The Determination of Organic, Inorganic, Total and Specific Tin Compounds in Water, Sediments and Biota 1992

Methods for the Examination of Waters and Associated Materials

HMSO

The Determination of Organic, Inorganic, Total and Specific Tin Compounds in Water, Sediments and Biota 1992

Methods for the Examination of Waters and Associated Materials.

Tin occurs in many forms. This booklet contains methods for toluene extractable organotin in waters, toluene extractable organotin in muds, sludges, weeds and fish and for speciation of organotin compounds in waters. It also contains three notes; one on speciation of tin compounds by high performance liquid chromatography-atomic spectroscopy, one on the determination of total, total inorganic and total organic tin compounds by cathodic stripping voltammetry. The third note which is chiefly for the examination of bottom deposits, but which can be adapted for waters, is capable of bringing common tin minerals into solution, as well as liberating tin compounds bound to clays and other intractable materials. This latter procedure is usually only used for relatively high concentrations of tin.

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Contents

About This Series

This booklet is part of a series intended to provide recommended methods for determining the quality of water and associated materials. In addition short reviews of the more important analytical techniques of interest to the water and sewage industries are included.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series is published as a series of booklets on single or related topics, thus allowing for the replacement or addition of methods as quickly as practicable without the need for waiting for the next edition. The rate of publication is also related to the urgency of the requirement for that particular method.

Although ideally, all methods published should be fully tested, this is not often possible without delay in publication. Furthermore, the limit of detection, range, precision and interference effects applying to instrumental methods can be dependent on the actual instrument used, as well as on sample type, reagent purity and operator skill, etc. Even methods tested in many laboratories have been known to acquire problems when new products appear (introducing new substances into effluents), changes in production methods affecting reagent quality, or the method used to analyse new types of sample (despite apparent similarity to samples already evaluated). As a guide, the following categories have been given to methods:

(i) tested, usually in five or more laboratories
— no grade indicated;

(ii) tested in one to three or four laboratories
— Tentative;

(iii) evaluated, but not fully tested, but publication is urgently required
— Note;

(iv) tested and found to be satisfactory by several laboratories, but in the opinion of experts requires a high degree of skill or has some other difficulty such that the method would be replaced if a better method were discovered.
— Provisional.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users and senior technical staff, to decide which method to use for the determination in hand. Whilst the attention of users is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has nine working groups, each responsible for one section or aspect of water cycle quality analysis. They are:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage works control methods
9.0 Radiochemical methods.

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and the main committee. The names of those associated with this method are listed at the end of this book.

Publication of new or revised methods will be notified to the technical press. A current list of publications can be obtained from the Secretary.

Every effort is made to prevent errors from occurring in the published text. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically. However, should any errors be found, please notify the Secretary.

DR D WESTWOOD
Secretary

20 January 1992

Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety and COSHH Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text, so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown to be often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', issued by the Royal Society of Chemistry, London: 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection', Public Health Laboratory Services Monograph 6, HMSO, London.

It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient, give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

Safety while Sampling

Prior consideration must be given, especially when sampling in confined spaces or where access is difficult, to guard against suffocation, drowning, falls and poisoning or infection by ingestion, inhalation or skin contact.

Good Laboratory Practice

The Department of Health issue a booklet entitled: Good Laboratory Practice; the United Kingdom Compliance Programme, 1989. This can be obtained by writing to that Department in London. It deals chiefly with toxicity studies, but much can be applied to analytical chemistry.

Total Tin in Waters and Sediments by Atomic Absorption or ICP Spectrometry

Introduction

Tin can occur in a variety of forms in the aqueous environment. It can occur as a constituent of bed rock, derived sediments, leached material and material from the related plant and animal assimilation processes. It can occur as leachate and sediment etc from any of the industrial and metallurgical uses of the metal and its salts. Soluble inorganic tin compounds often hydrolyse unless the pH is very low. Additionally, it can occur as organotin biocides, though usually, but not necessarily, in smaller quantities. Tin is usually four valent in nature, though soluble two valent inorganic compounds are known. The organic compounds consist of a varied series of mono, di and tri substituted alkyl and aryl salts and tetra substituted compounds. Tri substituted organotin can also form oxides. The commonest organo groups used commercially are butyl and phenyl; but many more organotins are known, some of which are also used industrially. Hence the chromatographic elution times for both GC and HPLC and the mass spectra can vary widely. Most, but not all, of these organocompounds are extractable in organic solvents. Their determination and identification are given in methods A, B, C and D in this booklet. Methods D, E and F determine both inorganic and organic tin. Most organic and inorganic tin compounds can be absorbed quite strongly by solids, especially by clays, glass and plastics. They are used as preservatives for both wood and metal, in antifouling compositions for surfaces, as mordants in dyeing and also in plating. As can be seen from Table 2, the strength of the absorption can vary widely, and with inhomogeneous materials can cause wide variation between duplicate analyses. This can make the assessment of the degree of pollution of bottom sediments very difficult, especially if tin minerals are present. Fortunately, most tin minerals have relatively high densities and so can be separated by flotation from the lighter clays and organic matter which more readily absorb the organotins. Note F describes how such separations can be made and goes on to give details of a method for bringing insoluble tin compounds into solution. It is not as sensitive as the other methods, but is of use if the determination of tin minerals is required, or gross contamination of a sediment which absorbs strongly has occurred.

Care is necessary to avoid accidental pick ups. Much glass now contains traces of inorganic tin, which should cause little problem if only organic tin is sought. However many plastic bottles contain traces of disubstituted organotins and both glass and plastic can absorb both organic and inorganic tin. Another source of contamination is tin from plating and solders which can contaminate water (see section A5.5). It should not be forgotten that tin IV chloride and bromide are volatile in steam.

The Grignard method for speciation was evaluated, but is not included here as it has been found to be more difficult for routine use than the hydride method and the extraction technique of Note D.

A Determination of Toluene Extractable Organotin in Waters

(Based on M and T Chemicals Inc, Method No AA–27)

1 Performance Characteristics of the Method

The performance data quoted was determined on bis (tributyltin) oxide (TBTO); but other tin compounds can be determined.

A1.1	Substances determined	Organotin compounds; the recovery of mono-alkyl tin compounds is poor.
A1.2	Types of sample	River, sea and drinking water.
A1.3	Basis of the method	The sample is acidified with acetic acid and the organotin compounds extracted into toluene. The extract is concentrated and analysed by electrothermal atomic absorption spectrophotometry (EAAS).
A1.4	Range of application	See Table 1. The range may be extended by dilution or by using a smaller volume of sample.
A1.5	Calibration curve	The instrument used for the performance tests gave a linear response over the range 0–5 ng of tributyl tin oxide injected. (See Fig 1).
A1.6	Standard deviation	See Table 1.
A1.7	Limit of detection	Calculated from the estimate of the standard deviation of the low spiked distilled water samples, the limit of detection was 0.02 $\mu g L^{-1}$ as Sn, for a 2 litre sample.
A1.8	Sensitivity	With a baseline fluctuation of 0.5%, 50% Full Scale Deflection was given by approximately 5 ng of TBTO injected (2.0 ng as Sn). The instrument response tends to decline as the furnace ages or becomes contaminated.
A1.9	Bias	None known.
A1.10	Interferences	None known.
A1.11	Time required for analysis	Eight samples may be extracted and analysed in a working day. If no concentration step is required 16 samples per day may be determined.

A2 Principle

The sample is acidified with glacial acetic acid and extracted with toluene. The extract may be concentrated, before analysis by electrothermal atomic absorption spectrophotometry (EAAS). (Refs 1.2.3)

A3 Interferences

None known. Pick up of diorganotins from some plastics can occur.

Figure 1 Linearity of response of the HGA-AAS to bis (tributyltin) oxide using TBTO standards

