Applied Organometallic Chemistry (1988) 2 33–46

0268–2605/88/02010033/$03.50

The analysis of inorganic and organometallic antimony, arsenic and tin compounds using an on-column hydride generation method

S Clark and P J Craig*
School of Chemistry, Leicester Polytechnic, PO Box 143, Leicester LE1 9BH, UK

Received 1 October 1987 Accepted 11 December 1987

A novel method of analysis of inorganic and organometallic compounds is reported. Essentially this utilizes the well-documented hydride generation technique, but in the present method the hydrides are generated from their involatile precursors (e.g. chlorides) on a GC column and separated from each other and from extraneous materials on the same GC column in a single process. Using the method, a solution of butyltin chlorides can be directly injected into a GC AA system to yield the volatile hydrides for separation, detection and quantification.

To date, species analysed by this method include inorganic As(III), Me_2AsOOH, inorganic Sb(III) and Sb(V), $MeSnCl_3$, Me_2SnCl_2, Me_3SnCl, Et_2SnCl_2, Et_3SnCl, $BuSnCl_3$, Bu_2SnCl_2, Bu_3SnCl and Pr_3SnCl.

With the use of the internal standard Pr_3SnCl and with the almost complete hydridization afforded by the technique, the procedure is shown to eliminate errors and to reduce the time involved in the analysis. The use of on-column derivatization also allows for the possibility that, in some cases, organotin hydrides reported to be found in the natural environment may, in fact, be organotin chlorides being reported as hydrides owing to inadvertent hydride production on the column. Some reports of successful gas chromatography for organotin halides could also conceivably be due to on-column hydride generation.

Keywords: Environmental analysis, hydride generation, organotin, organoarsenic, antimony

INTRODUCTION

The role of natural or anthropogenic inorganic and organometallic compounds in the natural environment is receiving increasing attention at the present time.[1]

Arsenic and antimony are both known to exist in several forms in the natural environment. Arsenic is sometimes found at the $\mu g\,dm^{-3}$ level in open ocean waters[2] and has been found at higher levels in marine biota. Marine biota accumulate this element and concentrations of 10–50 $mg\,kg^{-1}$ occur.[3] Methylarsenic species have been measured at the $ng\,dm^{-3}$ level in seawater and at the $mg\,kg^{-1}$ level in seaweeds, marine biota and sediment.[4] Leachates from lead smelters and effluents from mining and manufacturing have been shown to contain up to $mg\,dm^{-3}$ levels of antimony.[5] Methylantimony species have been reported at the $ng\,dm^{-3}$ level in some natural waters.[5,6] The presence of organotin compounds, which are widely used, for example, as stabilizers, biocides, bactericides and anti-fouling agents in paints and other formulations, is of interest as knowledge of their dispersal and fate in the environment increases. Two recent publications have been devoted to the environmental effects of organotin compounds.[7,8] In the natural environment there is a particular interest in butyltins.

One problem associated with the use of butyltin compounds in antifouling compositions lies in the inherently dispersive nature of their actions. These materials will prevent fouling of vessels and nets only if they dissipate from the surface so as to interact with the target organism. Much work has been dedicated to controlling the rate and method of dispersion of the butyltin into the water so as to achieve maximum effect with the lowest concentrations of organotin compound. The chief environmental concern over the use of tributyltin species (Bu_3Sn^+) in marine paints or preservatives (e.g. for fishing nets) lies in the effects on non-target organisms. For example, there is a correlation between low-level (i.e. in the $ng\,dm^{-3}$ region) concentrations of butyltins to the growth and development of oysters, fish and

*Author to whom correspondence should be addressed.

molluscs[9] and several countries have now placed restrictions on the formulation or use of tributyltin-containing paints.[10]

The chief problems for a proper assessment of the impact of Bu_3Sn^+ species in the aqueous environment are concerned with:

(a) the quantification of Bu_3Sn^+ and, following this,
(b) the environmental behaviour of this moiety.

Although several techniques now exist (see below) for the analysis of butyltins at low levels in aqueous media, analysis in sediments has been less studied. It should be realized that in the case of methylmercury compounds (CH_3Hg^+), over 90% of methylmercury species in aquatic systems are found in the bottom sediment.[11] Sediment may act as a reservoir, controlling availability to the water column and/or marine biota. Indeed, knowledge of concentrations in this matrix may be as significant as knowledge of concentrations in fresh or sea-water. For CH_3Hg^+ several analytical routes have been well established[12] but for Bu_3Sn^+ the techniques reported for analysis even in aqueous media tend to be inconvenient and time-consuming.[13]

The main properties of butyltins that allow their use as biocides also inhibit their easy detection and quantification in the environment, namely:

(a) effectiveness at low aqueous concentrations (ng dm^{-3} region),
(b) low volatility (Table 1), and
(c) a high affinity for soil or organic matter by Bu_3Sn^+.

Methods of analysis of these compounds have been reviewed elsewhere.[13] Essentially they consist of an extraction step, purification and further extraction by some form of derivatization, concentration and separation prior to detection. One of the most used derivatization techniques is hydride generation in which the chemically unknown counter-ion (or ligand) 'X' in Bu_3SnX is replaced by hydrogen, producing the more volatile hydride, Bu_3SnH. Hydride generation of organotin compounds has been a widely accepted method of analysis.[14] This method does not appear to have been reported for methylmercury or methyllead species, but is well known for arsenic, antimony, germanium etc.

Other derivatization techniques used have included generation of Bu_3SnR (R = Me—, Et—, Pr—, Hex—; or Bu— for methyltins) in a non-aqueous medium by Grignard techniques, usually following extraction with a hexane–tropolone mixture. Following derivatization, the organotin compound may be detected directly or pre-concentrated (usually by cryogenic trapping) prior to the detection step.[14] Pre-concentration is an additional and time-consuming step in the analysis, but it is often essential where low concentrations of the analyte exist (e.g. ng dm^{-3}). We found that pre-concentration by cryogenic trapping after hydride generation was made difficult by the low volatility of Bu_3SnH. Although trapping on a GC column packing was easily accomplished, quantitative and reliable revolatilization to a detection system proved difficult. Accordingly our thoughts turned towards an extraction method allowing concentration and direct injection of a liquid phase to the detector.

