

# Application of Crosslinked Chitosan in the Analysis of Butyl Tin Speciation

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**ABSTRACT:** A new method for the separation and preconcentration of butyl tin speciation with crosslinked chitosan (CCTS) and for its determination by hydride generation atomic absorption spectrometry was developed. At pHs 6.8, 4.4, and 3.0, monobutyl tin (MBT), dibutyl tin (DBT), and tributyl tin (TBT), respectively, were separated and preconcentrated with CCTS, eluted quantitatively with 10 mL of 1 mol L<sup>-1</sup> HCl, and determined. The method was applied to the discrimination and determination of MBT, DBT, and TBT

in water and sediment samples. The detection limits of TBT, DBT, and MBT were 21.2, 25.5, and 28.5 ng L<sup>-1</sup>, respectively. The analytical recoveries of MBT, DBT, and TBT added to the samples were 91–95% for water samples and 82–90% for sediment samples. The results were satisfactory. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1326–1328, 2004

**Key words:** adsorption; chitosan; crosslinking

## INTRODUCTION

The toxicity of elements or compounds is closely related to their speciation. For example, the toxicity of Cr(VI) is higher than that of Cr(III), and the toxicity of methyl mercury is 100 times higher than that of inorganic mercury.<sup>1</sup> Therefore, speciation analysis is very important for determining the environmental impact of elements or compounds. Organotin in water environments comes mainly from pesticides and paints that hinder the adherence of organisms to hulls. Tributyl tin (TBT) is usually used in hull paints as an additive reagent and is released into water.<sup>2</sup> TBT can be degraded and transformed into dibutyl tin (DBT) or monobutyl tin (MBT) by chemical, biological, and ultraviolet reactions; therefore, TBT, DBT and MBT generally coexist.<sup>3,4</sup> Their toxicity is ranked as follows: TBT > DBT > MBT.<sup>5</sup> Because the concentrations of butyl tin that are poisonous in water and sediments are low (1 ug L<sup>-1</sup> TBT has serious effects on aquatic organisms),<sup>6,7</sup> the different speciations of butyl tin (TBT, DBT, and MBT) need to be determined, and it is necessary to separate and preconcentrate butyl tin before the determination.<sup>8–10</sup>

Crosslinked chitosan (CCTS) is a synthesized product of chitosan (CTS) with a crosslinking reagent. It overcomes the disadvantage of CTS dissolving in acid and has better application prospects. Previously, we studied the adsorption properties of CCTS for Cr(VI) and Se(VI).<sup>11</sup> The experimental results showed that the adsorption rates of CCTS were 97% for Cr(VI) at pH 3.0 and 95% for Se(VI) at pH 4.0. That research concerned the removal of Cr(VI) and Se(VI) from wastewater and their preconcentrations in trace analysis.

In this study, the adsorption of CCTS for butyl tin was investigated. CCTS was found to have different adsorption abilities for different butyl tin speciations at certain pHs. The adsorption rates of CCTS for MBT, DBT, and TBT at pHs 6.8, 4.4, and 3.0, respectively, were greater than 95%. Therefore, a new method for separating and preconcentrating butyl tin speciation by CCTS was proposed. This method had a good separation effect and was low-cost. Hydride generation atomic absorption spectrometry (HGAAS) was used for the determination of butyl tin. The detection limit was greatly lowered, and trace butyl tin could be detected because of the preconcentration.

## EXPERIMENTAL

### Materials

CCTS (200 mesh) was synthesized according to a literature procedure.<sup>11</sup> MBT, DBT, and TBT solutions (1000 mg L<sup>-1</sup>) were supplied by Sigma-Aldrich (St. Louis, MO). Working standard solutions of lower concentrations were prepared after the serial dilution of

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the stock solutions. A 1%  $\text{KBH}_4$  (m/v) solution was prepared daily through the dissolution of  $\text{KBH}_4$  in a 0.5%  $\text{KOH}$  solution (m/v), the addition of 1 mL of 2%  $\text{La}(\text{NO}_3)_3$ , and filtration before use.  $\text{HCl}$  and  $\text{KOH}$  were high-purity; the other reagents were analytical-grade. Subboiling distilled water was used throughout the study.