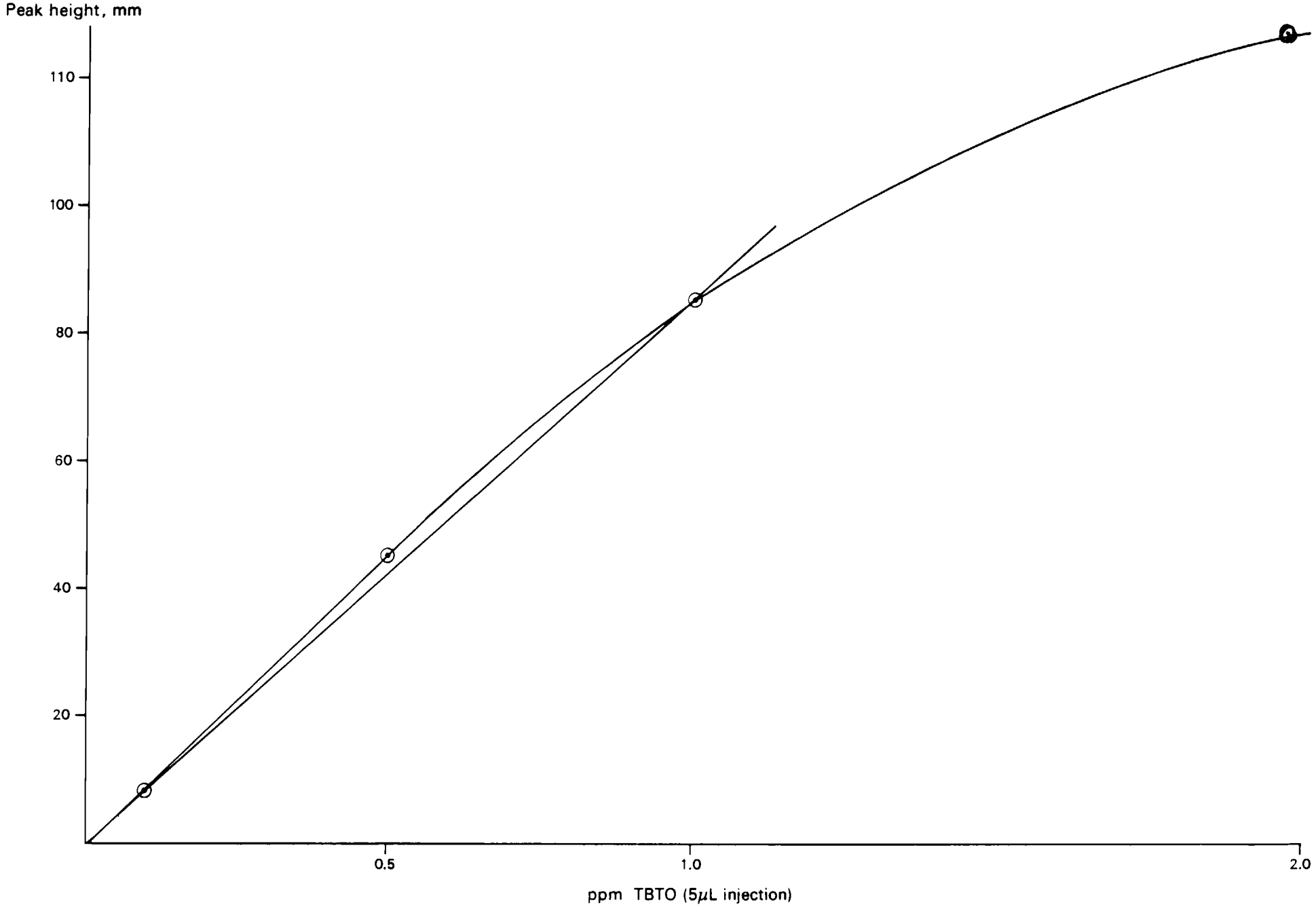


Table 1 Recovery and Standard Deviation from Water Samples

Sample	Mean & Range Organotin μgL^{-1} Sn	Mean Recovery %	S_w	S_b	S_t
			(degrees of freedom in brackets)		
Distilled Water (Blanks)	ND<0.02	—	—	—	—
DW + 0.024 μgL^{-1} Sn	0.024(8)	102	0.0044	0	0.0044
	0.017–0.030		(6)	(2)	(8)
DW + 0.24 μgL^{-1} Sn	0.26(5)	109	0.048	NS	0.051
	0.20–0.32		(3)		(5)
DW + 0.48 μgL^{-1} Sn	0.45(8)	94	0.057	0	0.057
	0.38–0.57		(6)		(8)
River Water	ND<0.02	—	—	—	—
RW + 0.024 μgL^{-1} Sn	0.021(5)	87.5	0.006	0	0.006
	0.017–0.028		(3)	(2)	(5)
RW + 0.24 μgL^{-1} Sn	0.25(5)	103	0.012	NS	0.022
	0.23–0.27		(3)		(5)
RW + 0.48 μgL^{-1} Sn	0.45(5)	91.25	0.025	0.088	0.09
	0.37–0.57		(3)	(2)	(5)

Data supplied by SAC Scientific.

A4 Hazards

Toluene is flammable and toxic. Organotin compounds are toxic. Glacial acetic acid is corrosive. Extractions should be made in a flameproof fume cupboard.

A5 Reagents

A5.1 Glacial acetic acid. Analytical grade reagent.

A5.2 Bis (Tributyltin) Oxide (TBTO) or Tributyl Tin Chloride. Analytical grade reagent.

A5.3 Toluene. Analytical grade reagent.

A5.4 Standard Solutions

A5.4.1 Stock Solution 100 mgL^{-1} as Tin. Weigh accurately a weight approximating to 0.0512 g TBTO. Dissolve in glacial acetic acid (A5.1) and make up to 200 mL with more acid. Do not attempt to weigh out exact amounts. See also B5.13.1.

A5.4.2 Intermediate Stock Solutions. By serial dilution into glacial acetic acid prepare 10 mgL^{-1} and 1.0 mgL^{-1} standard solutions. These are stable for at least 3 months.

A5.4.3 Working Solutions. Dilute appropriate aliquots of the intermediate standards with toluene (A5.3) to prepare working solutions to cover the range 0.025–0.2 mgL^{-1} as tin.

A5.5 Tin free water. Extract with toluene 2 litre batches of distilled water, prepared in an all glass apparatus.

A5.6 Sodium Sulphate. Anhydrous granular analytical grade reagent.

A6 Apparatus

A6.1 Sample bottles. 2.5 L all glass or with PTFE lined stoppers and calibrated at 2 litres.

A6.2 Pasteur pipettes.

A6.3 Shaking machine. (Capable of shaking 2.5 L bottles in a horizontal plane).

A6.4 Centrifuge tubes. 10 ml—glass, calibrated, with glass stoppers.

A6.5 Atomic absorption spectrophotometer adapted for electrothermal operation to be operated in accordance with the manufacturer's instructions. The use of an autosampler is beneficial.

A7 Sample Storage Samples should be analysed as soon as possible after sampling, store in a refrigerator if necessary. Addition of 50 mL of glacial acetic acid per 2 L will assist in the preservation of the sample. Absorption occurs to the bottle wall (see step A8.1.1).

A8 Analytical Procedure

Step	Procedure	Notes
A8.1	Extraction	
A8.1.1	To 2 litres of sample in the sample bottle add 50 ± 5.0 mL glacial acetic acid (A5.1) and agitate for a few seconds to mix. (This step is omitted if the acetic acid has been added previously for preservation.)	
A8.1.2	Add 20 ± 0.2 mL toluene (A5.3) and vigorously shake for 15 ± 1 min on a shaking machine. Allow the layers to separate. Add tin free water to bring the liquid level into the neck of the bottle.	
A8.2	Concentration	
	If the anticipated concentration in the sample is expected to be higher than 1.0 $\mu g L^{-1}$ proceed directly to 8.3	
A8.2.1	If preconcentration is required, transfer 10 ± 0.1 mL of the toluene extract into a 10 mL glass graduated centrifuge tube (A6.5). Lower the tube into a water bath controlled at 40 ± 2°C and reduce the volume of the solvent with the aid of a stream of dry, filtered nitrogen until the volume is 1 ± 0.05 mL (a dry block heater may be used) (notes a and b). This must be undertaken in a fume cupboard.	(a) Excess heat may not be used because of the risk of losses of the compound sought. (b) Centrifuge tubes should be accurately calibrated at the 1 mL mark.
A8.3	Measurement of Tin	
A8.3.1	Set up the atomic absorption spectrophotometer and heated graphite atomiser in accordance with the manufacturer's instructions at a wavelength of 286.3 nm (notes c and d). Establish the calibration of the instrument by atomising a series of standards (A5.4.3) to embrace the desired range.	(c) A solvent resistant sampling system must be used. Greater reproducibility is usually obtained when samples are injected automatically. (d) Enhancement of response may be achieved by tube pretreatment. See Section A9.
A8.3.2	Measurement Atomise the samples under the same conditions as used for calibration and determine the concentrations in the extracts by reference to the calibration response (notes e and f).	(e) Typical atomiser conditions are described in Section A10. (f) The results will be as tin. They may be expressed as TBTO by applying the factor 2.5.
A8.3.3	Performance checks Apply the entire procedure to aliquots of tin free distilled water (A5.5) and spiked samples to determine blank levels and recoveries (note g).	(g) Unacceptable levels of tin in the reagents must be investigated.

A8.4 Calculation

The concentration of tin (C) in the sample is given by:—

$$C = \frac{T \times v}{V} \times F\ \mu gL^{-1}\ Sn$$

Where T = concentration of tin in the toluene extract in mgL^{-1}
v = volume of extract in mL
V = volume of sample taken in litres.
F = concentration factor if step A8.2.1 is used (usually 0.1)
If step A8.2.1 is not required then F = 1.

A9 Pretreatment of Furance Tubes

A9.1 Prepare a 50 ± 5% w/v solution of lanthanum nitrate in distilled water.

A9.2 Clean non-pyrolitic carbon tubes by twice executing the drying, ashing and atomising sequence in the furnace. Allow to cool.

A9.3 Place the cleaned tubes in a glass boiling tube and cover with lanthanum nitrate solution. Tap the boiling tube to remove bubbles and allow to stand for a few minutes.

A9.4 Place the boiling tube in a beaker and add water to the beaker until the tube is about one third submerged.

A9.5 Heat the beaker to 60 ± 2°C and apply light vacuum to the boiling tube. Maintain these conditions for 30 ± 5 mins.

A9.6 Release the vacuum and remove the boiling tube from the beaker. Decant off the lanthanum solution and transfer the carbon tubes to a filter paper.

A9.7 Dry the carbon tubes overnight in an oven maintained at 105°C.

