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PREPARATION OF AMBERLITE XAD RESINS COATED WITH DITHIOSEMICARBAZONE COMPOUNDS AND PRECONCENTRATION OF SOME METAL IONS

SUWARU HOSHI, HIDEKI FUJISAWA, KATSUMI NAKAMURA, SEIJI NAKATA, MASAYUKI UTO and KUNIHIKO AKATSUKA

Department of Applied and Environmental Chemistry, Kitami Institute of Technology, 165,
Koen-cho-Kitami-shi, Hokkaido, 090 Japan

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Summary—The Amberlite XAD resins coated with dithiosemicarbazones were prepared and their collection behavior of metal ions from aqueous solution was investigated. Among the resins used, the reagent-loaded Amberlite XAD-7 was found to be superior for the collection of metal ions to other reagent-loaded resins used. The quantitative collection of mercury(II), palladium(II) and copper(II) was obtained from acidic medium, while cadmium(II) and lead(II) was obtained from neutral medium by the Amberlite XAD-7 resin coated with dimethylglyoxal bis(4-phenyl-3-thiosemicarbazone) (DMBS). These metal ions collected on the resin were easily eluted with a small volume of *N*,*N*-dimethylformamide as their DMBS chelates. This collection–elution method was applied to the determination of their metal ions by reversed-phase high performance liquid chromatography with a spectrophotometric detection.

Dithiosemicarbazone compounds (Fig. 1) react as tetradentate ligands with some divalent metal ions to form stable and kinetically inert chelates. Some of their compounds have been applied to the spectrophotometric determination of some metal ions,[1-3] and separation of their chelates by high performance liquid chromatography (HPLC).[4-6] The dithiosemicarbazones, however, have the disadvantage of low solubility in common solvents except solvents such as *N*,*N*-dimethylformamide and dimethylsulfoxide, *etc*. Therefore, it is difficult to use these compounds for preconcentration of metal ions.

In trace metal analysis, preconcentration or separation of the analyte from the matrix is frequently a necessity. The use of supports loaded with chelating reagents is particularly convenient because it is easy to prepare such resins, although their stabilities and collection abilities may be inferior to those of the chelating resins containing the various functionalized groups.[7] Therefore, the preconcentration and separation methods for trace metal ions have been developed by using various supports including Amberlite XAD resins,[8-11] silica gel,[12-14] ion-exchange resins[15-17] and polyurethane foams[18-21] loaded with a large number of reagents.

In this work, Amberlite XAD resins, which are commercially available with different properties, were used as a substrate for coating the dithiosemicarbazone compounds (Fig. 1), including glyoxaldithiosemicarbazone (GDS), glyoxal bis(4-phenyl-3-thiosemicarbazone) (GBS) and dimethylglyoxal bis(4-phenyl-3-thiosemicarbazone) (DMBS). They were tested for the collection of trace metal ions from aqueous solution and the elution as their dithiosemicarbazone chelates with a small volume of *N*,*N*-dimethylformamide (DMF) prior to the determination by reversed-phase HPLC with a spectrophotometric detection.

EXPERIMENTAL

Reagent and apparatus

The dithiosemicarbazone compounds were synthesized as reported in the literature,[2,22] and their reagent solutions were prepared by dissolving in DMF.

The Amberlite XAD-4(styrene-divinylbenzene type), -7(acrylic ester type) and -16(polystyrene type) (purchased from the Rohm and Haas Corp., bead size, 250–850 μm) was washed successively with 5*M* hydrochloric acid, distilled water and methanol and then dried at 40° for 24 hr in a vacuum dry oven.

Mercury(II) (1000 μg/ml), copper(II) (1000 μg/ml) zinc(II) (1000 g/ml), cadmium(II) (1000 μg/ml), lead(II) (1000 μg/ml) and palladium(II) (500 μg/ml) standard solutions were prepared by dissolving mercury(II) chloride, copper(II) sulfate, zinc(II) chloride, cadmium(II) sulfate, lead(II) chloride in $0.1M$ and palladium(II) chloride in $1M$ hydrochloric acid, respectively, standardized by titration with EDTA or spectrophotometrically, and were diluted as required. All other chemicals used were of analytical and HPLC grade.

