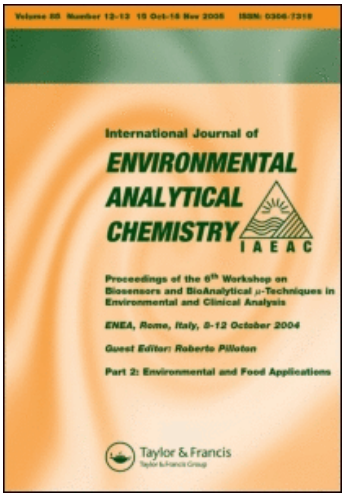

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Determination of "Heavy" Organotin Pollution of Water and Shellfish by a Modified Hydride Atomic Absorption Procedure†

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Tin speciation in aquatic environment is very complex. To the natural Sn^{IV} and methylated compounds, human activities add mainly butylated, octylated, phenylated or even methylated derivatives. The most environmentally significant, due to their high toxicity and direct introduction in water through biocidal use, are the tri-substituted ones. Several sophisticated speciation procedures have been proposed, they are not susceptible of common use.

We propose a simple and fast procedure allowing routine global distinction of "heavy" tin species that are most susceptible of exerting harmful effects. This AA method use the differences in volatility of stannanes generated by reduction with $NaBH_4$.

Sn^{IV} and the methylated species have very close response coefficients whereas "heavy" compounds respond very slightly at room temperature and are eliminated in a −40°C cold trap.

"Heavy" tin determination in water is thus obtained by the difference between two hydride AA experiments, one performed on the untreated sample ("light tin") and the other on a UV mineralised subsample (total tin). (The mineralisation of organotins is realised by UV irradiation—2 hours—in a quartz container—yields 95–100%.)

The analysis of shellfish tissue relies also on two experiments. Total tin is measured on a mineralised sample and "light tin" is obtained on a subsample "solubilised" with an Ultra Turrax homogeneizer in a diluted HCl solution.

KEY WORDS: Organotin compounds, water, shellfish, Atomic Absorption, spectroscopy.

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INTRODUCTION

Inorganic tin is either natural or due to anthropogenic input. Reported concentrations are in the range of 0.01 to 1 $\mu g l^{-1}$.[1] Organotin species may also have several origins. Biocidal use of organotin compounds, by far the more environmentally significant, involve trisubstituted compounds $R_3Sn^+X^-$ because these, together with R_4Sn, are extremely toxic, much more than di- or mono-substituted species. Their toxicity is widely dependent on the nature of R but only very slightly on that of the anion X. Biocides commonly used are tributylated (mainly) phenylated or octylated compounds. Stabilisers are di or monosubstituted compounds containing mainly butyl or octyl radicals. Methylated compounds are used in USA for this purpose but not in Europe to our knowledge.[3,4]

Degradation of organotin compounds in the aquatic environment seems to follow the general pathway

$$R_3Sn^+ \rightarrow R_2Sn^{2+} \rightarrow RSn^{3+} \rightarrow Sn^{IV}.$$

The final product, Sn^{IV}, is considered as atoxic at the concentration levels found in waters. But environmental methylation of organic tin has been demonstrated as well as the presence of methyl tin species in the aquatic environment.[5,6]

Evaluation of the potential risk of environmental deterioration by organotin pollution necessitates thus extremely sensitive and selective speciation methods that are very costly and time consuming (HPLC/GFAA,[7] derivatisation GC/specific detector,[8] etc). We have developed a simple and inexpensive semi-specific method suitable for a rapid screening of numerous samples for the presence of harmful anthropogenic organotin compounds in waters.

Hydrides and stannanes generated by addition of $NaBH_4$ to the acidified water sample are conducted to the quartz AA furnace through a cold trap retaining "heavy" species of low volatility, furnishing thus an adsorption related to "light" species. Subtraction of this result from a determination of total tin gives an evaluation of the amount of "heavy" anthropogenic species that are most susceptible of exerting harmful effects on the biota.

EXPERIMENTAL

Material

Hydride generation was realised by fast addition of 2.1 ml of a 5% $NaBH_4$ solution in 1% NaOH to the sample in 100–250 ml Pyrex erlenmeyers. Hydrides were then transferred to the quartz furnace through a transfer line (a) or (b). The (a) line is a silanised Pyrex tube (length 50 cm, ∅ 5 mm) using very short PE connections; it is used for the determination of total tin in mineralised samples.

The other transfer line, (b), is identical except for a short column of silica gel and a U-shaped cold trap maintained at −40°C in a propanol-2 bath. Mineralisation of water samples acidified by 0.2% HNO_3 was realised by UV irradiation (2 hours) in a quartz container.

Samples were taken in carefully cleaned polyethylene bottles, immediately acidified to pH = 1 with HNO_3 and kept at +4°C.

