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Tributyltin determination in marine sediments: a comparative study of methods

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Two independent speciation methods have been applied to the determination of tributyltin (TBT) in marine sediments: (1) acetic acid leaching/hydride generation/cold trapping/GC/quartz furnace AA; and (2) toluene–tropolone extraction/HPLC/ GFAA. TBT determines in a typically moderately polluted sediment (Porto Vecchio Bay, Corsica, France) are in very good agreement, as also are the determination of total recoverable tin by the first method and by a direct one using strong acid leaching followed by GFAA. These cross-verifications lead one to conclude that both speciation methods are convenient and allow for valid determination of TBT in marine sediments, with no loss of TBT. Method-induced modification of tin speciation has not been observed.

Keywords: Tin, speciation, tributyltin (TBT) determination, marine sediments

INTRODUCTION

Organotin compounds are widely used, for example as stabilizers, catalysts or biocides.[1] Natural waters, especially coastal marine waters, may be polluted by tributyltin (TBT) and its degradation products [mainly dibutyl- (DBT) and monobutyl-tin (MBT)], owing to current use of TBT-containing antifouling paints.[2] In situations where a high density of boats coexists with low-water-exchange conditions, TBT pollution may rise to levels so high as to influence biological activity.[3] Photolytic degradation of dissolved TBT to DBT or MBT compounds is known to occur more or less rapidly.[4] However, organotin compounds are strongly adsorbed onto particulates that scavenge them down to the surface sediment, where their photodegradation is probably very slow. Biodegradation phenomena that may be the most important procedures in the sediment also produce DBT and MBT — together perhaps with methylated compounds.[5] Owing to the very high toxicity for marine organisms of TBT, there is a great interest in TBT determination (i.e. speciation), and not simply in total tin or total organotin determinations, in environmental samples. There is thus a need for valid tin speciation methods both in water and sediment.

Whilst many papers deal with the organotin content of various environmental samples measured with numerous different analytical procedures, few contain a comparison of methods. There may therefore be doubt of the validity of some data as no cross-checking of methods is possible. The difficulties may come either from the extraction procedure used (incomplete recovery of the analyte) or from the measurement procedure (e.g. analyte loss or modification). Difficulties in the overall speciation procedures are commonly evaluated by recovery studies on spiked samples. The success of such procedures may be considered at most as a non-negative proof but it is certainly not sufficient as a quality assurance. Some authors do use an internal standard added to the spiked sample to justify the recovery evaluation: they may however only verify the constancy of their extraction yields. Donard *et al.*[6] compared acidic and basic aqueous extraction procedures using the same determination method and obtained an intrinsic variability of up to 57%. Weber *et al.*[7] found recoveries from 93 to 113% using a methanol/hydrochloric acid extraction procedure. Valkirs *et al.*[8] tried to compare different tin speciation methods, obtaining results that were only partly satisfactory, with some differences mounting to 550%. For these reasons we developed two independent tin speciation methods and have applied them simultaneously to the same sediment sample taken in a moderately polluted Mediterranean environment (Porto Vecchio Bay, Corsica, France). As a further verification the total tin content of this sample was determined by another method.

MATERIALS AND METHODS

Sample

A moderately polluted sediment, representative of a typical situation, was desired. The sediment sample was collected by a diver at 2 m depth outside Porto Vecchio harbour on 21 August 1988 using a polyethylene flask. It was air-dried, homogenized and maintained at 4°C. All analyses were performed during the following month. Repeated experiments at weekly intervals over one month demonstrated no change in the tin speciation. Conservation of the sample at room temperature seems also to be good over a period of one month.

Methods

The three speciation or determination methods used are schematized in Fig. 1. All were made using standard addition procedures.

