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Simultaneous Preconcentration and Determination of Trace Elements in Water Samples by Coprecipitation-Flotation with Lanthanum Hydroxide [La(OH)₃]

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The preconcentration and determination of trace Cd(II), Cu(II), Pb(II), Mn(II) and Zn(II) in water samples were studied by the precipitate flotation using La(OH)₃ as a coprecipitant. The analytes were quantitatively coprecipitated by adding 3.0 mL of 0.1 M La(III) solution in a 1,000 mL water sample and adjusting the pH to 9.5 with NaOH solution. After the addition of the 1:8 mixed surfactant solution of each 0.1% sodium oleate and sodium lauryl sulfate, the solution was stirred with a magnetic stirrer for 10 minutes. The precipitates were floated to the surface by bubbling with nitrogen gas and collected in a small sampling bottle. The precipitates were dissolved in nitric acid and then the solutions were diluted to 25.00 mL with a deionized water. The analytes were determined by flame atomic absorption spectrometry. This procedure was applied to the waste water analysis. This technique was simple, convenient and especially rapid for the analysis of a large volume of sample. And also, from the recoveries of better than 92% which were obtained from real samples, this method could be judged to be applicable to the preconcentration and quantitative determination of trace elements in water samples.

Introduction

Even though at trace levels, several heavy elements are fatally harmful to living things, but are sometimes necessary in their metabolism. And water is indispensable to keep the life of all the creatures. There are many kinds of elements in a water, especially natural water inflowed from various sources. And also the elements are absorbed into organisms together with water and cause various physiological phenomena.[1,2] Therefore, the information about such elements in waters is very important.

The requirement for the accurate determination of trace heavy elements has been increasing in environmental pollution studies. For it, the preconcentration is needed from bulk water prior to their measurements by a proper method. The volatilization, solvent extraction, adsorption, ion-exchange, and coprecipitation are commonly applied as the preconcentration techniques for the atomic spectrometric determination of them in water samples.[3~8] However, these methods need relatively long time and cumbersome operations for a large volume of sample by some techniques such as gentle heating, phase separation, filtration, elution and so forth.

In this work, a precipitate flotation technique was applied for the preconcentration of hydroxide-forming elements, in which the precipitates of hydrated metal oxide are floated with the aid of surfactant and small inert gas bubbles.[9~13] This technique is rapid and convenient compared to other concentration techniques and also the flotation of flocculent precipitates can be performed with an unskillful technique. Besides, it has another advantage to concentrate many elements, simultaneously.

Kim and Zeitlin[10] had determinated trace Cu(II) and Zn(II) in a sea water by the flotation of them coprecipitated with iron(III) hydroxide precipitates at pH 7.6 using dodecylamine as a surfactant. Mizuike and Hiraide[11] also used iron(III) hydroxide as a coprecipitant for the flotation of Sn(IV), Cu(II) and Zn(II) in an aqueous solution at pH 6-8 with paraffinic solution. On the other hand, hydrated zirconium oxide,[12] aluminum hydroxide and indium(III) hydroxide[13] as a coprecipitant as well as sodium oleate and sodium lauryl sulfate as a surfactant were used for the determinative flotation of various elements. And Ti(OH)₄, Bi(OH)₃, Th(OH)₄, CdS, PbS and so on have also been used.[14]

