DETERMINATION OF METAL IONS IN ENVIRONMENTAL WATERS BY FLAMELESS ATOMIC ABSORPTION SPECTROMETRY COMBINED WITH PRECONCENTRATION USING A SULFONATED DITHIZONE-LOADED RESIN

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Abstract - Flameless atomic absorption spectrophotometric methods combined with preconcentration by using tailor made chelate-forming resins have been developed for the determination of very low concentrations of several heavy metal ions in environmental water samples. The chelate-forming resin is prepared by loading a sulfonated dithizone (DzS) on an anion-exchange resin. DzS-loaded resin is useful for selective collection of heavy metal ions. The resin, in which metal ions are adsorbed, is introduced into a graphite-furnace in the determination of nickel(II), cobalt(II), copper(II) and palladium(II) and into a vessel for hydride generation in the case of lead(II), without eluting the metal ions from the resin. The proposed methods have been applied successfully to the determination of trace amounts of heavy metal ions in environmental water samples.

Key words preconcentration, graphite-furnace atomic absorption spectrophotometry, hydride generation atomic absorption spectrophotometry, ion-exchange, dithizone

Atomic absorption spectrophotometry has been widely used for the routine analysis. However, it does not have sufficient sensitivity for very low concentrations of heavy metal ions in environmental water samples. Its detection limits decrease by the combination with preconcentration techniques such as solvent extraction and collection with solid adsorbents. We have developed tailor made chelate-forming resins for the collection of trace amounts of heavy metal ions in environmental water samples by using commercially available anion-exchange resins and thiol type chelating agents such as sulfonic acid derivatives of dithizone (DzS), 8-mercaptoquinoline and bismuthiol-II. In this report, we have proposed simple methods for the determination of heavy metal ions such as nickel(II), cobalt(II), copper(II), palladium(II) and lead(II) in environmental water samples by flameless atomic spectrophotometry combined with preconcentration using DzS-loaded resin and direct introduction of the suspension of metal-adsorbed resin into the graphite-furnace and hydride generation vessel.

EXPERIMENTAL

Apparatus A Nippon Jarrel-Ash AA-880 atomic absorption spectrometer equipped with a flameless atomizer FLA-1000 was used. In the case of lead(II), a hydride generator HYD-1 and a hydride heat atomizer HYD-2 were equipped.

Reagents DzS was prepared as reported previously [1]. Amberlite IRA 400 (200-400 mesh) in chloride form was used as an anion-exchange resin. Metal stock solutions (1000 µg/ml) were obtained from Wako Pure Chemical Industries. Highly purified water was obtained by using a Millipore Milli-Q water system. All other reagents were of analytical reagent grade.

Preparation of DzS-loaded resin The anion-exchange resin (10 g) was added to an aqueous solution of DzS (10^{-3} M, 100 ml). The mixture was shaken by using a mechanical shaker until the supernatant solution became colorless. The resulting reddish DzS-loaded resin was separated, washed with water and methanol, and stored in a desiccator in which the humidity was adjusted to about 30%.

Analytical procedure Environmental water samples were filtered through a glass fiber filter (Whatman GF/C 47 mm) immediately after sampling. The pH value of the samples was adjusted to 5.0–7.0 by adding 0.05 M K_2PO_4 and KH_2O_4 . DzS-loaded resin (50 mg) was added to the sample (200–3000 ml). The mixture was incubated for 2–10 hr at room temperature. The resin was then separated from the mixture by filtration, washed with water and methanol, air-dried, and stored in the desiccator. The metal-adsorbed resin (20 mg) was suspended in 2.0 ml of distilled water, and the suspension (20 μ l) was introduced into a graphite-furnace in the determination of nickel(II), cobalt(II), copper(II) and palladium(II). In the case of lead(II), the metal-adsorbed resin (40 mg) was suspended in 40 ml of distilled water. The suspension was introduced into a vessel for hydride generation by a peristaltic pump with 15% hydrogen peroxide, 5% sodium borohydride (2.5% sodium hydroxide) and 1.2 M hydrochloric acid.

RESULTS AND DISCUSSION

Stability of DzS in the resin The mechanism of the immobilization of DzS molecules by the anion-exchange resin is based not only on ion-exchange but also on non-electrostatic interaction between styrene moieties of the resin matrix and DzS molecules. A schematic diagram of one DzS molecule immobilized on anion-exchange resin is shown in Fig. 1. DzS molecules were not released even in 1.0 M sodium chloride. However, DzS is unstable in strongly acidic medium such as in 0.5 M hydrochloric acid, because it is easily oxidized to form dehydrodithizone type compound [2].

