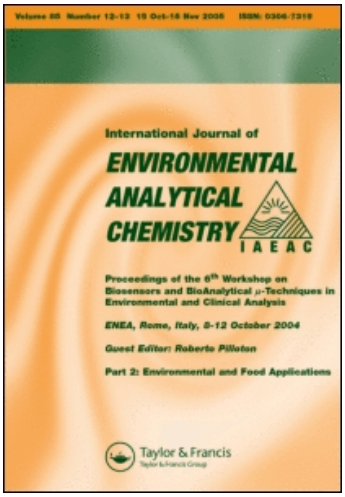

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Dogan, S. and Haerdi, W.(1980) 'Determination of Total Tin in Environmental Biological and Water Samples by Atomic Absorption Spectrometry with Graphite Furnace', International Journal of Environmental Analytical Chemistry, 8: 4, 249 — 257
To link to this Article: DOI: 10.1080/03067318008071894
URL: http://dx.doi.org/10.1080/03067318008071894

Intern. J. Environ. Anal. Chem., 1980. Vol. 8. pp. 249–257
0306-7319/80/0804-0249 $6.50/0

Printed in Great Britain

Determination of Total Tin in Environmental Biological and Water Samples by Atomic Absorption Spectrometry with Graphite Furnace†

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(*Received May 30, 1980*)

Analysis of traces of tin using several analytical techniques (X-ray fluorescence, neutron activation, polarographic techniques and atomic absorption) have been tested. Parameters such as simplicity, rapidity, sensitivity and interferences are compared in order to choose the most useful method for practical purpose. Finally, flameless atomic absorption was chosen for the determination of total tin concentration in different natural samples.

Digestion of biological samples (plant, plankton, fish, etc.) was achieved by using Lumatom^{R} (a trade organic chemical). Thus, the digested sample is directly injected into the graphite furnace. This digestion technique is suitable and rapid with a minimum of error (contaminations and losses). For tin analysis in water samples, a preconcentration of tin is carried out by coprecipitation with 1, 10-phenanthroline and tetraphenyl boron. The precipitate is separated and dissolved in alcohol or in Lumatom^{R}.

The sensitivity of this method is 0.1 ng absolute tin.

KEY WORDS: tin, environmental samples, flameless atomic absorption.

INTRODUCTION

Organotin compounds like those of other heavy metal ions are considered to be fairly toxic (used in plastics and in agriculture such as fungicides or

†Presented at the 10th Annual Symposium on the Analytical Chemistry of Pollutants, Dortmund (Germany), May 28–30, 1980.

bactericides), but the inorganic salts are less toxic.[1,2] However, it is well known that the inorganic salts may be converted into the organic ones by bacterial action in aquatic media[3] and thus a biological cycle is set up following a series of chain reactions. Hence it is important to know the concentration of tin present in natural systems in order to get an insight of its role in the pollution of the environment.

Atomic absorption spectrometry (AAS) using the hydride technique or flameless technique with electrothermal atomisation is frequently used for the determination of nanogram levels of tin. Fernandez[4] has determined tin and several other elements in the form of their hydrides using sodium borohydride as a reducing agent and he claims 7 ng as the absolute sensitivity for tin. Hodge *et al.*[5] and Braman *et al.*[6] have developed a sensitive method for the separation and determination of various organotin compounds in environmental samples using the hydride technique. Sensitive determinations of tin based on the flameless technique with electrothermal atomization have been described by Ohta and Suzuki[7] who used molybdenum tubes whereas Tominaga and Umezali[8] and Trachman *et al.*[9] used a graphite furnace. Several others have used flameless AAS coupled to a gas chromatograph[10] or high pressure liquid chromatograph[11] for quantitative determination and speciation studies of tin.

In the present work, the determination of traces of tin in environmental biological and water samples by means of flameless AAS is described. Among the analytical tools available for tin analysis (X-ray fluorescence, neutron activation, polarography and AAS), AAS seems to be the most practical method.

