

Studies of Some Ultratrace Elements in Antarctic Water via Crown Ether Crosslinked Chitosan

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Received 22 March 2002; accepted 20 December 2002

ABSTRACT: A new type of crown ether crosslinked chitosan was prepared by the reaction of chitosan with synthesized 4,4'-dibromodibenzo-18-crown-6. Its adsorption behaviors for some ultratrace elements at different sites in Antarctica were studied. The results indicated that the adsorption rates were greater than 95% at pH 7.5, the enrichment factor of the ultraelements was greater than 50, and the detection limits of graphite furnace atomic absorption spectroscopy were improved greatly. The proper analysis conditions were examined, and a new method of detecting

ultratrace elements in environmental water samples with dibromodibenzo-18-crown-6 crosslinked chitosan was developed. In addition, the elements could easily be eluted off after absorption by dibenzo-18-crown-6 crosslinked chitosan, and so it is possible for this method to be used as a routine and valuable analysis method in environmental inspections. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 806–809, 2003

Key words: crosslinking; adsorption

INTRODUCTION

In recent decades, people have gradually realized the importance of inorganic trace elements to human life. As civilization has developed, many inorganic elements have broken away from formal minerals and entered the environment, especially arsenic, lead, cadmium, chromium, and copper, which can do great harm to human beings if their contents reach beyond certain ranges. The relatively fewer anthropogenic activities in Antarctica make it an ideal site for studying the background contents of some inorganic elements. With respect to water quality, arsenic, lead, cadmium, chromium, and copper are the most common contaminating elements and are the primary indicators of environmental pollution. By studying the contents of these elements, we can determine the background of these chemical elements and heavy metal pollution scientifically, this being indispensable for the environmentalist trying to establish countermeasures of pollution and prevention. Therefore, analyzing these ultratrace elements in Antarctica is very significant.^{1–4} Methods for detecting arsenic, lead, cadmium, chromium, and copper have been developed, but these elements are difficult to detect directly without sufficient concentrations or a predisposal for low contents and great interference. Consequently, new analytical

methods for dealing with complex samples or new chemical reagents for efficiently concentrating and analyzing elements need to be developed.

Chitosan chelating with metal ions and its derivations have often been reported, but chitosan can be dissolved in acidic media and lost too easily to be recovered. Crown ethers have good selectivity for its particular molecular structure and variety of ring cavities during chelation with metal ions. However, the application of low-molecular-weight crown ethers has been restricted by their toxicity.^{5–7} In this study, dibenzo-18-crown-6 crosslinked chitosan (DCTS) was prepared with dibenzo-18-crown-6 (DBC) crosslinking with CTS. Lead, cadmium, copper, chromium, and arsenic from different sites of Antarctica were concentrated and simultaneously detected by graphite furnace atomic absorption spectroscopy (GFAAS) without other separations or more chemical reagents.

EXPERIMENTAL

Apparatus and reagents

Lead, cadmium, chromium, copper, and arsenic were determined with a Hitachi 180-80 polarized Zeeman atomic adsorption spectrophotometer (with a hollow cathode lamp for each element). The prepared solutions were vibrated on a TZ-83 desk oscillator. The pH values were measured with a mode DF-180 pH/MV meter.

Stock solutions (1 g L^{-1}) of each elements were prepared by dissolution in distilled and deionized water. Standard solutions of lower concentrations were prepared after serial dilution of the stock solu-

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Contract grant sponsor: State Education Committee Doctoral Foundation.

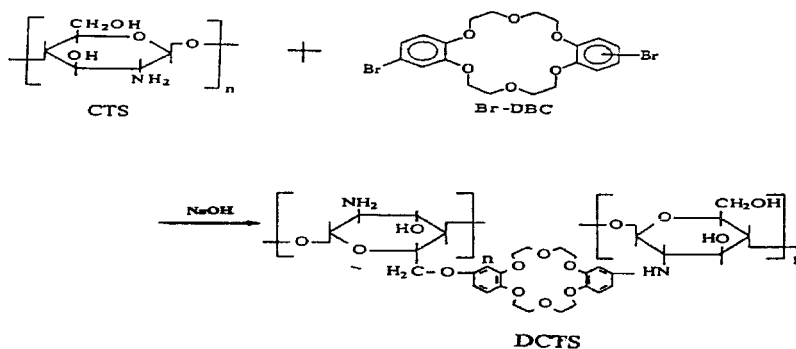


Figure 1 Reaction scheme for the synthesis of DCTS.

tions. 4,4'-Dibromodibenzo-18-crown-6 (Br-DBC) was synthesized according to ref. 8. HCl and HNO₃ were of premium purity, and the other chemicals were all analytically pure. The water used throughout the experiments was redistilled and deionized.