In this study, trace amounts of Cd(II), Cu(II), Pb(II), Mn(II), and Zn(II) were simultaneously floated by the coprecipitation with lanthanum hydroxide and nitrogen gas bubbling. But lanthanum hydroxide has not been used as a gathering agent for the flotation of multi-elements up to present. Not only the lanthanum forms very desirable flocculent precipitates, but also it has good capability to reduce the chemical interferences in the flame atomic absorption spectrometry. The various experimental parameters such as coprecipitant, surfactant, solution pH and bubbling rate of nitrogen gas were investigated as well as the interferences of concomitant
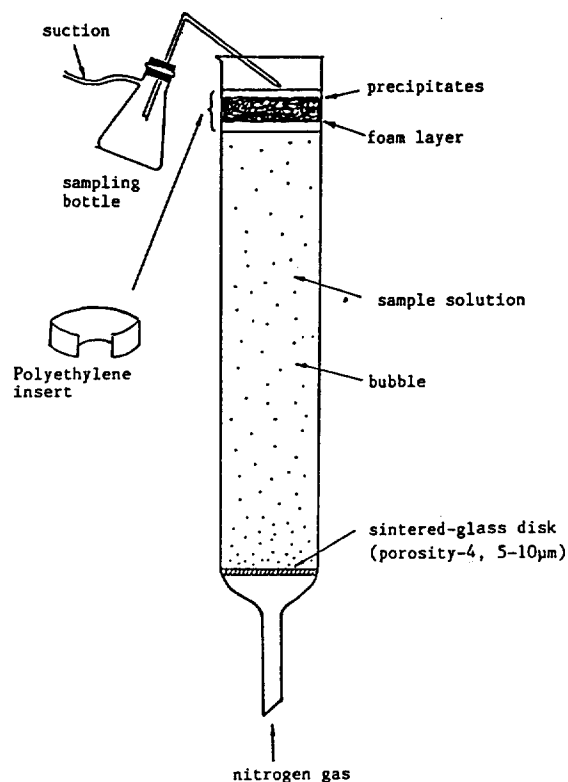
Figure 1. Flotation apparatus.

Figure 2. Effects of amount of coprecipitant [0.1 M La(II) solution] on the flotation of trace heavy elements. O: Cd (10 ng/mL); ▼: Cu (10 ng/mL); ●: Pb (60 ng/mL); □: Mn (40 ng/mL); ▽: Zn (10 ng/mL).

ions were eliminated. And the method developed was applied to real samples.

Experimental

Apparatus and reagents. A 1.0 L pyrex cylinder was used as a flotation cell (Figure 1). A bubbler was made of a sintered-glass filter (porosity 4), which produced numerous tiny nitrogen bubbles of less than 0.5 mm diameter.

Perkin-Elmer model 2380 atomic absorption spectrophotometer was equipped with 10 cm 1-slot burner. Hollow-cathode lamps were used as light sources. The atomic absorption equipment was operated under the following conditions: wavelengths (in nm) Cd 228.8, Cu 324.7, Pb 217.0, Mn 279.5, and Zn 213.9; gas flowrates of 3.0 L/min air and 14.0 L/min acetylene for Cd, Cu, and Mn, and 3.5 L/min air and 14.0 L/min acetylene for Pb and Zn; slit-width 0.7 nm.

A lanthanum solution, 0.1 M La(III), was prepared by dissolving lanthanum oxide in 0.2 M sulfuric acid. Stock solutions of other heavy elements, 1 mg/mL, were prepared in dilute nitric acid with cadmium (99.99%), copper (99.9%), manganese(II) nitrate, lead(II) nitrate, and zinc(II) nitrate.

A surfactant solution was prepared by mixing 0.1% ethanolic solutions of sodium oleate and sodium lauryl sulfate with 1 : 8 volume ratio.

All reagents used were above reagent-grade levels.