A10 Typical Spectrophotometer and Furnace Conditions

A.10.1 Spectrophotometer Conditions

Analytical Wavelength	— 286.3 nm
Source	— Hollow Cathode Lamp 15 mA, operating current 6 mA
Background connection	— essential
Slit Width	— 0.5 nm
Mode	— Peak Height
Signal	— Concentration
Integration Time	— 7 seconds
Inert Gas	— Argon or nitrogen
Sample Aliquot	— 5 μL
Tube Type	— Lanthanum coated

A10.2 Furnace Conditions

Step	1	2	3	4	5
Temp °C	50	85	600	900	2700
Ramp time secs	15	20	20	20	0
Hold time secs	10	10	5	5	7
Recorder			ON	ON	ON
Read					ON
Miniflow mL min^{-1}	50	50	50	50	
Gas Stop					ON

B Determination Of Toluene Extractable Organotin in Muds, Sludges, Weeds and Fish

B1 Performance Characteristics of the Method

B1.1	Substances determined	Organotin compounds excluding monoalkyl tin compounds.
B1.2	Types of sample	Bottom sediments, sewage sludges, weeds and fish tissues.
B1.3	Basis of the method	The sample is refluxed with methanol/hydrochloric acid, cooled, filtered and extracted with toluene. The toluene extract is dried and concentrated, before analysis by electrothermal atomic absorption spectrophotometry (EAAS). A 'clean-up' step is advantageous for some samples.
B1.4	Range of application	0-50 $\mu g\ kg^{-1}$ dry weight as Sn. The range may be extended by dilution of the extract or by using a smaller weight of sample.
B1.5	Calibration curve	The instrument used for the performance tests gave a linear response over the range 0–5 ng of bis (tributyltin) oxide (TBTO) injected.
B1.6	Standard deviation	See Table 2.
B1.7	Limit of detection	Muds = 5 $\mu g\ kg^{-1}$ dry wt as Sn Sludges = 120 $\mu g\ kg^{-1}$ dry wt as Sn Weeds = 5 $\mu g\ kg^{-1}$ wt as Sn Fish = 15 $\mu g\ kg^{-1}$ dry wt as Sn These limits were calculated from the low spiked samples except for the sludge where organotin occurred in the unspiked sample.
B1.8	Sensitivity	With a baseline fluctuation of 0.5%, 50% FSD was given by approximately 5 ng of TBTO injected (2 ng as Sn). The instrument response tends to decline as the furnace ages or becomes contaminated.
B1.9	Bias	None known.
B1.10	Interferences	None known.
B1.11	Time required for analysis	Four samples per working day.

B2 Principle

A sample equivalent to approximately 10 g dry weight of sample is prepared and refluxed with 50 mL methanol:hydrochloric acid (95:5 v/v) for 30 mins at 70–80°C. The mixture is cooled, filtered and 120 mL sodium chloride solution (10%) added to the filtrate. The organotin chlorides are extracted with 2 aliquots of 50 mL toluene. The extracts are combined, dried with sodium sulphate and concentrated using a Kuderna-Danish evaporator. A column clean up on silica gel is advantageous for some samples.

Table 2 Recovery and Standard Deviations from Solid Samples

Sample	Mean and Range Organotin $\mu g\ kg^{-1}$ dry Wt	Mean Recovery %	S_w	S_t
			(degrees of freedom in brackets)	
Mud (Ouse Tributary) (M)	ND<5	—	—	—
M + 12.8 $\mu g\ kg^{-1}$ Sn	14.6 (5) 12.3–15.9	114	1.07 (3)	1.37 (5)
M + 96 $\mu g\ kg^{-1}$ Sn	94 (5) 78–117	98	16.4 (3)	16.4 (5)
Raw Sewage Sludge (RSS) homogenized)	57.2 (5) 16–86	—	—	24.5 (5)
RSS + 12.8 $\mu g\ kg^{-1}$ Sn	85 (5) 77–91	217	5.38 (3)	6.10 (4)
RSS + 96 $\mu g\ kg^{-1}$ Sn	127 (5) 74–173	73	43.8 (3)	43.83 (5)
Water Weed (WW)	ND<5	—	—	—
WW + 12.8 $\mu g\ kg^{-1}$ Sn	12.4 (5) 9.4–15.0	96.7	1.16 (3)	2.56 (5)
WW + 96 $\mu g\ kg^{-1}$ Sn	96.1 (5) 77.8–114	100	5.65 (3)	12.9 (5)
Fish (F)	ND<15	—	—	—
F + 12.8 $\mu g\ kg^{-1}$ Sn	9.89 6.8–13.6	77	2.93 (6)	3.09 (8)
F + 96 $\mu g\ kg^{-1}$ Sn	99.4 51–152	103	25.3 (6)	35.0 (8)

Data supplied by SAC Scientific

Notes

1. Part of the variability with the sewage sludge data could be due to the difficulty in obtaining a homogeneous sample.
2. Tests with different kinds of river bottom material show that recovery of organic tin is highly dependent on the mineralogical type of the material.
Sand gives good recovery values.
Clays and some organic materials such as rotten leaves, wood and peat gave very poor recoveries.
Mixtures gave inbetween values, which could be variable depending on the degree of sample homogenity.

The extract (5 μL) is injected into an electrothermal atomic absorption spectrophotometer and the response compared to standards of organotin compounds (eg TBTO). (Refs 2&3).

B3 Interferences

None known. Some samples appear to contaminate the furnace and produce a diminished response. Several replicate injections of each sample extract should be made. Pick up of diorganotins can occur from some plastics.

B4 Hazards

Toluene and methanol are flammable and toxic. Organotin compounds are toxic.

B5 Reagents

B5.1 Methanol. Analytical grade reagent.

B5.2 Hydrochloric acid. Analytical grade reagent.

B5.3 Methanol/hydrochloric acid 95/5 v/v.

B5.4 Sodium chloride. Analytical grade reagent.

B5.5 **Water**—tin free; laboratory distilled water is normally suitable (see also Method A5.5).

B5.6 **Sodium chloride solution**—Dissolve 100 ± 10 g of sodium chloride in 1 ± 0.1 litre of water.

B5.7 **Toluene.** Analytical grade reagent.

B5.8 **Sodium sulphate.** Anhydrous granular, analytical reagent grade.

B5.9 **Silica-gel**—Merck 7754 or equivalent.

B5.10 **Hexane**—Pesticide grade.

B5.11 **Ethyl acetate** Analytical grade reagent.

B5.12 **Hexane/ethyl acetate 80/20 v/v.**

B5.13 **Standard solutions of organotin:—**

B5.13.1 *Bis (tributyltin) Oxide (TBTO).* In preparing stock solutions, weigh out by difference and record the true concentrations of the various solutions. Do not attempt to weigh out exact amounts.

B5.13.2 *Stock solution*—Dissolve 0.2 g TBTO in 200 mL toluene.

B5.13.3 Using microlitre syringes prepare standards of TBTO to cover the range 0.02-1 mg L^{-1} in toluene.

B6 Apparatus

B6.1 **Macerator**—suitable for rupturing and homogenising plant and animal tissue.

B6.2 **Reflux apparatus**—A 500 mL wide necked round bottomed flask with a ground glass joint is convenient, fitted with a water cooled condenser.

B6.3 **Water bath**—Capable of operation at 70–80°C.

B6.4 **Glass fibre filters**

B6.5 **Separating funnels**—500 mL capacity fitted with a PTFE stopcock.

B6.6 **Vacuum Kuderna-Danish evaporator**

B6.7 **Graduated centrifuge tubes**—10 mL capacity with 0.1 mL graduations.

B6.8 **Chromatography column** 20 cm × 0.6 cm id fitted with a sinter and tap.

B7 Sample Storage

Samples should be stored in a freezer and analysed as soon as possible after sampling.

B8 Analytical Procedure

Step	Procedure	Notes
B8.1	**Preparation of samples**	
B8.1.1	Mud samples are normally screened through a 100 mesh sieve (note a).	(a) For suggested preparative information see Ref 4.
	Macerate the fish, weed or sludge samples in a blender. Take a portion of the macerated material for a dry weight determination (note b).	(b) The addition of liquid nitrogen to the macerator containing the sample may assist in the break-up of the cells.

Step	Procedure	Notes
B8.2	Transfer a sample of the macerated material equivalent to approximately 10 g dry weight to a 500 mL round bottomed flask (B6.2). Add 50 ± 5 mL of methanol/hydrochloric acid (B5.3) and reflux at 75 ± 5°C for 30 mins.	
B8.3	Remove the apparatus from the water bath, cool and filter the mixture from the flask through glass-fibre filter paper (B6.4) into a 500 mL separating funnel (B6.5). Wash the flask with a further 20 ± 1 mL methanol/hydrochloric acid (B5.3) and pour the washings through the filter into the separating funnel. Wash the filter with a further 10 ± 1 mL methanol/hydrochloric acid and collect the filtrate in the same funnel.	
B8.4	To the filtrate in the funnel add 120 mL of sodium chloride solution (B5.6). Mix and add 50 ± 2 mL toluene (B5.7). Shake for 15 mins on a shaking machine, allow the layers to separate and transfer the lower aqueous layer into a second separating funnel. Add a further 50 ± 2 mL toluene, shake for 5 mins, allow the layers to separate, discard the lower aqueous layer and combine the two toluene extracts.	
B8.5	Run the toluene extract into a round bottomed flask containing anhydrous sodium sulphate (B5.8). Leave the flask for 20 mins and swirl occasionally to thoroughly dry the extract.	
B8.6	Decant the toluene extract into a vacuum Kuderna-Danish evaporator, wash the residual sodium sulphate with a further 20 ± 1 mL toluene and decant the washings into the same evaporator.	
B8.7	Evaporate the toluene to about 5 mL in the Kuderna (note c). Further concentrate the sample to 1.00 ± 0.02 mL with a stream of nitrogen in a fume cupboard.	(c) Evaporation of toluene is very slow at normal pressures. A vacuum Kuderna is preferred.
B8.8	Clean-up procedure For many samples this step may be omitted. It is advantageous when large amounts of co-extracted organic material is present.	
B8.8.1	Prepare a column (B6.8) containing a 12 cm × 0.6 cm layer of dry silica-gel (B5.9) capped with about a 1 cm layer of sodium sulphate (B5.8). Wash the column with 15 ± 0.5 mL hexane (B5.10) discarding the washings (note d).	(d) Each batch of silica-gel should be checked to ensure that all the organotin chlorides are recovered quantitatively.
B8.8.2	When the meniscus of the hexane reaches the top of the column add the sample, washing the tube with a further 1 ± 0.1 mL of toluene and adding the washings to the column.	
B8.8.3	When the meniscus reaches the top of the column add 20 ± 1 mL hexane and elute. Discard the hexane eluate from the column; this contains fatty co-extractants from the sample.	