EXPERIMENTAL

Preliminary studies showed that tin at ppb levels could not be determined by non-destructive methods (X-ray fluorescence and neutron activation), although tin is often present at these levels in environmental samples. The sensitivities of these two methods are not particularly good and in addition they are subject to interference from the matrix and the major elements present in the sample under investigation. Preconcentration prior to analysis may be carried out but it is time consuming for routine analysis and the use of various reagents and manipulations introduces large sources of error in analysis.[12]

Although the polarographic method is fairly sensitive, it is subject to a number of serious interferences. The sample must be digested in acid solutions or other digesting media. The nature of these digesting agents may interfere in the polarographic determination by either shifting the

half-wave potential or by masking the metal to be determined (e.g. lead interferes strongly). Metzger *et al.*[13] have determined tin in the presence of lead using 1 M HCl in methanol as supporting electrolyte. This method has limited practical applications and the method is not suitable for routine analysis of environmental samples. Nevertheless it is useful for carrying out species studies which should enable one to get information on their behaviour in natural systems. In some cases this method can be used for checking the results obtained by other methods. For this purpose Nembrini *et al.*[14] used AC anodic stripping voltametry for the determination of tin in biological samples.

Finally AAS was chosen for tin analysis because it is rapid especially with the digestion step used by us, highly sensitive, subject to few interferences and in addition it allows us to carry out routine analysis.

Apparatus and reagents

—Pye Unicam SP 1900 atomic absorption spectrometer equipped with a flameless atomizer, SP 9–01, and coated profile graphite tube were used. A hallow cathode lamp for resonance source (spectral line $\lambda = 286.3$ nm) and a deuterium lamp for background compensation were used. Nitrogen with a flow rate of $21.\text{min}^{-1}$ was used as an internal gas.
—Standard tin(IV) solutions were prepared by diluting $1\,\text{g.l}^{-1}$ stock solution of $SnCl_4$ in HCl (p.a. Merck).
—1, 10-Phenanthroline (p.a. Merck).
—Tetraphenyl boron (p.a. Fluka).
—Lumatom^R: a chemical containing a quarternary ammonium hydroxide in iso-propanol (commercially available: H. Kürner, D-6451 Neuberg, FRG).

Preparation of samples

The digestion of biological samples (plant, plankton, fish, organic component of sediments, etc.) was carried out by means of Lumatom^R. The sample (20–200 mg) was taken in a glass vial and digested in 1 ml of Lumatom^R at 50°C. After the complete digestion of sample (3 h. or more depending on the amount and nature of the sample), 20–50 μl of the sample was withdrawn using an Eppendorf pipette and injected into the graphite furnace. If required the solution may be diluted with iso-propanol or methanol.

This digestion procedure is simple, rapid with minimum sources of error from contamination and losses.

For tin analysis in water samples, we used the preconcentration technique described by Bergerioux and Haerdi.[15] In this procedure, 0.1–1.0 ml of 0.25 M 1, 10-phenanthroline and 0.1–1.0 ml of 0.2 M tetraphenyl boron (both the reagents were freshly prepared) were added to 50–1000 ml of water sample which had been previously filtered through 0.45 μm millipore filter. (The pH of this solution was adjusted to 5.0 before addition of coprecipitating reagents). The precipitate thus obtained was either filtered or centrifuged and dissolved in 1–5 ml aliquot of ammoniacal alcohol (methanol, ethanol or iso-propanol) solution, pH = 8–9 or in Lumatom^R. For large volumes of water, the dissolution of the coprecipitate must be carried out with Lumatom^R since there is the formation of a precipitate due to other ions present with ammoniacal alcohol solution.

RESULTS AND DISCUSSION

The optimum operating conditions for obtaining improved sensitivity in Lumatom^R digestion medium was determined. The effect of ashing temperature, ashing time and atomization temperature were studied using standard tin solutions in Lumatom^R. From the results shown in Fig. 1 it can be seen that optimum temperature for ashing without any loss of tin is observed at 800°C (ashing time: 40 sec). At this temperature contribution of the blank (Lumatom^R) is negligible.