Numerous detection techniques have been investigated,[14] i.e. ECD (electron capture detection), FPD (flame photometric detection), FID (flame ionization detection), MS and AA, some non-tin-specific, some tin-specific and one tin-species-specific (i.e. MS). Non-specific techniques (EC, FID) require extra care in procedure to remove co-eluting materials; some allegedly tin-specific techniques (e.g. FPD) may suffer interference from other environmentally existing species (e.g. sulphur compounds). MS is highly desirable as a confirmatory method but the most convenient technique is probably AA coupled to GC. Many GC AA couplings are available, including graphite and quartz furnaces which may be either flame or electrothermally heated. The combination of GC with AA provides a sensitive element- and near species-

Table 1 Volatility comparisons for butyltin species

Compound	Boiling point (°C)	
	Measured value	Estimated equivalent (760 mm Hg)[a]
Bu_3SnCl	146 (5.0 mm Hg)	305
Bu_2SnCl_2	155 (5.0 mm Hg)	310
$BuSnCl_3$	93 (10.0 mm Hg)	220
Bu_3SnH	79 (0.7 mm Hg)	280
Bu_2SnH_2	57 (5.0 mm Hg)	250
$BuSnH_3$	100 (760 mm Hg)	100

[a]Using pressure–temperature nomograph, BDH, UK catalogue 1986.

specific system for the analysis of organometallic compounds. Such systems have the separation capability of GC coupled with the specificity of AA.

We now report a novel method for analysis and quantification of inorganic and organometallic species, in particular the analysis of tributyltin-containing solutions.[15] Essentially it consists of **on-column** hydridization of extracted organotin **chlorides** to form their volatile hydrides, which are then separated and detected in a single procedure, on the same column and in a single step.

The method was first investigated when it was noticed that tributyltin **chloride** solutions were themselves giving substantial tributyltin **hydride** peaks in a coupled GC AA system. We surmized that the GC column had become contaminated by successive injections of analyte solutions containing residual amounts of sodium borohydride ($NaBH_4$) being used in conventional hydride generation analysis. To test this hypothesis, a dilute aqueous solution of tin(II) chloride ($SnCl_2.5H_2O$) was prepared and injected directly into the column: a peak at 0.6 min appeared, corresponding to that known to occur for stannane, SnH_4, under these conditions. A portion of this solution was then hydridized in a capped sealed vial and a sample of the headspace analysed. It too gave the stannane peak at 0.6 min. Final proof was given when acidic solutions of $SnCl_2$, Me_3SnCl, Me_2SnCl_2 and $MeSnCl_3$ were injected into a $NaBH_4$-doped GC column linked to a mass spectrometer. Mass spectra of the respective methyltin hydrides emanating from the column were obtained.

Until now, the hydride generation technique has always been performed in solution and the resulting hydride either driven out of solution by a stream of inert gas (purging) and cryogenically trapped before analysis,[14] or extracted into a non-aqueous solution and concentrated by evaporation and then hydridized before buffering and analysis.[14] Hydride generation and extraction have been performed simultaneously.[16] However, both these methods can lead to loss of the hydride and both involve time-consuming steps. The trapping method, in particular, has several limitations, the most troublesome being the revolatilization of the butyl hydrides, both in the reaction vessel and in the cryogenic trap. Condensation of the analyte in transfer lines is also a major problem.

The present *in situ* method of analysis eliminates several of these problems and is potentially a more practical, quicker and yet accurate method of analysis. The method of analysis described below (Experimental) consists of the extraction of an aqueous solution of tributyltin chloride with dichloromethane (CH_2Cl_2), concentration by evaporation, the addition of an internal standard followed by partial evaporation and then the direct injection of an aliquot into a $NaBH_4$-doped GC column. The hydride is formed in the heated injector and travels through the column for separation and detection.

Analyses of arsenic and antimony compounds have also been performed by this method in order to assess the potential applicability of this technique to other hydride-forming elements.

EXPERIMENTAL

Reagents

Water used in all experiments was distilled and gave blank readings in all analyses. All glassware for preparation, storage, etc., was washed with a detergent solution (Tepol L), then with aqua regia, and soaked in 10% nitric acid solution for at least 24 h before rinsing thoroughly with tap-water and then distilled water. Sodium borohydride ($NaBH_4$) pellets were used as obtained from the supplier (BDH, Poole, UK) in the preparation of the reducing agent by dissolving in distilled water. The solution was prepared fresh as needed. Alkyltin compounds and dimethylarsenic acid (cacodylic acid; Me_2AsOOH) were used as supplied (Aldrich Chemical Co. Ltd, Gillingham, UK). All solvents were of spectroscopic grade (BDH, Poole, UK). Bottled gases were used, the nitrogen being oxygen-free (white spot). Standard sea-water was supplied by IAPSO, Standard Seawater Service, Institute of Oceanographic Sciences, Surrey, UK.

Standards

Standard solutions of both Bu_3SnCl and Pr_3SnCl were prepared separately by dissolving in CH_2Cl_2 followed by subsequent dilution and mixing to give solutions in the working ranges 0.65–6.50 $\mu g\,cm^{-3}$ (ppm) Bu_3SnCl with 1.92 $\mu g\,cm^{-3}$ Pr_3SnCl as internal standard for

high-level calibration and 47–470 ng cm^{-3} (ppb) Bu_3SnCl with 32 ng cm^{-3} Pr_3SnCl as internal standard for lower-level calibration work.

Internal standard

Pr_3SnCl is used as an internal standard in the quantification of Bu_3SnCl as it is a close analogue of Bu_3SnCl and has similar properties. Its use in the analysis is necessary for the following reasons.

(a) Any evaporation of solvent between successive injections, leading to increased concentration of analyte, is compensated for to some extent as the concentration of internal standard should increase in proportion, thus yielding a constant Bu_3SnH/Pr_3SnH peak height ratio for a given initial Bu_3SnCl concentration.
(b) Any day-to-day variations in instrument sensitivity are catered for as these would affect both organotin species similarly, again giving a constant peak height ratio.
(c) Any variation in the efficiency of the hydride generation process is catered for as the variation is likely to affect both species to the same extent.
(d) When hydridization is performed ex-column, e.g. for comparison purposes, accurate measurement of injection volume is difficult due to bubbles of hydrogen in the syringe. The internal standard again allows for this as the actual volume injected is irrelevant to the Bu_3SnH/Pr_3SnH peak height ratio.

Apparatus

The GC AA quartz furnace apparatus used throughout the analysis is shown in Fig. 1. It consists of a gas chromatograph (GC) interfaced to an atomic absorption spectrophotometer (AA), details and operating parameters of which are given below and in Table 2.