Experimental procedure. In an erlenmeyer flask, 3.0 mL of 0.1 M La(III) solution was added to 1.0 L of an aqueous sample and the pH was adjusted to pH 9.5 with aqueous sodium hydroxide to coprecipitate the analytes with La(OH)₃. After 1.0 mL of the mixed surfactant solution was
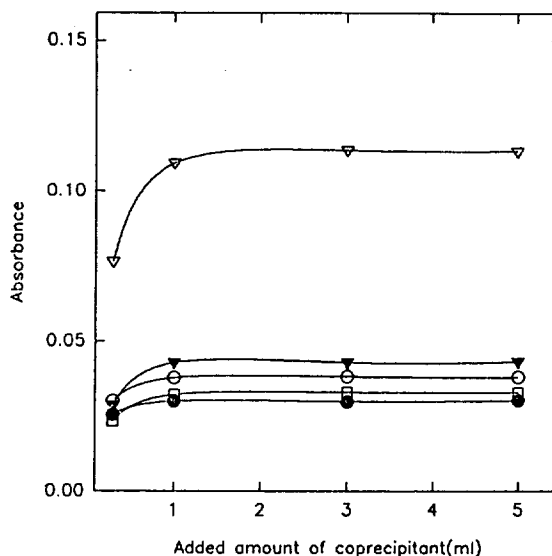
added, the solution was stirred for ten minutes. All the contents were transferred to a flotation cell and a nitrogen gas was bubbled at the flow-rate of 50 mL/min from the bottom of the flotation cell for three minutes. The floated pecipitates were collected on the micropore glass filter by suction and 10 mL absolute ethanol was added to break down the foams. After the precipitates were washed with 12 mL of 0.01 M sodium hydroxide solution, 4 mL of 2 M nitric acid was added to the glass filter to dissolve the precipitates, and the solution was marked in a 25.00 mL volumetric flask with a deionized water. The analytes were determined by flame atomic absorption spectrometry.

Results and Discussion

Coprecipitant. It was known that the amount of lanthanum was important as a coprecipitant to precipitate effectively trace Cd(II), Cu(II), Pb(II), Mn(II) and Zn(II) in an aqueous solution.

In order to investigate the suitable amount of the coprecipitant, the volume of 0.1 M La(III) solution added to 1,000 mL of the artificial sample including the analytes was changed from 0.3 to 5.0 mL (Figure 2). The effective coprecipitation was observed on the addition of more than 1.0 mL of the La(III) solution. This meant that the quantitative coprecipitation could be achieved by the addition of lanthanum to the sample solution about a thousand times of trace elements in mole ratio. This amount is relatively little compared to other coprecipitant[14] because the analytes were adsorbed as metal-hydrated oxide precipitates on the surface of the coprecipitant. Paneth-Fajans-Hahn's rule was obeyed in this case. In this work, 3 mL of 0.1 M La(III) solution was added to 1,000 mL of the sample solution as a coprecipitant.

Surfactant. Since lanthanum hydroxide precipitates are hydrophilic, their properties should be changed to hydrophobic to be floated effectively. For that, some surfactant having
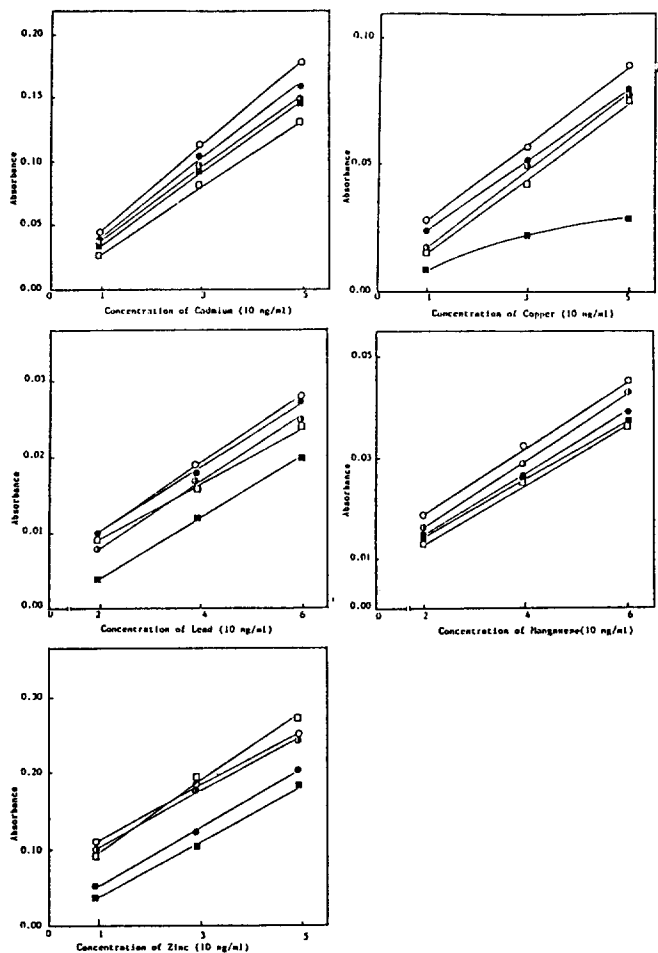
Figure 3. Effects of surfactants on the flotation of each element. ○: 1 : 8 sodium oleate/sodium lauryl sulfate. ○: sodium lauryl sulfate (1000 ng/m*l*). ●: 1 : 4 sodium oleate/sodium lauryl sulfate. □: sodium oleate (1000 ng/m*l*). ■: 1 : 2 sodium oleate/sodium lauryl sulfate.

