations. [c]TRIT, total recoverable inorganic tin. [d]TET, total extractable tin. TET = TOT + TRIT.

matter) by this procedure and an independent one (HPLC–GFAA) with success, the global agreement being confirmed by a third independent determination of total recoverable tin. We therefore propose method IV (pure acetic acid extraction) as the most efficient extraction method for TBT determinations in sediments by the hydride method.

The same method proved also to be the most efficient for the extraction of butyltin from oyster tissue (sample B), but no unequivocal proof of total extraction of TBT may be advanced.

Hydride generation from sediment extracts

All the results presented hereafter have been obtained using leaching method IV (pure acetic acid). Little mention is made in the literature of tin hydrides generation by $NaBH_4$ addition. It has been noticed that even small amounts of organic solvents may interfere[15] reducing or even cancelling the AA signals of tin hydrides. Our experience with sediment extracts demonstrates that they may seriously disturb the

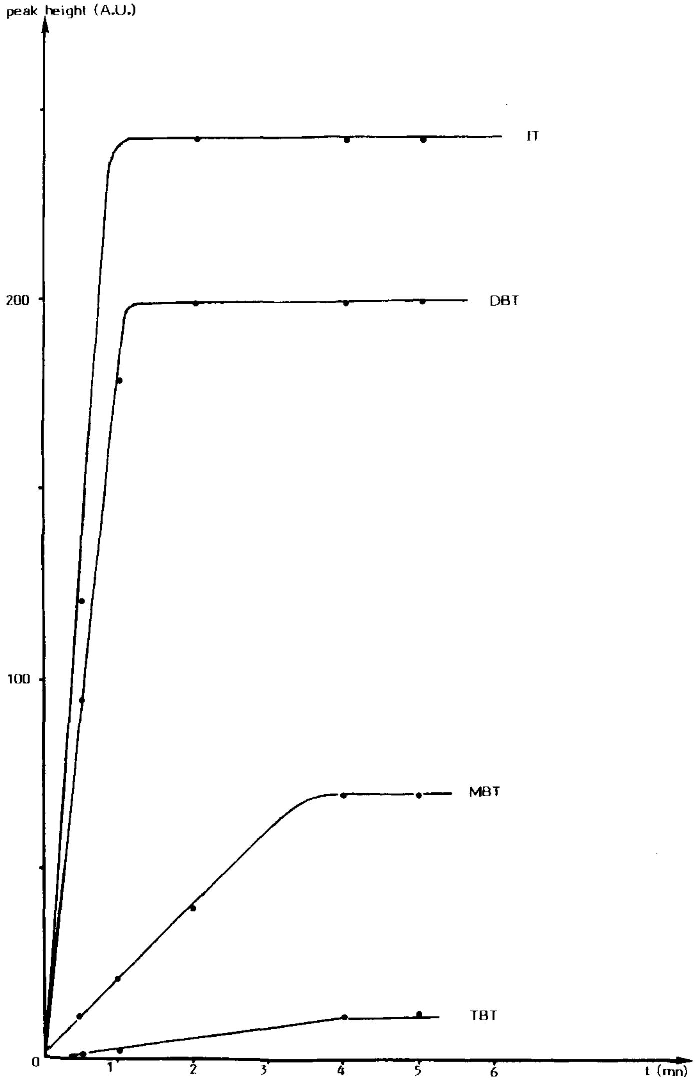

Figure 1 Effect of the amount of $NaBH_4$ on the generation of tin and butyltin hydrides from sample S_8: peak height is in arbitrary Absorbance Units (A.U.) versus time of $NaBH_4$ addition. The flow of the $NaBH_4$ solution is 2.24 cm^3 min^{-1}.

