

Determination of butyltin compounds in sediments by gas chromatography with flame photometric detector*

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Abstract—A method is described for the determination of butyltin species in sediments. The butyltin species were extracted from sediments with mixed solvent of benzene-hexane (2:1) after digesting with acetic acid under the sonication, then converted into volatile butyltin hydrides with solution of sodium tetrahydroborate. Butyltin hydrides were measured by gas chromatography with flame photometric detector. The detection limits were 4-10 ng tin per gram of sediment.

Keywords: butyltin species; sediments; gas chromatography.

1 Introduction

Organotin compounds have developed into important industrial commodities during recent decades. These compounds have been used for a variety of purposes as stabilizers for vinyl chloride polymers, catalysts, agricultural pesticides, and antifoulants etc. Environmental pollution, especially aquatic environmental pollution, caused by these compounds and their impact on the biota have raised the need for the development of reliable, rapid, sensitive analytical methods. Various analytical techniques have been used for the determination of organotin compounds in sediments (Tsuda, 1987; Desauziers, 1989; Maguire, 1984; Hattori, 1984). These include multiple extraction schemes followed by graphite furnace atomic absorption spectrophotometry, hydride purge and trap followed by flame atomic absorption spectrophotometry, and high performance liquid chromatography with a GFAAS detector. Gas chromatography, usually after suitable derivatization by Grignard reaction or hydride generation, can separate alkyltins, which can then be detected by flame photometric detectors, mass spectrometry, and a variety of non-specific detectors (Kojima, 1979; Hodge, 1979; Jewett, 1981; Siu, 1989). Maguire *et al.* (Maguire, 1987) reviewed mainly the aquatic environmental aspects of organotin compounds including methods of analysis, toxicity, environmental occurrence, persistence and fate. Several aspects of the chemistry and behavior of organotin compounds in general have been the subjects of excellent reviews. The further research includes direct determination of organotin chlorides by

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GC (Siu, 1989), quartz surface - induced luminescence of tin (Jiang, 1991), bio - degradation of organotin (Tian, 1989) and adsorption and desorption of organotins in sediments (Kram, 1989).

For developing an analytical method and for reporting preliminary results on concentrations of butyltin species in a variety of sediments, we developed a detection technique. Butyltin species are extracted into organic solvents and subsequently hydrided to form butyltin hydrides $\text{Bu}_n\text{SnH}_{(4-n)}$. These hydrides are easily separated, then detected by GC with flame photometric detector. The present method has the advantage of avoiding multiple step manipulations, which might introduce contamination or lead to loss of the analyte. The details of this method are reported in this paper.

2 Experimental

2.1 Instrumentation and GC condition

GC - 6AM gas chromatograph (Shimadzu Co., Japan) was used. The detector is a flame photometric detector with the sulphur interference filter (390 nm). A $2\text{m} \times 3\text{mm}$ (I. D.) glass column packed with 1.5% OV - 101 on Chromosorb G (80—100 mesh) was used under the following condition: oven temperature programme, initial 140°C hold 2 min, temperature ramp at $20^\circ\text{C}/\text{min}$, final 190°C hold 15 min; the injector and detector temperature were 200°C and 230°C respectively; nitrogen, hydrogen and air flow - rate, were 40 ml/min, 40 ml/min and 50 ml/min, respectively.

2.2 Reagents

All chemicals were reagent grade without further purification. Bis (dibutyltin) oxide (96%) was obtained from Ciba - Geigy. Tributyltin chloride (98.6%) and tetrabutyltin (99.4%) were obtained from M&T Chemicals Inc., USA. Each butyltin compounds was dissolved in methanol at a concentration of 1 mg tin/ml as a stock solution. Working standard solutions were diluted with methanol or distilled water before use.

2.3 Analytical procedure

A 2g of sediment plus described butyltin compounds spikes was sonicated with 10 ml of pure acetic acid for 1.5 h. The suspension was then extracted with 20 ml of benzene - hexane (2 : 1) after addition of 20 ml of water and shaken for 2 h. The organic phase was separated by centrifugation at 800 r/min for 10 min. A 10 ml volume of the organic phase was transferred into a separating funnel, then reacted with 5.5 ml of aqueous NaBH_4 after adding 20 ml of water and shaken for 15 min. A $2\ \mu\text{l}$ vol-

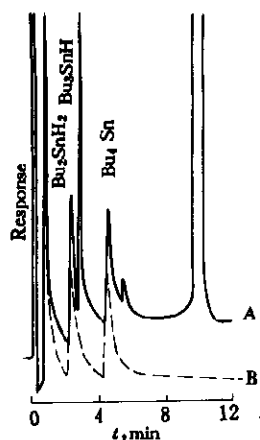


Fig. 1 Chromatogram of butyltin hydrides

A; butyltin species in sediment B; butyltin species

ume of the extract was injected into the chromatograph. Fig. 1 shows a typical chromatogram of butyltin hydrides.