Step	Procedure	Notes
B8.8.4	When the meniscus reaches the top of the column elute with 20 ± 1 mL hexane/ethyl acetate (B5.12) and collect the eluate in a small beaker.	
B8.8.5	Reduce the volume of the eluate to less than 10 mL by evaporation in a stream of nitrogen and quantitatively transfer into a 10 mL graduated tube (B6.7). Further evaporate to insipient dryness using a stream of nitrogen, (note e), and redissolve in 1.00 ± 0.02 mL of toluene.	(e) The tube may be gently warmed during evaporation but the temperature should not be allowed to rise above 40°C.

B8.9 Measurement of Tin

Proceed as in Section A8.3 in Method A. (note f)

(f) Take note also of Sections A9 and A10.

B8.10 Calculation

The concentration of organotin in the sample is given by:—

$$C = \frac{T \times v \times 100}{W \times \% \text{ dry matter}}$$

Where C = concentration (as Sn) in μg kg^{-1} dry weight.
T = concentration of tin in the toluene in μg mL^{-1}.
v = volume of toluene extract in mL.
W = Wet weight of sample taken in kg.

The % dry matter is determined by a separate determination. (see ref 5)

The result may be expressed as TBTO by multiplying the concentration found by 2.5.

C Determination of Some Organotin Species in Waters by Gas Chromotography

C1 Performance Characteristics of the Method

C1.1	Substances determined	Monoalkyl, dialkyl and trialkyl tin compounds. Aryltins are extracted by this procedure, but the limit of detection is higher. Tetraorganotins are not derivatized but are extracted and determinable.
C1.2	Types of sample	River and drinking waters, estuarine and sea water.
C1.3	Basis of method	Reduction to the hydride form with simultaneous extraction into dichloromethane (DCM). The extract is concentrated and analysed by gas-chromatography with flame photometric detection.
C1.4	Range of application	0–1 $\mu g\ L^{-1}$ as Sn. This range may be extended by dilution of the sample.
C1.5	Linearity	The range of linearity depends upon the instrument and detector in use.
C1.6	Standard deviation	For a saline water spiked with 50 ng L^{-1} of Tributyltin (TBT) the estimate of total standard deviation was 7.3 ng L^{-1} (16 degrees of freedom). The mean recovery was 89%. The mean recovery in fresh water was 90%. Recovery of monobutyltin chloride was 84% and for dibutyltin chloride 78%. Tests on fresh water show similar recoveries.
C1.7	Limit of detection	0.8 ng L^{-1} for bis(tributyltin) oxide (TBTO) on a 2L sample. (7 degrees of freedom).
C1.8	Sensitivity	Dependent upon the instrument and detector in use. For the instrument used in the performance testing 50% FSD was given by 0.2 ng TBT with a baseline fluctuation of 0.05%.
C1.9	Bias	None known.
C1.10	Interferences	Any co-extracted material or its derivative which has a similar retention time to any of the determinands and which gives a detector response will interfere. Normally, no interference is detected.
C1.11	Time required for analysis	Six samples per day.

C2 Principle

Alkyltin compounds are reduced to their hydrides with sodium borohydride and simultaneously extracted into dichloromethane (DCM). The DCM extracts are centrifuged and dried. After concentration, the extract is analysed by gas chromatography using a modified flame photometric detector.

C3 Interferences

None known

See section 3 of the preceding methods and also the Introduction for information on the risks of contamination.

C4 Hazards

DCM is narcotic; sodium borohydride is harmful; organotin compounds and their solutions are toxic. When the borohydride is added to the sample, hydrogen is released and the bottle becomes pressurised. The bottle should be covered in plastic mesh to minimise the consequences should a bottle crack. Hydrogen is flammable.

C5 Reagents

C5.1 Dichloromethane (DCM) Analytical grade reagent.

C5.2 Sodium borohydride. Pellets approx 6 mm diameter (BDH Spectrosol or equivalent).

C5.3 Organotin standards:

Monobutyltin chloride. Analytical grade reagent.
Dibutyltin chloride. Analytical grade reagent.
Tributyltin chloride. Analytical grade reagent.
Tripropyltin chloride. Analytical grade reagent. (Internal standard).

Other organotin standards as appropriate.

C5.3.1 Individual stock solutions of standards: Dissolve 25 mg of each compound (C5.3) in 25 ml DCM to produce a solution containing 1 gL^{-1} of each compound, including the internal standard.

C5.3.2 Individual working solutions: Add 10 μL of each stock solution (C5.3.1) to 10 mL DCM to produce solutions containing 1 $\mu g\ mL^{-1}$ of each compound. These solutions are necessary to establish the retention times relative to that of the tripropyl tin internal standard and to compare the responses of the compounds relative to that of the internal standard. The internal standard solution is used for spiking the samples.

C5.3.3 Composite working solutions: A composite working solution may be prepared containing 10 μL of each stock solution (C5.3.1) in 10 mL DCM (1 $\mu g\ mL^{-1}$). This composite may be used as a spiking solution to set up and test the method.

C6 Apparatus

C6.1 Sample bottles—2.5 litre capacity (Winchester type) fitted with a teflon-lined screw cap and graduated at 2 litres.

C6.2 Shaking machine—capable of shaking the sample bottles in a horizontal plane or of orbital type.

C6.3 Centrifuge—fitted with holders for 100 mL tubes and capable of operation at 2,500 rpm.

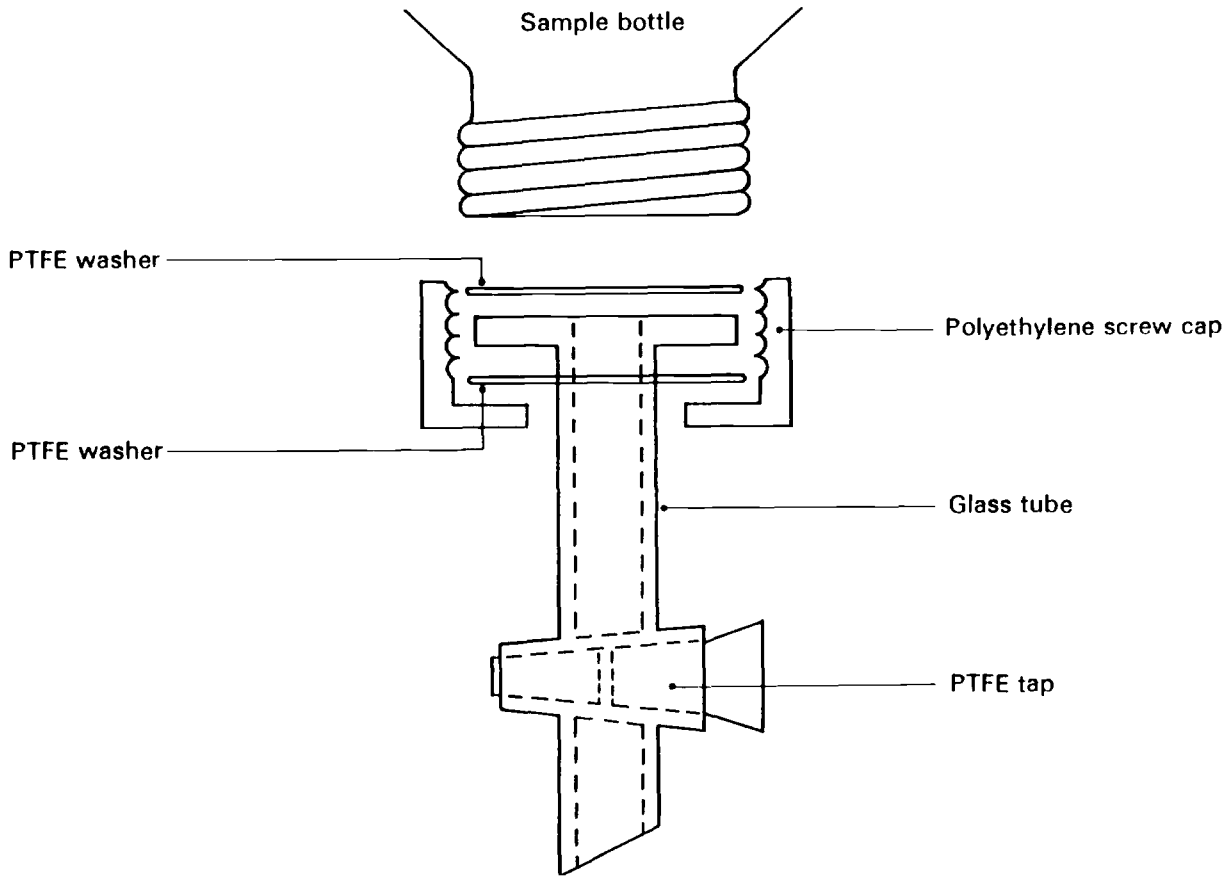
C6.4 Tap device for separating phases—see Fig 2.