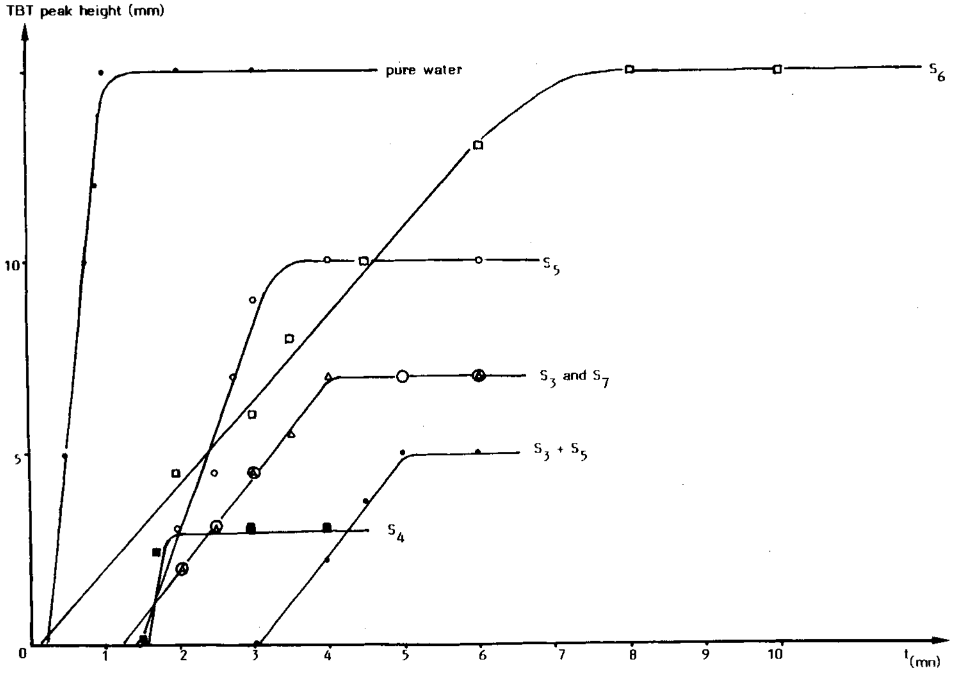

Figure 2 Effect of the amount of NaBH4 on the generation of Bu3SnH: peak height (A.U.) versus amount of NaBH4 expressed in time of flow (min) at 2.24 cm^3 min^{-1}. (S_3 + S_5) is a mixture of samples 3 and 5.

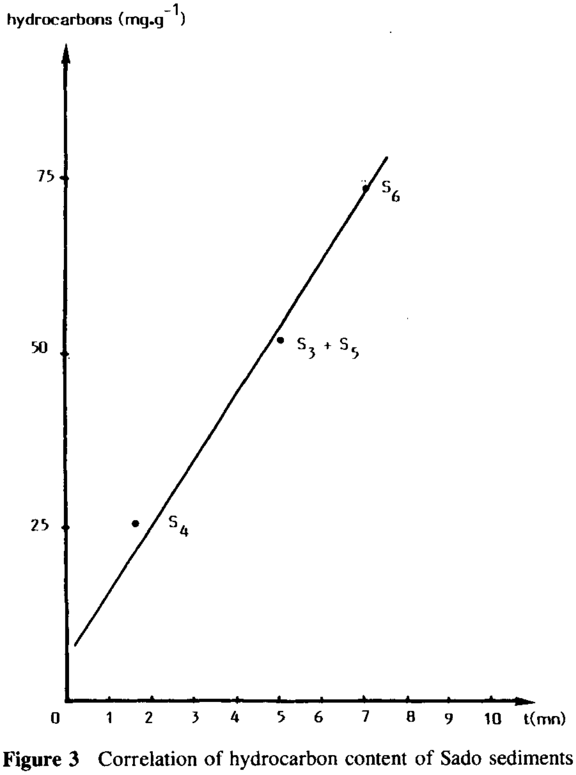

Figure 3 Correlation of hydrocarbon content of Sado sediments with NaBH$_4$ consumption. r = 0.998, (S_3 + S_5) is a mixture of samples 3 and 5.

hydride speciation procedure as applied to butyltin compounds, most probably because of competing reactions of hydride ions with tin species and some unidentified compounds. Figure 1 presents a series of rough experimental data obtained with the extract of an estuarine Rhine sediment (S_8). It is clear from this figure that the amount of NaBH$_4$ necessary to reach an optimal production of (organo)tin hydride differs between tin species. There seems to be a continuous decrease of their reactivity with increasing number of butyl radicals attached to the central tin atom.

In Fig. 2 are compared the effects of varying amounts of NaBH$_4$ introduced on the AA signal of TBT extracted from various sediments (S_3–S_7) sampled in the same area highly polluted by organic matter, or from pure water. Widely differing behaviours are noticeable. For some samples, addition of too low amounts of NaBH$_4$ completely fails to produce any AA signal corresponding to TBT.

Sado sediments (S_3, S_4, S_5, S_6) are polluted by hydrocarbons. Figure 3 relates the measured concentrations of hydrocarbons in these samples to the amount of NaBH$_4$ necessary to obtain optimal Bu$_3$SnH generation. There are only three points on the diagram, so the excellent correlation observed needs confirmation from further studies.