2.4 Calibration curves

10 ml of solutions containing different amount of butyltin compounds and 1 ml of NaBH_4 were extracted with 2 ml of benzene - hexane (2 : 1) solution for 15 min. The calibration curves were constructed by plotting the peak heights versus the amount of tin in butyltin compounds.

3 Results and discussion

It is more difficult to analyze butyltin species in sediment than in water, because sediment collected from different areas may have different chemical and physical properties and complicated composition. It is realized that separation and extraction of butyltin species from sediment is crucial for a successful determination method which should be suitable to different types of sediments.

3.1 Digestion of sediments

Direct extraction of butyltin species from sediment with organic solvents resulted in poor extraction efficiencies, so it is necessary to digest sediment samples before extraction. We tried several published digestion processes and found that only inorganic acids, such as HCl , HNO_3 , were not suitable as digestion agents to quantitative analysis of butyltin species in sediments. The quantitative recoveries could be obtained by using HCl and MeOH in proper proportion to digest sediments. Table 1 shows that the complete recoveries of $\text{Bu}_2\text{Sn}^{2+}$ and Bu_3Sn^+ were obtained when one part of HCl and nine parts of MeOH were used. We also found that the recoveries of the species would improve gradually with increase of MeOH content in HCl - MeOH . It must be pointed out that an increase amount of MeOH might cause such phenomenon analogous to emulsification which made the subsequent phase - separation very difficult or even almost impossible, an ideal recoveries of butyltin compounds and phase - separation were obtained when pure acetic acid was used as digestion agent. The following discussion will focus on the system using acetic acid as digestion agent.

Table 1 The effect of HCl - MeOH ratio on the extraction of butyltin species

Reagents	Ratio	Recoveries, %	
		$\text{Bu}_2\text{Sn}^{2+}$	Bu_3Sn^+
HCl		150	33
HCl - MeOH	9 : 1	96	46
HCl - MeOH	4 : 1	123	61
HCl - MeOH	2 : 1	164	72
HCl - MeOH	1 : 9	107.5	95.1

3.2 The concentration of acetic acid

The recoveries of butyltin species in spiked sediment at various concentrations of acetic acid were measured. The results showed that, in general, the recoveries of $\text{Bu}_2\text{Sn}^{2+}$ and Bu_3Sn^+ al-

most kept the same when the concentration of acetic acid was at the range of 25% to 100%, however, the recoveries of Bu_4Sn varied significantly being 28.6%, 42.7% and 95.8% with the concentration of acetic acid changing from 25%, 50% to pure acetic acid, respectively. It is obvious that pure acetic acid is more suitable as digestion agent for the determination of butyltin species in sediments.

3.3 The selection of extraction solvents

Many solvents, such as benzene - hexane, toluene, dichloromethane, tropolone in benzene, toluene - isobutylacetate, isooctane etc., have been used to the extraction of butyltin species from sediments. The benzene - hexane procedure used in this experiment is preferred as it extracts all three butyltin species efficiently and has low boiling - point which make the following concentration procedure easy and rapid. The recoveries of butyltin species extraction with mixed solvent benzene - hexane at different ratio are listed in Table 2. The results show that benzene is an ideal solvent for the extraction of $\text{Bu}_2\text{Sn}^{2+}$ and Bu_4Sn , the recovery for Bu_3Sn^+ is about 80%, hexane is ideal for Bu_3Sn^+ and Bu_4Sn extraction, but not good enough for $\text{Bu}_2\text{Sn}^{2+}$. Therefore, we used mixed solvent of benzene - hexane in order to overcome the inadequacy of benzene or hexane when used alone. The mixed solvent of one part hexane and two parts benzene was proved to be the most suitable extraction solvent for all of these three butyltin species.