Gas chromatograph

A Pye–Unicam 104 instrument fitted with a 2 m × 4 mm i.d. column packed with 10% OV 101 on Chromasorb W-HP (80–100 mesh) was used for the analysis of organotin compounds. Nitrogen carrier gas was monitored via a flowmeter and controlled by a needle valve. Oven and injector temperatures for Bu_3SnCl analysis were 180°C and 230°C respectively.

Atomic absorption spectrophotometer

A Varian AA instrument (Model 1000) used throughout this work was fitted with hollow cathode lamps (Juniper and Co. Ltd, UK).

The 10 mV output from the AA was connected to a chart recorder (Kipp and Zonan BD8, operated at 1 cm s^{-1}) such that 0.1 A units gave full scale deflection, i.e. recorder set at 1 mV (amplified 10-fold), and the AA operated on the highest possible damping—damp 'C'.

Gas chromatograph–mass spectrometer system

A magnetic deflection VG Micromass 16-F instrument, coupled to a Pye–Unicam 204 GC-D system, was used for speciation work.

Transfer line interface

The GC was interfaced to the AA via a heated stainless-steel transfer line. Teflon was tried initially but problems were encountered in maintaining gas-tight seals. The stainless-steel transfer line (0.75 m, 0.14 cm o.d., 0.07 cm i.d.; Phase Separations Ltd, UK) was electrically insulated from the coiled heating wire by a Teflon sleeve (0.28 cm o.d., 0.14 cm i.d.). The nichrome wire (7.4 m, 28 SWG) was held in position with PTFE tape and Teflon tubing (6 mm o.d., 4 mm i.d.). A wrapping of asbestos cord (Jencons Scientific Ltd, UK) served as thermal insulation. This was then covered with a layer of PTFE tape. Oven and transfer line temperatures were controlled to ensure volatility of the analyte without decomposition, by incorporation of a stainless-steel type 'K' thermocouple (Pyrotenax Ltd, UK) in the line, and this was also electrically insulated from the heating wire by PTFE tape. The transfer line was terminated with a Swagelock reducing union ($\frac{1}{16}$ in–$\frac{1}{4}$ in) fitted with a brass ferrule, and a self-sealing Teflon ferrule connection to the quartz furnace. Power to the transfer line was supplied by an independent variable transformer (22 V; 166°C).

Quartz furnace

The original quartz atomization cell (12 mm o.d., 10 mm i.d.) was supplied by the University of Essex, UK (Fig. 2). It was wrapped with nichrome wire (3.1 m, 28 SWG) and insulated using ceramic insulating beads (type MB1, Electrothermal Elements Ltd, Hinckley, UK). These served as electrical insulation preventing short circuiting which would otherwise have led

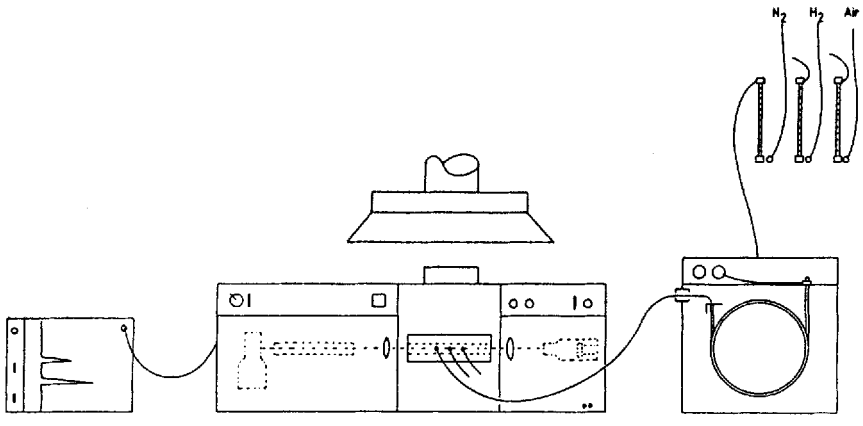

Figure 1 Interfaced GC AA apparatus.

to 'cold spots' and also as a method for spacing the windings evenly, leading to easier cell wrapping and uniform heating throughout the length of the cell. This was surrounded by a layer of asbestos cord and the whole arrangement held in a drilled firebrick (Fig. 3).

The furnace was held in position in the light beam of the AA by a specially designed cell holder, arranged to fit in place of the existing burner head and hence utilize the cell adjustment mechanism on the instrument, allowing for precise alignment of the atomization cell in the light beam. Power was supplied to the furnace by an independent variable transformer (65 V; *ca* 950°C).

Gases

The nitrogen flowed through the GC column and entered the furnace via the heated transfer line, bringing the analyte with it. Both hydrogen and air were needed for atomization of the organotin compounds and were conveyed to the furnace by Teflon lines (Pressure-Flex, Birmingham, UK) fitted with Swagelock reducing unions (Phase Separations Ltd, UK) at all glass–tube interfaces. The Swagelock unions were fitted with Teflon self-sealing ferrules. The hydrogen cylinder was fitted with a flash-back arrester safety device (Saffire, Waltham Cross, UK). The flow-rates of all gases are given in Table 2; they were controlled with precise needle valves (Phase Separations Ltd, UK) and monitored with float-in-tube type flowmeters (Jencons Scientific Ltd, UK).

Retention times

Retention times given in Table 3 for tin species are for a GC oven temperature of 180°C and a

Table 2 Summary of GC AA operating conditions for the analysis of organometallic compounds

Analyte Species[a]	Gas flow-rates ($cm^3\ min^{-1}$)			Temperatures (°C)				Wavelength (nm)	Slit width (nm)	Lamp current (mA)
	N_2	H_2	Air	Oven	Injector	Furnace	Line			
Arsenic compounds	20	250	25	50	Max.[b]	950	80	197.2	0.5	7.3
Antimony compounds	20	250	25	50	Max.[b]	950	80	217.6	0.2	7.0
Methyltin compounds	45	250	25	50	Max.[b]	950	80	286.6	0.5	5.5
Bu_3Sn^+ alone	60	300	15	180	230	950	180	286.6	0.5	5.5
Mixed butyltins	60	300	15	80–200[c]	Oven + 50	950	180	286.6	0.5	5.5
Et_2SnCl_2	60	300	15	100	Max.[b]	950	180	286.6	0.5	5.5

[a]N.B. All the above species were generated and analysed on either 10% OV 101, 3% OV 101 or 10% SP 2100. [b]Injector set to maximum—approximately 200°C above respective oven temperature. [c]24° min^{-1}.

nitrogen flow-rate of 60 $cm^3 min^{-1}$ on a 10% OV 101/Chromasorb WHP (80–100 mesh) column (2 m × 4 mm i.d.). Typical GC AA traces are shown in Fig. 4.

