Applied Organometallic Chemistry (1989) 3 105–114

0268–2605/89/03109105/$03.50

Optimization of butyltin measurements for seawater, tissue, and marine sediment samples

Martha O Stallard,*† Susan Y Cola* and Carol A Dooley‡
*Computer Sciences Corporation, 4045 Hancock Street, San Diego, CA 92110, USA and ‡Naval Ocean Systems Center, Code 522 Bldg 111, San Diego, CA 92152-5000, USA

Received 10 August 1988 *Accepted 6 October 1988*

Optimized techniques for measuring butyltins at the sub-part-per-trillion (ppt; 1:10^{12}) level in seawater and at the part-per-billion (ppb; 1:10^9) level in tissues and sediments are presented. Purge and trap/hydride derivatization followed by atomic absorption (AA) detection was optimized to give better sensitivity than was previously attained for seawater, yielding environmental detection limits of 0.08–0.2 ng dm^{-3}. Improvement in precision and reproducibility in measurement of butyltins in tissues and sediments was attained by adjustment of the concentration in an organic extract to minimize matrix effects and by use of internal standards. The tissues and sediments were homogenized and extracted with methylene chloride (CH_2Cl_2) after acidification. The butyltins in the organic layer were derivatized with hexylmagnesium bromide and analyzed by gas chromatography (GC) with a flame photometric detector (FPD). The absolute detection limits in tissues and sedimets were 0.1 ng for tributyltin (TBT), 0.12 ng for dibutyltin (DBT) and 0.29 ng for monobutyltin (MBT).

Keywords: Tributyltin, dibutyltin, monobutyltin, seawater, tissues, sediments, hydride, Grignard, gas chromatography, atomic absorption, flame photometric detection

INTRODUCTION

Increasing controversy over the use of tributyltin (TBT)-based antifouling paints and their potential impact on the marine environment has necessitated the development of techniques to measure part-per-trillion (ppt; 1:10^{12}) levels in seawater and part-per-billion (ppb; 1:10^9) levels in tissues and sediments. Two recent conferences[1,2] have produced reference documents on the chemistry, biology, toxicity, fate, distribution and behaviour of organotin compounds in the environment. Monitoring TBT in mussels and oysters is important as studies have shown sublethal effects at sub-part-per-billion levels (Thain in Ref. 1). Because of its lipophilic character, TBT is bioaccumulated by oysters and mussels. Bioconcentration factors from 5000 to 50 000 have been reported.[3] The measurement of TBT and its degradation products in the sediment is also relevant because TBT partitions to sediments which may act as a sink and future source of the compound. To evaluate environmental risks, practical, reproducible, and sensitive analytical methods are essential in order to measure and speciate low levels of butyltins in seawater, tissues and sediment.

There are several well-documented methods for TBT analysis in environmental water samples. Reported methods include simultaneous hydride derivatization and extraction[4] and extraction followed by Grignard derivatization.[5–10] Direct determination and speciation of tin and alkyltins in seawater can be achieved by hydride derivatization followed by purging and trapping the evolved hydrides. The tin hydrides are then volatilized and detected by hydrogen flame atomic absorption spectroscopy (AA) in a quartz burner.[11] Herein we report optimizations of our method,[12] which has increased the sensitivity 10-fold to sub-part-per-trillion levels. Intercalibration using different techniques has given comparable results for butyltin seawater concentrations.[13]

A recent intercalibration study (Stephenson *et al.* in Ref. 2, p. 1334) among seven laboratories illustrated the difficulties of TBT quantitation in tissues and

†Author to whom correspondence should be addressed.

sediments. TBT concentrations reported for tissues varied by factors of two to three and most laboratories were not able to participate in the sediment analysis. Our main concern in developing a suitable protocol for organotin analysis of tissues and sediments focused upon two points: precision and sensitivity. We decided to adapt the extraction/Grignard derivatization method[7–9,14–16] since derivated extracts were chemically and thermally stable. Using this method, TBTCl may be extracted from 5–10 g of tissue or sediment and quantitated without significant matrix effects provided Florisil clean-up, an internal standard, and a correct solvent/sample ratio are used.

EXPERIMENTAL

Seawater analysis

Reagents

Sodium borohydride ($NaBH_4$; 98%) from J.T. Baker was dissolved in 18-MΩ deionized water containing 1% sodium hydroxide AR from Mallinckrodt. The 4% $NaBH_4$ solution was prepared fresh daily. Baker-analyzed reagent-grade acetic acid was dissolved in 18-MΩ deionized water to make a 10% solution. UPC-grade helium and hydrogen and zero-grade air were used. Mono-, di-, and tri-butyltin chlorides (MBT, DBT, TBT) were used as supplied by Aldrich (Milwaukee, WI). Punctilious ethyl alcohol, (95%) 190 proof USP, was obtained from US Industrial Chemical (Anaheim, CA). Seawater for blanks and sample dilution was taken directly from the seawater flume at the Scripps Institution of Oceanography pier in La Jolla, CA.

