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SHORT PAPER

A simplified procedure for the determination of butyltin species in water

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A method is described for the analysis of solutions containing inorganic tin and butyltin compounds. It can be used to determine total tin at a concentration of 20 ng dm^{-3} using a 5 dm^3 sample. The method is based on solvent extraction with dichloromethane containing tropolone and determination of the tin as inorganic tin by atomic absorption spectroscopy using electrothermal atomization. The extracted butyltin compounds can be separated by paper chromatography and the tin content of the individual spot determined as above. Observations on the stability of butyltin compounds in water at the ~2 mg dm^{-3} (Sn) are included.

Keywords: Butyltin analysis, atomic absorption, electrothermal analysis, paper chromatography

INTRODUCTION

Tributyltin compounds have been used extensively as the active component of antifouling paints and materials for marine applications for the past 10–15 years.[1] Although recent legislation[2] in some countries has banned the use of these compounds in antifouling paints for small boats there will be a need, for some time to come, to monitor the butyltin species in water.

A number of methods for the determination of organotin species in water using gas chromatography (GC) or high performance liquid chromatography (HPLC) with flame photometric detection (FPD), either directly or after extraction of the sample to be analysed into organic solvent in the presence of a chelating agent such as tropolone, have been described.[3] However, in many cases where the presence of organotins as a contaminant in water is suspected, it is often sufficient to identify initially whether or not there may be a problem by determining the total tin content of the water. If this is found to be below a pre-determined acceptable level, then possibly no further analysis is required.

This paper describes a non-GC HPLC method using solvent extraction and atomic absorption spectroscopy with electrothermal atomization (AA ETA) for the determination of total butyltin species and inorganic tin in water with a limit of detection of 20 ng dm^{-3} when a 5 dm^3 sample is used. A paper chromatography method is also described for the quantitative speciation of the butyltin compounds present; the method is essentially as described for the determination of tributyltin species in wood.[4]

In the course of this and related work it was necessary to prepare standard aqueous solutions of bis(tributyltin)oxide (TBTO) at the 5 ppm (mg dm^{-3}) level. It was observed that aqueous solutions of TBTO at this concentration, when prepared via concentrated solutions of TBTO in a solvent such aa acetone or propan-2-ol, were not as stable as solutions prepared without these solvents. A more detailed account of these observations is given below.

EXPERIMENTAL

Apparatus

In this work a Pye SP9 atomic absorbtion spectrometer with an electrothermal atomisation (ETA) video furnace programmer was used. In addition a UV lamp was used if speciation was required.

Reagents

The following reagents were used: dichloromethane (general purpose); tropolone solution

(0.05% w/v general purpose in dichloromethane); sulphuric acid (sg 1.84, ~18.8 mol dm^{-3}, analytical grade); and nitric acid (sg 1.42, ~16.2 mol dm^{-3}, analytical grade).

For chromatographic separation, Whatman chromatography paper (No. 1 or 3MM) was used. The reverse phase was 10% v/v phenoxyethanol in industrial methylated spirit and the mobile phase used was 7.5% v/v glacial acetic acid in trimethylpentane. The indicator was Catechol Violet solution (0.1% w/v in industrial methylated spirit).

Procedure

Determination of total tin compounds

The aqueous sample (10–5000 cm^3 volume) was transferred to a suitable separating funnel [see Notes (1) and (2) below and shaken with 10 cm^3 of the tropolone solution for 5 min. The layers were allowed to separate and the organic layer run into a small beaker. The extraction was repeated with a further 10 cm^3 of the tropolone solution and the extracts combined in the beaker; 1–5 cm^3 of sulphuric acid was added (depending on the final volume of sample to be analysed by AAS) and also approximately 1 cm^3 of nitric acid; the sample was heated gently while nitric acid was added dropwise to destroy all the organic matter. Finally the solution was heated to the onset of sulphuric acid fumes, then cooled. After 5–10 cm^3 water had been added, the solution was boiled gently for about 1 min to destroy any nitrososulphuric acid remaining. If this solution was not colourless, it was evaporated to the onset of sulphuric acid fumes and the dropwise addition of nitric acid was continued as above. The solution was cooled to room temperature, 5–10 cm^3 water was added, it was cooled again and transferred to a suitable volumetric flask normally of 10–50 cm^3 volume depending on the amount of sulphuric acid used in wet ashing. The solution was diluted to the mark with water to give a final acid concentration of 10% sulphuric acid. The tin content of the solution was determined using AA ETA using the furnace programme summarized in Table 1. Calibration solutions were prepared containing 1–40 μg Sn per 100 cm^3 in sulphuric acid adjusted to give a 10% solution of the acid.