Column preparation for on-column generation

A column (packed as described above) was prepared and conditioned in the conventional manner (overnight flow of N_2, followed by temperature programming from 30 to 250°C at 4°C min^{-1}) before modification. Three methods of doping the column with $NaBH_4$ have been successful, the first of which is preferred due to its simplicity.

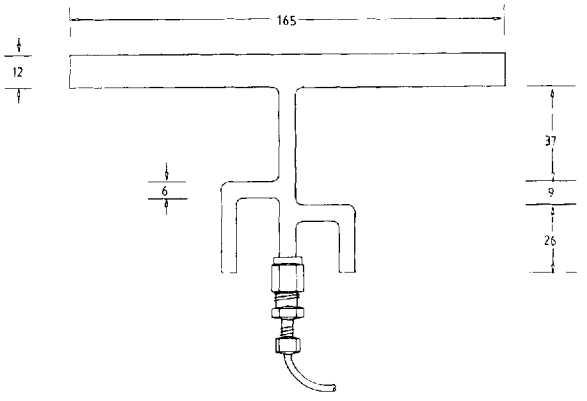

Figure 2 Quartz atomization cell (dimensions in millimetres).

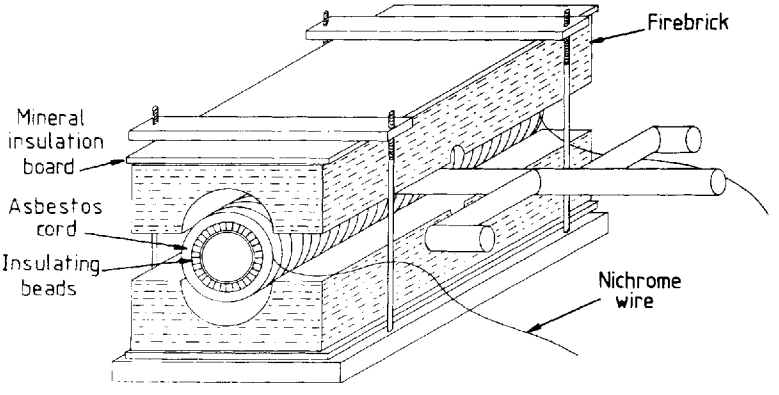

Figure 3 Electrically heated atomization cell.

Table 3 Retention times for tin species[a]

Compound	Retention time (min)
SnH_4	0.6
Pr_3SnH	1.1
Pr_4Sn	2.2
Bu_3SnH	2.7
Bu_4Sn	5.8
Bu_2SnH_2	1.0[b]
$BuSnH_3$	3.2[b]

[a]Conditions given in Table 2. [b]Temperature ramp: see Table 2.

(a) A $NaBH_4$ pellet was crushed using a mortar and pestle and this powder used to prepare a 4% aqueous solution. With the GC oven and injector both on 180 and 230°C respectively), 50 μl of this solution was injected in 5 μl aliquots. This was found to coat the top of the column adequately with the reducing agent with no appreciable problems.

(b) $NaBH_4$ was added physically; a small amount (0.2–0.3 mm column length) of crushed powder was added to the top of the column. This was found to be not as practical as (a) and it was also prone to over-doping, with the $NaBH_4$ becoming hard-packed and blocking the column.

(c) The quartz-wool added to the top of the column can be soaked in an aqueous solution of $NaBH_4$ and dried before use.

The presence of the $NaBH_4$ within the area of the heated injector appears to give better generation. Use of a 7 cm needle for injection of both reducing agent and analyte was found to give best results as this facilitates delivery to the hottest part of the injector.

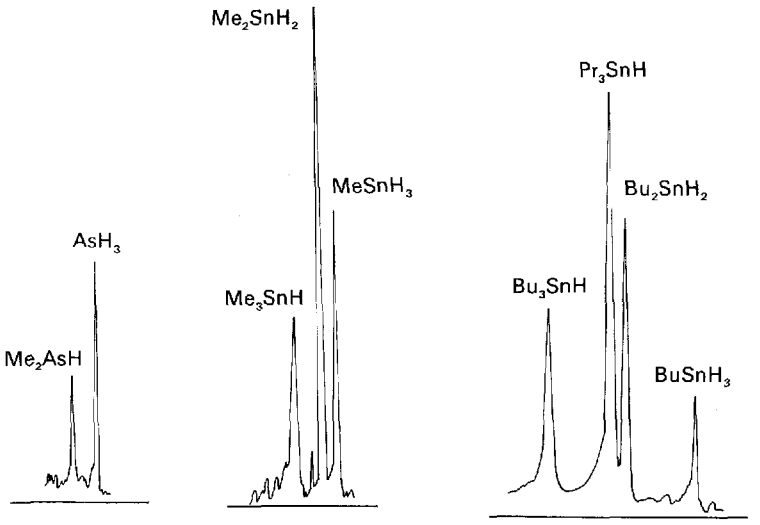

Figure 4 Some typical GC AA traces.

Comparison of on- and ex-column generation

In order to compare the amount of conversion of the chloride to the hydride by the on-column hydridization technique, individual Bu_3SnCl/Pr_3SnCl standards were first analysed by this method and then hydridized by the conventional ex-column method (adding 1 cm^3 of aqueous 4% $NaBH_4$, shaking and injecting a portion of the CH_2Cl_2 extract layer).

A direct comparison of Bu_3SnH production efficiency by both methods is difficult, as equal volumes of analyte cannot be injected due to hydrogen bubbles being present in the syringe, following the ex-column method.

Calibration

Standard solutions of Bu_3SnCl and Pr_3SnCl in CH_2Cl_2 were prepared from stock solutions by decadic dilution and analysed by direct injection into the GC AA system. The solution was analysed by at least triplicate injection of 5 μl aliquots and the ratio of Bu_3SnH to Pr_3SnH peak heights found.