Synthesis of DCTS

CTS (3.0 g) was dissolved in 160 mL of 1.5% (v/v) acetic acid. To this, Br-DBC (1.5 g), which was dissolved in 30 mL of chloroform, was slowly added with vigorous stirring, and then 50 mL of 15% (w/w) NaOH was slowly added in drops. After about 28 h of reaction at room temperature, a white colloid precipitated. The resulting precipitate was filtered off and washed thoroughly with water first and then with a little acetone. After being dried and ground, it was sieved with a 400-mesh sizing screen. DCTS has three possible structural formulas;⁹ Figure 1 shows the synthetic route and gives one possible molecular formula.

Operating conditions

With reference to the concentration range of each element determined by GFAAS, standard mixing solutions were prepared. A stabilized-temperature coated platform furnace, argon as a carrier gas, a sampling volume of 10 μ L (1% ascorbic acid as the matrix modifier of 5 μ L used for the determination of copper), a quickly ascending temperature of maximum power, and the cessation of gas at the atomization step were

all adopted. The best operation conditions for each element are shown in Table I.

Analytical procedure

Antarctic lake water (100 mL) was taken (pH 7.5) and added to DCTS (5 mg), and the mixture was vibrated for 15 min at room temperature. Then, it was filtered with a 0.45- μ m filter film, and the filter film was soaked. Each element was soaked out: (1) lead and cadmium were soaked with 2 mol L⁻¹ HCl, (2) cadmium was soaked again with 0.2 mol L⁻¹ NH₃ · H₂O, (3) arsenic was soaked with 8 mol/L, (4) copper was soaked with 2% ethylenediaminetetraacetic acid (EDTA), and (5) chromium was soaked with tartaric acid. Finally, each element was directly determined under the previously discussed operating conditions.

RESULTS AND DISCUSSION

Effect of complexion

According to the procedure mentioned previously, a series of standard mixing solutions containing 10 μ g L⁻¹ lead, 1 μ g L⁻¹ cadmium, 10 μ g L⁻¹ chromium, 10 μ g L⁻¹ copper, and 10 μ g L⁻¹ arsenic were adsorbed by DCTS together with EDTA, NH₃ · H₂O, NaOH, tartaric acid, HCl, or aqueous HNO₃ so that the effect of the concentration of DCTS could be analyzed. The results indicated lower adsorption rates and fewer

TABLE I
Optimum Instrumental Conditions for the GFAAS Determination of Each Element

Element	Wavelength (nm)	Slit width (nm)	Measure mode	Ash temperature (°C)	Atomic temperature (°C)	Working standard (μ g L ⁻¹)
Arsenic	193.7	2.6	Peak height	400	2800	10–100
Lead	283.3	1.3	Peak height	400	2000	5–30
Cadmium	228.8	1.3	Peak height	300	1500	0.1–4
Chromium	359.3	0.4	Peak height	700	2700	10–100
Copper	324.8	1.3	Peak height	600	2700	5–20

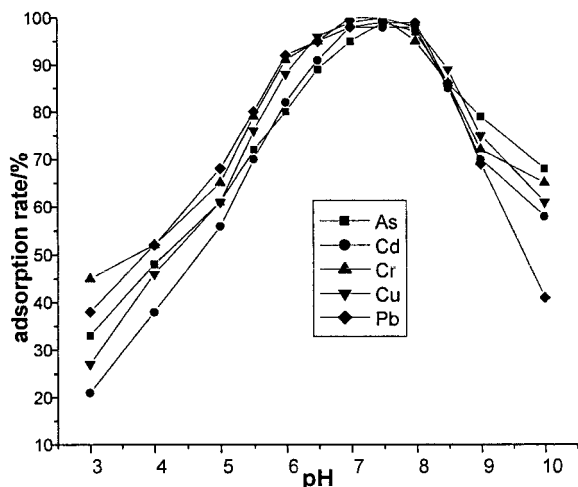


Figure 2 Effect of pH for each element.

influences, so DCTS was used to directly concentrate each element without other complexions.

