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MANAGEMENT PERSPECTIVE

Studies on butyltin compounds in the environment have intensified after the discovery of spatfall inhibition and shell growth anomalies on Pacific oyster culture. Subsequent investigations have found that butyltin compounds occur in fish and aquatic organisms in harbour areas because of their extensive uses in anti-fouling paint formulation.

There are many methods available for the determination of butyltin species in sediment. The variations of the methods are not in the methods of determination, but rather in the extraction of these compounds from the complex sample matrices. All these methods have not been critically compared or evaluated, mainly because of the lack of a suitable reference sediment for butyltin species. Recently, National Research Council of Canada has introduced a reference sediment (PACS-1) which contains certified values of butyltin species. With this sediment, comparison of the extraction efficiency now becomes feasible. The present paper presents an investigation of the recoveries of ten extraction techniques for butyltin species, using ethylation derivatization and GC-AAS as the method of determination. Of these ten methods, only three were found satisfactory for extraction of the dibutyltin and tributyltin species. None of the methods evaluated, however, could extract monobutyltin quantitatively from sediment.

The senior author, Shuzhen Zhang is a visiting scientist from Center for Eco-Environmental Sciences, Academia Sinica, Beijing, China, under the sponsorship of World University Service of Canada.

PERSPECTIVE GESTION

Les études sur les composés de butylétain dans l'environnement ont été intensifiées après la découverte d'une inhibition de la fixation du naissain et d'anomalies de croissance des coquilles dans les cultures d'huîtres géantes du Pacifique. Des enquêtes subséquentes ont permis de constater que l'on trouve des dérivés butylétain dans le poisson et les organismes aquatiques des zones portuaires à cause des importantes utilisations de formulations de peintures anti-salissures.

Il existe un grand nombre de méthodes disponibles pour le dosage des espèces de butylétain dans les sédiments. Ces méthodes diffèrent non pas par la technique de dosage, mais plutôt par celle de l'extraction de ces composés des matrices complexes des échantillons. Toutes ces méthodes n'ont pas été comparées ou évaluées de façon critique, surtout à cause du manque d'échantillons de référence appropriés de sédiments pour les espèces de butylétain. Récemment, le Conseil national de recherches du Canada a annoncé la disponibilité d'un sédiment de référence (PACS-1) qui contient des valeurs certifiées d'espèces de butylétain. Avec ce sédiment, la comparaison de l'efficacité des extractions est maintenant réalisable. Le présent document explique les recherches sur la récupération obtenue avec dix techniques d'extraction d'espèces de butylétain, basées sur la preparation de dérivés par éthylation et la CG-SAA comme méthode de dosage. De ces dix méthodes, seulement trois ont donné des résultats satisfaisants pour ce qui est de l'extraction des espèces de dibutylétain et de tributylétain. Toutefois, aucune des méthodes évaluées ne pouvait extraire quantitativement le monobutylétain des sédiments.

L'auteur principal Shuzhen Zhang est un chercheur invité du Centre des sciences éco-environnementales, Academia Sinica, Beijing, Chine, parrainé par Entraide universitaire internationale du Canada.

ABSTRACT

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 these methods have not been critically compared or evaluated, mainly because of the lack of a suitable reference sediment for butyltin compounds.

Recently, 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-AAS as the method of determination. Of these ten methods, only three were found satisfactory for extraction of the dibutyltin and tributyltin species. None of the methods evaluated, however, could quantitatively extract monobutyltin from sediment.

RÉSUMÉ

Il existe de nombreuses méthodes pour le dosage des composés de butylétain dans les sédiments. Ces méthodes diffèrent non pas au niveau des techniques de dosage, mais plutôt des techniques d'extraction de ces composés existant dans des matrices complexes. Toutes les méthodes n'ont pas été comparées ou évaluées de façon critique, surtout à cause du manque d'échantillons de référence appropriés contenant des composés de butylétain.

Récemment, le Conseil national de recherches du Canada a annoncé la disponibilité d'un sédiment de référence (PACS-1), qui contient des valeurs certifiées de composés de butylétain. La présente étude compare les taux de récupération d'espèces de butylétain obtenues à l'aide de dix techniques d'extraction, utilisant la préparation de dérivés par éthylation et la GC-SAA comme méthode de dosage. De ces dix méthodes, seulement trois ont été jugées satisfaisantes pour l'extraction des espèces de dibutylétain et tributylétain. Toutefois, aucune des méthodes évaluées ne pouvait extraire quantitativement le monobutylétain des sédiments.

Evaluation of Extraction Techniques for Butyltin Compounds in Sediment

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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 uses (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 in the determination itself but in the extraction of these compounds from the complex sample matrices. There are a number of techniques developed for the the extraction of butyltin from sediment. These methods, however, were developed in different laboratories for their own purposes primarily with two major considerations in mind; 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 technique (4).

Recently, 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 extraction methods for butyltin species from sediment using ethylation derivatization method and GC-AAS determination. Of these ten methods, some are directly taken from published work, some are modified in our laboratory in order to investigate the effects of chelating agents, and pH conditions before and after extraction.