Figure 4. Coprecipitation of trace heavy elements with lanthanium hydroxide as a function of pH. ○: Cd (10 ng/mL); ▼: Cu (10 ng/mL); ●: Pb (60 ng/mL); □: Mn (40 ng/mL); ▽: Zn (10 ng/mL).

hydrophobic functional groups should be added to form electrostatic linkage with hydroxide precipitates. The hydrophobic group can form a stable foam layer on the surface which prevent the redispersion of floated precipitates into the bulk solution. Therefore, a suitable surfactant must be chosen to be combined electrostatically with precipitates under the careful consideration of their electric charge. That is, anionic surfactants combine effectively with the possitive surface of precipitates which were formed in the solution having an excess cation, and *vice versa.*

In case of La(OH)$_3$, anionic surfactants such as sodium oleate and sodium lauryl sulfate are more effective than cationic surfactants because La(OH)$_3$ is made up of electrical double layer with the positive charge owing to superfluous lanthanum ions. Sodium oleate and sodium lauryl sulfate are known as suitable anionic surfactants.[15]

On the other hand, Hiraide and Mizuike[9] reported that sodium oleate and sodium lauryl sulfate had different functions in the precipitate flotation: sodium oleate had the function to float the precipitates and sodium lauryl sulfate formed stable foams on the surface of the solution. That is, if the precipitates are floated with sodium oleate only, then it
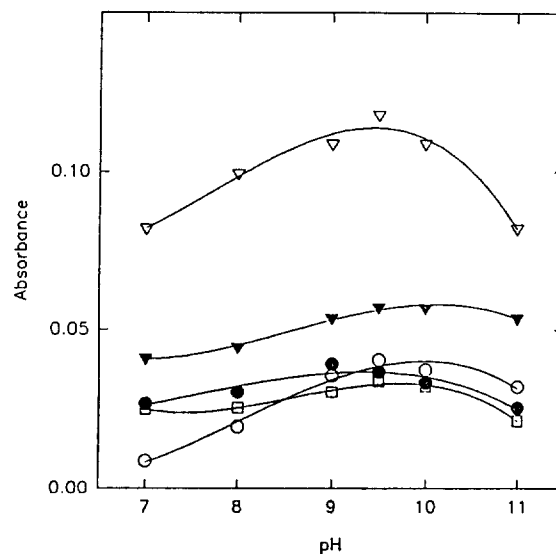
is possible to redisperse precipitates into the bulk of the solution due to the formation of the unstable foam layer. But, with sodium lauryl sulfate only, the precipitates could not be floated rapidly and completely. Hiraide *et al.*[16] had obtained good recoveries with the mixed surfactant of sodium oleate and sodium lauryl sulfate in the precipitate flotation of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb (II).

Therefore, sodium oleate, sodium lauryl sulfate, and their mixture were thoroughly investigated in this work. From above facts, it was also thought that the mixed surfactant were effective in the flotation of La(OH)$_3$ precipitates. In fact, the best efficiency was shown when 1 : 8 mixed solution of 0.1% ethanolic sodium oleate and laurly sulfate was added (Figure 3). This result meant that the cooperative effect had occurred between sodium oleate and lauryl sulfate.