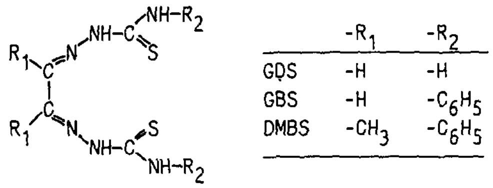
A Hitachi–Horiba Model F-7_{AD} pH meter was used for all pH measurements. IWAKI KM-Shaker was used for shaking. A Hitachi Model 170-10 atomic absorption spectrophotometer(AAS) was also used for the determination of metal ions in aqueous solution. The HPLC was performed at room temperature with Hitachi model L-6200, L-4200 ultraviolet-visible detector and D-2500 chromato-integrator. The column used was the ERC-ODS 1282(i.d. 6 mm × 250 mm height, Erma Co., Japan).

Preparation of the resins loaded dithiosemicarbazone compounds

The XAD resins (25 g) were added to 50 ml of each DMF solution containing 0.005–$0.01M$ of dithiosemicarbazones, and the mixture was stirred at room temperature for 2 hr. The resins loaded with each reagent was filtered off, washed with water, and dried at room temperature for 24 hr in a vacuum dry oven. The total loaded amounts of dithiosemicarbazone compounds on the resins were determined spectrophotometrically after elution with DMF from the resins.

Collection behavior of copper(II) ion on the reagent loaded resins

Add 0.5 g of each reagent-loaded resin and 20 ml aliquots of aqueous solution containing known amounts of copper(II) to a 30-ml screw-capped glass bottle, then shake for 2 hr. After filtration, the amounts of copper(II) adsorbed on the resins were decided by comparing the concentration of equal aliquot portion of the solution before and after collection by AAS.



	$-R_1$	$-R_2$
GDS	-H	-H
GBS	-H	$-C_6H_5$
DMBS	$-CH_3$	$-C_6H_5$

Fig. 1. Dithiosemicarbazone compounds.

Table 1. Total adsorption capacity of dithiosemicarbazone compounds on Amberlite XAD resins

	Amount loaded reagents (*μmole/g*)		
Supports	GDS	GBS	DMBS
XAD-4	8.4	15.0	15.1
XAD-7	14.6	19.8	22.9
XAD-16	15.2	28.1	28.3

Preconcentration of metal ions for the determination by HPLC

To screw-capped glass bottles (30–200 ml), add 0.1 g of DMBS-loaded Amberlite XAD-7 resin and 20–200 ml of each solution containing 0.6–3 g of mercury(II), copper(II), zinc(II), cadmium(II), lead(II) and palladium(II) adjusted to the desired pH. After shaking for a constant time, filter the solution with a polyethylene column (i.d. 9 mm × 65 mm height) fitted with a porous polyethylene disk with a 20-μm pore size, and then elute their DMBS chelates with 1 ml of DMF from the resin, and inject 5–10 μl of the DMF solution to HPLC.

RESULTS AND DISCUSSION

Properties of the dithiosemicarbazone compounds-loaded resins

The XAD resins are easily converted into resins loaded with dithiosemicarbazone compounds by mixing with each reagent–DMF solution for more than 30 min. The resins prepared were stable for several months if stored in a desiccator in the dark. Table 1 shows the total amount of the reagents in the resins. The loaded amount of each reagent on the resins increased in the order of XAD-16 > XAD-7 > XAD-4 in the same reagent and of DMBS > GBS > GDS in the same resin. The presence of phenyl substituents in the reagents enhances the adsorption on the resins, and it is also likely to be concerned with the properties such as framework and polarity of resins, and the hydrophobicity of the functional group in the reagents to the mechanism of adsorption of the reagents on the resins.