C6.5 Pasteur pipettes.

C6.6 Reactivials or equivalent 0.5 ml graduated.

C6.7 Gas chromatograph—Capillary column instrument with temperature programming and flame photometric detection, fitted with a 25 m SE 54 WCOT column.

Figure 2 Details of cap-tap



A suitable temperature programme is 40–200°C at 15°C min^{-1}. The filter in the detector is removed, leaving only the heat-screen to give a non-specific detector. Alternatively a narrow-band filter of 610 nm may be employed. No oxygen is required and the flame is hydrogen rich. The detector gas flow rates are usually about 100 mL min^{-1} H_2 and 70 mL min^{-1} air, but this will vary with the instrument used and will anyway, require fine tuning to secure optimum performance. Split, splitless or on-column injection may be used.

C7 Sample Storage

Samples should be analysed as soon as possible after sampling. If immediate analysis is not possible, samples should be stored in the dark in a refrigerator.

C8 Analytical Procedure

Step	Procedure	Notes
C8.1	To a 2 litre sample in the sample bottle add an appropriate amount of tripropyltin chloride solution (C5.3.1) followed by a pellet of sodium borohydride (C5.2) (notes a and b).	(a) When the borohydride is added, hydrogen is evolved. (b) 4% aqueous solution of borohydride may be used if preferred rather than the pellets.
C8.2	Add 50 ± 5 mL dichloromethane (C5.1). Cap the bottle and shake on a shaking machine for 15 min. CARE. The bottle is pressurised with hydrogen at this stage, handle with care; wear protective clothing. (note c).	(c) Wire gauze wrapped around or above the bottle may prevent injury should the bottle burst.
C8.3	Loosen the bottle cap and release the pressure. Replace the cap with the tap device shown in Fig 2 (C6.4) and allow the phases to separate with the	

Step	Procedure	Notes
	tap closed and the bottle in the inverted position. Open the tap and run the lower DCM layer into a 50 mL centrifuge tube.	
C8.4	Repeat steps 8.2 and 8.3 once more. Cap the tube and centrifuge at 2,500 rpm for 5 min (Note d). After centrifuging, any water in the tube is removed using a Pasteur pipette (C6.5).	(d) Because of the solubility of DCM in water, only about 20 mL will be recovered in the first extraction. The ratio of TBTO to the internal standard, however, remains constant.
C8.5	Evaporate the sample to 2–3 mL using a gentle stream of purified air or nitrogen at ambient temperature. Remove any excess water with a Pasteur pipette.	
C8.6	Add approximately 0.5 g of anhydrous sodium sulphate to the concentrated extract to remove any residual water and allow to stand for 20 min, swirling occasionally.	
C8.7	Transfer the dried extract into a 5 mL Reactivial (C6.6) leaving the sodium sulphate in the centrifuge tube. Using the purified air or nitrogen line, further concentrate the sample to 250 ± 50 μL (note e).	(e) The use of the internal standard renders quantitative transfers unnecessary.
C8.8	Repeat steps (C8.1–C8.7) using tin free blank water as the sample (note f).	(f) For the preparation of water free from tin, see Section A5.5.
C8.9	Repeat steps (C8.1–C8.8) using water spiked at appropriate levels with the alkyl tin compounds (note g).	(g) Standards in the range 1–200 ng L^{-1} in the original sample are usually appropriate.
C8.10	As appropriate, inject 1 μL of the blank, spiked samples and sample extracts on to the GC. Compare the retention times and peak heights of the peaks or areas with those of the internal standard. A chromatogram of some common alkyl tin hydrides is shown in Fig 3.	

C9 Calculation of concentration

Measure the peak heights or areas of the standards and internal standard and calculate the ratios of these heights or areas to that of the internal standard. Measure the retention times of the standard peaks for identification purposes. The concentration is calculated by the following equation

$$C = \frac{c \times h \times R}{H}$$

Where C = Concentration of the alkyltin compound in the original sample (ng L^{-1}).

h = Peak height or area given by alkyltin compound.

H = Peak height or area given by the internal standard.

R = Relative response of the alkyl tin compound to that of the internal standard.

c = Concentration of internal standard in the 2 litre sample (ng L^{-1}).

C10 Confirmation of the identity of alkyltin compounds by gas-chromatography/ mass spectrometry (GC/MS)

The extracts may also be run on GC/MS using the same chromatographic conditions as in the primary method. The FPD is replaced with a mass-spectrometer set up in the electron impact mode with unit resolution. Spectra at the appropriate retention times are examined for the clusters of fragments associated with the isotopes of tin.

Spectra are shown in Figs 4 a–c.