EXPERIMENTAL

Monobutyltin chloride, dibutyltin dichloride and tributyltin chloride were obtained from Alfa Products, Ward Hill, MA. Standard butyltin solutions (1000 μg/ml as Sn) were prepared by dissolving appropriate amounts of the butyltin in water. Internal standards addition technique was used in calculating the concentrations of butyltin in each extraction.

Reference sediment (PASC-1) was obtained from National Research Council of Canada, Ottawa. In each method to be evaluated, one gram of sediment was used for extraction of the butyltin species, following as close as possible the original procedure. One ml of the extract was removed for ethylation with 0.2 ml of ethylmagnesium bromide. Excess ethylmagnesium bromide was destroyed by shaking with 2 ml of 0.5 M H_2SO_4. The hexane phase was stored in a small vial containing anhydrous sodium sulfate for analysis by the GC-AAS method (5).

Analyses were run in four replicates. The averaged recovery results were compared to the certified values to assess their corresponding recoveries.

Extraction Methods.

Method 1.

Reference sediment (1 g) was extracted with 5 ml 0.5% tropolone in hexane for 1 hr after addition of 20 ml of water, 6 g NaCl, 2 g sodium benzoate and 1 g KI.

Method 2. Combination of (1) and Sasaki et al. 1988 (6)

(i) Sediment was shaken with 5 ml 0.5M HCl in methanol for 4 hr.

(ii) After addition of 10 ml of sat. aqueous NaCl solution, the mixture was extracted with 5 ml 0.5% tropolone in hexane for 2 hr.

Method 3. Rice et al. 1987 (7)

Sediment was extracted in Soxhlet with 5 ml hexane for 48 hr. after 5 ml H_2O and 6 g NaCl added.

Method 4. Maguire, 1984 (3)

Sediment was refluxed for 2 hr. with 20 ml 0.5% tropolone in hexane.

Method 5. Siu et al. 1989 (8)

(i) Sediment was sonicated with 4 ml 10M HCl and 8 ml of methanol for 1 hr.

(ii) The mixture was shaken vigorously for 3 min after addition of 5 ml isooctane.

(iii) Centrifuge at 2000 rpm for 10 min.

Method 6.

Same as method 5, except the use of 0.5% tropolone in hexane instead of isooctane in the

extraction.

Method 7. Dooley and Vafa, 1986 (9)

(i) Sediment was shaken with 10 ml 1:1 HCl for 1 hr.

(ii) The mixture extracted with 5 ml dichloromethane for 4 hrs. after the addition of 6 g of NaCl.

(iii) Solution was evaporated to dryness, after addition of 5 ml of hexane, to remove dichloromethane which interferes with the Grignard reaction. The final solution was in 5 ml of hexane.

Method 8. Desauzier, 1989 (4)

(i) Sediment was shaken with 5 ml acetic acid for 4 hr.

(ii) After addition of 20 ml of water, the mixture was extracted with 5 ml 0.5% tropolone in hexane for 1 hr.

Method 9. Modified Desauzier, 1989 (4)

(i) Sediment was shaken with 5 ml acetic acid for 4 hr.

(ii) After neutralization with 30% NaOH to pH=6.5, the mixture was extracted with 5 ml 0.5% tropolone in hexane for 1 hr.

Method 10. Siu et al. 1989 (10)

(i) Sediment was shaken with 2 ml of 10M HCl and 1 ml methanol for 1 hr.

(ii) The mixture was extracted with 2 ml of hexane-isobutylacetate (80:20) for 30 min after addition of 7 ml water.

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 for compatibility with the subsequent methods of determination, e.g. hydride generation method will prefer a workup solution in aqueous acidic medium, (3) the procedures used may not be exactly reproducible from laboratory to laboratory. The intention of this study, however, is to evaluate the extraction recovery of butyltin species by several published procedures, using a reference sediment. After extraction, the solutions are analyzed by the same determination technique, i.e. extraction with tropolone in hexane, followed by ethylation with ethylmagnesium chloride and GC-AAS determination. The reference sediment (PACS-1) used is a marine sediment, which has different composition than the 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 comparatively a small fraction being formed as a result of biological and chemical alkylation. Their occurrence in sediment is either superficially absorbed or organically complexed onto the sediment, or incorporated in the biological debris, and does not involve in mineralogical processes. Therefore, complete dissolution of the sediment as is often practised in most sediment analysis is not considered necessary. For extraction of organotin compounds from sediment, there are several basic approaches:

1. 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 their own merit and justification. For example, methods using 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 sediment with high organic content, the alkali or acid digestion is obviously more suitable. Table 1 summarizes the published techniques for butyltin compounds in a variety of environmental samples.

Extraction recovery results summarized in Table 2 indicated that several methods (2, 7, 8) are satisfactory for the extraction of DBT and TBT compounds. The extraction must be carried out in 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 tributyltin did not recover monobutyltin quantitatively. The analytical method using tropolone hexane extraction and ethylation on standard solutions has been proven satisfactory for all three butyltin species in water matrix (5); therefore, the deficiencies must be associated with the sediment extraction. From these experiments, we can conclude that none of the methods evaluated could recover monobutyltin from the reference sediment satisfactorily.