Collection behavior of copper(II)

The copper(II) was selected as a model ion to test whether or not it could be efficiently removed from aqueous solution by each reagent loaded resin. The adsorption of copper(II) was not reproducible with the GDS-loaded resins due to partial elution of GDS from the resins by contacting with aqueous solution. As shown in Fig. 2, copper(II) was quantitatively collected with DMBS-loaded XAD-7 resin by shaking for a short time, while its adsorptivity was lower in DMBS-loaded XAD-4 and -16 resins. The similar results were observed for the GBS-loaded resin systems. It is suggested that the XAD-7 may be moistened easily in aqueous solution compared to the XAD-4 and -16.

The adsorption behavior of copper(II) was examined by using the GBS- and DMBS-loaded XAD-7 resins which had high adsorption abilities. It can be seen from Fig. 3 that the adsorption behavior of copper is of the Langmuir type. The capacity of the GBS- and DMBS-loaded resins for copper(II) (q_∞, mg/g) at pH 4.0 was calculated by using the Langmuir equation

$$c/q = c/q_\infty + 1/q_\infty k$$

where q, c and k are the amount of copper(II) adsorbed (mg/l.), the equilibrium concentration (mg/l.) and the equilibrium constant (l./mg), respectively. The capacity of copper(II) for the GBS- and DMBS-loaded resins calculated from the q_∞ values were 19.7 and 21.0 μmol/g, respectively. From the amount of GBS and DMBS retained on the XAD-7 resins, the molar ratio of GBS and DMBS to copper(II) is 1:1. These results show that the dithiosemicarbazone compounds form 1:1 chelates with divalent metal ions.[1-3] On the basis of these results, the DMBS-loaded Amberlite XAD-7 was selected for further study.

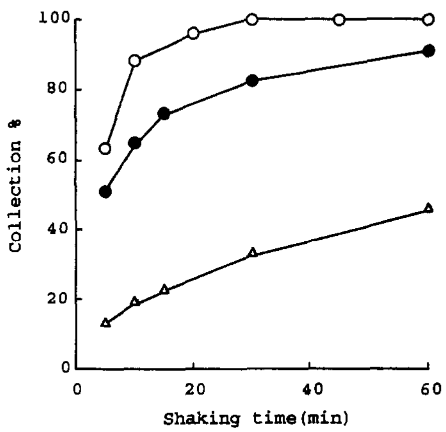


Fig. 2. Effect of shaking time for the collection of Cu(II) on DMBS-loaded XAD-7 (-○-), -16 (-●-) and -4 (-△-) resins (0.5 g) from 20 ml of solution containing 20 μg of Cu(II) at pH 4.

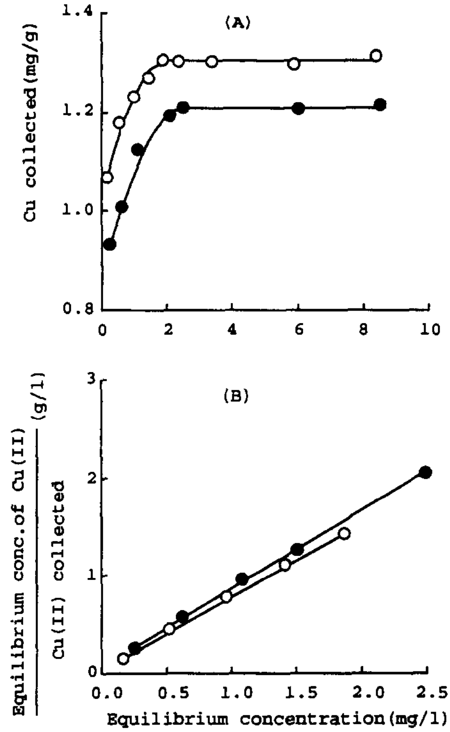


Fig. 3. Adsorption isotherms of Cu(II) on DMBS (-○-)- and GBS (-●-)-loaded XAD-7 resins (A), and Langmuir plot (B).