Figure 3 Typical gas chromatogram of butyl tin hydrides

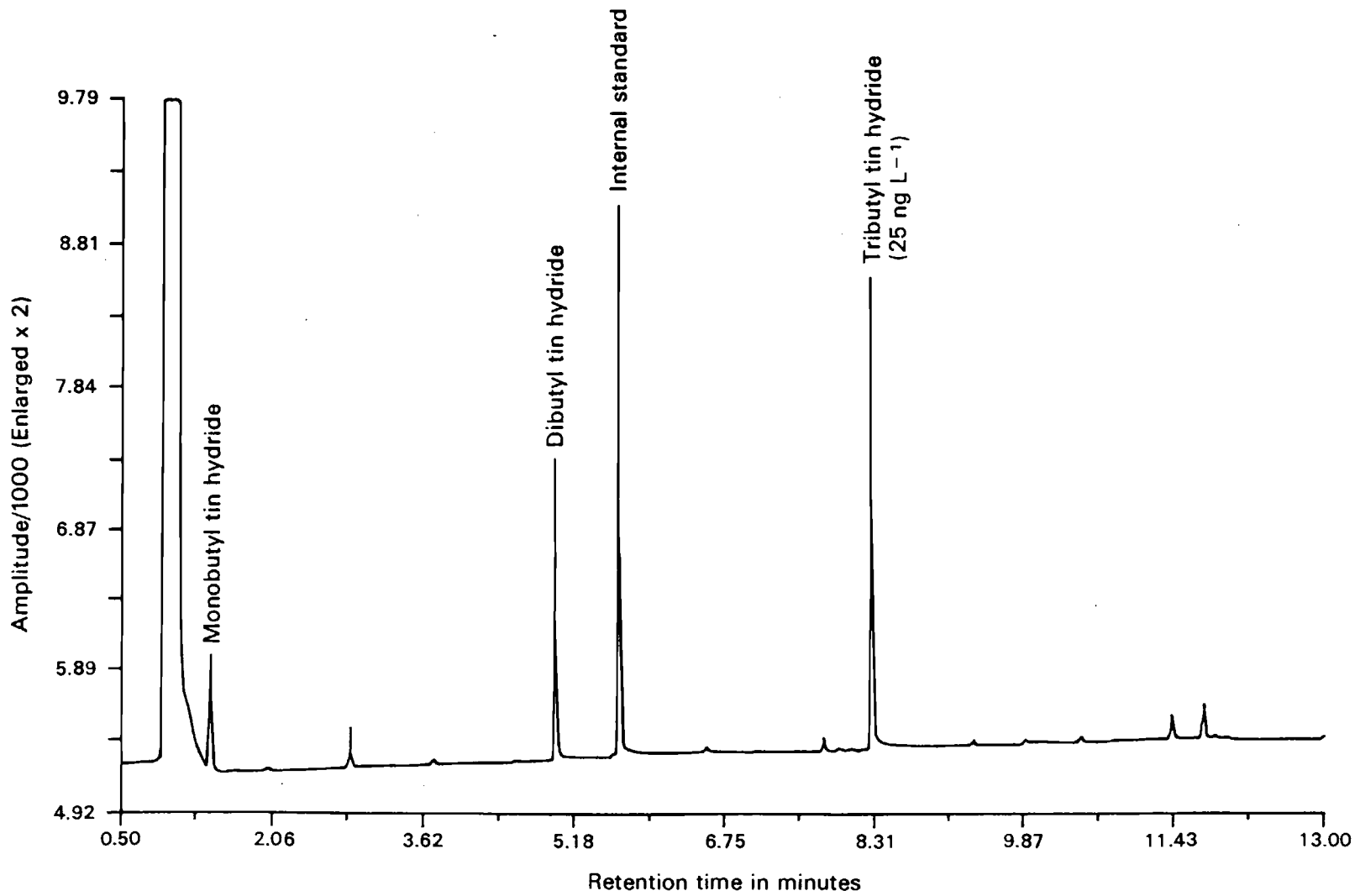


Figure 4a Mass spectrum of tributyl tin hydride

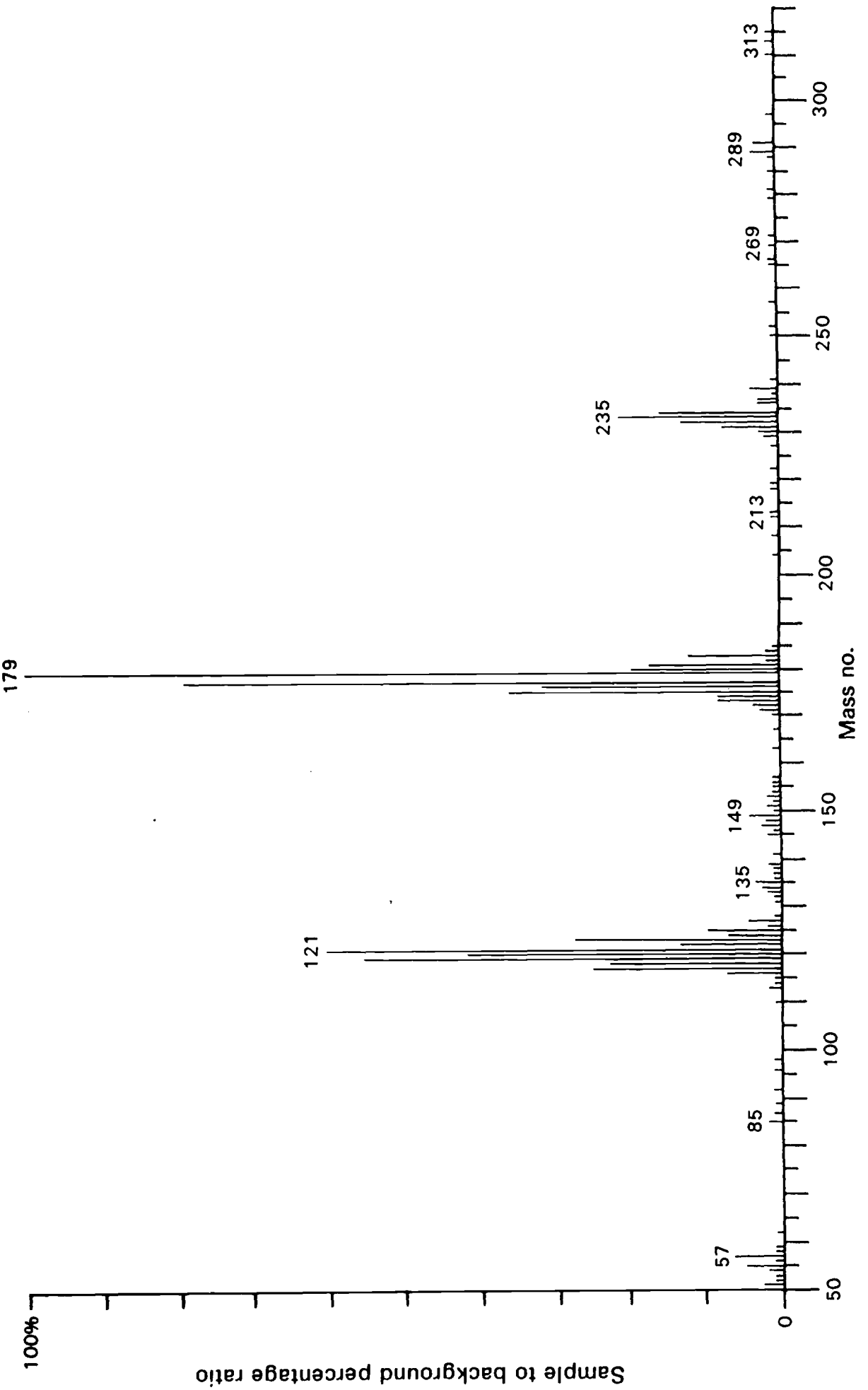


Figure 4b Mass spectrum of dibutyl tin hydride

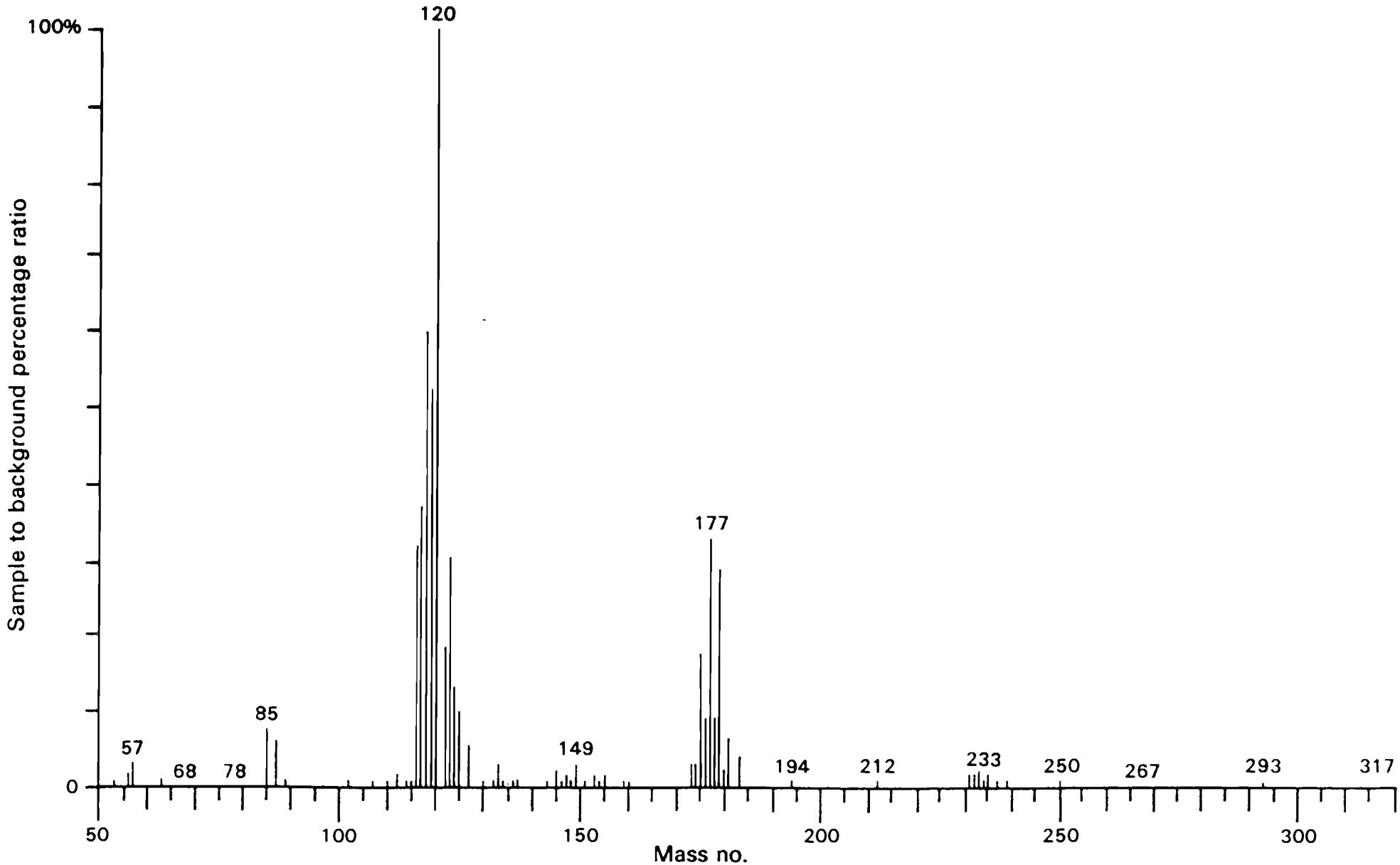
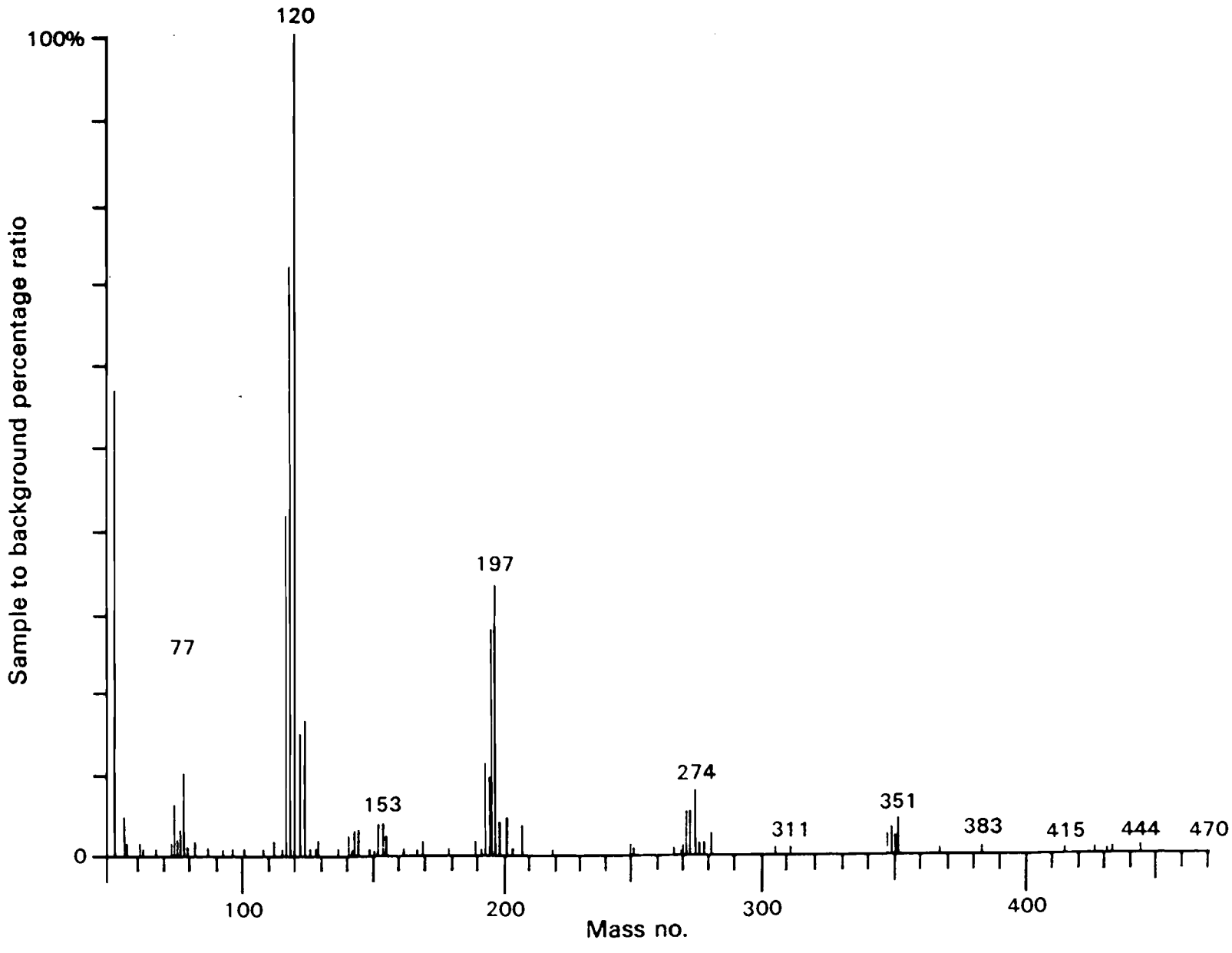


