Preconcentration and Determination of Trace Cd(II) and Pb(II) in a Water Sample by Organic Precipitate Flotation with 8-Hydroxyquinoline

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Received November 9, 1998

An organic precipitate flotation of Cd(II) and Pb(II) was investigated by the coprecipitation with lanthanum 8-hydroxyquinolinate. Trace amounts of Cd(II) and Pb(II) with a significantly large amount of La(III) were simultaneously precipitated in a 1,000 mL sample solution with the ethanolic 8-hydroxyquinoline solution. The pH was adjusted to 9.0 with 2 M ammonia solution. The precipitates were floated with the aid of tiny nitrogen bubbles and supported by the stable foam layer of sodium lauryl sulfate. The floats were collected on the fritted glass filter by a suction. The material collected was dissolved with 5.0 mL of ethanol and 1.5 mL of concentrated nitric acid, and then diluted to 25.0 mL with a deionized water. The analytes were determined by a flame atomic absorption spectrophotometry. The recoveries of the analytes spiked in the sample were 94.8% for Pb(II) and 92.0% for Cd(II). This flotation technique is simple and rapid, and also applicable to the determination of trace Cd(II) and Pb(II) at low ppb levels.

Introduction

The accurate determination of trace heavy metals for the investigation of environmental pollutants has been become more important together with an industrialization. Such heavy metals in natural water can differently affect the biological behavior of aquatic organisms and physiological phenomena of human beings according to the type of the element and the chemical form of dissolved species. Especially, necessity of a simple, rapid and accurate method is increased for the determination of trace Cd(II) and Pb(II) in a water because they deal a fatal blow. But their contents are usually so low in a natural water for the direct determination by an atomic absorption spectrophotometry (AAS) that the preconcentration of them is necessary to be determined. Ion-exchange chromatography, liquid-liquid extraction, co-precipitation and so on can be used as preconcentration techniques, but sometimes they are time-consuming or troublesome for a large volume of such a sample.

A flotation technique has been effectively employed for the preconcentration of trace elements.[1~7] When an organic precipitant such as dithizone or 2-mercaptobenzothiazole was added to an aqueous sample solution as a dissolved state in a miscible solvent with a water, trace analytes were quantitatively co-precipitated on organic precipitates and then floated by bubbling a gas without (sometimes with) surfactants.[6] And the organic molecule has an advantage of capability to react selectively with analyte ions and form the precipitate. Therefore, the trace elements can be readily separated from the solution of a complicated sample. Fukuda *et al.*[8] had co-precipitated and floated the trace Ag(I) in the solution of copper sample with p-dimethyl aminobenzylidene rhodamine. And Mizuike and coworkers[9] reported that a microgram level of cobalt in a zinc metal was separated in its sample solution by the precipitate flotation with 1-nitroso-2-naphthol. Hiraide *et al.*[10] had also floated the trace Ag(I) in a seawater by co-precipitation with 2-mercaptobenzothiazol. On the other hand, inorganic co-precipitants were also used in an organic precipitate flotation to promote the flotation of analyte elements, effectively.[11]

Recently, such co-precipitation and ion flotation techniques have been studied in our laboratory.[12~20] Among them, ammonium pyrrolidine dithiocarbamate (APDC) was used as an organic precipitant for the determination of trace Bi(III), Cd(II), Co(II) and Pb(II) in water samples together with Cu(II) as a co-precipitant.[20] And nitroso-R-salt was employed as an organic ligand for the ion flotation of several trace elements.[14]

In this work, 8-hydroxyquinoline was chosen as an organic precipitant for the determination of trace Cd(II) and Pb(II) in water samples. The 8-hydroxyquinoline can selectively and stoichiometrically react with Cd(II) and Pb(II) to form insoluble precipitates depending on the pH of solution, but the amount of their precipitates were small in size and not so flocculent for the flotation. Therefore, a large amount of La(III) was added to the solution as a co-precipitant because it could precipitate with 8-hydroxyquinoline in the same range of pH.

Here, experimental parameters such as a co-precipitant, pH, surfactant, stirring time and flow-rate of nitrogen gas were studied for the effective flotation. This procedure was applied to a waste water, and interferences of concomitant ions were investigated as well.

Experimental Section

Apparatus and reagents. The flotation cell is the same one as used in Ref. 19. The detachable polyethylene insert prevents the adhesion of floated precipitates on the inside wall of the cell.

A Perkin-Elmer model 2380 AAS with 10 cm burner(1-slot) was employed for the determination of analytes. The

equipment was operated under the following conditions: wavelengths Cd 228.8 nm and Pb 217.0 nm; slit-width 0.7 nm; air and acetylene flow rate of 2.7 : 13.9 L/min for Cd(II) and of 3.2 : 13.9 L/min for Pb(II).