Standards

Primary standards were prepared bimonthly by weighing mono-, di-, and tri-butyltin chlorides into volumetric flasks and diluting with ethanol. Each primary standard contained approximately 100 mg dm^{-3} of the butyltin chloride. The primary standards were stored at 4 °C in the dark. A mixed secondary working standard was prepared every other day by diluting 100 μL of each of the primary standards to 100 cm^3 resulting in a concentration of approximately 0.1 ng μL^{-1}. Standard curves were prepared daily by adding 10, 25, 50 and/or 100 μL of the mixed secondary standards to 500 cm^3 of blank seawater (Fig. 1). A standard was repeated after every sixth sample. Occasional standard additions were made to samples to confirm the absence of matrix effects. Results were calculated as the butyltin cation.

Equipment

Butyltin hydrides were detected with a Buck Scientific model 200 atomic absorption spectrometer fitted with a tin hollow-cathode lamp. This small, relatively inexpensive (< $8 000) spectrometer has good sensitivity for tin. The absorbance data were recorded on a Shimadzu CR3A Chromatopac recorder as peak areas. The spectrometer and the recorder were plugged into a Microstar energy converter to prevent erratic results from power surges. Cole Parmer 150 mm high-resolution flowmeters were used to control gas flow rates.

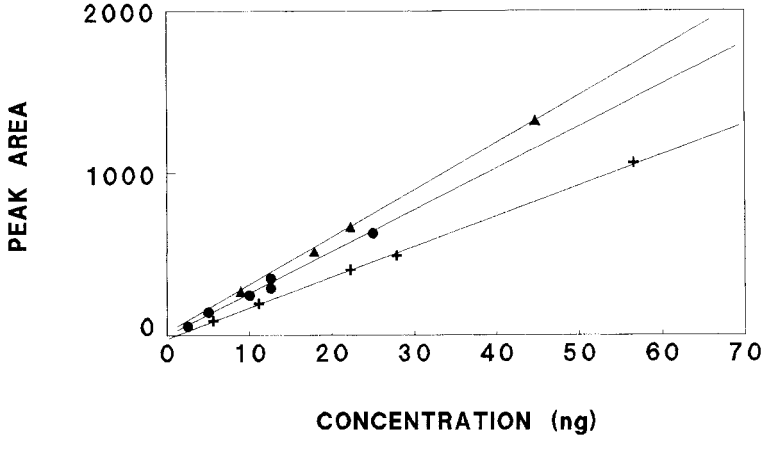

Figure 1 Cation calibration curve for butyltins in seawater. +TBT; ▲ DBT; ● MBT.

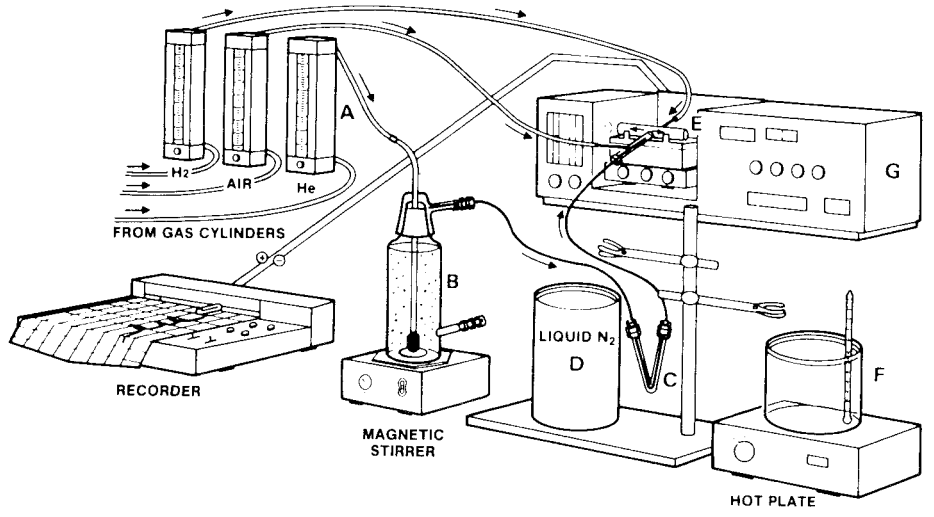

Figure 2 Hydride generation/atomic absorption sepctrometry system for measurement of organotin species. A, Helium carrier gas line; B, hydride generator, modified gas washing bottle; C, 3% OV-1 Chromosorb packed glass trap; D, liquid nitrogen for cryogenic cooling; E, quartz burner; F, 180°C high-temperature silicone oil bath; G, Buck atomic absorption spectrometer.