Influence of the solution pH

Then, a series of standard mixing solutions containing $10 \mu\text{g L}^{-1}$ lead, $1 \mu\text{g L}^{-1}$ cadmium, $10 \mu\text{g L}^{-1}$ chromium, $10 \mu\text{g L}^{-1}$ copper, and $10 \mu\text{g L}^{-1}$ arsenic were adsorbed by DCTS at different pH values; their concentrations were determined, and their adsorption rates were obtained. Figure 2 shows that the optimum pH value for the maximum adsorption of the five elements was 7.5.

Balance time

After a series of standard mixing solutions containing $10 \mu\text{g L}^{-1}$ lead, $1 \mu\text{g L}^{-1}$ cadmium, $10 \mu\text{g L}^{-1}$ chromium, $10 \mu\text{g L}^{-1}$ copper, and $10 \mu\text{g L}^{-1}$ arsenic were adsorbed by DCTS at different adsorption times, their concentrations were measured. Figure 3 shows that

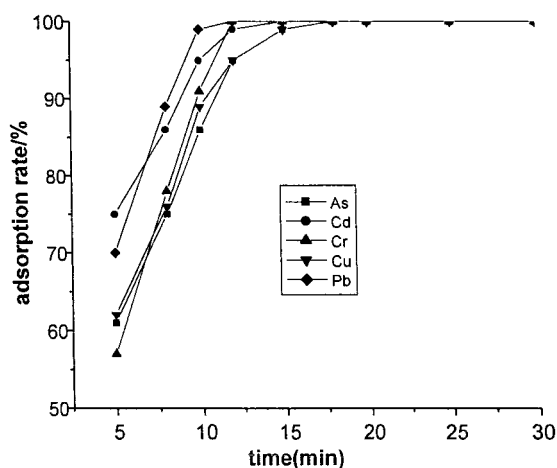


Figure 3 Effect of the balance time.

TABLE II
Performance Data for the Analysis of DCTS for Each Element ($n = 5$)

Element	Enrichment factor	Detection limit (3σ)/pg	RSD (%)	Recovery (%)
Lead	V_a/V_b	0.4	2.5	103
Cadmium	V_a/V_b	0.03	2.1	96
Chromium	V_a/V_b	2	1.8	100
Copper	V_a/V_b	0.5	2.2	101
Arsenic	V_a/V_b	6	3.2	99

V_a , sample volume; V_b , soakage volume.

the best adsorption time for simultaneously measuring the five elements was 15 min.

Mass of DCTS

After a series of standard mixing solutions containing $10 \mu\text{g L}^{-1}$ lead, $1 \mu\text{g L}^{-1}$ cadmium, $10 \mu\text{g L}^{-1}$ chromium, $10 \mu\text{g L}^{-1}$ copper, and $10 \mu\text{g L}^{-1}$ arsenic were adsorbed by DCTS of different masses, their concentrations were measured. The results showed that the adsorption rates of the five elements could be greater than 95% when the mass of DCTS was higher than 4 mg. Therefore, the mass of DCTS was 5 mg.

Adsorption capacities of DCTS for each element

After a series of standard mixing solutions with different concentrations of each element were adsorbed by DCTS, their concentrations were measured. The results showed that the adsorption capacities of DCTS for lead, cadmium, chromium, copper, and arsenic were 60.2, 101.6, 44.8, 39.3, and 56.1 mg g^{-1} , respectively.

Desorption to each element

Desorption of tartaric acid, HCl, and HNO_3

After several filter films were soaked with 2 mL of tartaric acid, HCl, and HNO_3 of different concentrations, the elemental concentrations of the soakage were measured. The results showed that the desorption rates of HCl (2 mol L^{-1}) for cadmium and lead were 72 and 100%, that of HCl (8 mol L^{-1}) for arsenic was 95%, and that of 20 g/100 mL tartaric acid for chromium was 100%. The other desorption rates were all lower.