Analysis of synthetic sea-water for Bu_3Sn^+ species only

Synthetic sea-water solutions were doped with a known amount of Bu_3SnCl/ethanol solution (50 cm^3 sea-water to 1 cm^3 ethanol). These were shaken in a separating funnel and allowed to stand for 1 h. Acid (1 cm^3 of conc. HCl—36%) was added followed by 2×2.5 cm^3 portions (individually added) of CH_2Cl_2 and the aqueous solution extracted. The pooled extract was transferred to a 5 cm^3 'V' vial. The solution was then evaporated to near-dryness (50 μl) by a steady stream of N_2. Pr_3SnCl/CH_2Cl_2 solution (1 cm^3), as internal standard, was then added by pipette and the vial capped. The solution was concentrated by evaporation where necessary and analysed by at least triplicate injection of 5 μl aliquots into the GC AA system. The ratio of Bu_3SnH to Pr_3SnH peak heights was found. Taking into account the actual concentration of Pr_3SnCl in the vial, a simple correction was made for the Pr_3SnCl concentration during calibration and thus the concentration of Bu_3SnCl found. Control experiments were performed involving the analysis of the undoped sample matrix. Using 2 dm^3 of the water sample, 5 cm^3 of HCl and 40 cm^3 of CH_2Cl_2, the sensitivity of the method could be increased (see Results).

Separation of mixed butyltin species

Synthetic sea-water (2 dm^3) was doped with mixed butyltin chlorides in ethanol (1 cm^3), shaken in a separating funnel and allowed to stand for 1 h. Acid (5 cm^3 of conc. HCl) was added, followed by two portions (individually added) of 0.05% tropolone/CH_2Cl_2 (35 cm^3 and 5 cm^3) and the aqueous solution extracted and analysed as before.

Loss of analyte during concentration

In order to assess the degree of loss (if any) of Bu_3Sn^+ and/or Pr_3Sn^+ during evaporation of CH_2Cl_2 (an essential concentration step in this analysis), losses were studied. Studies were performed on alkyltin chlorides, hydrides and tropolone complexes. Aliquots (5 μl), from a known volume (2 cm^3 in most cases) of solution containing both Pr_3Sn^+ and Bu_3Sn^+ moieties of interest, were analysed by replicate injection into the GC AA system. This volume was then evaporated with a gentle stream of nitrogen at room temperature to approximately 50 μl. The solution was made up to the initial volume with fresh solvent and re-analysed. This was performed at least twice for each of the derivatives.

Analysis of arsenic and antimony compounds

In order to validate the method further, analyses of various arsenic and antimony compounds were performed. The compound in question was analysed by both conventional headspace techniques and by direct injection of 5 μl aliquots of a solution ($\mu g\,cm^{-3}$ level) into a doped column (see Results and Discussion).

RESULTS AND DISCUSSION

In the present study Bu_3SnCl has been quantitatively analysed from a matrix. All three methyl- and butyl-tin cations have been generated and separated by this method (Tables 2–5) and other inorganic and organometallic compounds have been investigated and shown to undergo derivatization by this technique. Work is under way with the analysis of other organometals and metalloids.

Column life

The lifetime of a column doped with $NaBH_4$ was difficult to assess as we were continually injecting solutions of differing organometallic concentration and make-up. During the course of our work the hydride generation efficiency of the doped column depreciated. A regular (once-weekly) re-doping was found sufficient for our purposes. On occasions the hydridization capacity of the column completely disappeared, but was rectified by replacing the top few centimetres with fresh packing, re-conditioning and re-doping. To date we have noticed no depreciation in the column's separatory capabilities as a result of the doping (more than six months of daily use).

Comparison of on- and ex-column generation

The results of this work are tabulated (Table 4) and plotted (Fig. 5). It can be seen that for any given Bu_3SnCl concentration, the measured parameter, i.e. the Bu_3SnH/Pr_3SnH peak height ratio, is slightly greater for the ex-column generation, which suggests either

(a) that Pr_3SnCl is generated more efficiently than Bu_3SnCl on the column, or
(b) that Bu_3SnCl is generated more efficiently than Pr_3SnCl off the column.

In general, though, it is estimated that on-column generation is at least 90% as efficient as the ex-column method, with presumably fewer transport losses.

Variability of generation and limits of detection

Table 5 gives figures for the variability of the method for different organotin species. The range of absorbence for a given amount of compound injected is given, together with the standard deviation. When comparing absorbence per unit mass values, one must allow for stoichiometric differences of tin content between species and for this reason they are expressed in $ng\,Sn^{-1}$. It must also be borne in mind that the unit absorbence obtained is a combination of two factors:

(a) the extent of hydridization of the compound, which determines the amount of analyte that reaches the detector, and
(b) the atomization characteristics of the particular hydride species within the quartz cell.

Decreasing difficulty in generating the hydrides in the order $Me > Me_2 > Me_3$ was found and may account for the decreasing standard deviation of absorbences with addition of each alkyl group. The lowest standard deviation was noticed for Me_3SnCl, the highest for the Bu_3Sn–tropolone

Table 4 Bu_3SnCl calibration by on-column and ex-column generation techniques

On-column				Ex-column	
Low level[a]		High level[b]		High level[b]	
$[Bu_3SnCl]$ (ng cm^{-3})	Mean peak height ratio	$[Bu_3SnCl]$ ($\mu g\ cm^{-3}$)	Mean peak height ratio	$[Bu_3SnCl]$ ($\mu g\ cm^{-3}$)	Mean peak height ratio
47	1.11	0.65	0.15	0.65	0.25
94	1.34	1.30	0.28	1.30	0.45
141	1.87	1.95	0.48	1.95	0.73
188	2.49	2.60	0.60	2.60	0.95
282	3.21	3.25	0.77	3.25	1.18
329	3.89	3.90	1.04	3.90	1.43
376	4.04	4.55	—	4.55	1.58
423	4.56	5.20	1.47	5.20	1.79
		5.85	1.69	5.85	1.96
		6.50	1.84	6.50	2.23

[a]Against $[Pr_3SnCl]$ at 32 ng cm^{-3}. [b]Against $[Pr_3SnCl]$ at 1.92 $\mu g\ cm^{-3}$.
Notes. All concentrations given are initial concentrations before evaporation of solvent. Peak heights are the mean of at least triplicate injection. Ratios are Bu_3Sn^-/Pr_3Sn^+.