Apparatus and optimization

The optimized system (Fig. 2) consists of a modified 500-cm^3 gas washing bottle (hydride generator) with an outlet on the top and an injection port on the side. Teflon tape was wrapped around $\frac{1}{8}$-inch o.d. Teflon tubing to form a secure seal when the tubing was threaded through the top outlet and pulled snug.* This tubing was then pressure-fitted into the end of a 3-mm i.d. glass U-tube (2.5–3-inch sides) which formed the cryogenic trap for the tin hydrides. Avoiding the use of Swagelok fittings which can form dead spaces improved the analysis. The gas washing bottle must also be filled within 1.5 inches from the neck of the bottle to minimize dead space. We have found the tall cylindrical shape of the modified gas washing bottle coupled with the use of a Kimax 12C frit to disperse the helium bubbles provided the most efficient combination to scrub the evolved tin hydrides from the sample. Coarser frits yield larger bubbles that do not remove the hydrides as efficiently. Finer frits gave rise to too much back pressure, thus causing problems in controlling the helium flow. The most effective helium flow rate was found to be 50–60 $cm^3\ min^{-1}$. Flow rates below 40 $cm^3\ min^{-1}$ did not provide efficient scrubbing and those above 70 $cm^3\ min^{-1}$ produced too much water vapor.

Active sites in the trap which bind the hydrides and cause peak reduction or broadening must be avoided. This was done by thoroughly cleaning and silanizing the traps. We have encountered variability in sensitivity depending on how well the glass traps have been silanized. The method we have found to be most successful was to clean the traps thoroughly by soaking in a critical cleaner such as hot 2% RBS 35 (VWR Scientific, San Francisco Ca.), rinsing with distilled water and drying. The traps were then washed with hexane and methanol and dried in an oven. While still warm they were filled with silanizing fluid (Supelco Silon CT) and allowed to sit for at least 30 min. The traps were then thoroughly flushed with hexane and methanol and conditioned in a 200 °C oven for 10–15 min. Then 20–30 mg of 3% OV-1 on Chromosorb W-HP 80/100 mesh was added to the traps and this packing material was secured with silanized glass wool plugs.

We have also investigated the use of Teflon traps with the same internal diameter as the glass traps. The Teflon traps gave similar sensitivity to silanized glass traps. However, the Teflon did not conduct heat well and water vapor condensed in ends of the trap resulting in greatly reduced sensitivity after a few runs. We believe that an electrothermal heater (Clavell *et al.* in Ref. 1, p. 1152) will make possible use of the Teflon traps.

The trap was connected to a quartz burner with another Teflon tube. It was obvious from the work by

* 1 inch = 2.54 cm.

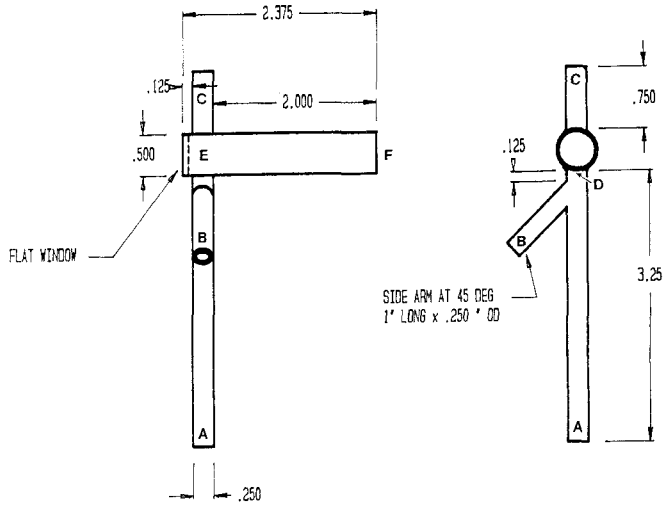

Figure 3 Closed-end quartz burner (dimensions in inches). A, Sample entry; B, air entry; C, hydrogen entry; D, position of glass capillary tip in Teflon tube that introduces tin hydrides into burner; E, hottest portion of burner (500°C); F, open end (400°C).