Notes

(1) When the volume of the sample is 500 cm^3 or more it is essential to saturate the sample with dichloromethane before extraction with tropolone solution (the solubility of dichloromethane in water is 7–8 cm^3 dm^{-3}).

(2) Samples of 5 dm^3 or more may be extracted in 2 and 1 dm^3 aliquots and all the extracts combined.

Table 1 Furnace programme

	Temperature (°C)	Time (s)	Rate (°C s^{-1})
First dry	120	30	100
Second dry	375	15	10
Ash	700	10	200
Atomize	2800	3	>2000
Clean	2900	3	>2000

Ramp control 4, 7, 3, 0, 0 respectively.

Speciation and determination of butyltin species

It is essential to exclude light from the sample during analysis because the butyltin–tropolone complex is light-sensitive. Thus all glassware, including the separating funnel, must be covered with (for example) aluminium foil.

The sample (10–5000 cm^3) was transferred to a suitable separating funnel and extracted with dichloromethane/tropolone solution as described in the determination of total tin. The dichloromethane extracts were combined in a small beaker and the solution was carefully evaporated to about 5 cm^3. It was then cooled and quantitatively transferred to a 10 or 25 cm^3 volumetric flask, and diluted to the mark with dichloromethane. A suitable aliquot was transferred to a 10 cm^3 beaker and carefully evaporated to about 0.2–0.3 cm^3, ensuring that the beaker was not heated above 55–60°C. There are no evaporative losses if this procedure is adhered to.

A paper for chromatography[5] was prepared by immersing in the reverse-phase solution and allowing it to dry in air for about 15 min. The 0.2–0.3 cm^3 of solution was transferred quantitatively to the paper, the beaker was rinsed with a few drops of dichloromethane and these washings were added to the spot on the paper.

The chromatogram was developed in trimethylpentane/acetic acid solution by either ascending or descending chromatography. It was then removed from the developing tank, allowed to dry for a few minutes, sprayed with the Catechol Violet solution, and exposed to UV light for 10–15 min. The appearance of blue spots

indicated the presence of organotin compounds.[5] The R_f values of the butyltin species are: monobutyl/inorganic tin ~0; dibutyltin ~0.2 (see Note, below); and tributyltin species ~0.9.

The chromatogram was cut to separate the blue areas and each area was transferred to a 150 cm^3 beaker, 1.0–5.0 cm^3 sulphuric acid (sg 1.84) and approximately 1 cm^3 of nitric acid (sg 1.42) were added, and each 'spot' was wet-ashed and its tin content determined as described in the determination of total tin above.

Reproducibility data are given in Table 2.

Note The presence of the tropolone alters the R_f value of the dibutyltin species from ~0.5 to ~0.2. R_f values of the other species are not significantly affected.

RESULTS AND DISCUSSION

At the time that this method was being developed the National Bureau of Standards (USA) were organising an International Interlaboratory comparison of the measurement of tributyltin in water.[6] The solution as distributed was a nominal 2.5 ppm TBTO (≡1 ppm Sn) in sterile water and participants were asked to dilute the sample for analysis.

The overall average total tin from approximately 30 laboratories was 1.00 ± 0.05 ppm Sn. The results obtained on the sample using the method described for total tin are shown in Table 2. The dilutions were made by taking 1.0 cm^3 of the sample and diluting with distilled water to the appropriate volume.

Similar dilutions with distilled water were made and the samples extracted and the species present separated chromatographically and determined for tin content by the method described. The results obtained are shown in Table 3 and, as can be seen, no appreciable breakdown of tributyltin species was observed in the samples.

