CELLULOSE CHEMISTRY AND TECHNOLOGY

SOLID-PHASE EXTRACTION OF Pb FROM COMMON SALT AND WATER SAMPLES BY CELLULOSE MODIFIED WITH ANHYDROUS EDTA

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A regenerated cellulose fiber functionalized by anhydrous EDTA has been synthesized, then it was employed as a solid-phase extraction material for preconcentration and determination of trace Pb in common salt and water samples. The chelating cellulose (Cell-EDTA) was characterized by infrared spectrometry and elemental analyses. In order to obtain quantitative recoveries of Pb, various analytical parameters, such as pH, amounts of solid-phase, equilibration rate, sample volume, eluent volume, flow rate etc. were investigated. The effects of some metal ions on the sorption of Pb were also examined. The maximum sorption capacity of 0.68 mmol/g was obtained. A preconcentration factor 200 (using 2000 mL of sample and 10 mL of eluent) was achieved. The proposed method was applied to determine the trace amount of Pb in common salt and water samples. The detection limit of Pb was 1.5 µg L^{-1} as the concentration in 500 mL solution (20-fold preconcentration).

Keywords: EDTA-type chelating cellulose, Pb, solid-phase extraction, preconcentration, common salt

INTRODUCTION

Pb is known to be a harmful contaminant with toxic effects for the living organisms. Even small amounts of Pb can cause many health problems, often over a period of months or years. Pb is especially dangerous for children. The most common sources of Pb exposure include: Pb in paint, water distribution systems, soil and dust, food, and Pb used in hobby activities. Trace Pb is present in many environmental and food samples, therefore its separation and determination are of great importance. For a low level of Pb in various samples, a preconcentration and separation step prior to determination is required to reach an appropriate level of sensitivity and reduce the interferences from the other elements present. Nowadays various separation/preconcentration techniques, including solvent extraction, coprecipitation, aqueous two-phase extraction and solid-phase extraction have been developed for the trace heavy metals analysis in various samples. Among these methods, solid-phase extraction has been attracting attention as an excellent preconcentration technique for trace metal ions, due to its handling simplicity, rapidity and yielding of a higher enrichment factor. Chelex 100[1,2] and Muromac A-1[3,4] are popular adsorbents chemically modified with iminodiacetic acid, which is often used in solid-phase extraction of trace metals. In addition, many different types of adsorbents, such as poly(acrylamidoxime) resin,[5] activated carbon,[6] XAD-16-PAN resin,[7] chitosan modified ordered mesoporous silica,[8] TiO_2,[9] alumina,[10] CM-PEHA resin,[11] MCI GEL CHP resin,[12] NOBIAS Chelate-PA1[13,14] etc., have also been used for preconcentration of trace Pb and other metals. Cellulose is used well as a support material of solid sorbent for trace metals, due to its stability, hydrophilicity and insolubility to water or organic solvents. Cellulose is cheap, biodegradable and the most abundant biopolymer of all naturally occurring organic compounds. Our research has focused on the use of modified fibrous cellulose using chelating reagents for the removal of trace metal ions.

In our previous studies, the cellulose-based sorbents containing iminodiacetic acid (Chelest Fiber IRY),[15,16] EDTA,[17] thioglycollic acid[18] and N-methyl glycin[19] have been reported for trace metal preconcentration. V. Gurnani and co-workers[20] have studied cellulose based macromolecular chelator having pyrocatechol for enrichment of multielements. K. Pyrzyńska and co-workers[21] have examined cellulose sorbent functionalized with phosphoric acid for vanadium species. D. W. O'Connell and co-workers[22] have functionalized imidazole chelating group onto grafted polymeric cellulose and studied its removal ability for Cu. G. I. Tsysin *et al.*[23] synthesized cellulose fibrous sorbents, containing a diethylenetriamine tetraacetate groups and employed it for preconcentration of heavy metals from natural waters.

EDTA is a widely applicable complexing agent, as it forms strong complexes with many metals. In analytical chemistry, EDTA is used in complexometric titrations and analysis of water hardness or as a masking agent to sequester metal ions that would interfere with the analysis. In this work, EDTA type chelating cellulose (abbreviated as Cell-EDTA) was synthesized by adding a slight improvement to the previous method. Because Cell-EDTA can easily be synthesized by a one-step procedure, the synthetic method is more advantageous than that of Chelest Fiber IRY based on cellulose.