Donard *et. al.* [17] that the design of the quartz burner could influence sensitivity. We tested their burner design along with several others. We found that the closed-end burner with gas entry off-center gave optimum sensitivity (Fig. 3). External heating of this burner design with a nichrome wire coil did not seem to increase sensitivity. It took the system longer to stabilize after being initially turned on with the heated burner designs. The position of the tube that introduces the tin hydrides influenced sensitivity. A glass capillary (0.5–0.75 inch long) was forced into the end of the Teflon tube from the trap to prevent the end from burning. The tip of the capillary was positioned at the edge of the quartz burner barrel (D in Fig. 3) and fastened into place with a Swagelok reduction fitting at the sample entry (A in Fig. 3). We believe that the increased sensitivity of this burner design results from concentrating the evolved tin hydrides in a small area (E in Fig. 3) resulting in more tin atoms in the lightpath and therefore increased light absorption. This area is also the hottest part of the burner. The open end (F in Fig. 3) of the burner was ignited with a piezoelectric Lab Lyter. It was important to check periodically to ensure that the hydrogen flame was burning. The quartz burner was wrapped with a 2 mm thickness of Fiberfrax ceramic fiber (Lab Safety Supply, Janesville, WI) and mounted on a custom-made adjustable aluminum frame placed on the AA burner head. We have found this ceramic fiber to be a good replacement for potentially carcinogenic asbestos. The burner was then positioned to give maximum light transmission.

Operating procedure

Seawater samples of 10–500 cm^3 were introduced into the hydride generator and diluted with blank seawater until the level was within 1.5 inches of the neck of the vessel. The samples were then acidified to approximately pH 5.5 by the addition of 10% acetic acid. The magnetic stirrer was started and helium bubbled through the sample while the glass trap was placed in liquid nitrogen. The trap was immersed just sufficiently to cover the packing material to avoid accumulation of water vapor, and 5 cm^3 of 4% sodium borohydride in 1% sodium hydroxide was then injected through the septum and the evolved tin hydrides purged into the cryogenic trap with helium.

After the sample had purged for 5 min, the trap was removed from the liquid nitrogen and the various tin and alkyltin hydrides were detected sequentially, according to their boiling points, as they volatilized from the trap into the quartz burner. The first tin species volatilized from the trap as it came to room temperature was tin hydride (SnH_4). The methyltin hydrides were followed by monobutyltin hydride ($BuSnH_3$). We have not routinely quantified inorganic tin or methyltins because they were almost always present in small quantities in seawater and generally they were not anthropogenic in origin. After the mono-

butyltin hydride was detected the trap was placed in a water bath at 50 °C to volatilize the dibutyltin hydride (Bu_2SnH_2) as a sharp peak. Volatilization of tributyltin hydride (Bu_3SnH) was achieved by heating the trap in a 180 °C silicone oil bath. The butyltin hydrides were atomized in a hydrogen/air flame using the quartz burner discussed earlier. The hydrogen and air flow rates were 220 and 140 $cm^3\ min^{-1}$ respectively. The tin species were detected by atomic absorption spectroscopy at a wavelength of 286.3 nm and a tin hollow-cathode lamp current of 8 mA. Use of the 224.6 nm wavelength gave somewhat better sensitivity but resulted in considerably more baseline noise. It was very difficult to resolve small peak areas with the greater baseline noise so we found that although we had to sacrifice some sensitivity, use of the 286.3 nm wavelength gave better results.

All lines and the trap were periodically flushed with dry helium to remove water vapor. This was important to retain sensitivity and increase the life of the trap. The traps must be thoroughly dried by helium purging between runs. Although we have run at the rate of four samples per hour, we have found more consistent results were obtained at three samples per hour.

Tissue and sediment analysis

Reagents

Mono-, di-, and tri-butyltin chlorides (MBTCl, DBTCl, TBTCl) and 2.0 mol dm^{-3} n-hexylmagnesium bromide were obtained from Aldrich. n-Hexane, glass-distilled dichloromethane, ACS-certified methanol, and Ultrex hydrochloric acid were obtained from VWR.

Standards

TBTCl, DBTCl, and MBTCl stock solutions were prepared bimonthly by weighing mono-, di-, and tributyltin chlorides into volumetric flasks and diluting with hexane.

Tripentyltin bromide (TPTBr), the internal standard, was prepared by bromination of tetrapentyltin which was prepared from pentylmagnesium bromide and tin tetrachloride.[18,19]

Equipment

Instrument conditions were as follows. The Hewlett–Packard 5890 gas chromatograph was equipped with a flame photometric detector. The filter, obtained from Dietrich Optical, had a range of 625–2000 nm. Flow rates through the detector were 100 $cm^3\ min^{-1}$ for air and 170 $cm^3\ min^{-1}$ for hydrogen. Nitrogen make-up gas plus helium carrier gas had a combined flow rate of 35 $cm^3\ min^{-1}$. The column head pressure was 28 psi (193 kPa). The injector and detector temperatures were 225 °C and 250 °C, respectively. The oven program was set as follows: after an initial temperature of 50 °C for 2.00 min, the oven was ramped at 30 °C min^{-1} to a final temperature of 200 °C and held for 8.00 min. A bake-out at 240 °C for 6.00 min was then programmed. The column was a Supelco SPB-1 fused-silica capillary 30 m long and with a 0.25 mm i.d.