And the optimum amount of the surfactant was also investigated for the effective flotation. The absorbances of the analytes were almost constant on the addition of more than 1.0 mL of the mixed surfactant solution, but at more than 2.0 mL, so much foam was formed that long time was consumed to filter the solution. Therefore, 1.0 mL of the mixed surfactant solution was added in this experiment.

pH of sample solution. The coprecipitation of trace analytes with La(OH)$_3$ is largely dependent upon the pH of the sample solution because the formation of La(OH)$_3$ also relys on the pH of the solution. Therefore, the effective flotation occurs in the pH range at which the stable La(OH)$_3$ can be precipitated.

An expriment was performed to optimize the pH range by changing the pH from 7.0 to 11.0 with 0.5 M NaOH solution(Figure 4). From the figure, the best efficiency for the coprecipitation and flotation of the analytes was shown around pH 9.5. But the efficiency was decreased above pH 10.0 because the hydroxo complexes of analytes such as zinc and lead were formed in the concentrated OH- solution[17] as
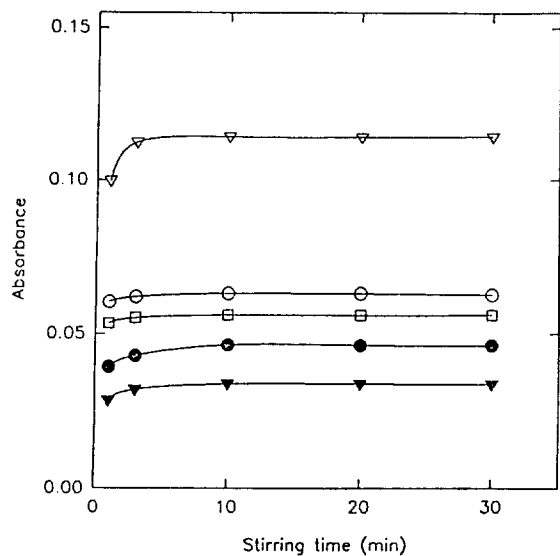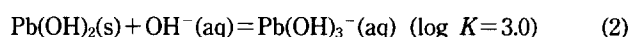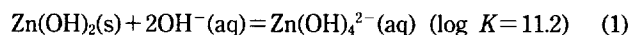
Figure 5. Effects of stirring time on the flotation of trace heavy elements. ○: Cd (10 ng/mL); ▼: Cu (10 ng/mL); ●: Pb (60 ng/mL); □: Mn (40 ng/mL); ▽: Zn (10 ng/mL).

Figure 6. Relationship between nitrogen gas flow-rate and flotation efficiency. ○: Cd (10 ng/mL); ▼: Cu (10 ng/mL); ●: Pb (60 ng/mL); □: Mn (40 ng/mL); ▽: Zn (10 ng/mL).

followings:

$$Zn(OH)_2(s) + 2OH^-(aq) = Zn(OH)_4{}^{2-}(aq) \quad (\log K = 11.2) \quad (1)$$

$$Pb(OH)_2(s) + OH^-(aq) = Pb(OH)_3{}^-(aq) \quad (\log K = 3.0) \quad (2)$$

And also the interaction between precipitates and surfactants was decreased by the possible change of the charge of the first electric layer on the surface of precipitates so that some hindrances were happened in the flotation.

The pH of the solution could not adjusted with the ammonia because five analytes did not precipitate by the formation of their ammine complexes[18].

Stirring time. It is necessary to stir thoroughly the solution to enhance the coprecipitation and floatation of analyte ions with La(OH)₃. So, the efficiencies were investigated changing the stirring time from 1 to 30 minutes (Figure 5). The figure showed that the absorbances of all analytes were almost constant on stirring for more than five minutes. Thus, it could be known that the analytes were rapidly coprecipitated with La(OH)₃ because their precipitation was the same as lanthanum hydroxide. In this work, the flotation was carried out after ten minute stirring.