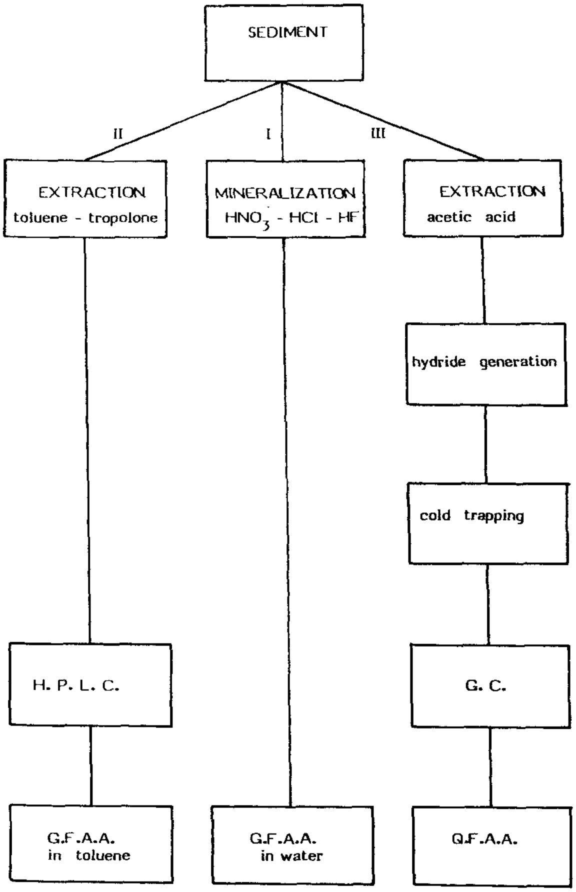

Figure 1 Scheme for the three determination methods.

Method I

This method is intended to determine total recoverable tin (TRT). A 1 g subsample is treated by hydrofluoric–hydrochloric–nitric acids (HF–HCl–HNO$_3$) mixture (18.3 mol dm^{-3}, 1.5 mol dm^{-3}, 0.6 mol dm^{-3} respectively) in a warmed PTFE flask until the volume is reduced to ca 1 cm^3 (3 h). Water is added and after centrifugation the volume is adjusted to 25 cm^3. Determination of tin is made by GFAA (IL 451 + IL 555 + IL Fastac) using a potassium dichromate–nitric acid (K$_2$Cr$_2$O$_7$/HNO$_3$) matrix modifier (1.36·10^{-3} mol dm^{-3}, 0.29 mol dm^{-3}) respectively).[9] The detection limit is 1.0 ng cm^{-3} in the aqueous solution i.e. 25 ng g^{-1} in the sediment. This last detection limit may be much improved if necessary by using larger sediment samples. The relative standard deviation (RSD) at 10 times the detection limit is 9%.

Method II

This is a speciation procedure allowing only separate determinations of TBT and DBT out of a complex mixture. A 12 g subsample is shaken for 15 h in a glass-stoppered 50 cm^3 Pyrex flask with 10 cm^3 of a 50 mg dm^{-3} tropolone solution in toluene. After filtration the toluene is vacuum-evaporated down to a 2 cm^3 volume. Tin species contained in a 250 μL subsample are separated by HPLC (Varian 5000 equipped with a Nucleosil 5 CN: column and precolumn) using a 7.5 mg dm^{-3} tropolone solution in toluene as eluant (1 cm^3 min^{-1}). Separated tin species in the HPLC effluent are determined as total tin by on-line GF AA (Varian Spectra-30/GTA-96) using on-line addition of a matrix modifier (0.05% picric acid in toluene; w/vol; 0.2 cm^3 min^{-1}).[10] The overall detection limit (IUPAC, $k = 3$) is 20 ng cm^{-3} (as tin) for TBT species in the subsample injected in HPLC, i.e. a 3.3 ng g^{-1} detection limit in the sediment. The overall relative standard deviation (RSD) for TBT determinations at 10 times the detection limit is 9%. This original procedure, which has no common step at all with the procedure below, has been developed essentially as a cross-verification method.