Sample preparation

All glassware for preparation and storage was soaked overnight in RBS cleaning solution, rinsed with tap water, and soaked overnight in dilute nitric acid. Sediments and tissues were stored frozen in polycarbonate tubes. Extractions were carried out in disposable polypropylene centrifuge tubes. A sample set typically consisted of 12 samples, a blank, and a standard addition set.

Tissue Excess of water was decanted from the tissues. Approximately 5 g of wet tissue were homogenized using a Tekmar tissuemizer. This tissue was weighed to the nearest 0.1 g in tared 50-cm^3 polypropylene centrifuge tubes, and 10 cm^3 of 1.5 mol dm^{-3} HCl and 20.0 cm^3 of methylene chloride were added to each tube. The capped tubes were mixed on a vortex mixer for 2 min and placed on a rotary mixer for 3 h. After centrifugation, a 2.0-cm^3 aliquot was removed from the bottom layer with a Pasteur pipet and dried under air in a 35 °C water bath.

The extracts were redissolved in 2 cm^3 of hexane and the internal standard, tripentyltin bromide, was added. A second internal standard, tripropyltin chloride, was sometimes added before extraction of the tissue. n-Hexylmagnesium bromide (250 μL of 2.0 mol dm^{-3}) was added to each extract. After 10 min, 2 cm^3 of 0.2 mol dm^{-3} sulfuric acid were added to hydrolyze the remaining Grignard reagent. The top layer was removed and eluted on Supelco florisil columns (and Supelco manifold) with hexane. The extracts were dried under air as before and reconstituted in 200 μL of hexane.

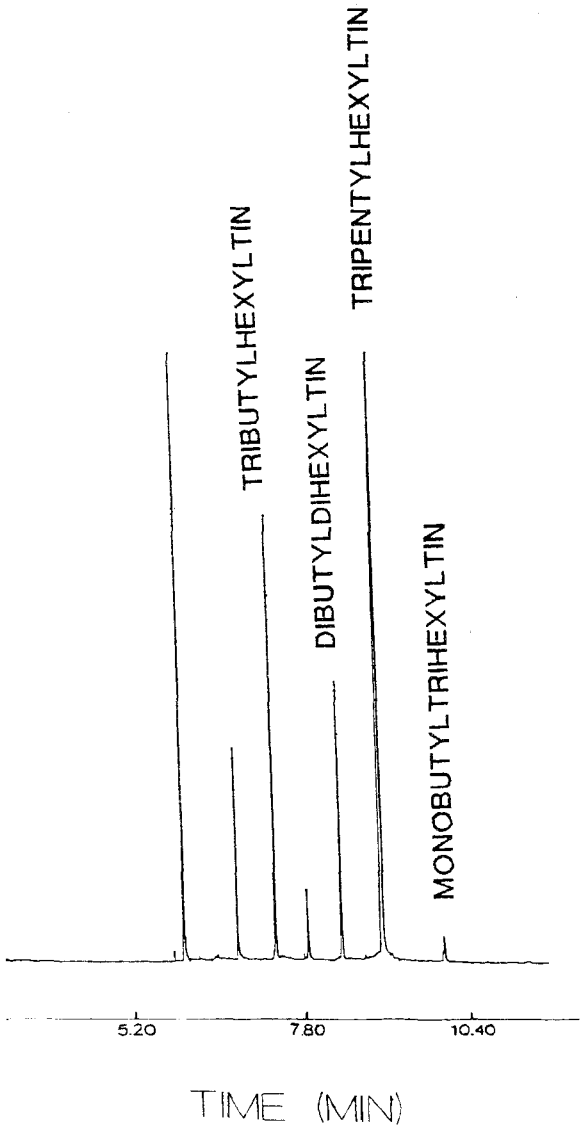

Figure 4 A typical environmental chromatogram from a moderately TBT-impacted San Diego Bay sediment.

