Concentration of Trace Heavy Metal Ions in Water by Ion Flotation Using 1,10-Phenanthroline

Toshiyuki HOB0, Katsurou YAMADA and Shigetaka SUZUKI

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukasawa, Setagaya, Tokyo 158

An ion flotation-atomic absorption spectrometric method is described for the determination of six heavy metal ions: Fe(III), Ni(II), Co(II), Cu(II), Cd(II) and Zn(II), in water. Heavy metal ions in 1000 ml samples were chelated with 1,10-phenanthroline at pH 4.0 and were floated with the aid of sodium lauryl sulfate and nitrogen bubbles. Each metal ion concentration was determined by a conventional flame atomic absorption spectrometry after diluting to 10 ml. The linear calibration curve of each ion was obtained in the concentration range of 4×10^{-8} M– 8×10^{-7} M. The proposed method was successfully applied to the determination of these ions in hot spring waters.

Keywords Ion flotation, heavy metals, 1,10-phenanthroline, atomic absorption spectrometry

Usually flotation is classified into two submethods¹, precipitate flotation and ion flotation. The former has been investigated more intensively than the latter.^{2–8} It has been applied to the analysis of various kinds of samples. The most distinctive feature of the precipitation flotation is that relatively higher number of elements can be collected at one time. The elements collected have been determined through specific methods such as atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry.

On the other hand, ion flotation is a rather selective concentration method. Formerly, we applied it to the concentration of Cr(VI)⁹, sulfide¹⁰, nitrite^{11,12}, Fe(III)¹³ and other ions.¹⁴ Those species collected were measured by spectrophotometry. To make the ion flotation less selective in concentration will be helpful. Based on the former investigation of ion flotation of Fe(III) ion by using 1,10-phenanthroline, we attempted to apply the method to the simultaneous concentration of several elements which seem to behave similarly to Fe(III) ion. Fe(III), Ni(II), Co(II), Cu(II), Cd(II) and Zn(II) were the elements examined. The method developed was successfully applied to the analysis of hot spring waters.

Experimental

Flotation system

A schematic diagram of ion flotation system is presented in Fig. 1. The foam separator is made of Pyrex glass cylinder (570 mm×70 mm i.d.) fitted with a

sintered glass filter (G3) to generate small bubbles.

Instruments

For the atomic absorption spectrometric measurement, a Shimadzu model AA-610 atomic absorption spectrophotometer with an air-acetylene flame burner was used. An inductively coupled plasma atomic emission spectrometric measurement was occasionally

Fig. 1 Schematic diagram of flotation system. a, nitrogen cylinder; b, flow meter; c, drain; d, foam separator; e, foam collector; f, flange; g, sintered glass; h, plunger pump; j, SLS solution reservoir.

carried out to examine the flotation efficiency under coexistence of several metal ions. The instrument used was a Jarrell-Ash model 975 PRASMA ATOM-COMP.

Chemicals

All chemicals used were of the highest grade available. The water used was purified by distillation and ion exchange. For the preparation of slightly acidic aqueous stock solutions of metal ions (1×10^{-4} M), ammonium iron(III) sulfate dodecahydrate, ammonium nickel(II) sulfate hexahydrate, cobalt(II) sulfate heptahydrate, copper(II) sulfate pentahydrate, cadmium metal and zinc metal were used. Their concentrations were ascertained by EDTA titrations. 1,10-Phenanthroline used was $C_{12}H_8N \cdot HCl \cdot H_2O$ and a 0.1 M aqueous solution of it was prepared. Aqueous solutions of hydroxylamine sulfate (10 w/v%) and sodium lauryl sulfate (SLS, 1 mg ml⁻¹) were also prepared.

Recommended procedure

Take 1000 ml of sample into a beaker. Add 2 ml of (1+1)sulfuric acid, 5 ml of 10% hydroxylamine sulfate and 3 ml of 10^{-2} M 1,10-phenanthroline solution. Adjust the pH to 4.0 with 6 M ammonia and stir the solution for 10 min. Pour the solution into the foam separation tube to which nitrogen gas is being fed at a low flow rate. After adjusting the nitrogen gas flow rate to 145 ml min⁻¹, add 1 ml of 1% SLS aq. solution from the top of the separator and at the same time start feeding the 1% SLS solution through the lower side tube at the flow rate of 0.335 ml min⁻¹. Collect the foam coming out of the separator in a 50 ml beaker which contained 2 ml of 1-propanol as the foam breaker. Continue the separation for 15 min. Measure the metal contents in the solution obtained by atomic absorption spectrometry after diluting to 10 ml with water or after digesting with nitric acid and diluting with water.

