Notes

Preconcentration of Heavy Metal Ions Using Synergistic Extraction with Dithizone and Tributylphosphine Oxide on the Basis of HSAB Rule

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Synergistic extraction with a mixture of dithizone and tributylphosphine oxide (TBPO) has been applied to the preconcentration of Co^{II} and Cd^{II} in river waters.^{1,2} Chelate extraction constants (K_{ex}) could be rationalized by HSAB (hard and soft acids and bases) rule³, into which a new dual parameter scale for strength (S_{A}) and soft (σ_{A}) factors of a metal ion (M^{z+}) was introduced:⁴

$$\log K_{\text{ex}} + zpK_{\text{a}} = S_{\text{A}}S_{\text{B}} + \sigma_{\text{A}}\sigma_{\text{B}} \quad (1)$$

where the subscripts A and B denote Lewis acid and base, and pK_{a} is the acid dissociation exponent of a chelating agent. In this work, a method for simultaneous preconcentration of Cd^{II} , Co^{II} , Cu^{II} , Ni^{II} , Pb^{II} and Zn^{II} using dithizone extraction was designed based on the HSAB rule, and was applied to inductively coupled plasma atomic emission spectrometry (ICP-AES).

Experimental

Apparatus

A Shimadzu Model ICPS-1000III ICP atomic emission spectrometer equipped with a plasma torch for organic solvent was used. The operating conditions of the spectrometer are summarized in Table 1. A Horiba Model F-80 pH analyzer and an Iwaki KM type shaker were used for pH measurements and shaking of separatory funnels, respectively.

Table 1 Operating conditions of the ICP spectrometer

RF power, W	1.4
Argon flow rate, l/min	
coolant gas	14
plasma gas	1.2
carrier gas	0.6
Observation height, mm	15
Analytical line, nm	
Pb 220.353 I	Zn 213.856 I
Cd 214.438 I	Co 228.616 II
Cu 324.754 I	Ni 221.647 II

Reagents

Standard metal(II) solution: a weighed amount of metal powder (Soekawa Chemical Co., Ltd., 99.9%) or metal(II) salt (Wako Pure Chemicals Co., Ltd.) was dissolved in (1+1) nitric acid or water and then diluted to 1 dm³ with water. The working solutions were prepared by diluting the stock solution.

Dithizone-TBPO solution: a weighed amount of dithizone (Wako Pure Chemicals Co., Ltd.) and TBPO (Tokyo Chemical Ind. Co., Ltd.) were dissolved in xylene to obtain 1.5×10^{-3} and 1.0×10^{-1} mol dm⁻³ solution, respectively.

Acetate buffer solution (pH 6.0): a 0.2 mol dm⁻³ acetic acid solution and a 0.2 mol dm⁻³ ammonium acetate solution were mixed at an appropriate proportion.

All other chemicals used were of analytical reagent grade. Deionized water was used throughout.

Preconcentration procedure

To 300 cm³ of a water sample solution in a separatory funnel was added 3 mol dm⁻³ ammonia. The pH was preliminarily adjusted to *ca.* 6.0. Then, 10 cm³ of acetate buffer solution and 3 cm³ of dithizone and TBPO solution were added, and the mixture was shaken for 30 min. After the phases were allowed to separate, each of the two phases was applied to ICP-AES and the pH of the aqueous phase was measured.

Results and Discussion

The extraction of a divalent metal ion with dithizone (H_2dz) proceeds according to Eq. (2):

where the subscript org denotes the organic phase. By assuming $D = [\text{M}(\text{Hdz})_{2,\text{org}}][\text{M}^{2+}]^{-1}$, Eq. (3) can be obtained:

$$\log D = \log K_{\text{ex}} + 2\log [\text{H}_2\text{dz}]_{\text{org}} + 2\text{pH}. \quad (3)$$

Into this, Eq. (1) is introduced; the resulting equation is

Table 2 pH limit for preconcentration

Cd ^{II}	Co ^{II}	Cu ^{II}	Ni ^{II}	Pb ^{II}	Zn ^{II}
5.6	3.6	-0.6	3.5	4.5	7.7

Fig. 1 Extraction curve for Zn^{II}.

as follows:

$$\log D = S_A S_B + \sigma_A \sigma_B - 2pK_a + 2\log[H_2dz]_{org} + 2pH. \quad (4)$$

In the case that the volume ratio of the aqueous phase to the organic phase is 100, $\log D$ should exceed 4 for the quantitative extraction of a metal ion, namely 99% extraction. Since $S_B=0.46$, $\delta_B=0.44$, $pK_a=4.47$,⁴ and $[H_2dz]_{org}=1.5 \times 10^{-3} \text{ mol dm}^{-3}$, pH limit for preconcentration of an analyte can be calculated by using Eq. (4). The results of calculations are given in Table 2. Among the values given in Table 2, the pH limit for Zn^{II} is higher than 6.0, indicating that quantitative preconcentration of Zn^{II} may be unsuccessful. Thus, TBPO was used for synergist to obtain quantitative extraction of Zn^{II} at pH 6.0. Figure 1 shows the extraction curve obtained with a mixture of dithizone and TBPO. The extraction of Zn^{II} is quantitative at pH=6.0. The quantitative extraction of other divalent metal ions than Zn^{II} has already been confirmed empirically. In conclusion,

Table 3 Analytical results for the Watarase River water samples

	Found ^a /μg dm ⁻³	D. L.	Added/μg	Rec., %
Cd	0.57±0.002	0.054	0.090	121
Co	0.73±0.05	0.41	0.30	127
Cu	85.0 ±0.45	0.18	5.1	110
Ni	17.0 ±0.6	0.57	3.0	122
Pb	3.2 ±0.035	0.87	0.17	116
Zn	88.0 ±0.07	0.042	5.2	108

a. Average and standard deviation of three to six determinations.

judging from the above discussion, the proposed method for preconcentration will be practically useful.

Analytical results are given in Table 3, where sample was taken from the Watarase River, and filtered through 0.45 μm membrane filter. The filtrate was stored in a polyethylene bottle and analyzed as soon as possible. Results of accuracy test by the standard addition method and reproducibilities in Table 3 are satisfactory. Here, rather high recovery is attributable to the decrease in the volume of the organic phase after shaking with the aqueous phase. These facts suggest that design of preconcentration based on the HSAB rule is feasible.

References

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