### Apparatus

Atomic absorption spectrometry measurements were performed with a 180-80 spectrometer (Hitachi Corp., Osaka, Japan). The pH values were measured with a Delta 320-S pH meter (Mettler-Toledo, Greifensee, Switzerland). An LD5-2A centrifuge (Beijing Medical Centrifuge Factory, Beijing, China), a KQ-50B ultrasonic cleaner (Kunshan Ultrasonic Instruments Co., Ltd., Kunshan, China), and a CHA-S thermostatic shaker (Changzhou Guohua Electric Appliance Co., Ltd., Changzhou, China) were used in this experiment.

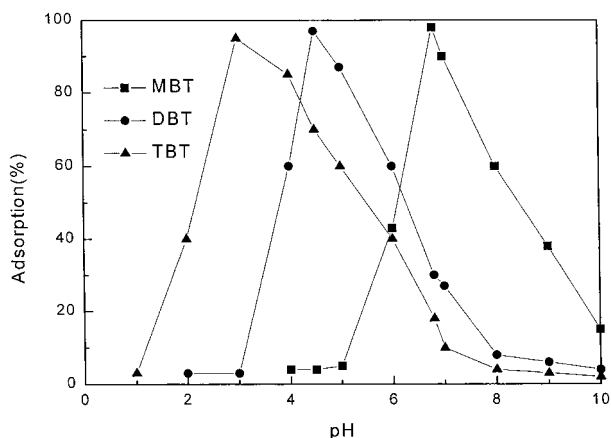
### Procedure

CCTS (10 mg) was added to a test solution of pH 3.0. The mixture was shaken for 20 min on a shaker and filtered; filtrate 1 and CCTS 1 were obtained. After the pH of filtrate 1 was adjusted to 4.4, the same procedure was performed, and filtrate 2 and CCTS 2 were obtained. When filtrate 2 was at pH 6.8, filtrate 3 and CCTS 3 was obtained in the same way. Then, CCTS 1, CCTS 2, and CCTS 3 were eluted with 10 mL of 1 mol  $\text{L}^{-1}$   $\text{HCl}$ , and their subsequent eluent was measured with HGAAS.

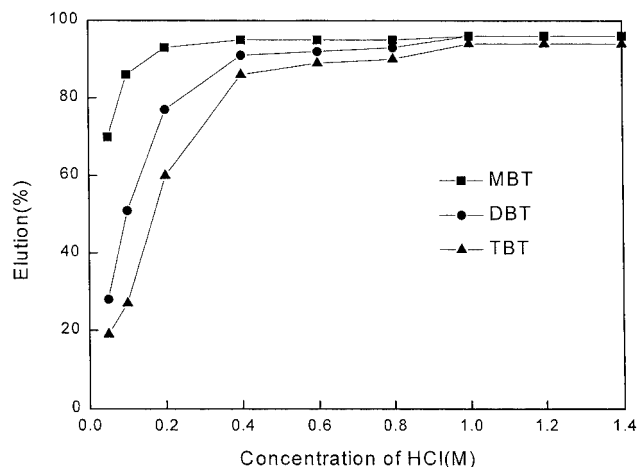
## RESULTS AND DISCUSSION

### Effect of pH on the separation and preconcentration efficiency of butyl tin speciation

The performances of the separation and preconcentration of CCTS for butyl tin speciation are closely related



**Figure 1** Effect of the pH on the adsorption of butyl tin speciation.



**Figure 2** Effect of the  $\text{HCl}$  concentration on the elution of butyl tin speciation.

to the acidity of the solution,<sup>11</sup> Figure 1 shows the influence of pH on butyl tin speciation adsorption by CCTS when the concentrations were 20  $\mu\text{g L}^{-1}$ . The pH values for the optimum adsorption of CCTS for TBT, DBT, and MBT were different. The adsorption rates of TBT, DBT, and MBT were greater than 95% at pHs 3.0, 4.4, and 6.8, respectively and the latter was almost not adsorbed at the pH of the optimum adsorption of the former. On this basis, the method for separating and preconcentrating butyl tin speciation by CCTS was designed.