Flow-rate of nitrogen gas. The bubbling with nitrogen gas is very important for the flotation of precipitates to the solution surface.[19] Even if the precipitates are flocculent and become hydrophobic by combining with surfactants, they are really not floated without any aid of nitrogen gas bubbling. The nitrogen gas should be bubbled as tiny bubbles, for the bubbles are captured in the interstices of the precipitates to float even when the surfaces are slightly charged. Because large bubbles rise rapidly and cause breakup of the precipitates, the overlapped region becomes very narrow in the absence of ethanol[19] and there is the possibility to affect the efficiency of flotation by the flow-rate of nitrogen gas.

Therefore, the influence of the gas flow-rate on the flotation was investigated in the range of 20 to 80 mL/min (Figure 6). The best efficiency was observed around the rate
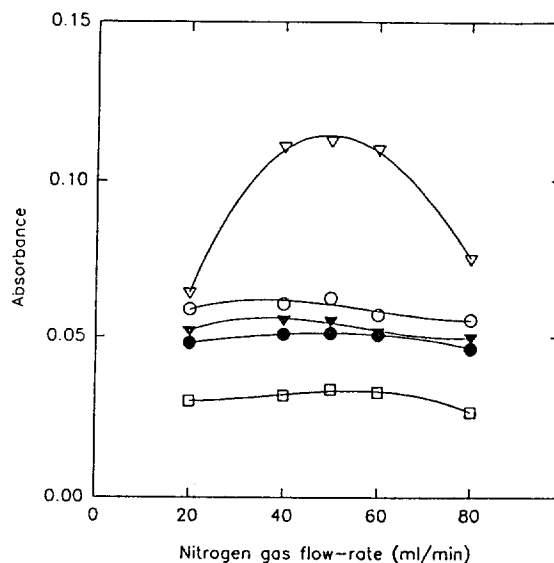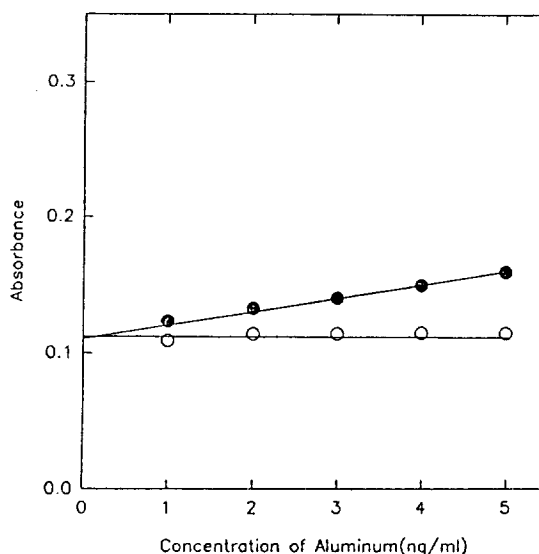

Figure 7. Interfering effects of aluminum on the determination of Zn(II). ●: Interfered; ○: Released.

of 50 mL/min. Below 20 mL/min, not only a few bubbles were produced, but also the floating force was too weak. Thus, so much time was spent for the flotation. Above 60 mL/min, some large bubbles were produced so that the sample solution became unstable by convection and the foam layer was broken by the strong rising force of gas bubbles. Parts of floated precipitates were redispersed into the bulk solution. As a result, the flotation was carried out at about 50 mL/min of nitrogen gas flow-rate.

Influences of concomitant ions. Interfering effects of various other ions as well as their elimination were studied in this proposed procedure.

