Notes

Coprecipitation of Copper(II)-Humic Complexes with Indium Hydroxide**Masataka HIRAIDE, Hiroshi HOMMI and Hiroshi KAWAGUCHI***Faculty of Engineering, Nagoya University, Nagoya 464-01, Japan***Keywords** Water analysis, coprecipitation, indium hydroxide, copper(II)-humic complexes, humic acid, fulvic acid

Concentration of traces of heavy metals is often required prior to the instrumental determination to lower the detection limits and to improve the precision and accuracy of analytical results. Coprecipitation with indium hydroxide is one of the most effective multielement preconcentration techniques in water analysis.^{1,2} It is directly combined with inductively-coupled plasma (ICP) atomic emission spectrometry because of the simple emission spectrum of indium¹ and also combined with graphite-furnace atomic absorption spectrometry because of ease of removal of indium as bromide at the ashing stage.³

Traces of heavy metals in natural waters, however, exist in various physicochemical forms⁴, which may exhibit different separation behavior in coprecipitation. According to the previous work², hydrated heavy metal ions, hydroxo complexes, inorganic colloids and suspended particles are simultaneously coprecipitated with indium hydroxide at pH 9.0 to 9.5. The behavior of metal-humic complexes, however, is not quite clear because neither coprecipitation of fulvic acid complexes nor interference of soluble silica (monosilicic acid) has been discussed at all.

Humic and fulvic acids are the major organic constituents in natural waters and interact with metal ions to form water-soluble complexes.⁵ Actually, 60–70% of the copper dissolved in river water was found to be humic complexes.^{6,7} In the present work, therefore, coprecipitation of copper(II)-humic complexes as well as humic and fulvic acids was studied in detail in the presence of soluble silica. Analytical results for copper in river water obtained by coprecipitation closely agreed with those obtained by evaporation, indicating that nearly all copper species can be collected on indium hydroxide.

Experimental*Apparatus*

A Shimadzu UV-180 spectrophotometer with 5-cm cells was used for the measurement of absorbance of humic and fulvic acids. A Seiko I & E SPQ-6100A

ICP-mass spectrometer was used for the determination of heavy metals.

Reagents

A humic acid solution (0.50 mg ml⁻¹) was prepared by dissolving humic acid (Nakarai Chemicals) in 0.1 M potassium hydroxide and filtering through 0.4-μm Nuclepore filters; the absorptivity of the solution was 12 mg⁻¹ cm². Fulvic acid⁸ was dissolved in water (1 mg ml⁻¹); the absorptivity was 0.86 mg⁻¹ cm².

An indium solution (10 mg In ml⁻¹, in 0.1 M nitric acid) was prepared from 99.9999% indium metal (Rear Metallic). A silica solution (1 mg Si ml⁻¹) was prepared by dissolving sodium silicate in water.

A macroreticular anion-exchanger, diethylaminoethyl Sephadex A-25 (Pharmacia Fine Chemicals), was ultrasonically washed in 0.1 M hydrochloric acid, followed by washing in water. The supernatant solution was neutralized with 1 M sodium hydroxide; then the slurry was transferred into a column (5 mm diam. × 30 mm).

Procedure

To a 50-ml sample was added 0.5 ml of indium solution and the pH was adjusted to different values with 0.01 and 0.1 M potassium hydroxide. The solution containing indium hydroxide was stirred for 5 min; then the precipitate was centrifuged at 3000 rpm for 10 min. The supernatant solution was collected and reserved for the determination of humic substances by spectrophotometry at 400 nm or determination of heavy metals by ICP-mass spectrometry (ICP-MS). The precipitate in the centrifuge tube was dissolved in 1 ml of 1 M nitric acid; then the solution was diluted to 2 ml with water for ICP-MS.

Results and Discussion

Indium hydroxide was precipitated at different pH values from water containing humic or fulvic acid. The humic recovery was obtained spectrophotometrically as described in *Procedure*. Similar experiments were

carried out with iron(III) hydroxide. Figure 1 illustrates the effect of pH on coprecipitation. Both hydroxides were formed at pH 6, where humic substances were collected quantitatively. Humic and fulvic acids were recovered in greater than 90% yields at the pH up to 9.5 or 8.0 with indium or iron(III) hydroxide, respectively. The recovery, however, rapidly decreased at higher pH's.