RESULTS AND DISCUSSION

Determination of total tin

Organotin compounds eventually present in environmental water samples or in biological matter solutions were converted to Sn^{IV} by UV irradiation. For a two hours irradiation time (16 lamps UV: Rayonet Photochemical Reactor lamp, the S.O.N.E. Ultraviolet Co., Middletown, USA) we check that all organotin compounds were decomposed (recovery as mineral tin 100%). Optimisation of the operating parameters for tin determination leads us to 0.2 ng mass detection limit, i.e. for a 250 ml water sample a concentration detection limit of 0.8 ng l^{-1} (IUPAC k = 3). This limitation, although perfectly suitable for our purposes is essentially due to the blank level, determinated by tin pollution of the $NaBH_4$ solutions. No serious interference has been registered up to now.[9]

Determination of "light" tin

When direct hydridation of aqueous solutions of organotin

compounds is performed the corresponding stannanes are produced following

$$R_pSn^{(4-p)+} + (4-p)H^- \rightarrow R_pSnH_{(4-p)}.$$

The molecular weights of the possible hydride and stannanes, thus their volatilities, vary widely. A detailed study of the behaviour of these stannanes as a function of the temperature of the transfer line has been realised. Using transfer line (b) with a $-40°C$ cold trap large differences in the response coefficients are obtained (Table I). The relative sensitivity, r, is defined here as the ratio of the AA signals of S_0—signal for 10 ng of tin introduced as individual organotin compound—to S_i—signal obtained for the same mass of tin as inorganic tin.

$$r = \frac{S_0 - B}{S_i - B} \quad B \text{ is the blank.}$$

Consideration of the data presented in Table I indicates that what we define as "light" tin is mainly due to inorganic tin and methylated species. The harmful trisubstituted butyl, phenyl and octyl compounds do not interfere in this determination; the corresponding disubstituted species have negligible response; only the hardly toxic monobutylated compound presents a non negligible response.

In the European environment, where methyltin compounds are not in use, "light" tin corresponds thus with a very good approximation to the sum of natural tin species and the final non toxic degradation products of industrial organotin compounds. In countries where use is made of Me_2SnX_2 compounds as stabilisers (mainly USA) interpretation of these data is somewhat different.

Evaluation of water pollution by anthropogenic organotin compounds

It follows from the preceeding discussion that outside of USA the difference $(Sn_T - Sn_L)$, i.e. "heavy" tin (Sn_H) represents approximately the amount of potentially harmful anthropogenic organotin compounds. In USA, this difference is only an evaluation of the

TABLE I

Relative sensibility of hydride AA determination of environmentally significant organotin compounds.

Tin as	$SnCl_4$	$MeSnCl_3$	Me_2SnCl_2	Me_3SnCl	$BuSnCl_3$	Bu_2SnCl_2	Bu_3SnCl	Ph_3SnCl_2	Oct_2SnCl_2	TBTO
$r \times 100$	100	94	84	77	64	24	0	0	0	3

amount of anthropogenic butylated, phenylated, octylated or cyclohexylated compounds. Sn_H is nevertheless quite significant as it includes all of the most harmful species.

Application to water samples

Some examples of application to actual marine water samples are presented in Table II.

TABLE II

Total, "light", "heavy" tin in the surface waters of two Mediterranean harbours.

Sampling place	Date	Sn_T (ppt)	Sn_L (ppt)	$Sn_H = Sn_T - Sn_L$ (ppt)
Toulon harbour	27/05/85	249	23	226
Porto Vecchio harbour	05/04/85	270	53	217

These two samples were taken in harbours where hundreds of leisure boats are anchored. In both sites the renewal rate of water is low due to negligible tidal effects.

Application to biological matter: oysters poisoned with TBTO

Oysters were exposed to panels recovered by antifouling paints containing TBTO in sea water for many weeks. During this time, of course, many oysters died and malformations appear in the shell.[10,11] On the living oysters the coarse speciation was made as following.

The whole oyster body is lyophilised (without shell) and homogenised. An homogenised fraction is solubilised in hydrochloric acid 0.04 N with a gentle warming. (Under these conditions we checked that a sample of TBTO is not hydrolysed: no change in response.) The measurements are effected after dilution by suprapure water. The results are given in Table III.

We can see that oysters concentrate tin as inorganic and organic tin and this concentration can become important with time.

TABLE III

Tin concentration (ppb) in oyster's body exposed to panels covered with antifouling paints containing TBTO in sea water.

Exposition in days	0	8	18	25	32	39	146
Sn_T (ppb)	0	212	900	587	1062	1887	5400
Sn_L (ppb)	0	112	724	269	485	575	2400
Sn_H (ppb) as $Sn_T - Sn_L$	0	100	176	318	637	1342	3000

So, it seems that such a coarse speciation method may be a very useful tool for studies about poisoning by organotin compounds.

Analysis time is short (a few minutes per determination) so that if a convenient UV irradiation apparatus is available, up to six samples may be analysed per hour.

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