It was considered that Al and Cr(III)[20] having the large heat of oxide formation would affect the reaction between
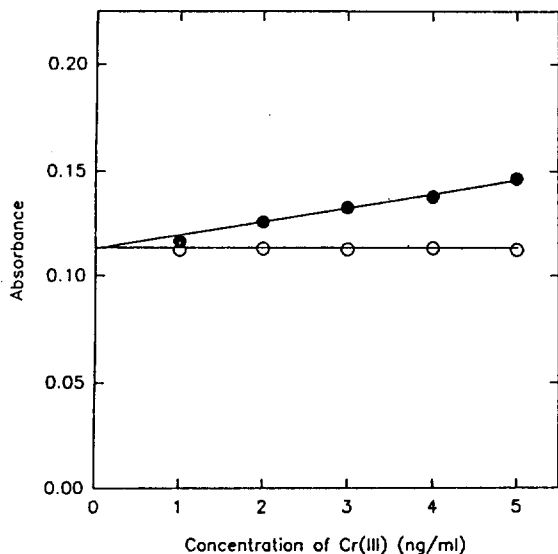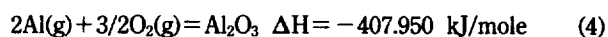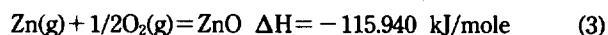
Figure 8. Interfering effects of chromium(III) on the determination of Zn(II). Zn(II): 10 ng/mL. ●: Interfered; ○: Released.

Figure 9. Calibration curve of each element.

neutral analyte atoms and oxygen in the flame of AAS. Their interferences were investigated by adding Al and Cr(III) up to 5 mg/L into 1.0 L of the artificial sample solution containing the analytes, respectively. The absorbance for zinc only was slightly increased as the concentrations of Al and Cr(III) were increased (Figure 7, Figure 8). The zinc was supposed to be more sensitively affected because it had so large heat of oxide formation compared with other analytes that the oxidation of zinc was delayed under the coexistence of more oxidizable aluminum and chromium. But other analytes were nearly not influenced because they were easily atomized regardless of presence of Al and Cr.

In order to describe above fact, the equilibrium réactions could be considered as followings[21]:

$$Zn(g) + 1/2O_2(g) = ZnO \quad \Delta H = -115.940 \text{ kJ/mole} \quad (3)$$

$$2Al(g) + 3/2O_2(g) = Al_2O_3 \quad \Delta H = -407.950 \text{ kJ/mole} \quad (4)$$

$$3Cr(g) + 3/2O_2(g) = Cr_2O_3 \quad \Delta H = -278.030 \text{ kJ/mole} \quad (5)$$

That is, the equilibrium reactions of Eq. (4) and (5) happen so predominantly compared to Eq. (3) that the equilibrium of Eq. (3) would shift to left by the deficiency of O_2 in the flame. Therefore, the zinc would be easily atomized in the flame.

Such an interfering effect could be released by adding lanthanum more than 100 times in mole ratio to zinc because it had larger heat of oxide formation ($\Delta H = -434.330$ kJ/ mole) than Al and Cr(III).

In other hand, Fe(III) did not interfere with the absorbance measurement of analytes up to at least 20 mg/L, and Fe(II) is so rapidly oxidized with oxygen in aqueous solutions[22] that its interference could be negligible. And Mg (up to 20 mg), Cl^- (200 mg), and SO_4^{2-} (20 mg) did not interfere with the determinations. Nakashima and Yagi[12] reported that for the determination of 80 ng/L cadmium and 20 mg/L zirconium, any interferences were not caused by Na^+, K^+, Ca^{2+}, Mg^{2+} and SiO_3^{2-} up to 10 mg/L, Sr^{2+}, Ba^{2+} and H_3PO_4 up

to 1 mg/L, and Cr(VI), Mo(VI), Hg^{2+}, Co^{2+}, V(V), Ni^{2+}, Bi^{3+}, As^{3+}, Sb^{3+}, Se(IV), and Sn(IV) up to 0.2 mg/L. Really, most elements usually exist at the level of micro or nanogram per liter or less in natural water samples. Therefore, the flotation and determination of the analytes could be performed ignoring these interferences.

Analytical results and recoveries. This method was applied to a waste water to examine the applicability of the recommended procedure. The sample and standard solutions were coprecipitated and floated with the conditions mentioned above. Here, the standard solutions were prepared by adding proper amounts of analytes in 1.0 L deionized water.