In the determination of trace metal ions in common salt samples, it is necessary to separate/concentrate the analyte in advance to avoid the effect of NaCl. Even with the modern analytical instruments, the direct determination of low concentrations of metals in NaCl is difficult because of the high matrix effect. So far, a number of pretreatment methods for the determination of trace metals in common salts have been reported.[24-27] The development of a rapid and simple analysis of the trace heavy metals contained in the common salt sample is an important research subject from the viewpoint of food safety and food control. The purpose of this study is to establish the separation/preconcentration of trace Pb in common salt and water samples using Cell-EDTA as solid-phase extraction material.

EXPERIMENTAL

Apparatus and reagents

A flame atomic absorption spectrometer (Hitachi model A-2000) with a deuterium background correction was used for the analysis. The Pb hollow cathode lamp was run under the conditions suggested by the manufacturer. A micro-tube pump (Tokyo Rikakikai EYELA model MP) equipped with a silicon tube (2.5 mm i.d.) was used to propel the solution. IR spectra were recorded over the range 4000-400 cm^{-1} with a JASCO FT/IR-4200 spectrophotometer, using KBr pellets. A SevenEasy pH meter (METTLER TOLEDO) with a combined glass electrode was employed for measuring the pH of the solutions.

Reagents

All chemicals were of analytical reagent grade, unless otherwise stated. Nitric acid diluted to 1.0 mol/L was used as eluent. The working standard solutions of Pb were prepared by appropriate stepwise dilution of the stock standard solution of 1000 mg/L (Wako Pure Chem., Japan). Regenerated cellulose fiber was purchased from Chelest Inc., Japan.

Preparation of Cell-EDTA

The Cell-EDTA was prepared according to the procedure described elsewhere[16] with a minor modification. Regenerated fibrous cellulose whose size and morphology had been controlled was used as support material. The chelating ligand of EDTA was directly combined with the cellulose in a one-step synthetic procedure.

100 mL dimethyl sulfoxide was added to the mixture of regenerated cellulose fiber (10 g) and anhydrous EDTA (10 g). The mixture was heated in a round bottom flask for 2 hours at 90 °C. After heating, the reaction mixture was filtered, and the cellulose fiber immobilized with EDTA was sufficiently washed with deionized water. The resulting product was then dried in air at 60 °C for 10 h.

Analysis (%): found for cellulose: C, 40.5; H, 6.64; found for Cell-EDTA: C, 40.3; H, 6.25; N, 1.6. The amount of EDTA groups bound to the cellulose surface was determined by a method based on the nitrogen content. From the chemical analysis, the EDTA content was found to be of about 0.57 mmol/mass of EDTA-Cell (g) by the following calculation: $1.6 \times 1000 \times 10^{-2} \times (2 \times 14)^{-1}$. The structure of Cell-EDTA is presented in Fig. 1.

Synthesis of Cell-EDTA-Pb complex

To a solution containing 2.0 g of $(CH_3COO)_2Pb \cdot 3H_2O$ in 100 mL of water, 0.3 g of Cell-EDTA (EDTA group: 0.57 mmol/g) were added. The Cell-EDTA-Pb complex was synthesized using a Pb excess. The pH of the solution was adjusted to 5 with sodium acetate, and was magnetically stirred for 1 h in a water-bath at 65 °C. The obtained Cell-EDTA-Pb complex was thoroughly washed with deionized water, and then dried overnight at 70 °C.

Preparation of the column

A polypropylene column (78 mm×15 mm) packed with 1.0 g of adsorbent was used as the operation column. Both ends of the adsorbent in the column were suppressed with polyethylene disk filter to prevent its dispersion, when the sample solutions passed through the column. The height of the column section containing 1.0 g of adsorbent was of about 20 mm. Before using the column, it was washed with 20~30 mL of 0.5 mol/L HNO_3, and deionized water until the effluent was neutral.