Table 5 Variability of on-column generation technique and relative absorbences and limit of detection (LOD)

Compound	Amount (ng)	n	Absorbence ($\times 10^3$)[b] Range	Mean	S.D.	(Per ng Sn)	Calculated LOD (ng) [c]	[d]
$MeSnCl_3$	15.00	8	15.5–42.5	29.9	8.1	4.01	0.75	0.37
Me_2SnCl_2	7.35	8	68.5–86.0	75.6	6.1	18.93	0.15	0.08
Me_3SnCl	7.50	8	20.5–29.0	24.8	2.8	7.49	0.45	0.27
Pr_3SnCl	13.00	9	52.0–65.8	57.7	5.8	10.53	0.34	0.14
Bu_3SnCl	15.25	9	30.0–40.0	35.1	3.7	6.26	0.65	0.24
Pr_3Sn^+[a]	13.00	14	47.5–77.5	64.8	8.6	11.81	0.30	0.13
Bu_3Sn^+[a]	15.25	14	18.5–57.8	27.3	11.4	4.87	0.84	0.31

[a]As Tropolone complexes, but figures are calculated as chlorides. [b]Absorbence figures, i.e. peak heights, per ng reflect two effects—generation and atomization of analyte. [c]Calculated LOD based on an acceptable peak height of 3 mm (1.5×10^{-3} A). [d]Calculated per ng Sn.

complex. The compound with the lowest calculated limit of detection (LOD) was Me_2SnCl_2, with little difference between Me_3SnCl and Bu_3SnCl.

In carrying out investigations into this method it was noticed that:

(a) a trace quantity of acid in the injected analyte solution is essential for the derivatization of $BuSnCl_3$, Bu_2SnCl_2 and compounds of arsenic and antimony, and

(b) some species (especially the trialkylated tins) require less acid for generation and at times appear not to need acid at all; this may be due, in part, to small traces of acid on the column.

Calibration

Linear calibration of the Bu_3SnH/Pr_3SnH ratio plotted against Bu_3SnCl concentration over two orders of magnitude was achieved with calculated

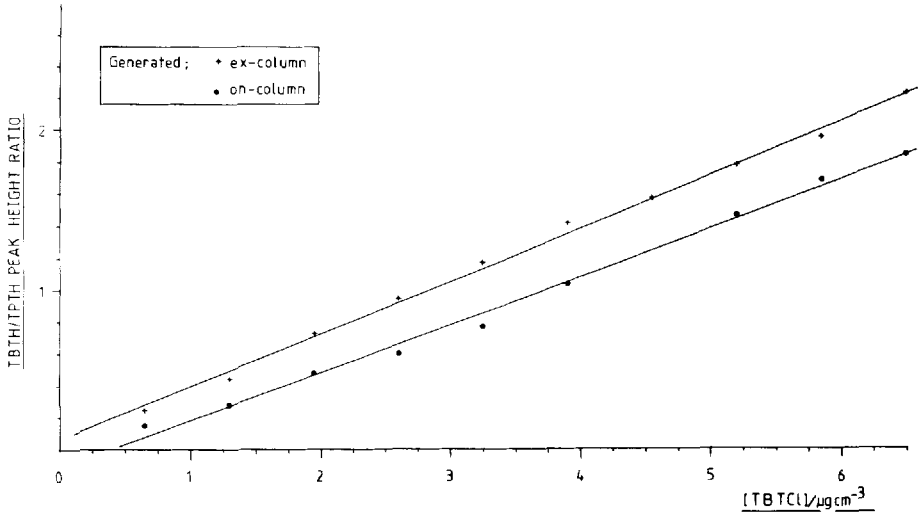

Figure 5 Comparison of hydridization techniques.

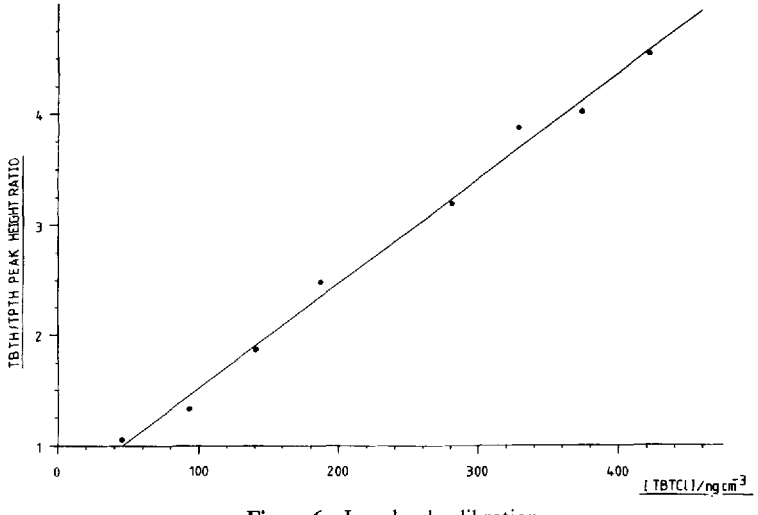

Figure 6 Low-level calibration.

detection limits (before optimization) of around 0.3 ng Pr_3SnCl (=0.1 ng Sn) and 0.7 ng Bu_3SnCl (=0.3 ng Sn) at the detector (based on three times the noise level—*ca* 3 mm). We believe this can be improved by optimization of all instrument parameters and, further, by the use of a more sensitive detector (e.g. FPD). Calibration figures are given in Table 4, and plotted in Figs 5 and 6.

Analysis of mono- and di-butyltin compounds

Both $BuSnCl_3$ and Bu_2SnCl_2 can be generated on-column and separated from each other and from Bu_3SnCl using a temperature ramp (see Experimental).

Sea-water analysis for butyltin species

This method may be adapted for the detection of all butyltin cations together, or it may be adapted to detect selectively Bu_3Sn^+ only. The extraction is not successful for Bu_2Sn^{2+} or $BuSn^{3+}$ without the use of a complexing agent. We used tropolone for this purpose.

Good recovery of Bu_3SnCl without use of tropolone from 50 cm^3 of sea-water was achieved

over the entire calibrated range (Table 6). Between 66 and 95% was recovered with slightly better recovery at the nanogram level than at the microgram level (i.e. a mean of 85% as opposed to 72%). A 50 cm^3 sample of sea-water containing 20 ng (i.e. 400 ng dm^{-3}) can be analysed (based on extraction with 5 cm^3 CH_2Cl_2 followed by evaporation down to 50 μl and injection of 5 μl)—further evaporation is possible but gives problems in sampling (water pick-up) and prevents replicate injection, as the sample volume is too small. Using the same method with a 2 dm^3 water sample, 5 cm^3 HCl and 40 cm^3 CH_2Cl_2, Bu_3Sn^+ can be detected at the 40 ng dm^{-3} level. Results are given in Table 6, showing the reproducibility of recovery at high (μg cm^{-3}) and low (ng cm^{-3}) levels with a range of 66–95% recovery, and a standard deviation of 9%.