Method III

This is a speciation procedure allowing simultaneous determination in a single experiment of all tin species producing volatile compounds during sodium borohydride reduction under helium purge. A 1 g sediment subsample is shaken with 20 cm^3 of concentrated acetic acid (17.48 mol dm^{-3}) in a glass-stoppered 50 cm^3 Pyrex bottle for 15 h. After centrifugation, 1 cm^3 of the supernatant solution is introduced to a Pyrex reaction vessel and diluted with 99 cm^3 of water.[11] The vessel is purged with helium (1 min), then 2 cm^2 of a 5% solution of $NaBH_4$ in 10% sodium hydroxide are added by a peristaltic pump. Stannanes (SnH_4), organotin hydrides, volatile organotin compounds (Bu_4Sn, Me_4Sn, for example) are carried by the flux through a Pyrex line to a Pyrex U-shaped tube (30 cm length, 5 mm i.d.) packed with Chromosorb GAW-HP, 80–100 mesh, coated with 10% OV-101 maintained in liquid nitrogen. After 1 min the column is removed from liquid nitrogen and then submitted to controlled heating. Volatile tin compounds are then successively released from the GC column, carried by the helium flux to a point where oxygen and hydrogen are added, and then to an open and electrically heated (950°C) quartz cell aligned in an IL 151 AA spectrometer furnished with a hollow tin cathod lamp. Atomic absorption of tin is measured at 286.15 nm. The mass detection limit, in the conditions described above, varies from 70 to 400 pg depending on the tin species involved, i.e. from 0.7 to 4 ng dm^{-3} in the 100 cm^3 sample submitted to hydride reduction. The detection limits in the sediment vary therefore between 1.4 and 8 ng g^{-1}. Considerable improvements of these detection limits are easy but are not necessary for our purposes. The RSD is 7%. This procedure is one of the most frequently used tin speciation methods (except for the use of acetic acid as both an extractant and an acidification agent for hydride generation) which we have already successfully used for sediment and biological samples.[12] However, owing to the rather crude treatments (acidification, powerful reduction, heating) to which the organotin compounds are submitted, one must consider the possibility of analyte loss by degradation, by exchange of organic groups, etc.

RESULTS AND DISCUSSION

Typical speciation chromatograms obtained from the Porto Vecchio sediment by speciation Methods II and III are presented in Figs 2 and 3 respectively. Analytical results are compared in Table 1 with total recoverable tin obtained by Method I.

Total recoverable tin

Total recoverable tin (TRT) obtained after a vigorous acid leaching is 220 ± 20 ng g^{-1}. TRT may be lower than total tin, as a solid residue remains after

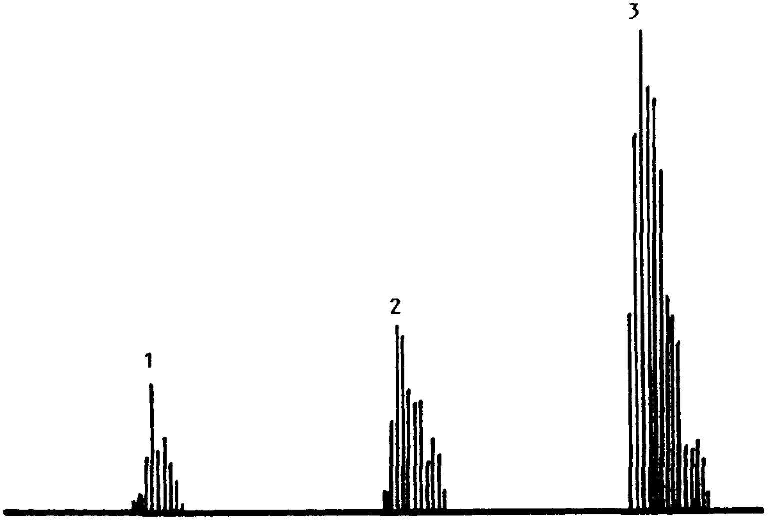

Figure 2 HPLC–GF AA chromatograms obtained from Porto Vecchio sediment by Method II. Curve 1, sample; curves 2 and 3, standard additions of TBT (49 ng and 185 ng respectively).

