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SHORT PAPER

Evaluation of extraction techniques for butyltin compounds in sediment

Shuzhen Zhang,* Y K Chau, W C Li and A S Y Chau
National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, Canada, L7R 4A6

There have been many methods available for the determination of butyltin compounds in sediment. The variations of these methods are not in the methods of determination but rather in the extraction of these compounds from the complex matrices. All of these methods have not been critically compared or evaluated, mainly because of the lack of a suitable reference sediment for butyltin compounds.

Recently, the National Research Council of Canada has introduced a reference sediment (PACS-1) which contains certified values of butyltin compounds. The present study compares the recoveries of ten extraction techniques for butyltin species using ethylation derivatization and GC AA as the method of determination. Of these ten methods, only four were found satisfactory for extraction of the dibutyltin and tributyltin species. None of the methods evaluated, however, could quantitatively extract monobutyltin from sediment.

Keywords: Butyltin, analysis, sediment, extraction, ethylation

INTRODUCTION

Studies on butyltin compounds have intensified after the discovery of spatfall inhibition and shell growth anomalies on Pacific oyster culture.[1] Subsequent investigations have found that butyltin compounds occur in environmental samples, particularly in harbour areas, because of their extensive use.[2,3]

Speciation and determination of butyltin compounds have been well established and have been applied to different environmental materials including sediments. For the analysis of biological samples and sediments, the major consideration is not of the determination itself but of the extraction of these compounds from the complex sample matrices. There are a number of techniques developed for the extraction of butyltin from sediment. These methods, however, were developed in different laboratories with their own purposes, and were based primarily on two major considerations: first, the method of extraction so developed must be compatible with the determination technique used; secondly, the type of sediment dealt with might require special digestion procedures. Thus, the procedure developed in one laboratory for their sediment may not be suitable for other laboratories and other types of sediments. All these extraction techniques, however, have not been critically compared or evaluated, mainly because of the lack of a suitable reference sediment for butyltin species. There is only one limited study available on the comparison of acid leaching procedures for recovery of butyltin from sediments using the hydride generation ($NaBH_4$ derivatization) technique.[4]

Recently, the National Research Council of Canada introduced a reference sediment (PACS-1) which contains certified values of butyltin species. With this sediment, comparison of extraction techniques now becomes feasible. The present paper presents an investigation of the recoveries of ten selected extraction methods for butyltin species from sediment using the ethylation derivatization method and GC AA determination. Of these ten methods, some are taken directly from published work, and others are modified in our laboratory in order to investigate the effects of chelating agents and pH conditions for extraction and derivatization.

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* Visiting Scientist, Center for Eco-Environmental Sciences, Academia Sinica, Beijing, China.

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EXPERIMENTAL

Monobutyltin trichloride (MBT), dibutyltin dichloride (DBT) and tributyltin chloride (TBT) were obtained from Alfa Products, Ward Hill, MA, USA. Standard butyltin solutions (1000 μg cm^{-3} as Sn) were prepared by dissolving appropriate amounts of the butyltin in water, and stored in the dark at 4°C. The internal standards addition technique was used in calculating the concentrations of butyltin in each extraction.

The reference sediment (PACS-1) was obtained from the National Research Council of Canada, Ottawa. In each method to be evaluated, 1 g of sediment was used for extraction of the butyltin species, following as closely as possible the original procedure. A 1 cm^3 portion of the extract was removed for ethylation with 0.2 cm^3 of ethylmagnesium bromide. Excess ethylmagnesium bromide was destroyed by shaking with 2 cm^3 of 0.5 mol dm^{-3} H_2SO_4. The hexane phase was kept in a small vial containing anhydrous sodium sulphate, and stored in the dark for analysis by the GC AA method.[5] Analyses were run in four replicates. The averaged recovery results were compared with the certified values to assess their corresponding recoveries.

Extraction methods

All the extractions were carried out in a mechanical shaker in the fume cupboard under subdued laboratory lighting conditions.

Method 1
Reference sediment (1 g) was extracted for 1 h in the fume cupboard with 5 cm^3 of 0.5% tropolone in hexane after addition of 20 cm^3 of water, 6 g sodium chloride, 2 g sodium benzoate and 1 g potassium iodide.

Method 2: combination of method 1 and Sasaki *et al.* (1988)[7]
(i) Sediment was extracted with 5 cm^3 0.5 mol dm^{-3} HCl in methanol for 4 h.
(ii) After addition of 10 cm^3 of saturated aqueous sodium chloride solution, the mixture was extracted with 5 cm^3 0.5% tropolone in hexane for 2 h.