Sources of error in quantification

Several potential sources of error are documented for this procedure.

(a) Choice of internal standard

An internal standard has to mimic the properties of the analyte as closely as possible and such fundamental properties as boiling point, polarity and general chemical behaviour affect its suitability. The evaporation of CH_2Cl_2 from a Bu_3SnCl/Pr_3SnCl solution is an essential step in the method, during concentration of the analyte solution. The possibility exists that loss of analyte may occur. This error will be compensated for by a similar loss of internal standard only if their boiling points, polarity and affinity for the solvent are of similar magnitude. If not, preferential loss of one component will occur and erroneous results will ensue. In order to estimate losses, a solution containing suitable concentrations of both tripropyl and tributyl species was prepared so that analysis could be performed before evaporation. Concentrations used were 3.05 and 2.60 μg cm^{-3} of Bu_3SnCl and Pr_3SnCl respectively.

Little difference in losses from evaporation of either 1 cm^3 or 2 cm^3 of solution was observed. This indicates that the vast majority of losses occur during the final stages of evaporation, i.e. when a Bu_3Sn^+ concentration >6.1 μg g^{-1} is reached. In order to have a 1 cm^3 extract of this concentration when analysing environmental matrices (2 dm^3 water, 1 g sediment), we calculate that levels would have to be in excess of 600 ng dm^{-3} and 3000 ng g^{-1} respectively, i.e. significant losses during evaporation will *not* occur for matrices having concentrations lower than these levels (based on 2 dm^3 and 1 g analysed with 50% recovery). If 20 g of sediment is analysed (50% recovery into 5 cm^3 CH_2Cl_2), then significant losses would not occur below 120 ng g^{-1}.

From these studies it is possible to apply a correction factor when estimating initial concentrations, but it must be remembered that evaporation is not a precise technique and this is an estimation. However, from the above, with normal environmental samples with low levels of organotins, and using an internal standard, a correction factor for evaporation is not necessary.

As can be seen from Tables 7 and 8, both Pr_3Sn^+ and Bu_3Sn^+ moieties are partially lost during evaporation of CH_2Cl_2 solvent. It is interesting to note that the Bu_3Sn^+ loss decreases in the order of $H^- > Cl^- >$ tropolone complexes. Preferential loss of the tripropyl derivative is noticeable in all three series. From this evidence alone it would appear that the tropolone derivatives should be used but, unfortunately, these are not generated as efficiently as the chlorides, give greater variation in reproducibility (Table 5), have the biggest disparity of evaporative loss between tripropyl and tributyl derivatives (Table 8) and also give rise to dismutation products (see Dismutation with tropolone below).

Table 6 Recovery of Bu_3SnCl from sea-water using on-column generation technique

Sample	Added[a] Bu_3SnCl (ng)	Measured[b] Bu_3SnCl (ng cm^{-3})	Bu_3SnCl recovery[c] (%)
1	94	61	82
2	188	124	86
3	282	166	76
4	376	270	95
5	12 500	8 200	78
6	12 500	7 100	66
7	12 500	7 500	68
8	12 500	8 100	76

[a]Bu_3SnCl was added to 50 cm^3 of sea-water by addition of a 1 cm^3 ethanol solution. [b]Measured concentrations are calculated for CH_2Cl_2 solution before evaporation. [c]Figures for recovery are calculated by accounting for solvent recovery and excess loss of Pr_3SnCl standard on evaporation.

Table 7 Summary of losses of organotin compounds on evaporation from dichloromethane (%)

	Hydrides		Chlorides		Tropolones	
Study	Pr_3	Bu_3	Pr_3	Bu_3	Pr_3	Bu_3
1	49.1	43.1	69.0	40.6	64.4	36.4
	39.2	29.3	54.3	34.8	57.7	24.5
	—	—	62.2	35.6	—	—
2	46.8	41.4	57.4*	26.7*	29.6	5.2
	44.6	26.5	53.8	29.3	39.2	18.3
	—	—	46.9	20.4	16.3	3.0
3	—	—	60.8*	37.7*	26.5	—
	—	—	56.5	36.0	46.5	22.3
	—	—	40.5	16.4	45.3	31.7
Mean	44.9	35.1	55.7	30.8	40.7	20.2

Notes. (a) Figures given are for evaporation of a 2 cm^3 solution of 3.05 $\mu g\,cm^{-3}$ Bu_3SnCl, 2.60 $\mu g\,cm^{-3}$ Pr_3SnCl in CH_2Cl_2 (except *—only 1 cm^3 evaporated). (b) Conditions were as follows: evaporation down to 50 μl with a 'gentle stream' of nitrogen, ambient temperature (26°C), approx. 9.5–10.0 min for 2 cm^3, 5 min for 1 cm^3. (c) Estimates of losses are calculated on the reduction of mean peak heights before and after evaporation. (d) These concentration levels are higher than those normally encountered in the environment, where losses are not significant (see text).

Table 8 Excess loss of propyltin moieties compared with the analogous butyltin derivatives (%)

Study	Hydrides	Chlorides	Tropolones
1	22	67	100
2	34	107	223
3	—	75	46
Mean	28	83	123

The choice of internal standard is therefore a compromise, and Pr_3SnCl may eventually not prove to be the best for the analysis of Bu_3Sn^+.

(b) Internal standard concentration

Clearly the ratio of Bu_3SnH/Pr_3SnH peak heights is an arbitrary value and depends on the concentration of both species at the time of analysis. Studies have shown, however, that when quantifying for Bu_3SnCl it is desirable to have the concentration of Pr_3SnCl as close as possible to that used when the calibration was performed. This gives a more accurate estimation of the analyte concentration as it eliminates error in the correction step necessary. This view is borne out by the results given in Table 9. It can be seen that the concentration difference of Pr_3SnCl between calibration and analysis is too large in the first instance.

(c) Bu_3SnCl adhesion to glass surfaces

In a latter stage of the analysis, Bu_3SnCl in CH_2Cl_2 solution is dispensed into a 'V' vial and the solvent evaporated from 5 cm^3 to *ca* 50 μl. As such a large surface area of glass is in contact with a very small amount of analyte, it is possible that adhesion loss to glass occurs here as the solvent is evaporated. Quantification of Bu_3Sn^+ should not be affected due to compensation by the internal standard, but such losses would raise the achievable limit of detection.