Results and Discussion

Flotation conditions analogous to the one reported for Fe(III) ion¹³ were employed. In that case, 2 ml of 10% hydroxylamine sulfate proved to be enough to reduce 4×10^{-7} M Fe(III) and did not interfere with the flotation at all. Further, 3 ml of 1,10-phenanthroline solution was shown to be sufficient for quantitative results. As for the addition of 1% SLS solution, it was necessary to add both from the top at the beginning and continuously from the bottom at a flow rate of more than 0.17 ml min⁻¹. Unless it was added from the top, several large scums which originated from $[Fe(phen)]^{2+}(LS)^-$ remained on the surface of the separator and prevented the quantitative flotation. Accordingly, 2 ml for 10% hydroxylamine sulfate solution, 3 ml for 1,10-phenanthroline solution and

0.335 ml min⁻¹ for 1% SLS solution were chosen as appropriate conditions for the following experiments.

Effect of pH

The hydrogen ion concentration has a significant effect on the formation of chelate and on the flotation process. Therefore, the effect of pH on the recoveries of those metal ions was examined. Typical results are shown in Fig. 2. The pH ranges in which the recoveries were quantitative are 2.7–8.7, 3.0–8.4, 3.0–8.6, 3.0–6.0, 2.5–8.1 and 3.3–8.0 for Cu(II), Cd(II), Co(II), Zn(II), Ni(II) and Fe(III), respectively. Those six metal ions apparently floated all together when the pH of the solution is controlled between 3.3 and 6.0.

Effect of nitrogen flow rate and separation time on recovery

Nitrogen flow rate is an important factor for high

Fig. 2 Effect of pH on ion flotation of Cu(II), Cd(II), Co(II) and Zn(II). Concentration of each ion, 4×10^{-7} M; N₂ flow rate, 145 ml min⁻¹; flotation time, 15 min.

Fig. 3 Effect of N₂ flow rate on Zn(II) recovery and concentration ratio. Zn(II) concentration, 4×10^{-7} M; pH 4.0; flotation time, 15 min.

Fig. 4 Effect of flotation time on the recoveries of Cu(II) and Zn(II) ions. Cu(II) and Zn(II) ion concentrations, each 4×10^{-7} M; pH 4.0; N_2 flow rate, 145 ml min^{-1} .

recovery and high concentration ratio, and short separation time. Effects were examined at a fixed separation time of 15 min, while the flow rate was varied between 60 ml min^{-1} and 184 ml min^{-1} .

Results for Zn(II) ion are illustrated in Fig. 3. Similar results were obtained for other metal ions. The recovery reached a maximum when the flow rate increased to more than 104 ml min^{-1} , and the more the flow rate, the less the concentration ratio. Considering other results such as those for Cu(II) ion, which should be floated at a higher rate than 140 ml min^{-1} , 145 ml min^{-1} was chosen as appropriate for the nitrogen gas flow rate.

The effect of separation time was also examined. Results on Cu(II) and Zn(II) ions are presented in Fig. 4. As shown in the figure, the curves obtained were different from each other. For example, the recoveries at 3 min after the front of the foam passed by the top of the separation tube were 30, 59, 33, 36 and 48% for Cu(II), Cd(II), Co(II), Zn(II) and Fe(III), respectively. Maximum and quantitative recoveries of them were attained after 12 min, except for Zn(II) ion which needs only 9 min. Fifteen minutes was chosen for the separation time.

From those results, the recommended procedure mentioned earlier was established.