It is apparent from figure 1-A that at ashing temperature of 800°C, 40 sec is adequate for complete removal of Lumatom^R. Longer times will be required for large volumes of injections and shorter times for solutions diluted in alcohol. Ashing times of 25 sec should suffice for aqueous or alcohol solutions not containing Lumatom^R (e.g. in water analysis samples). The following conditions were finally adopted for the measurement of tin:

Drying :100°C (30 sec)
Ashing :800°C (40 sec. For animal tissue samples longer time should be used to ensure complete calcination of the sample).
Atomization :2860°C (5 sec)
Tube clean :3000°C (5 sec)

Remarks

1.—With regard to atomization temperature (figure 2), it can be seen that the absorbance increases as temperature increases.

But with our instrument at high temperatures (about 3000°C) a signal due to the electronics of the instrument is observed. This makes

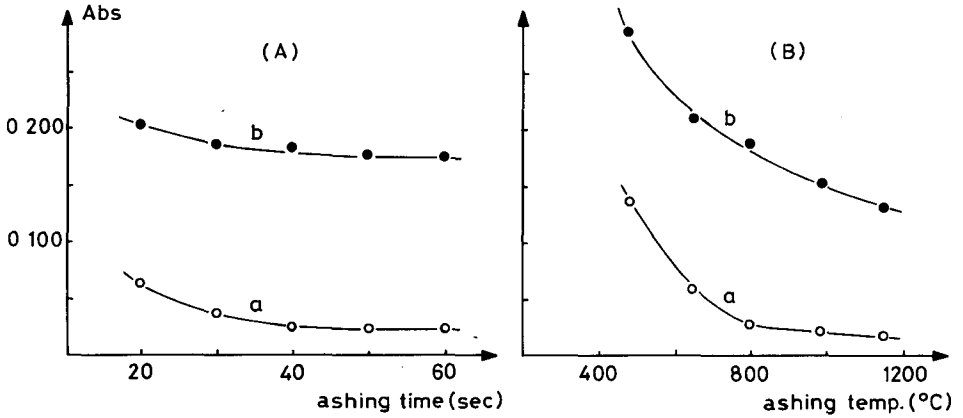

FIGURE 1 Effect of ashing time and ashing temperature on the sensitivity of tin determination (temperature of atomization: 2860 C). Total tin: 5 ng in Lumatom^R (curves b) Blank: Lumatom^R (curves a) Injected volume: 20 μl.

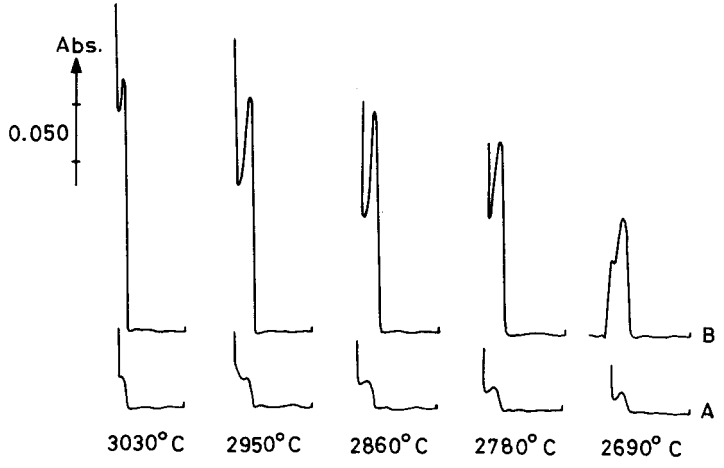

FIGURE 2 Effect of atomization temperature on the sensitivity of tin determination (ashing temperature: 800°C; ashing time: 40 sec). Total tin: 5 ng in Lumatom^R (peaks B) Blank: Lumatom^R pur (peaks A) Injected volume: 20 μl.

the resolution of the tin peak difficult especially at low concentrations of tin.

2.—During the drying and ashing steps the opening through which samples are injected should be closed in order that nitrogen can pass through the graphite tube. This will enable to drive off the fumes efficiently. Just before the atomization step the hole is re-opened so that the sensitivity is not diminished.