Storage of aqueous solutions of TBTO

As part of this and other work it became necessary to prepare and store standard aqueous solutions of TBTO at the ~5 ppm level. The simplest way to prepare such a standard solution is to initially dissolve a known weight of the TBTO in an organic solvent that is miscible with water and then to dilute a small aliquot (say 0.5–

Table 2 Results of the determination of total tin on a National Bureau of Standards, USA (NBS) sample as received and diluted

Sample	Sn found in diluted solution (ppm)	Sn concentration in original sample (ppm)
As received	—	0.96, 0.97
100 × dilution	0.009, 0.01	0.90, 1.00
300 × dilution	0.0034, 0.0036	1.04, 1.08
1000 × dilution	0.0011, 0.0010	1.04, 1.00
Average		1.01 (R.S.D. 5.3%)[a]

[a]R.S.D., relative standard deviation.

Table 3 Results of the speciation of the NBS sample

Diluted Sn concn (ppm) (Vol. extracted, cm^3)	Species found as Sn (μg)			Total Sn (μg)[a,b]	Recovery (%)
	Bu/inorganic*	Bu_2*	Bu_3		
0.03 (500)	0.4	0.3	13.6	14.3	95
0.015 (1000)	0.5	0.5	13.6	14.6	97
0.001 (5000)	0.0	0.4	3.8	4.2	84

[a]Total tin is amount of tin (μg) found in the volume of solution (cm^3) given in parentheses.
[b]$3\sigma \equiv 0.2\ \mu g$ Sn (= L.O.D. at detector). 20 μL is injected to the instrument.
*These levels are about the level of the experimental error.

2.0 cm^3) to the required volume with water. It was observed that these solutions tended apparently to lose tin especially if stored at low temperature. It was thought that this might be due to adsorption on the walls of the container; however, in experiments keeping the NBS sample in pyrex glass vials both at room temperature and at −15°C, it was shown that these samples were quite stable over a period of seven days. Also, the NBS sample itself had been stored in a pyrex vial for over a year without any apparent loss of tin. It should be noted that the NBS solution was prepared by passing sterile water through a chromatographic column packed with Chromosorb WHP and loaded with TBTO.[6] It was also observed that aqueous solutions prepared from an acetone solution of TBTO tended to be less stable than those obtained from a propan-2-ol solution (see Tables 4 and 5).

To ascertain the whereabouts of the lost tin in the frozen samples kept at −15°C, the walls of the container were treated with acid and the solution analysed for tin. As can be seen in Table 5, approximately 4 μg of tin was found on the walls of the beaker; this represents over 70% of the 'missing' tin.

Table 4 Effect of temperature and storage time on the stability of aqueous solutions of TBTO (5 ppm) prepared by different routes

Solvent for TBTO	Storage time (h)	Storage temp. (°C)[a]	Sn found ($\mu g\,cm^{-3}$)
Acetone	0	RT	2.0
	72	RT	1.9
	72	−15	1.5
	168	RT	1.7
	168	−15	1.4
Propan-2-ol	0	RT	2.0
	72	RT	2.0
	22	−15	1.5

[a]RT, room temperature.

CONCLUSIONS

(1) A satisfactory and simple method for the determination of tin and butyltin species in water has been developed. In the method described total inorganic tin and butyltin species can be determined in water samples by solvent extraction and determination of the tin content of the wet-ashed extract by AAS/ETA. The limit of detection using a 5 dm^3 sample is ~20 ng dm^3.

(2) Aqueous solutions of TBTO at the 2–5 ppm level prepared by initially dissolving the compound in a water-miscible organic solvent followed by dilution with water may not be stable over a period of time, especially if stored at low temperatures.

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Table 5 Effect of storage temperature and time on the stability of aqueous solutions of TBTO (2.5 ppm) prepared by different routes

Solvent for TBTO	Storage time (h)	Storage temp. (°C)	Sn found ($\mu g\,cm^{-3}$)	Sn found on sides of the vessel (μg)
Acetone	0	RT	0.9	—
	168	RT	0.8	—
	168	−15	0.6	~4
Propan-2-ol	0	RT	1.1	—
	168	RT	0.9	
	168	−15	0.6	~4
Water (NBS)	0[a]	RT	1.0	—
	168	RT	1.05	—
	168	−15	1.1	—

[a]Sample had been stored for over a year before the experiment was performed.

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