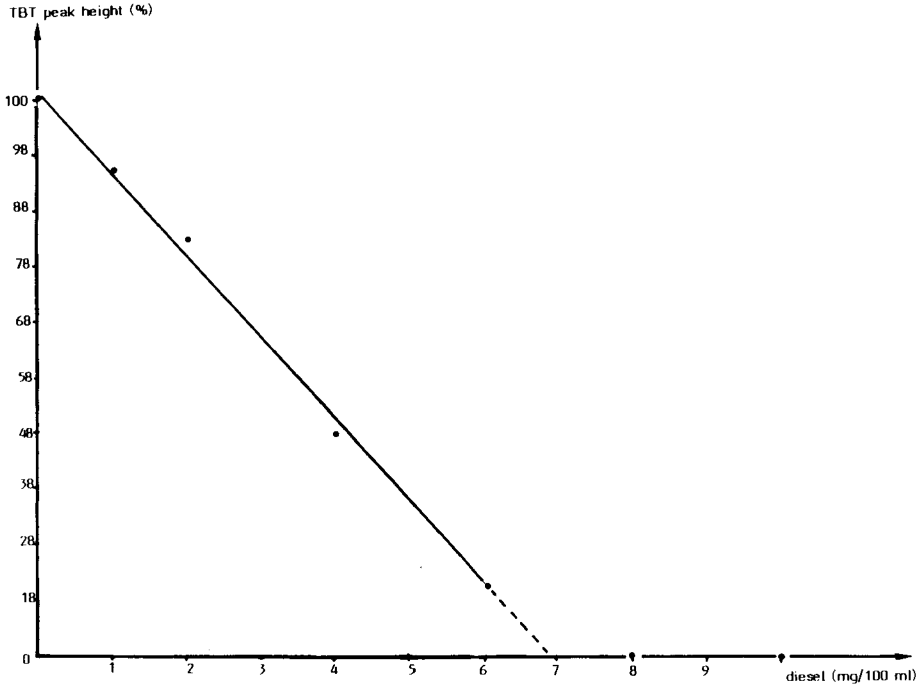

Figure 4 Peak height (relative absorbance) observed for 15 ng TBT with increasing gas-oil (diesel) amounts in aqueous solution (100 cm^3).

However, a primary confirmation of these effects on hydride generation may be found in Fig. 4. This figure reports the results of a series of experiments in which gas-oil (diesel oil) was added directly to the sample in the hydride generation flask. The AA signal of Bu_3SnH is severely affected by amounts of hydrocarbon representative of what may be found in harbour sediments. A large increase of the amount of $NaBH_4$ added may be necessary to recover the normal sensitivity of the method for TBT as shown in Fig. 2.

CONCLUSION

Speciation of tin in sediments and tissues by the hydride GC AA method is possible. The best extractant for TBT determination is pure acetic acid. Reaction of sodium hydroborate with components of the matrix such as hydrocarbons may occur and inhibit (organo)tin hydride generation, depending on the extent of tin atom substitution. Care should then be taken to ensure a satisfactory determination of tributyl cation.

REFERENCES

1. Champ, M A and Bleil, P F US Department of Commerce, NOAA Report, March 1988
2. Donard, O F X, Randall, L, Rapsomanikis, S and Weber, J H *Int. J. Env. Anal. Chem.*, 1986, 27: 35
3. Randall, L, Han, J S and Weber, J H *Env. Technol. Lett.*, 1986, 7: 571
4. Donard, O F X, Rapsomanikis, S and Weber, J H *Anal. Chem.*, 1986, 58: 772
5. Lavigne, R Thesis University of Pau, France, June 1989
6. Rapsomanikis, S and Harrison, R H *Appl. Organomet. Chem.*, 1988, 2: 151
7. Chau, Y K *Sci. Tot. Environ.*, 1988, 71: 57
8. Tsuda, T, Nakanishi, H, Morita T and Takebayashi, J *J. Ass Soc. Off. Anal. Chem.*, 1986, 69(6): 981
9. Tugrul, S, Balkas, T I and Goldberg, E D *Mar. Poll. Bull.*, 1983, 14(8): 297
10. Han, J S and Weber, J M *Anal. Chem.*, 1988, 60: 316
11. Ebdon, L, Hill, S and Griepink, B *Env. Technol. Lett.*, 1988, 9: 965
12. Quevauviller, Ph, Lavigne, R, Pinel, R and Astruc, M *Env. Poll.*, 1989, 57: 149
13. Quevauviller, Ph, Vale, C, Lavigne, R and Astruc, M In: *Proc. Heavy Metals in the Hydrological Cycle*, Astruc, M and Lester, J N (eds), Lisbon, 6–8 Sept. 1988, pp 425–432
14. Astruc, A, Lavigne, R, Desauziers, V, Pinel, R and Astruc, M *Appl. Organomet. Chem.*, 1989, 3: 267
15. Ashby, J R and Craig, P J *Sci. Tot. Environ.*, 1989, 78: 219