Figure 4c Mass spectrum of triphenyl tin hydride



D Speciation of Tin using coupled High-Performance Liquid Chromatography—Atomic Spectroscopy

Tin species may be separated by high performance liquid chromatography using a silica base cation-exchange column and then introduced directly into an air-hydrogen flame of a flame atomic absorption spectrometer (1), or an inductively coupled plasma-mass spectrometer (2) for detection. In both cases conventional instrumentation is used operating on-line and in real time. The interface between the two instruments consists of a short length of silicon rubber tubing between the end of the HPLC column and the nebuliser. When used with FAAS a small hole is made in the tubing to facilitate discrete volume nebulisation, ie allowing the nebuliser to draw air between aliquots of sample to balance the flow from the column with that of the natural uptake of the nebuliser. No other modifications are necessary although the addition of a slotted tube atom trap will improve detection limits in FAAS and in the case of ICP-MS a reduced argon flow plasma torch may be used.

In both of the above techniques organotin compounds are quantitatively extracted into chloroform and pre-concentrated prior to analysis. To facilitate injection onto the HPLC column, the chloroform is evaporated and the sample redissolved in methanol. Detection limits of 200 ng and 1.6 ng as tin are achieved using HPLC-FAAS and HPLC-ICP-MS respectively.

Instrumental operating conditions

HPLC system—		
Mobile phase	80 + 20 methanol-water, 0.1 M with respect to ammonium acetate	
Stationary phase	Partisil 10 μm SCX packed into a 25 × 0.4 cm column	
Flow-rate	1.5 mL min^{-1}	
Injection volume	175 μL (ICP-MS) or 1.5 mL (FAAS)	
ICP-MS—	Standard torch	Low flow torch
Forward power	1.8 kW	1.0 kW
Reflected power	40 W	10 W
Nebuliser flow	0.8 $Lmin^{-1}$	0.65 $Lmin^{-1}$
Coolant gas flow	15 $Lmin^{-1}$	9 $Lmin^{-1}$
Intermediate gas flow	0.9 $Lmin^{-1}$	0.9 $Lmin^{-1}$
Cool bath	−10°C	−10°C
Data acquisition mode	Survey scan	Local mass set to 120.2 μ
FAAS—		
Wavelength	286.3 nm	
Lamp current	6 mA	
Band Pass	1 nm	
Hydrogen	2.6 $Lmin^{-1}$	
Air	4.0 $Lmin^{-1}$	

E Determination of organotin using voltammetry

Total dissolved tin and inorganic (reactive) tin can be determined in natural waters using cathodic stripping voltammetry (van den Berg et al., 1989(8). In this technique the reduction current of the tropolone complex with tin is measured after adsorptive collection of the complex on a hanging mercury drop electrode. Reactive tin is measured at pH2 and represents dissolved inorganic tin. Total dissolved tin is determined after UV-irradiation of the sample to destroy organic compounds; organotin is fully converted to inorganic tin by this procedure. The method is very sensitive with a limit of detection of 6 ng L^{-1} (total tin) and only a small sample volume (20 mL) is required.

Dissolved organic surface active material interferes in samples from estuarine origin with the determination of reactive tin. The inorganic tin concentration can therefore often not be determined specifically in the un-irradiated sample. For this reason it is recommended to pass the sample through a Sep-pak C-18 column which specifically adsorbs organotin whilst allowing inorganic dissolved tin to pass through (van den Berg and Khan, unpublished data)(9). Total dissolved tin is then determined in the usual manner after UV-irradiation of the sample to remove remaining interfering organics. The dissolved organotin concentration is calculated by difference of the total dissolved tin concentrations in the sample before and after the Sep-pak treatment. The inorganic tin concentration in natural waters is normally very low (<10 ng L^{-1}) so its contribution to the total dissolved tin concentration is small in the presence of organotin pollution. The sample volume required for this determination is approximately 40 mL and the limit of detection for organotin is 10 ng L^{-1}. The sample throughput is approximately 10 samples day^{-1}.

F Note on the Determination of Total Tin in Waters and Sediments by Atomic Absorption or ICP Spectrometry

F1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results 1980, also published in this series).

F1.1	Substances determined	All forms of tin likely to occur in raw and potable waters and in sediments, especially inorganic forms.
F1.2	Types of sample	Raw and potable waters, sediments.
F1.3	Basis of the method	Separation by solubility and other means, bringing of insoluble matter into solution by acid, or by ammonium iodide fusion followed by determination using atomic absorption or ICP techniques.
F1.4	Range of application	Up to at least 80% Sn (Cassiterite is c78% Sn).
F1.5	Standard deviation	Dependent on equipment used, range and wavelength, but generally less than 10% relative standard deviation except close to the limit of detection.
F1.6	Limit of detection	Dependent on sample and equipment but typically below 2 mgL^{-1} for water and 0.05% for solids.
F1.7	Bias	None known.
F1.8	Interferences	None known.
F1.9	Time required for analysis	The total analytical time for 20 pre-treated samples is approximately 2 hours. The corresponding operator time is approximately 45 minutes, assuming automatic data calculation. The pretreatment time varies depending on the nature of the sample.

F2 Principle

The sample is, if necessary, separated into soluble (passing through a 0.45 μm filter) and insoluble forms. Insoluble material is treated either with dilute acid to dissolve absorbed tin, or fused with ammonium iodide prior to similar extraction. The final determination is either by a form of AAS or ICP Spectrometry.

F3 Interferences

Whether tin will be extracted by acid or not depends on the form in which it is present. Solubilization by the ammonium iodide procedure is virtually complete. Iron, copper, magnesium, manganese, antimony, zinc, aluminium, bismuth, lead, nickel, arsenic, cobalt, cadmium, chromium, vanadium, lithium, sodium, potassium, barium and calcium have all been shown to be without effect on the AA or ICP stages, provided the correct procedures are used.

F4 Hazards

The usual precautions for acid digestions, vacuum filtration and tube fusions, including use of shields, containment and fume hoods are essential. Similarly, all precautions necessary for AAS (especially using nitrous oxide—acetylene, or electrothermal sources) and ICPS are obligatory.

F5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section F6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

F5.1 Water The water used for blank determinations and for preparing reagent and standard solutions should have a tin content that is negligible compared with the smallest concentrations to be determined in the sample. Deionized water or water distilled from an all glass apparatus is suitable. Beware of tin lined stills and tanks and tin containing glassware. See also Section A5.5.

F5.2 Hydrochloric acid approx 2M Take 200 ± 5 mL of hydrochloric acid (d_{20} 1.16) and dilute with water to 1L (± 10 mL) in a measuring cylinder. Mix well. Store in a polyethylene bottle.

F5.3 Ammonium iodide (finely ground)

F5.4 Stock standard tin solution (1 mL contains 1 mg tin). Weigh out 1.00 ± 0.005 g of pure tin. Cover with water and dissolve in the minimum of cold hydrochloric acid to ensure a final pH of less than 1. Transfer quantitatively to a 1L calibrated flask and make up to volume with water. Mix well.

F5.4.1 Working standard solutions. Prepare a series of suitable dilutions in water, maintaining a pH of just less than 1. Do not use nitric or sulphuric acids. (See Section F9.2 and F9.4.1).

F6 Apparatus

F6.1 An 0.45 μm filter and filtration apparatus. A number of typical filters should be pretested with blank water and with standards; the filters and the blanks are then analysed, to ensure that the filters neither absorb nor leach out tin.

F6.2 Pyrex or other hard glass tubes 18 × 180 mm.