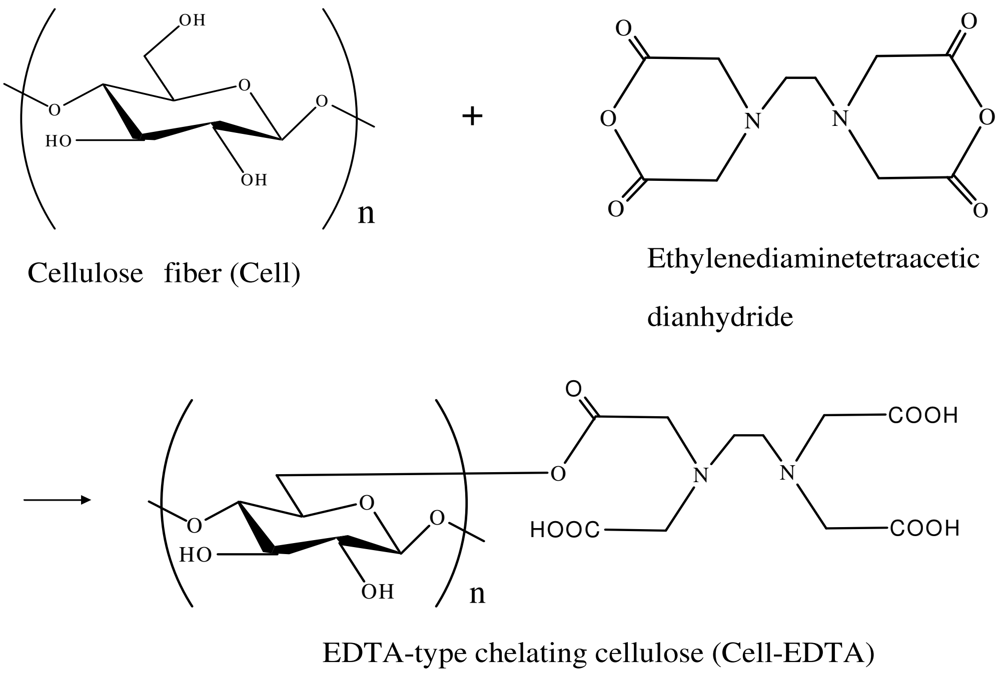


Figure 1: Synthesis of EDTA-type chelating cellulose(Cell-EDTA)

General preconcentration procedure

To an 80 mL of sample solution containing 200 µg of Pb, 10 mL of 1 mol/L CH_3COONH_4 was added. Then the pH of the solution was adjusted to about 3.5 with acetic acid or aqueous ammonia solution. The resulting volume was maintained at 100 mL. The buffered sample solution was passed through the micro-column packed with chelating cellulose sorbent at a flow rate of 15 mL/min controlled by a micro-tube pump. After passing the sample solution, the column was rinsed twice with 10 mL of deionized water to eliminate the excess reagent. The Pb retained on the sorbent was then eluted with a 15 mL portion of 1.0 mol/L nitric acid at a flow rate of 4 mL/min. Subsequently, the eluent was diluted to 25 mL in a volumetric flask. The Pb in the solution was determined by FAAS. The procedure of optimization was carried out changing one parameter, while the other parameters were kept constant.

Applications to common salt and water samples

Accurately weighed saline samples (100 g) were dissolved in 700 mL distilled water and 5 mL of 14 mol/L nitric acid was added, and then they were heated on a hot plate at 100 °C for 15 min. After cooling the sample solution to room temperature, it was diluted to 1000 mL with deionized water. 100 mL aliquots of sample solution were analysed according to the general preconcentration procedure.

The water sample collected from Tama River, Tokyo, was filtered through a membrane filter with a pore size of 0.45 µm, and then 500 mL aliquots of filtrate were used for Pb analysis.

RESULTS AND DISCUSSION

IR spectrum

FT-IR spectroscopy was employed to ascertain the immobilized EDTA and chelated Pb onto the surface of the adsorbent. The IR spectra of the original cellulose fiber, Cell-EDTA and Cell-EDTA-Pb are presented in Fig. 2 and Fig. 3. In the IR spectra of the prepared Cell-EDTA and Cell-EDTA-Pb complex broad absorption bands at around 3400 cm^{-1} arise from the vibration of OH group. The strong peak at 1634 cm^{-1} in cellulose fiber and Cell-EDTA indicate the presence of uncoordinated water, while in the Cell-EDTA-Pb complex this peak due to water is found as a shoulder band near 1589 cm^{-1}. The peak at 1731 cm^{-1} in Cell-EDTA is assigned to C=O stretching. The strong peak at 1589 cm^{-1} and weak peak at 1371 cm^{-1} in the Cell-EDTA-Pb complex are attributed to asymmetric vibration of OCO^- group (ν_{as}) and symmetric vibration of OCO^- group (ν_s) respectively. The peak at 1731 cm^{-1} due to $\nu_{C=O}$ in Cell-EDTA-Pb is weaker than that of the Cell-EDTA. These results indicate that hydrogen ions in the –COOH groups are substituted by Pb.