Method 3: Rice *et al.* (1987)[8]
Sediment was extracted in a Soxhlet with 5 cm^3 hexane for 48 h after 5 cm^3 water and 6 g sodium chloride had been added.

Method 4: Maguire (1984)[3]
Sediment was refluxed for 2 h with 20 cm^3 0.5% tropolone in hexane.

Method 5: Siu *et al.* (1989)[9]
(i) Sediment was sonicated with 4 cm^3 of 10 mol dm^{-3} HCl and 8 cm^3 of methanol for 1 h.
(ii) The mixture was shaken vigorously for 3 min after addition of 5 cm^3 of iso-octane.
(iii) The mixture was centrifuged at 2000 rpm (550*g*) for 10 min.

Method 6: modified Siu *et al.* (1989)[9]
This method is the same as method 5, except for the use of 0.5% tropolone in hexane instead of iso-octane in the extraction.

Method 7: Dooley and Vafa (1986)[10]
(i) Sediment was shaken with 10 cm^3 HCl (1:1, v/v) for 1 h.
(ii) The mixture was extracted with 5 cm^3 dichloromethane for 4 h after the addition of 6 g of sodium chloride.
(iii) The solution was evaporated to dryness, followed by addition of 5 cm^3 of hexane, to remove dichloromethane which interferes with the Grignard reaction. The final solution was in 5 cm^3 of hexane.

Method 8: Desauziers *et al.* (1989)[4]
(i) Sediment was shaken with 5 cm^3 acetic acid for 4 h.
(ii) After addition of 20 cm^3 of water, the mixture was extracted with 5 cm^3 0.5% tropolone in hexane for 1 h.

Method 9: modified Desauziers *et al.* (1989)[4]
(i) Sediment was shaken with 5 cm^3 acetic acid for 4 h.
(ii) After neutralization with 30% NaOH to pH 6.5, the mixture was extracted with 5 cm^3 of 0.5% tropolone in hexane for 1 h.

Method 10: Siu *et al.* (1989)[11]
(i) Sediment was shaken with 2 cm^3 of 10 mol dm^{-3} HCl and 1 cm^3 of methanol for 1 h.
(ii) The mixture was extracted with 2 cm^3 of hexane/isobutyl acetate (80:20, v/v) for 30 min.

RESULTS AND DISCUSSION

It is a difficult task to compare sediment extraction methods because: (1) sediment compositions are different; (2) sediment extraction procedures are normally developed to be compatible with the

Table 1 Summary of extraction methods of BuSn from sediment and biological samples

Species[a]	Medium	Method	Author
BuSn	Sediment	Digest in HNO_3, HF/HCl	Hodge *et al.* (1979)[12]
TBT	Tissue	Homogenized, HCl + EtOAc, NaCl	Arakawa *et al.* (1981)[13]
TBT, DBT	Sediment	Reflux 30 min in HCl/MeOH	Hattori *et al.* (1984)[14]
BuSn	Sediment	Benzene + tropolone, reflux 2 h	Maguire (1984)[3]
BuSn	Oyster	HCl, stir, extract with CH_2Cl_2	Dooley *et al.* (1986)[10]
TBT, DBT	Salmon	Hexane, no tropolone	Short and Thrower (1986)[15]
MeSn, BuSn	Sediment	2.5 mol dm^{-3} HCl, 2.5 mol dm^{-3} $CaCl_2$	Randall *et al.* (1986)[16]
TBT	Oyster Sediment	Hexane extract, 24 h (Soxhlet) 48 h	Rice *et al.* (1987)[8]
BuSn	Sediment	Ethereal tropolone	Muller (1987)[17]
TBT	Sediment, biological	HCl, stirred, extracted with CH_2Cl_2, use GF AA	Stevenson and Smith (1988)[18]
TBT, DBT	Fish	HCl/MeOH; hexane	Sasaki *et al.* (1988)[7]
Tin(IV)	Biological	EtOAc + HCl + NaCl	Tsuda *et al.* (1988)[19]
BuSn	Sediment	MeOH/HCl sonication: (1) Toluene/i-BuOAC/tropolone (2) Hexane/i-BuOAc	Siu *et al.* (1989)[11]
TBT	Sediment	(1) MeOH/HCl sonication, iso-octane extraction (2) Butanol sonication	Siu *et al.* (1989)[9]
BuSn	Sediment, biological	Cold HOAc, 4 h	Desauziers *et al.* (1989)[4]

[a] Abbreviations: BuSn, butyltin species; MeSn, methyltin species; TBT, tributyltin; DBT, dibutyltin.

subsequent methods of determination preferred by the researcher, e.g. use of the hydride generation method will suggest a work-up solution in an aqueous, acidic medium; and (3) the procedures used may not be exactly reproducible from laboratory to laboratory. The intention of this study, however, is to evaluate the extraction recoveries of butyltin species by several published procedures, using a reference sediment. After extraction of the sediment, the extracts are analysed by the same determination technique, i.e. ethylation with ethylmagnesium chloride for GC AA determination. The reference sediment (PACS-1) used is a marine sediment, which has a composition different from that of a freshwater sediment. In spite of these discrepancies, it is hoped that through this comparison an optimum sediment extraction method can be established.