-----: ion-exchange, non-electrostatic interaction and metal binding

Fig. 1. Schematic diagram of DzS molecule immobilized on anion-exchange resin

Uptake of metal ions by DzS-loaded resin The optimum pH ranges were 1 to 10 for palladium(II), 5 to 10 for copper(II), 6 to 10 for cobalt(II), and 6.5 to 10 for lead(II) and nickel(II). Readiness of metal ion uptake decreases in the order of palladium(II) > copper(II) > cobalt(II) > lead(II) > nickel(II), which is in accord with the order of the extractability in a dithizone-carbon tetrachloride extraction system [3]. Uptake of metal ions by DzS-loaded resin is based on the formation of metal complexes of the same coordination structure as that of dithizone.

Determination of metal ions by graphite-furnace atomic absorption spectrophotometry When solid adsorbents are used for preconcentration of metal ions, the metal ions are usually eluted from the adsorbents prior to measurement procedure. However, elution procedure increases the time required for analyses, and involves risks of contamination. We propose here a graphite-furnace atomic absorption spectrophotometric method combined with a kind of solid sampling technique, that is, direct introduction of resin suspension

into the graphite-furnace. The analytical procedure for the determination of metal ions except lead(II) was shown in Fig. 2. Calibration curves obtained by using the metal-adsorbed resin suspensions were almost the same as those obtained by using standard aqueous solutions of the corresponding metal ions.

Fig. 2. Procedure for the determination of metal ions by graphite-furnace atomic absorption spectrophotometry

Determination of lead(II) by hydride generation atomic absorption spectrophotometry In order to determine the optimum conditions to convert lead(II) into its hydride in the presence of DzS-loaded resin, the effects of concentrations of hydrochloric acid, sodium borohydride, and hydrogen peroxide on absorption intensity were investigated. In the cases of hydrochloric acid and hydrogen peroxide, the optimum concentration ranges were 1.0 to 1.6 M and 10 to 20%, respectively. On the other hand, in the case of sodium borohydride, generation of lead hydride increased with increasing the concentration of sodium borohydride under the conditions. To prevent the quartz cell from deteriorating, the concentration of sodium borohydride was adjusted to 5%. These effects of the reagents on the generation of lead hydride in the presence of DzS-loaded resin was almost the same as those in the absence of DzS-loaded resin. This finding suggests that the lead(II) ions are no longer adsorbed in the resin. Calibration curve obtained by using the lead-adsorbed resin suspension was almost the same as that obtained by using the standard aqueous solution of lead(II).

Effect of chelating agents on the generation of lead hydride Chelating agents such as EDTA and 8-mercatoquinoline sulfonic acid, and chelating resin such as Chelex-100 interfere seriously with the generation of lead hydride. On the other hand, DzS and DzS-loaded resin do not. The results are summarized in TABLE 1. The effective conversion of lead(II) into its hydride in the presence of DzS and DzS-loaded resin may be attributed to the unstableness of DzS in strongly acidic medium.

Determination of metal ions in an environmental water sample The concentrations of nickel(II), cobalt(II), copper(II), palladium(II) and lead(II) in a spring water sample collected in Osaka, Japan were determined by the proposed methods. The results are summarized in TABLE 2.

CONCLUSION

A graphite-furnace atomic absorption spectrophotometric method combined with preconcentration using tailor made chelate-forming resins such as DzS-loaded resin and direct introduction of the resin suspension can be applied successfully to the determination of low concentrations of heavy metal ions except lead(II) in environmental water samples. Lead(II) adsorbed in DzS-loaded resin is determined by hydride generation atomic absorption spectrophotometry.

TABLE 1. Effect of chelating agents and chelating resins on the generation of lead hydride

Chelating agent 0.1 mM	Relative absorbance Pb(II): 500 ng/ml
none	1.00
DzS	1.02
MQS ^a	0.62
EDTA	0.01
DzS-loaded resin ^b	1.03
Chelex-100 ^b	0.00

^a8-mercaptoquinoline-5-sulfonic acid

^bsuspension of lead-adsorbed resin: 1 mg resin per one ml of distilled water

TABLE 2. Heavy metal contents in a spring water sample

Metal	Found, ppb(*ppt) $\pm$ s.d.
copper(II)	4.9 $\pm$ 1.6
cobalt(II)	*33 $\pm$ 2
nickel(II)	0.66 $\pm$ 0.03
palladium(II)	*22 $\pm$ 2
lead(II)	1.2 $\pm$ 0.0

The sample was collected in September, 1990 in Osaka.

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