Other problems encountered

Several problems were encountered in the development of this method. Problems were experienced with syringe erosion, column blocking, flowmeters sticking, transfer lines leaking, and heating element burn-out.

Analysis of arsenic and antimony compounds

The work performed on various compounds of arsenic and antimony is summarized in Table 10. Authenticity of products is by virtue of element specific detection coupled with retention times coincident with those of species seen in the headspace analyses and proven by MS.

Table 9 Effect of internal standard concentration on Bu_3Sn^+ quantification

Concentrations ($\mu g\,cm^{-3}$)			
Bu_3SnCl (actual)	Pr_3SnCl[a] (actual)	Bu_3SnCl (measured)	Error (%)
6.52	15.36	7.94	+22[c]
2.60[b]	3.84[b]	2.76	+6[c]

[a]Pr_3SnCl concentration at calibration = 1.92 $\mu g\,cm^{-3}$. [b]Mean of 15 injections. [c]I.e. it is advisable to choose Pr_3SnCl levels close to those anticipated for Bu_3SnCl.

Table 10 Summary of experimental work performed on investigation of on-column hydridization of arsenic and antimony compounds

Compound (concentration, $\mu g\ cm^{-3}$)	Solvent	Results	
		Hydride generation ex-column into headspace: analysis by GC AA/FID/MS	Direct injection of solution into GC AA/FID
Cacodylic (dimethylarsinic) acid, $(Me)_2AsOOH$ (3.8)	CCl_4	—	No detectable peak(s)
	$CHCl_3$	—	No detectable peak(s)
	Water (no buffer)	No detectable peak(s)	No detectable peak(s)
	Water + acetate buffer, pH4.8	Peak at 1.4 min MS shows hydride $(Me)_2SsH$	—
	Water + HCl ($0.025\ mol\ dm^{-3}$), pH 1.6	ditto	Peak at 1.4 min
Arsenic acid, $AsO(OH)_3$ (11)	$CHCl_3$	—	No detectable peak(s)
	Water (no buffer)	—	No detectable peak(s)
	Water + acetate buffer, pH 4.8	Very small peak at 0.7 min	
	Water + oxalic buffer, pH 1.2	Peak at 0.7 min MS shows hydride AsH_3	No detectable peak(s)
	Water + HCl ($0.025\ mol\ dm^{-3}$) pH 1.6	ditto	No detectable peak(s)
Arsenic oxide As_2O_3 (4.4)	Water + HCl ($0.025\ mol\ dm^{-3}$), pH 1.6	Peak at 0.7 min MS shows hydride AsH_3	Peak at 0.7 min
	Water + HCl ($0.025\ mol\ dm^{-3}$) + oxalic buffer	Peak at 0.7 min MS shows hydride AsH_3	—
Antimony trichloride, $SbCl_3$ (14.6)	Water + HCl ($0.025\ mol\ dm^{-3}$), pH 1.6	Peak at 0.8 min MS shows hydride SbH_3	Peak at 0.8 min
	Water + HCl ($0.025\ mol\ dm^{-3}$) + oxalic buffer	Peak at 0.8 min MS shows hydride SbH_3	—
Antimony pentoxide, Sb_2O_5 (~ 10)	Water + HCl ($0.025\ mol\ dm^{-3}$) + oxalic buffer	Peak at 0.8 min MS shows hydride SbH_3	—
	Water + HCl ($0.025\ mol\ dm^{-3}$), pH 1.6	Small peak to 0.8 min MS shows hydride SbH_3	Peak at 0.8 min
Antimony potassium tartrate, $KSbOC_4H_4O_6$ (26.8)	Water + HCl ($0.025\ mol\ dm^{-3}$), pH 1.6	Peak at 0.8 min MS shows hydride SbH_3	Peak at 0.8 min

Notes. (a) 'Control' headspace analyses were performed with air (i.e. syringe), water, buffer and sodium borohydride. All gave negative results. (b) All solvents/acidic solutions were injected separately prior to every analysis undertaken. All gave negative results. (c) All analyses were performed in triplicate. (d) An attempt at doping the column with oxalic acid buffer and $NaBH_4$, followed by injection of aqueous solutions was made, but with no success. (e) By preparing solutions of these concentrations, it was possible to estimate that all compounds were detectable at the nanogram level. (f) — Not attempted.

Analysis of environmental samples for Bu_3Sn^+

Water samples from the River Yealm at Newton Ferrers, Devon, UK, and from Sutton Marina, Plymouth, UK, were analysed. Bu_3Sn^+ levels are given in Table 11. We believe this method to be the simplest and most convenient yet described for the analysis of tributyltin in the aqueous natural environment.

Dismutation with tropolone

Use of tropolone to assist extraction of trimethyltin compounds has been shown to produce tetra- and di-methyltin products by a dismutation process.[17] We find that tropolone is unnecessary for the analysis of tributyltin in water. However, we also note that tributyltin is dismutated by tropolone. Hence analysis of di- and mono-butyltin with tropolone may be complicated by additional dibutyltin formed from tributyltin present. We are investigating this with a view to quantification.

Table 11 Bu_3SnCl levels found in environmental samples

Site	Sample analysed	[Bu_3SnCl] (ng dm^{-3})
River Yealm, Newton Ferrers, 12 Nov. 1987	1 19 Nov. 1987	164
	2 20 Nov. 1987	162
	Mean	163
Sutton Marina, Plymouth 12 Nov. 1987	1 16 Nov. 1987	412
	2 17 Nov. 1987	580
	3 18 Nov. 1987	316
	4 19 Nov. 1987	332
	5 24 Nov. 1987	156
	6 26 Nov. 1987	522*
	7 27 Nov. 1987	434*
	Mean	393

Notes. (a) A 2 dm^3 sample volume was analysed. Samples were stored at pH 1–2 in amber bottles in the shade at room temperature. (b) Each result given is calculated from the mean of three injections into the GC AA. (c) No correction for % recovery of Bu_3SnCl has been made in the calculation of concentrations. We assume 80–100% recovery. (d) All extractions were performed with 40 cm^3 of CH_2Cl_2, except *– with 40 cm^3 of 0.025% tropolone/CH_2Cl_2.

Acknowledgements SC is pleased to acknowledge funding from SERC; PJC gratefully acknowledges travel funding from the Royal Society (London) and the US Navy.

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