The significant sources of organotin compounds in the environment are mainly anthropogenic with a comparatively small fraction being formed as a result of biological and chemical methylation. Their occurrence in sediment is either via superficial absorption or by organically complexation onto the sediment, or by incorporation in the

Table 2 Recovery of butyltin compounds from reference sediment (PACS-1) by different extraction techniques

PACS-1 (reference sediment, National Research Council, Canada) certified values ($\mu g\ g^{-1}$): $BuSn^{3+}$, 0.28 ± 0.17; Bu_2Sn^{2+}, 1.16 ± 0.18; Bu_3Sn^{+}, 1.27 ± 0.22.

	Concentration found ($\mu g\ g^{-1}$)[a]		Recovery (%)[b]	
Method	Bu_2Sn^{2+}	Bu_3Sn^{+}	Bu_2Sn^{2+}	Bu_3Sn^{+}
1	0.23 ± 0.04	0.24 ± 0.03	19.4	18.9
2	0.97 ± 0.09	1.00 ± 0.14	83.6	78.7
3	0.18 ± 0.01	0.38 ± 0.02	15.5	29.9
4	0.77 ± 0.24	1.08 ± 0.18	66.4	85.1
5	—	1.14 ± 0.09	—	89.7
6	—	1.34 ± 0.17	—	105.5
7	1.36 ± 0.22	1.09 ± 0.06	117.2	85.8
8	1.09 ± 0.11	1.08 ± 0.11	94.0	85.0
9	0.64 ± 0.10	1.52 ± 0.57	55.2	119.7
10	1.14 ± 0.2	1.33 ± 0.06	98.4	104.7

[a] Analyses in replicate ($n = 4$), expressed as Sn in $\mu g\ g^{-1}$ (dried wt).

[b] Recoveries were calculated with reference to the certified values.

— Not detected.

biological debris, and there is no involvement in mineralogical processes. Therefore, complete dissolution or total breakdown of the sediment, as is often practised in most sediment analyses, is not considered necessary. For extraction of organotin compounds from sediment, there are several basic approaches:

(1) Direct extraction of sediment with an organic solvent with/without a chelating agent.
(2) Acid leaching of sediment.
(3) Alkali leaching of sediment.
(4) A combination of any of these techniques.

There are many methodologies developed around the above techniques, and each one so developed has its own merit and justification. For example, methods using the hydride generation technique in the final determination tend to use acid digestion for extracting organotin because of the necessity of sending the samples in aqueous medium to the hydride generator. For methods which use alkylation in preparing the derivatives for GC separation, it is necessary to have the samples in an organic solvent for alkyl derivatization. For sediments with high organic contents, the alkali or acid digestion is more suitable. Table 1 summarizes some of the published techniques for butyltin compounds in a variety of environmental samples.

Extraction recovery results summarized in Table 2 indicate that several methods (2, 7, 8, 9) are satisfactory for the extraction of DBT and TBT compounds. The extraction must be carried out in an acidic medium. The recoveries of monobutyltin were erratic and non-reproducible by all the methods tested. Those methods that have good recoveries for dibutyl- and tributyl-tin did not recover monobutyltin quantitatively. The analytical method using tropolone/hexane extraction and ethylation on standard solutions has been proved satisfactory for all three butyltin species in a water matrix;[5] therefore, the deficiencies must be associated with the sediment extraction. In a recent investigation of sediment extraction with tropolone in dichloromethane, followed by GC AA determination,[6] quantitative recovery for tributyltin was also reported. It is unfortunate that recoveries of dibutyltin and monobutyltin were not investigated in this study, and we did not investigate the recoveries of this method because it was similar to several of the extraction methods we included using tropolone in hexane.

From the investigations in this study, we can conclude that none of the methods evaluated could recover monobutyltin from the reference sediment satisfactorily. Inorganic tin(IV) was not extracted by all the methods investigated, although it is known that tin(IV) can be extracted by tropolone/hexane from water matrix.[5] Further investigations are required in these aspects.

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