SEM characterization

The surface morphologies of the cellulose and functionalized cellulose samples have been examined using the scanning electron microscope. The surface of the samples was clear and differences between original cellulose fiber and Cell-EDTA were not observed, as shown in Figs. 4 (a) and (b). The diameter of functionalized cellulose seemed to become slightly thicker than that of the original cellulose.

Influences of pH

In the solid-phase extraction studies, the pH of the aqueous solution is one of the important factors for the retention of trace metal ions. The influence of the pH on the adsorption of Pb onto chelating cellulose modified with EDTA was studied over the pH range 1.0-6.0 by the column process, described in the general preconcentration procedure. The recovery of Pb as a function of sample solution pH is given in Fig. 5. The recovery is maximal for the extraction at pH 1.9-6.0. A pH of about 3.5 was selected for subsequent work. The desorption of the Pb from the Cell-EDTA column was also examined using 1.0 mol/L nitric acid solutions in the range of 3-20 mL. It was observed that quantitative elution of Pb from the column was achieved with ca. 6 mL of 1.0 moL/L nitric acid solution, at a flow rate of 4.0 mL/min. Thus, we selected 10~15 mL of 1.0 mol/L nitric acid as the optimum eluent volume for desorption of Pb.

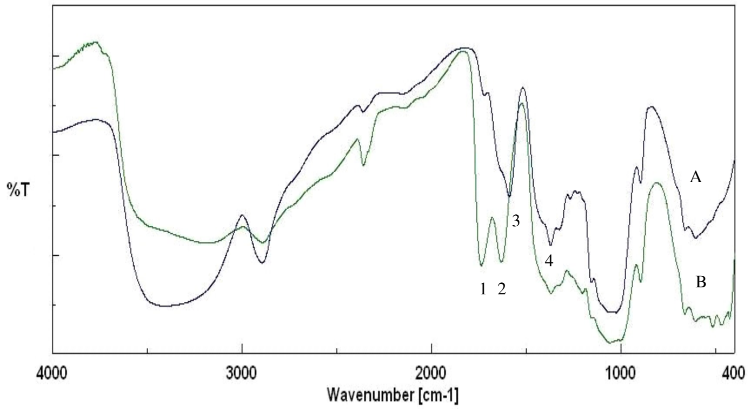


Figure 2: FT-IR spectra of (A) Cell-EDTA-Pb and (B) Cell-EDTA (1: 1737 cm^{-1}, 2: 1634 cm^{-1}, 3: 1589 cm^{-1}, 4: 1371 cm^{-1})