F6.3 Glass weighing bottle or scoop.

F6.4 Tube heater for 18 × 180 mm tubes inclined at c15° to the horizontal.

F6.5 Test tube tongs.

F6.6 Wooden cooling rack (tin free).

F6.7 Thermostatically controlled water bath (capable of 85 ± 2°C).

F6.8 3 cm glass rod (6 mm diameter).

F6.9 Cotton wool (tin free)

F6.10 Optical microscope (mineralogical attachments are useful).

F6.11 Flotation apparatus, scoop or spoon.

F6.12 Filters with a range of filter paper.

F6.13 Standard laboratory glassware.

F7 Sampling and Sample Preservation

All equipment must be pretested and shown to be tin free. Plastic should not be used. Store samples in tin free glass bottles with glass or PTFE stoppers. Store solids in similar wide mouthed jars. If aqueous samples are to be filtered, do so as quickly as possible after sampling, then stabilize, whether filtered or not, by acidification to a pH of < 2.5 with hydrochloric acid.

F8 Pretreatment

The pretreatment required varies widely with the nature of the sample and the information required. Aqueous samples may contain both organic and inorganic tin. Most organic tin is solvent extractable (see the earlier procedures), but monoalkyl and monoaryl tin salts remain with the inorganic soluble salts. Suspended matter and sediments may contain both soluble inorganic and organic tin compounds absorbed onto organic matter or mineral particles such as clays, or consist of tin minerals such as cassiterite. (This latter is of common occurrence in parts of Britain and is an unusually heavy mineral).

If extractable organotin is not required in this total value, use the aqueous or solid residues from the preceding determinations.

F8.1 Clean water samples

Optically bright samples need only acidification. If samples are warmed, analysts should avoid nitric and sulphuric acids as they may cause oxidation to the four valent state and promote hydrolysis; hydrochloric acid is sometimes avoided as it increases tin volatility; see, however, the section on determination. Record the volumes of sample and acid used. Proceed to Section F9.

F8.2 Turbid water samples

Filter a known volume of sample through a 0.45 μm filter (see Section F6.1 for pretesting). Treat the filtrate as in Section F8.1 above. If the suspended solid is to be analysed treat as in Section F8.3 onwards below.

F8.3 Solid samples

If desired, it is possible to subdivide the solids into cassiterite-free and cassiterite-rich material. Cassiterite is naturally occurring stannic oxide d_{20} 6.99. It is usually dark brown in colour, but is creamy white if pure. Tin pyrite (stannite) also occurs in Britain (d_{20} 4.4) and can be separated with cassiterite. A preliminary examination of a small typical sample under a microscope may be helpful when making this decision. If a separation is to be made, see Section F8.4, if not, see Sections F8.5 and F8.6 for mild and severe leaching procedures respectively.

F8.4 Separation of solid material by density

Hazard—the flotation liquids are toxic and have unpleasant smells. The whole procedure must be carried out in a good fume hood and in a container tray large enough to contain any spillage and all the vessels used. Avoid skin contact. Use of gloves is not recommended.

F8.4.1 Air dry the samples at not more than 5–10°C above ambient. If necessary grind to pass a 100 mesh British Standard sieve.

F8.4.2 Pour about 50 mL of either bromoform (d_{20} 2.9) or diiodomethane (d_{20} 3.3) into a 100 mL beaker. Pour some of the sample onto the liquid in the beaker and agitate. Organic matter and most minerals especially clays will float. The tin minerals will sink. Decant off the floating material into a separate beaker without entraining the settled material on the bottom. Continue the separation, adding more flotation liquid as required. Finally, recover the separated solid fractions by filtration. Recovered flotation liquid may be kept for reuse. Allow the solids to dry. Carry out steps F8.5 or F8.6 on the lighter fraction and, if needed, step F8.6 on the heavier fraction. Weigh each fraction and record the weights prior to digestion.

F8.5 Mild digestion procedure

Do not use nitric, sulphuric or perchloric acids for this procedure (see Section F8.1 above, hot perchloric acid can explode with organic matter). Transfer either the filter from Section F8.2 or the appropriate separated fraction from Step 8.4.2 to a 200 mL beaker, add 100 mL of hydrochloric acid (F5.2) and simmer gently, preferably using a watch glass containing some water to minimize evaporation losses, in a fume hood for 2–3 hours (or as long as experience with this type of sample shows is necessary for virtually complete extraction). Cool and filter through an appropriate pore size glass filter paper (prewashed with hydrochloric acid). Wash with hydrochloric acid (3×10 mL is suggested, but the amount used should be proportional to the amount of solid being washed). Transfer quantitatively to a suitable volumetric flask and make up to volume with distilled water. Proceed to Section F9.

F8.6 Full digestion procedure

F8.6.1 Dependent on the expected tin content, weigh out exactly, an appropriate weight of dried solid.

Approx % Sn	Approximate weight of sample weighed out mg
0.2	500
2	100
6	150
60	5

F8.6.2 Weigh out 0.50 ± 0.02 g of finely ground ammonium iodide, into a hard glass test tube (F6.2). Add the portion of sample and shake gently to mix thoroughly.

F8.6.3 During the above, bring the tube furnace to 450–500°C. Then insert the loaded tube. Note the time. After 1 minute, rotate to mix. After a total of 10 minutes, remove the tube from the furnace using the test tube tongs. When cool enough to place in the wooden rack without damage to the rack, leave in the rack to complete cooling.

F8.6.4 When cold, add 10.00 ± 0.05 mL of approx 2M hydrochloric acid and shake gently. Simmer in a water bath set at 85°C for 30 ± 1 minute. Agitate 3 or 4 times during the digestion. Then return the tube to the wooden rack and allow to cool to room temperature.

F8.6.5(a) Put a small plug of cotton wool (F6.9) in the mouth of the test tube and, using the glass rod, push the plug down the tube into the solution at the bottom, removing any crystals adhering to the walls. Push the plug right to the bottom of the tube, leaving a clear dark brown liquid above it. Proceed to Section F9.

F8.6.5(b) Alternatively filter through a small filter paper.

F9 Determination of Tin

F9.1 Blanks

Prepare blank samples exactly as samples using the same acids, ammonium iodide etc. For the initial stage of the fusion (F8.6) use an empty tube.

F9.2 Calibration standards

Prepare these from the standard tin solutions (F5.4.1). They must contain the same concentrations of the same acids and, if appropriate, of ammonium iodide as the samples. (Note: this is essential as the tin response in Sections F9.4(i) or (ii) is enhanced by iodine and ammonium iodide).

F9.3 Control standards

These should be carried through the various procedures being checked.

F9.3.1 Aqueous samples

Prepare, as for calibration standards, one high and one low concentration standard for the expected range.

F9.3.2 Solid samples ('Light' material)

Take an appropriate amount of material similar to the sample matrix (such as peat or kaolin) and analyse as above. Then spike a similar portion with a known amount of standard sample solution, dry and analyse. Use spike recovery as the control.

F9.3.3 Solid samples ('Heavy' material)

Weigh out 5.00 ± 0.05 mg of Stannic Oxide analytical reagent grade (SnO_2). The theoretical result is 78.76%Sn.

F9.4 Determine the tin content of the appropriate liquid by:
(See Note below)

(i) Electrothermal Atomic Absorption Spectrophotometry (see F9.4.1 below), or

(ii) Nitrous Oxide—Acetylene Flame Atomic Absorption Spectrophotometry at 235.5 nm, or

(iii) Inductively Coupled Plasma Emission Spectrophotometry (see the booklet in this series[10]) or

(iv) Inductively Coupled Plasma Mass Spectrometry (see the booklet in this series[10]).

Note: Samples and standards sometimes tend to contain crystals of free elemental iodine. If this happens they must be filtered immediately prior to being analysed by any of the four above techniques.

F9.4.1 EAAS conditions

Follow manufacturer's instructions. The following are courtesy of Varian Ltd.

Concentration range	0.1–5 $\mu g\ mL^{-1}$
Concentration sensitivity	0.6 $ng\ mL^{-1}$
Sample size	5 μL
Lamp current	5 mA
Wavelength	224.6 nm or 286.3 nm
Spectral Band Width	0.2 nm

Background correction is not necessary

Sheath Gas	Nitrogen
Hydrogen Flow	3L min^{-1}

Dry and Ash Settings	Temp(°C)	Time (sec)
Dry	100	50
Ash	600	20

Atomizer Settings			
Element	Temp(°C)	Hold	Ramp
Sn	2,300	2	500

Use the method of standard additions with standard additions of 1.0, 2.5 and 5.0 $\mu g\ mL^{-1}$ Sn.

Customary safety precautions appropriate to the method must be observed.

F10 Calculation

From the tin content of the final solution calculate back to the tin content in the appropriate portion of the initial sample.

References

1. Method AA27. (M and T Chemicals Inc.)

2. Hattori I.et al. *J.Chromatog* **315**. 341–9 1984

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Address for Correspondence

However well a method is tested there is always the possibility of a user encountering a hitherto unreported problem.

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This booklet was produced by the Working Groups for Metallic and Organic Impurities in cooperation. Initially the Pesticides Panel of the Organic Impurities Working Group drafted methods A, B and C aided by the Metals Working Group. Method F arose entirely from a small panel of the Metals Working Group. The final editing of methods A, B and C and all work on methods D and E was done by the recently formed Organometallics Panel of the Organic Impurities Working Group.

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