Flotation of mixture

Coflotability of those metal ions was examined in the concentration range of 4×10^{-8} M– 8×10^{-7} M of each metal ion. In this experiment, inductively coupled

Table 1 Determination of six heavy metal ion concentrations in hot spring waters

	Concentration/M			
	Sample ^a I	II	III	IV
Fe ³⁺	—	2.2×10^{-7}	1.5×10^{-7}	7.0×10^{-7}
Cu ²⁺	8.0×10^{-8}	8.5×10^{-8}	2.5×10^{-8}	1.9×10^{-8}
Ni ²⁺	2.8×10^{-8}	1.0×10^{-8}	1.7×10^{-8}	2.0×10^{-8}
Cd ²⁺	0.3×10^{-8}	0.4×10^{-8}	1.1×10^{-8}	0.8×10^{-8}
Co ²⁺	1.3×10^{-8}	ND	0.2×10^{-8}	1.1×10^{-8}
Zn ²⁺	2.0×10^{-7}	8.8×10^{-7}	2.0×10^{-6}	4.2×10^{-7}

a. Samples were collected at: Miyanoshita station, Hakone-machi (I, June 27, 1983), Ninotaira hot spring, Hakone-machi (II, February 8, 1983), Yugawara hot spring, Yugawara-machi (III, February 8, 1983), and Oohiradai hot spring, Hakone-machi (IV, February 8, 1983).

plasma atomic spectrometry was used for the determination of floated ions. All metal ions proved to be quantitatively floatable and their working curves were all linear within the range examined.

Application

The method was applied to the determination of six metal ions in the hot spring waters in Hakone and Yugawara areas. Contents of these heavy metal ions in hot spring water are so low that few reports on their concentration were available. The samples were acidified ($\text{pH} < 2$) with sulfuric acid and brought back to the laboratory and analyzed after they were filtered through a membrane filter (pore size $0.45 \mu\text{m}$). The results on the six metal ions are presented in Table 1. A standard addition method was employed for the flotation-atomic absorption spectrometric measurements. As shown in the Table, the concentrations of Co(II) and Cd(II) ions are very low and that of Zn(II) ion is rather high.

The method proposed is applicable to actual samples. The other heavy metal ions which form chelates easily with 1,10-phenanthroline could be floated by the present method; so far, it has been confirmed that Pd(II) and Mn(II) ions are also quantitatively floated at pH 4.1–6.1 and 5.1–8.1, respectively. Silver(I) ion, however, did not give satisfactory results, probably due to the presence of chloride ion which came from 1,10-phenanthroline.

References

1. A. Mizuike and M. Hiraide, *Pure Appl. Chem.*, **54**, 1566 (1982).
2. M. Hiraide, T. Ito, M. Baba, H. Kawaguchi and A. Mizuike, *Anal. Chem.*, **52**, 804 (1980).
3. M. Hiraide, K. Sakurai and A. Mizuike, *Anal. Chem.*, **56**, 2851 (1984).
4. E. H. DeCarlo, H. Zeitlin and Q. Fernando, *Anal. Chem.*, **53**, 1104 (1981).
5. E. H. DeCarlo, H. Zeitlin and Q. Fernando, *Anal.*

- Chem.*, **54**, 898 (1982).
6. R. S. Shreedhara Murthy and D. E. Ryan, *Anal. Chem.*, **55**, 682 (1983).
 7. S. Nakashima and M. Yagi, *Anal. Chim. Acta*, **157**, 187 (1984).
 8. M. Aoyama, T. Hobo and S. Suzuki, *Anal. Chim. Acta*, **153**, 293 (1983).
 9. M. Aoyama, T. Hobo and S. Suzuki, *Anal. Chim. Acta*, **129**, 237 (1981).
 10. M. Aoyama, T. Hobo and S. Suzuki, *Bunseki Kagaku*, **31**, E7 (1982).
 11. M. Aoyama, T. Hobo and S. Suzuki, *Bunseki Kagaku*, **31**, E99 (1982).
 12. M. Aoyama, T. Hobo and S. Suzuki, *Anal. Chim. Acta*, **141**, 427 (1982).
 13. K. Yamada, M. Aoyama, T. Hobo and S. Suzuki, *Bunseki Kagaku*, **33**, 99 (1984).
 14. S. Suzuki, T. Hobo and Y. Asaumi, *Bunseki Kagaku*, **31**, 13 (1982).

(Received April 15, 1986)

(Accepted May 23, 1986)