The calibration curves were plotted with the standard solutions (Figure 9). But the calibration curve of zinc was directly constructed with standard solutions without any treatment because the concentration of zinc was too high in the waste water. A background correction was done subtracting the blanck absorbance from measured absorbances. All calibration curves were linear up to 20 ng/mL for Cd, 50 ng/mL for Cu(II), 80 ng/mL for Pb, and 100 ng/mL for Mn(II). According to the result (Table 1), the contents in a waste water were 0.7 ng/mL for Cd, 6.6 ng/mL for Cu(II), 6.0 ng/mL for Pb, 18.3 ng/mL for Mn(II), and 710 ng/mL
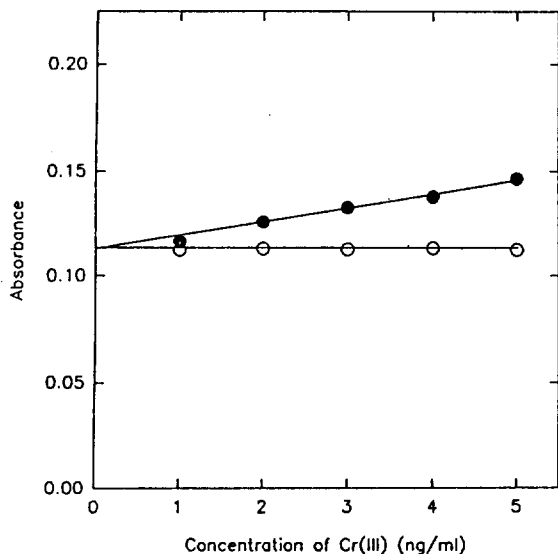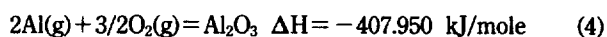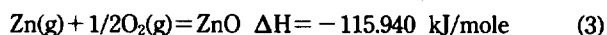
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Preconcentration of Trace Elements by Coprecipitation-Flotation

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Table 1. Flotation of Heavy Elements in 1 L of Waste Water

Element	Added (μg/mL)	Found (μg/mL)	RSD	Recovery (%)
Cd	0	0.7		
	5	4.8	1.7	96
	10	9.6	2.8	96
Cu	0	6.6		
	10	9.2	2.7	92
	20	18.7	2.2	93
Pb	0	6.0		
	20	18.4	4.1	92
	50	45.8	2.7	92
Mn	0	18.3		
	20	18.6	5.5	93
	30	28.0	4.3	93
Zn	0	710.0		

for Zn, respectively.

And the recoveries of analytes spiked with given amounts were also examined by above procedure. Table 1 shows recovery data for the analytes except Zn. These results indicate that this analytical system could be successfully applied to the preconcentration and determination of Cd, Cu(II), Mn(II), Pb, and Zn at sub-microgram levels in an aqueous solution.

Conclusions

Trace amounts of Cd, Cu(II), Mn(II), Pb, and Zn were determined in a waste water by the flotation of them coprecipitated with La(OH)$_3$. The coprecipitation was done at pH 9.5 adjusted with NaOH solution. La(III) of more than 1,000 times of each analyte was needed to coprecipitate analyte ions quantitatively so that 3.0 mL of 0.1 M La(III) solution was added in 1.0 L sample. The precipitates were effectively floated by adding 1 : 8 mixed surfactant solution of 0.1% of sodium oleate and 0.1% of sodium lauryl sulfate and by bubbling nitrogen gas. The content was stirred for 10 minutes before it was transferred to a flotation cell. The analytes were determined by flame atomic absorption spectrophotometry. The interferences of Al and Cr(III) in the determination of zinc could be released by adding much excess lanthanum compared to the interferring elements. The recoveries of more than 92% for each element showed that this procedure could be applicable for the quantitative determination

of trace elements in water samples.

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