River water generally contains appreciable amounts of soluble silica, which interfere with coprecipitation of humic substances, especially in alkaline solutions, as shown in Fig. 2. For example, in the case of indium hydroxide, humic or fulvic acid decreased in recovery from 95% to 70% at pH 9.5

Coprecipitation with indium hydroxide is recommended at the pH range of 9.0 to 9.5, where various heavy metal ions are simultaneously and quantitatively

coprecipitated, leaving alkali and alkaline earth metals in the solution.¹ Therefore, copper(II)-humic complexes were prepared to examine whether metal-humic complexes behave similarly to humic or fulvic acid. A copper(II) solution (pH 3–4) was mixed with a humic or fulvic acid solution (pH 7) and the pH was adjusted to 7.0 with 0.1 M potassium hydroxide. About a half of the copper (45–55%) was complexed with humic substances, which was obtained by analyzing the effluent by ICP-MS after the sorption of negatively charged humic complexes on a Sephadex A-25 column.^{9,10} As shown in Table 1, nearly complete recoveries were obtained for copper at pH 9.5, in the absence or the presence of soluble silica. Coprecipitation was also quantitatively achieved even at pH 10.5, where the recovery of humic or fulvic acid was only 30% in the presence of silica. At present, it is unclear whether the copper is coprecipitated as humic complexes or as inorganic species of copper released from the complexes.

The above findings and our previous work² prove that coprecipitation with indium hydroxide can give the total copper present in water. The coprecipitation method was compared with the evaporation method for

Fig. 1 Coprecipitation of humic substances with indium or iron(III) hydroxide. Sample volume 50 ml; humic acid $5 \mu\text{g ml}^{-1}$ (○, ●); fulvic acid $50 \mu\text{g ml}^{-1}$ (△, ▲); indium or iron(III) $100 \mu\text{g ml}^{-1}$.

Fig. 2 Coprecipitation of humic substances in the presence of soluble silica. Sample volume 50 ml; humic acid $5 \mu\text{g ml}^{-1}$ (○, ●); fulvic acid $50 \mu\text{g ml}^{-1}$ (△, ▲); silica $10 \mu\text{g Si ml}^{-1}$; indium or iron(III) $100 \mu\text{g ml}^{-1}$.

Table 1 Coprecipitation of copper(II)-humic complexes with indium hydroxide

Sample ^a (50 ml) containing/ μg		Cu coprecipitated, %	
		pH 9.5	pH 10.5
Cu	2.5	98	97
Humic acid	250		
Cu	2.5	99	99
Fulvic acid	250		
Cu	2.5	99	98
Silica	500 (as Si)		
Humic acid	250		
Cu	2.5	99	99
Silica	500 (as Si)		
Fulvic acid	250		

a. 45–55% of Cu was complexed with humic or fulvic acid.

Table 2 Determination of copper in river water

Cu/ $\mu\text{g l}^{-1}$	
Coprecipitation ^b	Evaporation
Kiso River ^a	
0.4, 0.4, 0.6 (av. 0.5)	0.4, 0.5, 0.6 (av. 0.5)
Shonai River ^a	
1.1, 1.2 (av. 1.2)	1.2, 1.2 (av. 1.2)

a. Passed through a $1\text{-}\mu\text{m}$ Nucleopore filter.

b. At pH 9.5.

the determination of copper in filtered river water samples. In the latter, 20 ml of sample was gently evaporated to dryness and the residue was dissolved in 2 ml of 0.5 M nitric acid. The results obtained by the two methods are in good agreement with each other, as shown in Table 2. Compared with evaporation, coprecipitation allows higher concentration factors to be attained with less time consumed.

Coprecipitation with indium hydroxide can also be applied to determine total concentrations of other heavy metals, because Co(II), Ni(II), Zn(II), Cd(II) and Pb(II), 50 $\mu\text{g l}^{-1}$ each, were coprecipitated in greater than 92% yields from water containing humic acid (5 mg l^{-1}).

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