Table 2 The effects of benzene - hexane ratio on the extraction of butyltin species

Solvents	Ratio	Recoveries, %		
		$\text{Bu}_2\text{Sn}^{2+}$	Bu_3Sn^+	Bu_4Sn
Benzene		110.9	81.5	108.7
Hexane		71.5	110.1	104.3
Benzene/hexane	4 : 1	92.8	85.2	101.8
Benzene/hexane	3 : 1	134.6	69.2	105.2
Benzene/hexane	2.5 : 1	120	93.7	94.9
Benzene/hexane	2 : 1	91.8	114.9	94.8
Benzene/hexane	1 : 1	85.1	117.2	91.9

3.4 Sonication and extraction time

Many sediment characteristics such as its composition, grain size distribution, especially adsorption and desorption properties, would greatly influence the time of sonication and extraction. We found that two hours was long enough to get satisfactory extraction of species. We also found that good recoveries were obtained by shorter treatment time, even 0.5 h, for certain sediments.

3.5 The effects of NaBH_4 amount on hydridization reaction

Experiments showed that the amount of NaBH_4 is the key factor to the hydride formation reaction. The recoveries of species became lowered with no more than 5 ml of NaBH_4 added, this is because a part of acetic acid was dissolved into organic phase when butyltin species were digested with acetic acid and the added NaBH_4 was consumed by the dissolved acetic acid which made hydride formation reaction incomplete. The recoveries of butyltin species were low as well, espe-

cially for Bu_3Sn^+ , when more than 6 ml of NaBH_4 was added, the white suspended substance was formed between the two phases. We concluded that the suitable amount of NaBH_4 (5% w/v) was 5–5.5 ml. It must be mentioned that the NaBH_4 solution should be gently added drop by drop in order to avoiding excessive violence of reaction and loss of butyltin hydrides. Table 3 summarizes the effect of different amount of NaBH_4 on the hydridization of butyltin compounds.

3.6 Improvement of detection limits

The absolute detection limits (defined as three times signal over the baseline noise) were found to be about 0.08 ng of tin for Bu_4Sn and about 0.2 ng of tin for the hydrides of $\text{Bu}_2\text{Sn}^{2+}$ and Bu_3Sn^+ . For the analysis of sediments containing lower butyltin concentration, the detection limits may be lowered by a pre-concentration step. This is demonstrated as follows: a 10 g sediment sample spiked with butyltin species was extracted with the usual procedure, the extract was evaporated to 1 ml at about 35–65°C in a rotary evaporator, 2 μl of sample solution was injected in the GC, in this case, the detection limits were 4 ng tin/g sediment for Bu_4Sn , and 10 ng tin/g sediment for $\text{Bu}_2\text{Sn}^{2+}$ and Bu_3Sn^+ .

Table 3 The effects of NaBH_4 amount on the hydridization of butyltin species

NaBH ₄ added, ml	Recoveries, %		
	$\text{Bu}_2\text{Sn}^{2+}$	Bu_3Sn^+	Bu_4Sn
3	80.9	19.9	67.6
4.5	77.1	94.7	106.7
5	86.1	100.6	102.8
5.5	99.2	94.3	104.9
6	96.7	46.8	89.9

3.7 Application to environmental samples

Environmental samples spiked with standard butyltin species were analyzed by the proposed method. The recoveries of butyltin species for these samples are given in Table 4. Quantitative recoveries for most of samples were obtained.

Table 4 The recoveries of butyltin species for spiked sediment samples

Sediments *	Recoveries, %		
	$\text{Bu}_2\text{Sn}^{2+}$	Bu_3Sn^+	Bu_4Sn
#107 Sediment	91.8	114.9	94.8
Jinshan mouth	90.2	98.6	103.5
D4 sediment	106.5	74	106
D5 sediment	89.4	105.3	—
Xiaomiaohong	111.8	113	107.8
Liaodong harbour	101.2	100.5	111.4

* Spiked with 1.5 $\mu\text{g/g}$ $\text{Bu}_2\text{Sn}^{2+}$, 1.5 $\mu\text{g/g}$ Bu_3Sn^+ and 1.0 $\mu\text{g/g}$ Bu_4Sn

4 Conclusion

A method for determining butyltin species in sediment has been developed. The best digestion agent for butyltin determination in sediment is pure acetic acid. Butyltin species are extracted with benzene - hexane mixed organic solvent (2 : 1), and then hydrided with 5—5.5 ml NaBH₄ (5% w/v). This procedure provides a simple, rapid and sensitive GC - FPD methods for butyltin species determination in sediments.

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