Collection and elution of metal ions on DMBS-loaded Amberlite XAD-7 resin

The collection behavior of metal ions with DMBS-loaded Amberlite XAD-7 resin was investigated. As shown in Fig. 4, palladium(II), mercury(II) and copper(II) were quantitatively

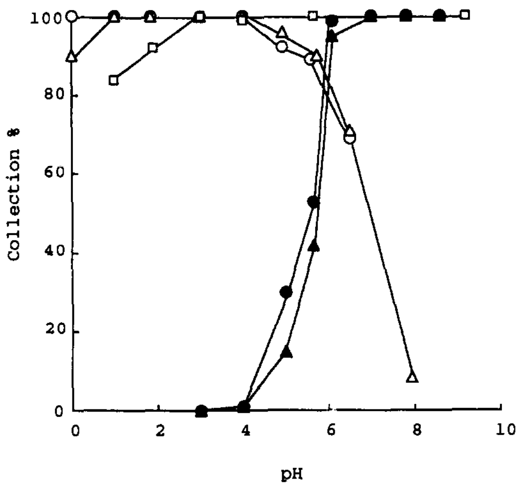


Fig. 4. Effect of pH on the collection of metal ions with 0.1 g of DMBS-loaded XAD-7 resin. The concentration of metal ions in 20 ml of sample solution are 1 μg for Hg(II) (○), 0.8 μg for Cu(II) (□), 0.6 μg for Pd(II) (△) and Cd(II) (●), and 3 μg for Pb(II) (▲). The shaking time is 60 min.

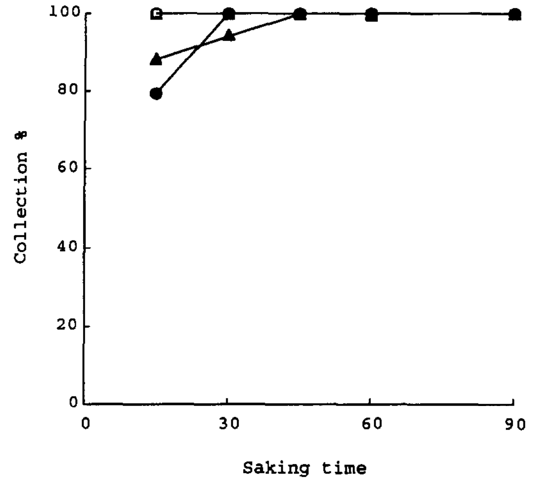


Fig. 5. Effect of shaking time on the collection of metal ions. The pH conditions are 2 for Hg(II) and Pd(II), and 8 for Cu(II), Cd(II) and Pb(II). Other conditions are same as those for Fig. 4.

collected from acidic medium to the resin, cadmium(II) and lead(II) from neutral medium. The collection of zinc(II) was not reproducible and the maximum collection was less than 90% even at pH 8, although the reasons for this was not clear. The optimum pH ranges were very similar to those for the chelation in 80(v/v)% DMF-water mixed solution except for zinc (II).[5] Figure 5 shows the effect of the shaking time for the quantitative collection of metal ions at the optimum pH conditions. The quantitative collections were achieved within 15 min for mercury(II), palladium(II) and copper(II), 30 for cadmium(II), and 45 for lead(II). As shown in Fig. 6, up to 150-fold for mercury(II) and palladium(II), and 100-fold concentrations for copper(II), cadmium(II) and lead(II) could easily be achieved when eluted with 1 ml of DMF.

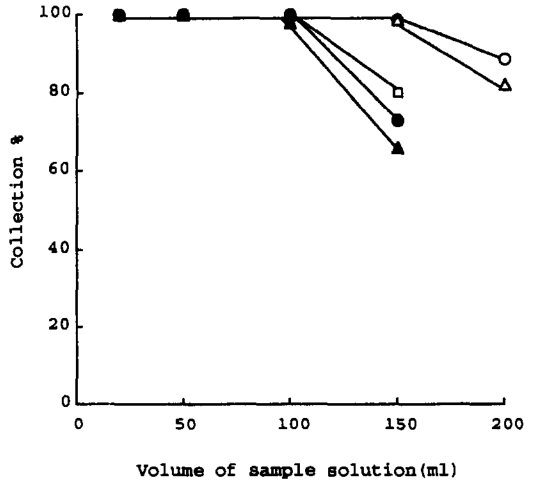


Fig. 6. Effect of sample volume on the collection of metal ions. The conditions are same as those for Fig. 5 except volume of sample solution. The shaking time is 60 min.