Inorganic Sn(IV) was not extracted by all the methods investigated, although it is known that

Sn(IV) can be extracted by tropolone from water matrix (5). Further investigations are required in these regards.

Table 1. Summary of extraction methods of BuSn from Sediment & Biological Samples

Species	Medium	Method	Authors
BuSn	Sediment	Digestin HNO_3,HF-HCl	Hodge et al, 1979 (11)
TBT	Tissue	Homogenize, HCl+EtOAc,NaCl	Arakawa et al, 1981(12)
TBT, DBT	Sediment	Reflux 30 min in HCl-MeOH	Hattori et al, 1984(13)
BuSn	Sediment	Bz + Tropo, reflux 2 hr	Maguire 1984 (3)
BuSn	Oyster	HCl stir, extract with CH_2Cl_2	Dooley et al, 1986 (9)
TBT, DBT	Salmon	Hexane, no Tropolone	Short & Thrower, 1986 (14)
MeSn, BuSn	Sediment	2.5M HCl, 2.5M $CaCl_2$	Randell et al, 1986 (15)
TBT	Oyster Sediment	Hexane extract, 24 h (Soxhlet) 48 h	Rice et al, 1987 (7)
BuSn	Sediment	Ethereal-Tropolone	Muller, 1987 (16)
TBT	Sediment, biological	HCl stirred, extracted with CH_2Cl_2 use GFAAS	Stephenson & Smith (17) 1988
TBT, DBT	Fish	HCl-MeOH; Hexane	Sasaki et al, 1988 (6)
Sn(IV)	Biological	EtOAc + HCl + NaCl	Tsuda et al, 1988 (18)
BuSn	Sediment	MeOH-HCl sonication (1) Toluene-i-BuOAC-Tropo (2) Hexane-i-BuOAc	Siu et al, 1989 (10)
TBT	sediment	(1) MeOH-HCl sonication i-octane extraction (2) butanol sonication	Siu et al, 1989 (8)
BuSn	Sediment biological	cold HOAc, 4 hr	Desauziers et al 1989 (4)

BuSn- butyltin species; MeSn - methyltin species; TBT - tributyltin; DBT - dibutyltin.

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

	Concentration found (ug/g)		Recovery (%)*	
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	85.06
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	0.59±0.16	1.47±0.06	50.9	115.7

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

Analyses in replicate (n=4), expressed as Sn in μg/g (dried wt.)

*Recoveries were calculated with reference to the certified values.

REFERENCES

1. Alizieu, C, TBT detrimental effects on syster culture in France - evolution since antifouling paint regulation. In: Organotin Symposium, Oceano-86 Conference, Washington, D C, 1986. Proc. vol. 4, IEEE, New York, pp.1130-1134.

2. Siligman, P F, Grovhoug, J G, Valkirs, A O, Stang, P M, Fransham, R, Stallard, M O, Davidson, B and Lee, R F Appl. Organomet. Chem., 1989, 3: 31-38.

3. Maguire, R J Environ. Sci.& Technol., 1984, 18: 291-294.

4. Desauziers, V, Leguille, F, Lavigne, R, Astruc, M and Pinel, R Appl. Organomet. Chem., 1989, 3: 469-474.

5. Tian, Shizhong, Chau, Y K and Liu, D Appl. Organomet. Chem., 1989, 3: 249-255.

6. Sasaki, K, Ishizaka, T, Suzuki, T and Saito, Y J. Assoc. Off. Anal. Chem., 1988, 71: 360-363.

7. Rice, C D, Espourteille, F A and Huggett, R J Appl. Organomet.Chem., 1987, 1: 541-544.

8. Siu, K W M, Gardner, G J and Berman, S S Anal. Chem., 1989, 61: 2320-2322.

9. Dooley, C A and Vafa, G Butyltin compounds and their measurement in oyster tissues. In: Organotin Symposium, Oceano-86 Conference, Washington, D C, 1986. Proc. vol. 4, IEEE, New York, pp. 1171-1176.

10. Siu, K W M, Maxwell, P S and Berman, S S J. Chromatogr., 1989, 475: 373-379.

11. Hodge, V F, Seidel, S L and Goldberg, E D Anal.Chem., 1979, 51: 1256-1259.

12. Arakawa, Y, Wada, O and Yu, T H Toxicol. Appl. Pharmacol., 1981,60: 1-7.

13. Hattori, Y, Kobayashi, A, Takemoto, S, Takami, K, Kuge, Y, Sugimae, A and Nakamoto, M J. Chromatogr., 1984, 315: 341-349.

14. Short, J W and Thrower, F P Mar. Pollut. Bull., 1986, 17: 542-545.

15. Randall, L, Han, J S and Weber, J H Environ. Technol. Lett., 1986,7: 571-576.

16. Muller, M D Anal. Chem., 1987, 59: 617-623.

17. Stephenson, M D and Smith, D R Anal. Chem., 1988, 60: 896-898.

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