Desorption of EDTA, NaOH, and $\text{NH}_3 \cdot \text{H}_2\text{O}$

After several filter films were soaked with 2 mL of EDTA, NaOH, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ of different concentrations, their concentrations in the soakage were measured. The results showed that the desorption rate of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (0.2 mol L^{-1}) for cadmium was around

TABLE III
Analytical Results ($\mu\text{g L}^{-1}$) of Water Samples ($n = 12$)

Sample No	Lead	Cadmium	Chromium	Copper	Arsenic
Site A	0.85 ± 0.03	0.035 ± 0.002	0.70 ± 0.01	1.20 ± 0.01	0.75 ± 0.03
Site B	1.42 ± 0.02	0.055 ± 0.001	0.50 ± 0.01	0.65 ± 0.02	0.40 ± 0.03
Site C	0.55 ± 0.03	0.075 ± 0.003	0.85 ± 0.03	2.00 ± 0.02	1.30 ± 0.04
Site D	1.05 ± 0.02	0.085 ± 0.002	1.00 ± 0.01	2.85 ± 0.04	1.10 ± 0.04
Site E	1.75 ± 0.04	0.090 ± 0.003	1.15 ± 0.02	0.35 ± 0.01	0.30 ± 0.04
Site F	0.76 ± 0.02	0.100 ± 0.001	0.38 ± 0.02	0.70 ± 0.03	0.62 ± 0.02
Data range	0.05–2.00	0.008–0.110	0.30–1.20	0.30–3.00	0.05–1.50

The data range included all the Antarctic water samples that we detected.

85% and that of 2% EDTA for copper was 100%, whereas the rates of the others were lower.

Effects of coexisting ions

The effects of several coexisting ions on the adsorption rates of the five elements were tested, and the results indicated that there was no interference when Na^+ ($1.0 \times 10^4 \text{ mg L}^{-1}$), K^+ and Mg^{2+} ($2.2 \times 10^3 \text{ mg L}^{-1}$), Ca^{2+} , Mn^{2+} , and Zn^{2+} ($8 \times 10^2 \text{ mg L}^{-1}$), Fe^{3+} , Al^{3+} , Co^{2+} , and Ni^{2+} ($5 \times 10^2 \text{ mg L}^{-1}$), Cl^- ($4 \times 10^3 \text{ mg L}^{-1}$), and NO_3^- and SO_4^{2-} ($3 \times 10^3 \text{ mg L}^{-1}$) were added to 100 mL of standard mixing solutions containing $10 \mu\text{g L}^{-1}$ lead, $1 \mu\text{g L}^{-1}$ cadmium, $10 \mu\text{g L}^{-1}$ chromium, $10 \mu\text{g L}^{-1}$ copper, and $10 \mu\text{g L}^{-1}$ arsenic.

Analytical performance

According to the aforementioned procedures, data for the detection limits (after concentration), enrichment factors, relative standard deviations, and recoveries were detected. The results are shown in Table II.

Analyses of antarctica water samples

According to the aforementioned procedures, water samples (sampled according to People's Republic of China Standard GB8538.2-87) from Antarctica and blank samples were analyzed in parallel. The analytical results are shown in Table III (the blank values were close to those of redistilled and deionized water).

CONCLUSIONS

DCTS has an adsorption ability for some metal elements; the pH value is an important factor for the

adsorption. In this study, DCTS was applied to concentrate and analyze trace elements such as lead, cadmium, chromium, copper, and arsenic. At a specific pH value, the adsorption rates could reach 100%. This method shows higher precision, greater delicacy, and a better enrichment factor (a value greater than 100 can be achieved if necessary with a larger volume of a water sample). Coexisting ions of higher concentrations will not interfere with the determination. One more advantage of this procedure is that the elements can easily be eluted off and be determined directly by GFAAS. Therefore, DCTS may be used one day for the routine testing of water quality.

The authors greatly acknowledge the researchers at the Institute of Hydrobiology of the Chinese Academy of Sciences (Wuhan, China) for their kind efforts in providing the Antarctica water samples used in this study.

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