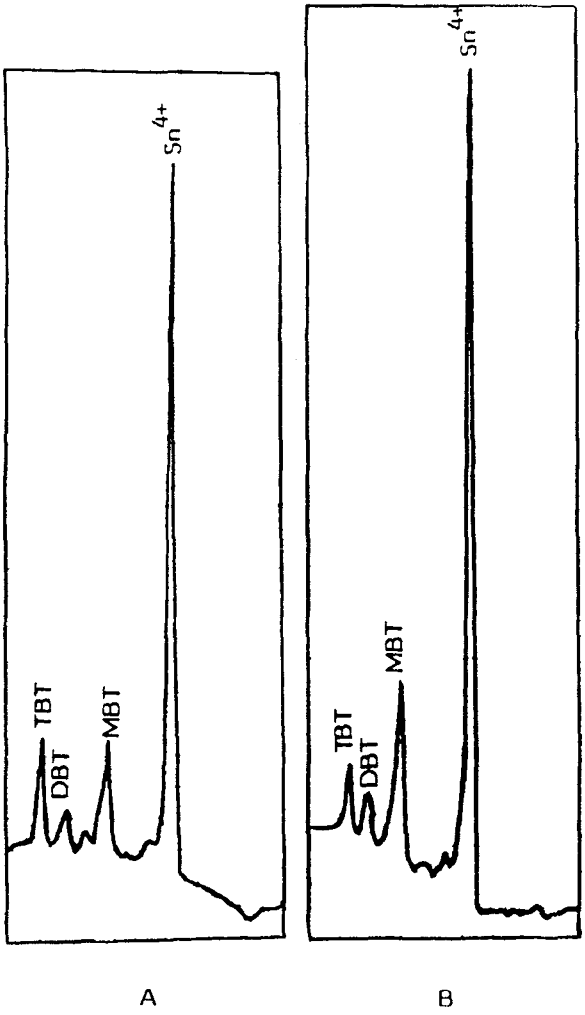

Figure 3 Hydride–GC–QFAA chromatograms obtained from (a) Porto Vecchio sediment; (b) Porto Vecchio overlying seawater.

the acid leaching. However, in these conditions, there is no loss of tin introduced as spikes of organotin compounds. Thus TRT should represent the sum of organotin compounds and recoverable inorganic tin. This assumption seems to be validated by comparing TRT obtained by Method I with the sum of the individual determinations of tin species by Method III (200 ± 20 ng g^{-1}). This, in turn, tends to validate the weaker acid leaching procedure used in Method III. This last leaching procedure of sediment by concentrated acetic acid has been the object of a development study, where it was compared with already published methods, that demonstrated its interest for tin speciation.[11] The slightly lower value obtained by Method III may even be explained by the presence of methylated tin species that were not quantified and included in the summation, as their individual concentrations were below the detection limit but not zero, as may be seen from Fig. 3. One may thus conclude that nearly perfect agreement between the determinations by Methods I and III exists for total tin. There is therefore no loss of tin during the complicated procedure of Method III.

Tin speciation

Speciation of tin by Method III is much more detailed and sensitive than by Method II. This last method was only able to determine tributyltin (TBT) and to indicate that the presence of DBT was slightly under the detection limit. Both determinations of TBT are in very good agreement. This conclusion, which has also been confirmed by several other coupled results obtained from comparative analysis of artifical or spiked water or sediment samples, is very important: as Methods I and

Table 1 Speciation of tin in Porto Vecchio sediment

Method	TRIT	MBT	DBT	TBT	TRT	Other compounds[a]
I	NA	NA	NA	NA	220 ± 20	
II	NA	NA	<DL	21 ± 4	NA	NA
III	140 ± 11	23 ± 4	13 ± 2	25 ± 2	(200 ± 20)	<DL

Abbreviations: TRIT, total recoverable inorganic tin; MBT, DBT, TBT, mono-, di-, tri-butyltin ions; TRT, total recoverable tin; NA, not analysed by this method; DL, detection limit (see text). Concentrations reported in ng g^{-1} as tin (dry weight).

[a] Methylated tin compounds have not been positively detected.

II have no common step, it may be concluded either that both methods suffer from fortuitous equal errors or that they are both satisfactory. The last hypothesis seems to be the most likely. However, if TBT determinations are perfectly coherent, this is not the case for DBT analysis. Similar problems have been encountered with spiked sediment samples (but not with spiked water samples) indicating therefore that it is most probably the extraction step of DBT from sediment that fails in Method II. The comparison, in Figs 3a and 3b, of the tin speciation chromatograms obtained for a sediment and for the overlying water indicates interesting similarities.

CONCLUSION

Tributyltin (TBT) determinations in sediment samples by independent speciation methods have been demonstrated as very coherent. Moreover the sum of the individual tin species concentrations determined by the hydride/GC/AA speciation procedure compares perfectly with a total recoverable tin determination. The two speciation methods used may therefore be supposed to be able to allow exact determination of TBT in marine sediment samples.

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