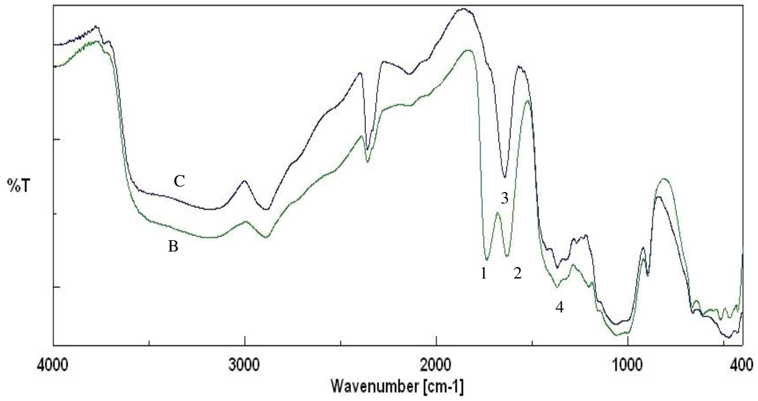
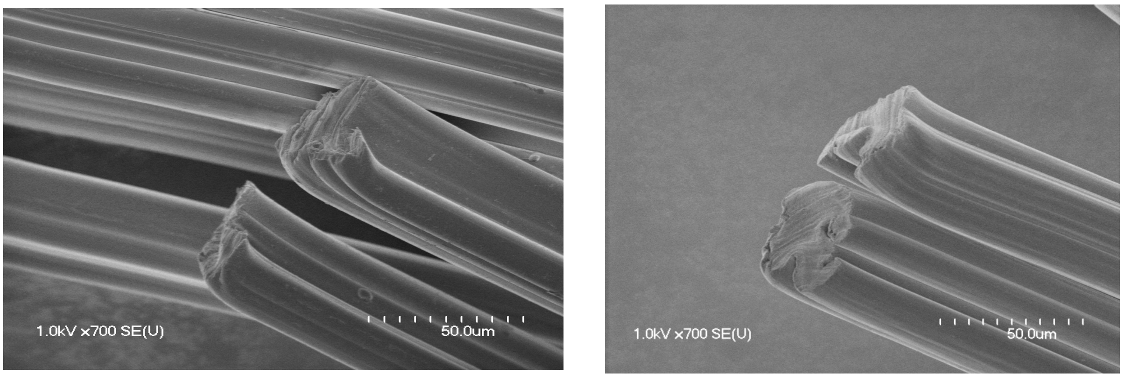


Figure 3: FT-IR spectra of (B) Cell-EDTA and (C) original cellulose fiber (1: 1737 cm^{-1}, 2 and 3: 1634 cm^{-1}, 4: 1368 cm^{-1})



a) b)

Figure 4: Scanning electron micrographs of (a) original cellulose fiber and (b) Cell-EDTA; magnification of 700× each

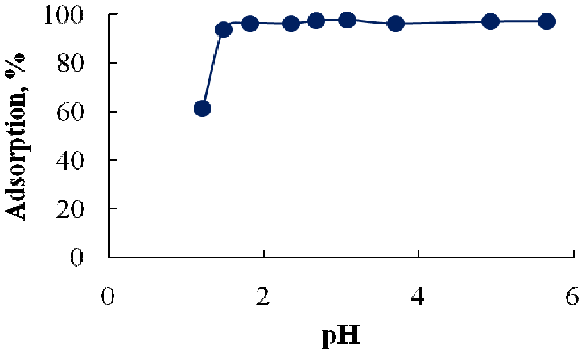


Figure 5: Effect of pH on the adsorption of Pb (Adsorbent: 1.0 g, Pb: 200 µg, flow rate: 15 mL/min, sample volume: 100 mL)

Flow rate of sample solutions

The effect of flow rate of the sample solution through the column was examined in the range of 4.0-25 mL/min. The retained Pb on the column was eluted with 15 mL of 1.0 mol/L nitric acid at a flow rate of 4.0 ml/min. The results showed that 200 µg of Pb in the solution was quantitatively recovered in the studied flow rate range. Thus flow rates of 15 mL/min and 4.0 mL/min were employed for the sample solution and for the eluent, respectively. Regeneration is one of the key factors in evaluating the performance of the adsorbents. Our experimental results indicate that the stability permitted over 50 adsorption-desorption cycles, without significant decrease in the recovery of Pb.

Effect of different ions

The effect of various cations (Mg, K, Ca, Cr, Fe, Co, Ni, Cu, Zn, Cd, In) on the adsorption of Pb onto the modified cellulose was investigated. The foreign ions were individually added to a solution containing fixed amounts of Pb. In the adsorption of Pb, both metal ions of Cu and Fe had a slightly greater influence than other metal ions, as shown in Table 1. This is due to the high reactivity of both metals to the adsorbent.

Enrichment factor and loading capacity

The sample volume is one of the important parameters to obtain a high concentration factor. The influence of sample volume on the retention behaviors of Pb was studied in the range of 100~2000 mL. In all cases, Pb could be quantitatively retained by the adsorbent. The retained Pb in the column was quantitatively eluted with ca. 10 mL of 1.0 mol/L nitric acid, therefore the possible preconcentration factor was 200. Also, as has already been reported,[15] in Chelest Fiber IRY, a concentration factor of at least 200 can be attained. In the general preconcentration procedure, however, the eluate was diluted to 25 mL with deionized water and supplied to an AAS analysis of Pb.