Calibration curve

The calibration curve is linear over the range 0.4–14.0 ng absolute both in Lumatom^R and aqueous solutions (volume injected: 20 μl). 0.1 ng of tin can be determined without any difficulty and lower amounts can be detected by using the expended scale of the instrument.

Determination of tin in biological samples

The digesting technique based on Lumatom^R was used for biological samples: canned juice, aquatic plants, plankton, fish and sediments. All the analyses were carried out by spiking the sample with standard solutions.

Juice of canned fruits

Direct determination of tin in canned juices may be performed but

reproducible results are not obtained owing to the presence of significant proportions of suspended particules in the solution. Therefore analysis was done after digesting the sample in Lumatom^R (0.2 ml aliquot of the juice in 1 ml of Lumatom^R). The digested sample is injected into the graphite furnace after making appropriate dilution with iso-propanol. The results of analysis of some of the juices of canned fruits available commercially are given in Table I. The results were also checked by polarography.[14]

TABLE I

Determination of tin in some juices of canned fruits.

Sample	pH	Total tin (ppm)	
		AAS	polarography
Juice of halved peach (family size bottle)	3.90	99	105
Juice of sliced peach	3.96	30	28
Juice of halved pear	3.63	43	45
Juice of sliced pineapple	3.98	86	83
Juice of fruit cocktail	3.74	57	51
Juice of quartered mandarine	3.30	68	70
Juice of peeled tomato	4.56	52	50
Orange drink (concentrate)	3.10	1.2	not determined

Aquatic biological samples and sediments

Analysis of tin in some aquatic plants, plankton, fish and sediments of Lake Léman (at Geneva) were carried out. It must be noted that cellulose of the plants is not very soluble in Lumatom.^{R} However, reasonably homogenous solutions could be obtained if the samples are finely ground. The solutions when injected give reproducible results (complete calcination of the sample is done in the graphite tube during the ashing step).

The analysis of sediments 'sieved in 100 μm mesh sieved and dried at 60°C) consisted of two steps: a) Digestion in Lumatom^R gave an estimate of the concentration tin in the organic matter, b) the mineralization of the sample in acid media (aqua regia) prior to analysis yielded the quantity of total tin in the sediments.

Some of the results are given in Table II.

TABLE II

Concentration of tin in some aquatic plants, planktons, fishes and sediments from the lake Léman (at Geneva).

Sample	date of sampling	Sn (ppm)[a]
Plant:		
– Potamogeton Lucens	17.7.1975	12.8
	31.7.1976	4.3
	12.9.1977	8.7
	13.7.1978	9.5
–Potamogeton Perfoliatus	17.7.1977	7.5
	13.7.1978	9.0
Plankton:		
–Plankton mixed (Ceratium and Cladocera)	8.9.1975	5.0
—Zooplankton (Cladocera)	16.5.1978	3.1
	(acid digestion)[c]	3.3
Sediments:		
—Sandy samples:	1979	
Lumatom solubilization		0 – 0.03
Acid digestion		54 – 56
—Samples rich in humus:	1979	
Lumatom solubilization		0.1 – 2.2
Acid digestion		80 – 100

Fish	Weight (g)	Length (cm)	Sn (ppm)[b]
Bleak	400 – 600	30 – 35	0.4 – 0.7
Trout	3660 (empty)	62	5.0
(acid digestion)[c]			5.2
Tench	2780	46	4.1
Pike	5112(empty)	75	6.6
(acid digestion)[c]			8.4

[a]values for dried weight;
[b]values for wet weight;
[c]acid digestion is carried out with HNO_3 conc. in teflon decomposition vessel.

Remarks

1.—The plant samples were washed with 4‰ formol solution, dried at 40°C and then finely ground.
2.—The plankton samples were lyophylised.
3.—The fish samples were directly digested after homogenization.
4.—0.2–0.3 g sediment sample in 3–5 ml aqua regia were heated in a water bath at 90°C for about 1 h., then the solution was diluted to 10 ml with water and centrifugated. The supernatant solution was injected into the graphite furnace with or without dilution of the sample depending on the amount of tin present in the sample.

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