### Balance times of butyl tin speciation adsorption by CCTS

A series of 30-mL test solutions containing 10  $\mu\text{g L}^{-1}$  TBT, DBT, and MBT were prepared. The solution pHs were adjusted to 6.8, 4.4, and 3.0, and then 10 mg of CCTS was added. The solutions were shaken on a shaker for different times, and then the adsorption efficiency of butyl tin speciation was determined. The results showed that the balance times were 20 min for CCTS adsorbing TBT and DBT and 30 min for CCTS adsorbing MBT.

### Effect of the $\text{HCl}$ concentration on the elution of butyl tin speciation

Different concentrations of  $\text{HCl}$  (10 mL) were used to elute butyl tin speciation adsorbed by CCTS. Figure 2 indicates that TBT, DBT, and MBT that adsorbed onto CCTS could be eluted quantitatively with 10 mL of 1 mol  $\text{L}^{-1}$   $\text{HCl}$ .

### Effect of the sample volume on the preconcentration efficiency of butyl tin speciation

Our experiments showed that butyl tin species adsorption of greater than 95% could be achieved when

**TABLE I**  
**Analytical Results**

Sample	Found			Spiked (ng)			Measured (ng)			Recovery (%)		
	MBT	DBT	TBT	MBT	DBT	TBT	MBT	DBT	TBT	MBT	DBT	TBT
Tap water	ND	ND	ND	100	100	100	92	94	95	93	94	95
East Lake water	120 ± 13	ND	ND	100	100	100	91	92	93	90	92	93
Yangzi River water	146 ± 15	205 ± 17	315 ± 26	100	100	100	95.7	90.8	93.2	95.7	91	93
Yangzi River sediment	52.4 ± 4.7	115.8 ± 11.1	183.2 ± 15.1	100	100	200	85.7	88.2	163	86	88	82
East Lake sediment	86.0 ± 7.9	37.4 ± 2.8	ND	100	100	200	90.1	86.2	169	90	86	85

$n = 6$ . The units are ng/L for water and ng/g for sediment. ND = not detected.

the sample volumes ranged from 30 to 500 mL, but the preconcentration efficiency of the butyl tin species was reduced when the solution volume was greater than 500 mL. CCTS could be used for the preconcentration of ultratrace amounts of TBT, DBT, and MBT from large-volume solutions.

### Evaluation of interference

It is well known that copper, nickel, and so forth can interfere with the hydride generation method. The effects of 16 diverse ions on the preconcentration and determination of  $5 \mu\text{g L}^{-1}$  butyl tin speciation were tested in this work, and the results showed that no interferences was found for the following ions [the concentrations ( $\text{mg L}^{-1}$ ) are given in parentheses]:  $\text{Cr}^{3+}$  (3),  $\text{Ni}^{2+}$  (10),  $\text{Pb}^{2+}$  (15),  $\text{Cu}^{2+}$  (20),  $\text{Fe}^{3+}$  (15),  $\text{Mn}^{2+}$  (30),  $\text{Mg}^{2+}$  (60),  $\text{Ca}^{2+}$  (40),  $\text{Al}^{3+}$  (25),  $\text{Zn}^{2+}$  (12),  $\text{Na}^+$  (3000),  $\text{K}^+$  (3000),  $\text{SO}_4^{2-}$  (1000),  $\text{Cl}^-$  (4500),  $\text{CO}_3^{2-}$  (150), and  $\text{PO}_4^{3-}$  (80).

### Analytical applications

#### River sediment analysis

A sediment sample (2.00 g) was placed in a centrifuge tube, and a 25-mL mixture of HCl and  $\text{CH}_3\text{OH}$  (1:4 v/v) was added. The mixture was centrifuged at 4000 rpm after being treated for 20 min with an ultrasonic cleaner. A 10-mL sample solution was taken out and diluted to 100 mL with water,<sup>12</sup> it was then analyzed according to the procedure mentioned previously.

#### Water sample analysis

A water sample (200 mL) was directly analyzed according to the procedure mentioned previously. Be-

cause no standard reference materials for water and sediment were available, the accuracy of the method was tested via the spiking of the samples. The analytical results are listed in Table I. The results show that the recoveries were reasonable for ultratrace analysis, and the method was reliable.

### CONCLUSIONS

A novel method for the separation, preconcentration, and determination of butyl tin speciation in water and sediment was proposed, featuring a low detection limit, a good separation effect, and a low analysis cost. The analytical results were satisfying. This research has practical value.

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