Table 1
Effect of foreign ions on the adsorption of Pb

Ions	Added, mg	Recovery, %
Mg	1.0	94.5
	2.0	94.8
K	1.0	96.0
	2.0	95.0
Ca	1.0	95.5
	2.0	97.5
Cr(VI)	1.0	96.3
	2.0	95.3
Fe(III)	1.0	93.0
	2.0	91.0
Co(II)	1.0	96.5
	2.0	95.0
Ni	1.0	95.3
	2.0	95.8
Cu	1.0	95.8
	2.0	87.0
Zn	1.0	95.0
	2.0	96.8
Cd	1.0	96.8
	2.0	96.5
In	1.0	96.5
	2.0	90.5

Adsorbent: 1.0 g, Pb: 100 μg, sample volume: 100 mL, sample flow rate: 15 mL/min, pH 3

In order to study the maximum adsorption capacity of the Cell-EDTA, 50 mL sample solution containing an excess amount of Pb (5.3 mmol) was passed through the column (adsorbent 0.3 g) at a flow rate of 15 mL/min. After that, the column was washed with deionized water to remove the excess Pb and then the adsorbed Pb was desorbed as mentioned above. The eluate was diluted to an appropriate amount with deionized water for FAAS determination of Pb. The capacity of the sorbent for Pb was found to be of 0.68 mmol/g. Although this adsorption capacity is slightly lower, as compared with the 1.0 mmol/g of Chelest Fiber IRY, which is sufficient for the enrichment of trace elements, the appropriate concentration level can be measured.

Table 2
Recovery of Pb from spiked common salt and water samples (mean, n = 3)

Sample	Sample (g)	Pb^{2+}added (μg)	Pb^{2+} found (μg)	Recovery (%)
NaCl	10	0.0	n.d.	
	10	100	101.4±2.2	101.4
Amajio	10	0.0	n.d.	
	10	50	50.6±0.3	101.2
Okinawanosio	10	0.0	n.d.	
	10	100	99.0±0.8	99
Nagasakinosio	10	0.0	n.d.	
	10	50	50.0±1.1	100
Hakatanosio	10	0.0	n.d.	

	10	100	96.4±1.5	96.4
Tap water	500	0.0	n.d.	
	500	30.0	28.0 ± 0.2	93.3
River water	500	0.0		
	500	30.0	29.1 ± 0.0	97.0

The limits of detection of the proposed method for the determination of Pb was studied by passing 500 mL of blank solutions from the column under the optimal experimental conditions. The detection limits of Pb in our recommended analytical procedure calculated as three times the SD (N = 10) of the blank was found to be 1.5 µg/L as the concentration in 500 mL of solution (20-fold preconcentration). This value corresponds to a Pb content of 0.75 µg/g, when the amount of common salt sample is 10 g.

Analytical applications

The solid-phase extraction procedure presented for Pb was applied to water samples and several common salts produced from Japanese seawater. The preparation of the sample solution and the solid-phase extraction of Pb were performed as mentioned in Experimental section. The concentration of Pb in all the water and common salt samples was found below the detection limits. The accuracy of the method was verified by spiking the sample with 10 µg of Pb and performing an analysis by the proposed procedure. The recovery values for added Pb were found to be higher than 93% on triplicate measurements, as shown in Table 2. These results satisfactorily confirmed the validity of the proposed method.

CONCLUSION

The immobilization of EDTA onto regenerated cellulose fiber, and the adsorption properties of this Cell-EDTA for Pb were investigated. The Cell-EDTA was synthesized in a one-step procedure by reacting an anhydrous EDTA and fibrous cellulose in dimethyl sulfoxide solvent. The advantages of this synthesis method are simple procedure, short time and mild conditions.

Quantitative adsorption in a wide pH range, fast adsorption and desorption kinetics, and high sorption capacity of the adsorbent demonstrate its significant potential as an adsorbent in the removal of trace Pb from aqueous solutions. Furthermore, the Cell-EDTA sorbent can be used at least 50 times without any loss in its adsorption properties. The quantitative recovery of Pb in spiked common salt samples with a relative standard deviation of 0.6~2.2% reflects the validity and accuracy of the method.

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