Sediment After excess water had been decanted and the sediment had been air-dried overnight, approximately 5 g of the partially dried sediment were placed into a tared polypropylene centrifuge tube, ground with a pestle to break up any clumps, and weighed to the nearest 0.1 g; 10 cm^3 of 1.5 mol dm^{-3} HCl in methanol and 20.0 cm^3 of methylene chloride were added to each tube. The capped tubes were mixed on a vortex mixer for 2 min. After venting gases, the tubes were placed on a rotary mixer for 3 h. Sediment preparation was completed in the same manner as tissues. Figure 4 shows typical results.

Table 1 Calibration data

Compound	*N*	Average rf (±SD)	Limit of detection (ng)
TBT	5	1.39 (±0.16)	0.10
DBT	5	1.19 (±0.20)	0.12
MBT	4	0.48 (±0.14)	0.29

All peak areas are normalized against the internal standard, TPT. *N* represents the number of calibration standards used to determine the average response factor (rf) values. The concentration range for TBT is 0.148–1.288 $\mu g\ cm^{-3}$.

Table 2 TBT spiked recoveries of mussels and sediments from San Diego Bay

Measured ($\mu g\ cm^{-3}$)	Actual ($\mu g\ cm^{-3}$)	Recovery (%)
(A) Mussels		
0.13	0.12	108
0.24	0.29	83
1.07	1.18	91
3.21	3.15	103
(B) Sediments		
0.30	0.23	130
0.57	0.54	105
1.09	1.01	93
1.83	1.80	102

Calibration

Calibration for tissues and sediments as seen in Table 1 was based upon the response factors of four calibration standards in the concentration range 0.125–1.25 $\mu g\ cm^{-3}$ where the response factor (rf) was calculated as follows:

$$\text{rf} = \frac{\text{X peak area}}{\text{internal standard peak area}} \times \frac{\text{concentration of internal standard}}{\text{concentration of X}}$$

Calibration standards were processed and quantified every two weeks to check analytical control (using linear regression analysis and rf) as well as the condition of the instrument. Generally the rf will not deviate by ±20% thoughout the life of the column. The butyltin peak areas are normalized against the internal standard, tripentylhexyltin.

Spiked recoveries

Table 2 illustrates spiked recovery data for mussels and sediment from San Diego Bay. Diluted TBTCl stock solution was added in linear volumetric amounts to four 10 g aliquots of homogenized tissue and sediment. One blank aliquot of tissue and sediment was processed as well to check if recoveries were similar for different spike concentrations (i.e. by linear regression). The spiked samples were refrigerated overnight before processing.

Optimization of methylene chloride extraction/ Grignard derivatization for solids analysis

There were several advantages in using the methylene chloride extraction/Grignard derivatization method. Methylene chloride is a semipolar solvent that extracted TBT with greater than 90% recovery. DBT-spiked recovery from sediment was better than 90% but MBT had less than 12% recovery and the standard deviation was greater than ± 100%. A complexing agent such as tropolone would increase the extraction efficiency of other alkyltins but did not increase the recovery of TBT and caused non-linear recoveries in standard addition tests. More importantly, the tetraalkyltin derivatives were thermally stable in the GC injector. Our experience and studies using a GC MS have shown that anion exchange occurs for both alkyltin halides and alkyltin hydrides,[20] dependent upon the history of the injector. In addition, the tetraalkyltin derivatives were chemically stable over a 10-day period (if frozen), and were amenable to Florisil clean-up which removes some of the more polar compounds as well as particulates.

The disadvantages of using this method are that signal damping may occur due to co-eluants in the detector flame, and that evaporative losses of TBTCl may be significant at high alkyltin concentrations. In particular, we noticed a signal damping of the internal standard relative to other peaks that resulted in higher quantitated butyltin concentrations. Given a solvent/sample ratio of 20 cm^3/5 g, we also noticed that concentrating the extracts by 20-fold or more caused an erratic internal standard recovery. Since spiked recoveries of the internal standard from sample blanks were better than 90%, the apparent lower recoveries might have been an artifact caused by co-eluting compounds in the detector flame.[21] Concentrating the matrix one- or two-fold reduced this effect and sensitivity of the method was not significantly compromised. Usually a comparison of a linear regression analysis of standard additions against that of calibration standards indicated whether significant matrix effects were present. Studies by Craig *et al.*[20] have shown that significant evaporative losses of TBT^+ occurred at concentrations greater than 3000 ng g^{-1}. To avoid this, we reduced the concentration and drying time needed by drying and derivatizing a 2-cm^3 aliquot of the methylene chloride layer. Extracts were removed before complete dryness. Standard deviations for spiked recoveries and ambient environmental samples were normally 20% or less and average spiked recoveries were greater than 95% (Tables 2 and 3).