After the quantitative collection of metal ions, the elution of metal ions as their DMBS chelates with 1 ml of DMF were investigated. Each metal chelate was quantitatively eluted with first 1 ml of DMF. Figure 7 shows the chromatograms of the metal–DMBS chelates in some mobile phase conditions after the collection from 20 ml of aqueous solution adjusted to pH 2 or 8 and elution with 1 ml of DMF. The HPLC conditions are the same as those already described.[5] Addition of sodium acetate in the mobile phase required the reproducible chromatogram for cadmium(II) and lead(II) due to the dissociation of their DMBS chelates in acidic medium. Thus, it was possible to determine exclusive or simultaneous determination of their metal ions by selecting the mobile phase of HPLC and pH of aqueous solution. Cadmium(II) and lead(II) collected on the resin were also eluted with 5 ml of 1*M* hydrochloric acid solution. The resin, once used in batch operation of collection and elution for cadmium(II) and lead(II), could be re-used at least six times without losing the ability for the quantitative collection of their metal ions.

Many polymeric substances coated with sulfur-containing ligands have been developed for preconcentration of mainly heavy metal ions from aqueous solution.[9,12,16,18–20,23,24] The DMBS-loaded resin has advantages and disadvantages compared with other resins coated with sulfur-containing ligands. The collection of metal ions on the resin is time-consuming, and the elution of mercury(II), palladium(II) and copper(II) collected on the resin with acid solution is very difficult because of the formation of very stable DMBS chelates even in strong acidic medium. However, the elution as their DMBS chelates with a small volume of DMF is very easy, thus a high concentration factor can be obtained, and the regeneration of the resin loaded with DMBS is very simple after washing the resin used, and the resin prepared is very stable. The present method may be applicable to the preconcentration of metal ions for the spectrophotometric determination and the reversed-phase HPLC with a spectrophotometric detection. Further investigation for practical samples is required.

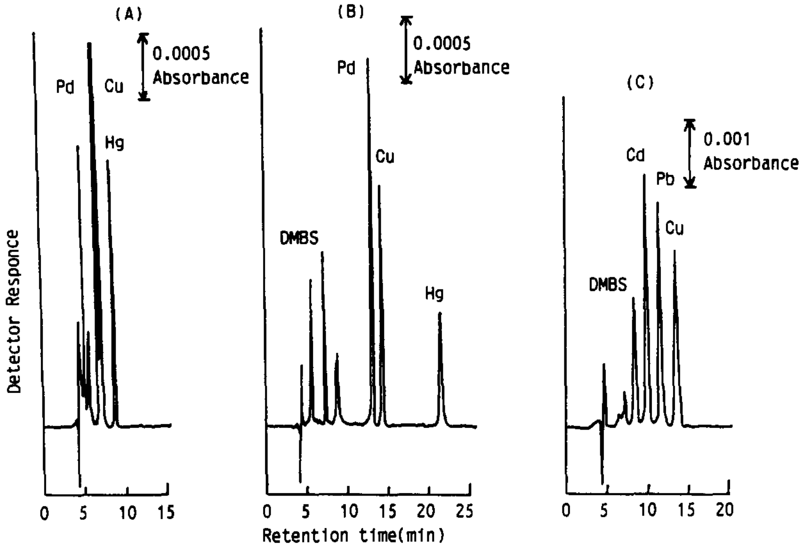


Fig. 7. Chromatograms of the metal-DMBS chelates. Mobile phase: (A) 80(v/v)% acetone-water; (B) 70(v/v)% acetone-water; and (C) 70(v/v)% acetone-water containing 0.001*M* sodium acetate; Flow rate: 1 ml/min; Injected volume: (A) and (B) 5 μl; (C) 10 μl.

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