RESULTS AND DISCUSSION

Figure 5 shows typical results of the analysis of a seawater sample with fairly low butyltin concentrations. Calibration standards are linear to at least

Table 3 Data from San Diego Bay mussels (μg g^{-1} wet weight)

Station	MBT (±SD)	DBT (±SD)	TBT (SD)
SDM4 19	0.076 (±0.004)	0.169 (±0.007)	0.252 (±0.020)
SDM4 53B	0.257 (±0.029)	0.538 (±0.025)	1.067 (±0.220)
SDM4 2B	BDL ±[a]	0.087 (±0.016)	0.068 (±0.011)

Three replicates are analyzed for each station. Each replicate consists of approximately five homogenized mussels for a total of 15 mussels per station.
[a]Below detection limit.

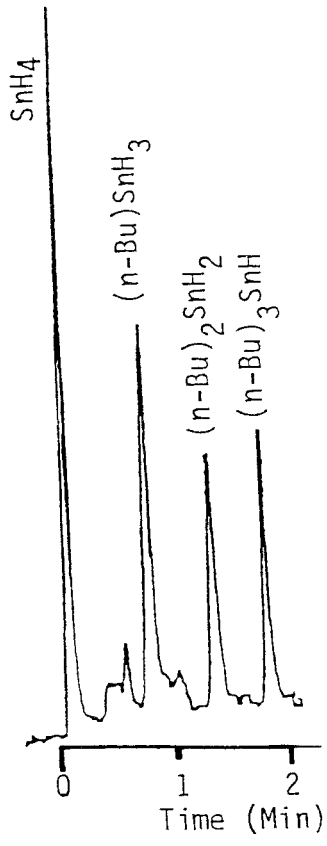

Figure 5 Speciation of butyltins in seawater. Quantities of the compounds as the cation are as follows: $(nBu)Sn^{3+}$, 1.3 ng; $(nBu)_2Sn^{2+}$, 64 ng; $(nBu)_3Sn^{+}$ 1.3 ng.

70 ng dm^{-3} as shown in Fig. 1. Seawater samples from marinas where high butyltin concentrations were expected were diluted with blank seawater to keep the values on the calibration curve, rather than exceeding the limits of linearity.

Our current absolute detection limits were obtained by running a series of blank seawater samples spiked with about 0.5 ng of each butyltin compound. The detection limits based on three standard deviations (σ) of these near-background standard additions were 100 pg for tributyltin, 40 pg for dibutyltin, and 65 pg for monobutyltin calculated as the cation. This resulted in environmental detection limits in seawater of 0.08–0.2 ng dm^{-3} as the cation assuming a sample volume of 500 cm^3. This compares well with the previous lowest TBT detection limit of 1.2 ng dm^{-3} as the cation assuming a sample volume of 100 cm^3.[22,23] Our absolute tributyltin sensitivity ranged from 180 pg to 80 pg. This range reflects differences in the five systems we use for monitoring butyltin concentrations.

Table 3 reports *Mytilus edulus* tissue monitoring data from San Diego Bay. Station SDM4 19 is located near a commercial marine dry dock facility. Average TBT water concentrations were 20 ng dm^{-3} (Seligman *et al.* in Ref. 1). Station SDM4 2B is located at the mouth of San Diego Bay where TBT concentrations were 3 ng dm^{-3} (Seligman *et al.* in Ref. 1). Station SDM4 53B is located in a small yacht harbor where TBT water concentrations are 50–100 ng dm^{-3}. Similar monitoring studies by Huggett *et al.*[14] have shown TBT concentrations as high as 1.5 $\mu g\ g^{-1}$ wet weight in oysters taken near a marina. Mussels taken from Sarah Creek (between two marinas and a boatyard) had a mean value of 0.834 $\mu g\ g^{-1}$ wet weight.[14] A comparison of the detection limits of some analytical methods (Table 4) along with a California Fish and Game intercalibration study (Stephenson *et al.*, Ref. 2, p. 1334) indicates that several methods might be useful for monitoring TBT in tissue and sediment provided care is taken to minimize matrix effects and thus quantitation errors. Recovery data for these methods (tissues) are as follows: 100% (Ref. 24), 105% (Ref. 25), 96% (our study), 93% (Ref. 26). As mentioned previously, standard additions before extraction (to check procedural variability) or after extraction (to check matrix effects) serve as a good indicator of analytical control.

Table 4 Comparison of some analytical methods

Method	Limits of detection (ng g^{-1} wet weight)	Ref.
Hydride generation/AA	11–25	24
CH_2Cl_2/AA	2.5	25
CH_2Cl_2/Grignard/FPD	10–20	Present study
CH_2Cl_2/hydride/FPD	10	26

CONCLUSION

In view of recent legislation in California and other states banning the use of TBT antifouling paints on pleasure craft, the ability to measure low levels of TBT will be important in order to monitor compliance and the effects of the ban. By changing burner design and removing active sites from the trap, we have attained

sub-part-per-trillion detection limits of butyltins in seawater. We hope to adapt this hydride method to measure and speciate other organometallic toxicants such as lead, arsenic and selenium in the marine environment.

Improvement in the measurement of butyltins in tissues and sediments was achieved by optimizing extraction parameters and reducing matrix effects. Use of internal standards and quality control checks have also improved our analytical variability.

Acknowledgements This work was funded by the Office of Chief of Naval Research and the David Taylor Ship Resarch and Development Center under the Navy Energy Research and Development Program Element 63724N. Kathy Shulte aided in designing monitoring protocols and John Testa helped by synthesizing internal standards. Cesar Clavell was very helpful in providing design and computer assistance. Aldis Valkirs, Peter Stang, Mark Kram and Steve Frank helped to test the optimizations. Marca Doeff and Aldis Valkirs were very helpful as proofreaders.

REFERENCES

1. *Proceedings, Oceans 86*, Vol 4, Organotin Symposium. Copies available from IEEE Service Center, 445 Hoes Lane, Pisataway, NJ 08854, USA
2. *Proceedings, Oceans 87*, Vol 4, Organotin Symposium. Copies available as for Ref. 1
3. Salazar, M H and Salazar, S M 1988, *Proceedings Oceans 88*, Vol. 4, p 1188 Organotin Symposium. Copies available from IEEE, 345 E. 47th Street, New York, NY 10017
4. Matthias, C L, Bellama, J M, Olson, G J and Brinckman, F E *Environ. Sci. Technol.*, 1986, 20: 609
5. Maguire, R J and Huneault, H *J. Chromatog.*, 1981, 209: 458
6. Meinema, H A, Burger-Wiersma, T, Versluis-de Haan, G and Geevers, E C *Environ. Sci. Technol.*, 1978, 12(3): 288
7. Mueller, M D *Fresenius Z. Anal. Chem.*, 1984, 317: 32
8. Mueller, M D *Anal. Chem.*, 1987, 59: 617
9. Maguire, R J, Tkacz, R J, Chau, Y K, Bengert, G A and Wong, P T S *Chemosphere*, 1986, 15(3): 253
10. Unger, M A, MacIntyre, W G, Greaves, J and Hugget, R J *Chemosphere*, 1986, 15(4): 461
11. Hodge, V F, Seidel, S L and Goldberg, E D *Anal. Chem.*, 1979, 51: 1256
12. Valkirs, A O, Seligman, P F, Vafa, G, Stang, P M, Homer, V and Lieberman, S H *Naval Ocean Systems Center Technical Report* No 1037, 1985
13. Valkirs, A O, Seligman, P F, Olsen, G, Brinckman, F E, Matthias, D T and Bellama, J M, *Analyst*, 1987, 112: 17
14. Rice, C D, Espourteille, F A and Huggett, R J *Appl. Organomet. Chem.*, 1987, 1: 541
15. Sasaki, K, Ishizaka, T, Suzuki, T and Saito, Y, *J. Assoc. Off. Anal. Chem.*, 1988, 71(2): 360
16. Maguire, R J *Environ. Sci. Technol.*, 1984, 18: 291
17. Donard, O F, Rapsomanikis, S and Weber, J H *Anal. Chem.*, 1986, 58: 772
18. Davis, A G and Smith, P J The synthesis, reactions and structures of organometallic compounds. In: *Comprehensive Organometallic Chemistry*, Wilkinson, G W (ed), Pergamon Press, New York, 1982, pp 519–627
19. Ingham, R K, Rosenberg, S D and Gilman, H *Chem. Rev.*, 1960, 60459
20. Clark, S, Ashby, J and Craig, P J *Analyst*, 1987, 112: 1781
21. Aue, W A and Flinn, C G *J. Chromatogr.*, 1977, 142: 145
22. Randall, L, Donard, O F and Weber, J J *Anal. Chim. Acta*, 1986, 184: 197
23. Donard, O F X, Randall, L, Rapsomanikis, S and Weber, J H *Int. J. Environ. Anal. Chem.*, 1986, 27: 55
24. Han, J S and Weber, J H *Anal. Chem.*, 1988, 60: 316
25. Stephenson, M D and Smith, D R *Anal. Chem.*, 1988, 60: 696
26. Sullivan, J J, Torkelson, J D, Wekell, M M, Hollingworth, T A, Saxton, W L and Miller, G A *Anal. Chem.*, 1988, 60: 626