Standard solutions were prepared with pure cadmium and lead nitrate of guaranteed grade (GR). 8-Hydroxyquinoline solution was prepared with 3.0 (w/v)% in ethanol, and 0.1 M La(III) solution was prepared by dissolving lanthanum oxide in 0.2 M sulfuric acid. Ethanolic sodium lauryl sulfate (0.1%) was used as a surfactant. All other reagents of GR were used without any further purification. A deionized water with Milli-Q system was used for this work.

Procedure. After filtrated a waste water, 5 mL of 8-hydroxyquinoline and 1.5 mL of 0.1 M La(III) solution were added to 1,000 mL of the water sample in an erlenmeyer flask. The pH of the solution was adjusted to 9.0 with 2 M ammonia solution for the precipitation, and 1 mL of 0.1% sodium lauryl sulfate was added as a surfactant. After the solution was stirred for 10 minutes with a magnetic stirrer, all of the contents was transferred into a flotation cell. The erlenmeyer flask was washed three times with small portion of a deionized water, and the wash water was also added into the flotation cell. The solution was bubbled with nitrogen gas at the flow-rate of 20 mL/min for 4 minutes to float the precipitates, completely. The floats were separated from mother liquor into a sampling bottle by a suction, and the precipitates were collected on the fritted glass filter by filtration and dissolved with 5.0 mL of ethanol and 1.5 mL of a concentrated nitric acid. And the solution was marked to 25.0 mL in a volumetric flask with the deionized water for the determination of Cd(II) and Pb(II) by flame AAS.

Results and Discussion

Role of La(III) in precipitation. Usually, most of organic precipitants for the flotation are insoluble in an aqueous solution and can collect some elements as a metal-organic precipitate. Among them, 8-hydroxyquinoline can be existed as an ionic form in an aqueous solution and form precipitates quantitatively with several metal ions. But the amount of its precipitates formed with Cd(II) and Pb(II) in a waste water is extremely little and the flocculent precipitates are not formed, quantitaitvely. Therefore, an adequate amount of La(III) to react with 8-hydroxyquinoline at the same pH as in the precipitation of Cd(II) and Pb(II) is necessary to get flocculent precipitates. In this case, La(III)-8-hydroxyquinolinate precipitate has the role as a gathering agent of trace analytes. The flotation efficiency is dependent upon the amount of La(III) added. An excess 8-hydroxyquinoline should be added to co-precipitate Cd(II) and Pb(II) together with the precipitation of La(III).

Therefore, the amount of La(III) was studied under the condition that 5 mL of 3.0% 8-hydroxyquinoline had been added to 1.0 L of the deionized water having 30 g Cd(II) and 100 g Pb(II). 0.1 M La(III) of 0.1 to 2.0 mL was added to the solution (Figure 1). The effective gathering was shown from the addition of 1.0 mL La(III) solution, but the absorbances
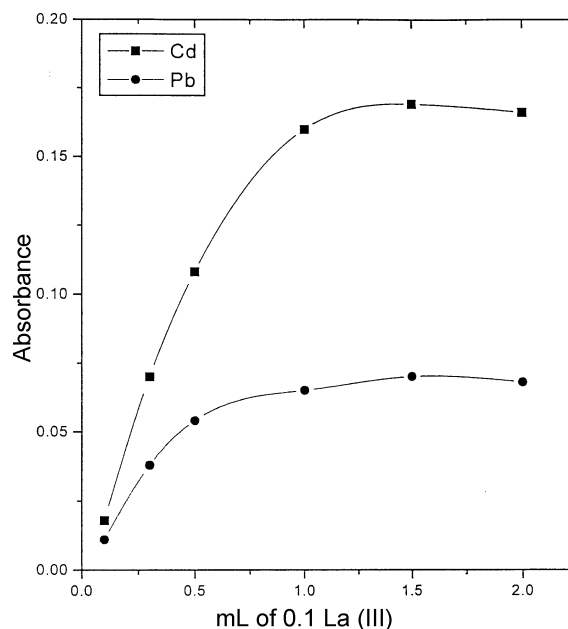
Figure 1. Flotation efficiencies according to the amount of 0.1 M La(III) solution as a gathering agent. Cd(II): 30 ng/mL; Pb(II): 100 ng/mL.

of Cd(II) and Pb(II) were constant on the addition of more than about 1.0 mL. This amount was relatively little compared to the precipitant used in an inorganic precipitate flotation. Such a result was because precipitates were easily coagulated due to the small polarity of metal 8-hydroxyquinolinate in an aqueous solution. If too much La(III) was added, then the flotation and filtration would be increased because of a large amount of La(III) 8-hydroxyquinolinate precipitate formed.

pH of solution. It was known that metal 8-hydroxyquinoline precipitate was selectively formed with an ion depend-
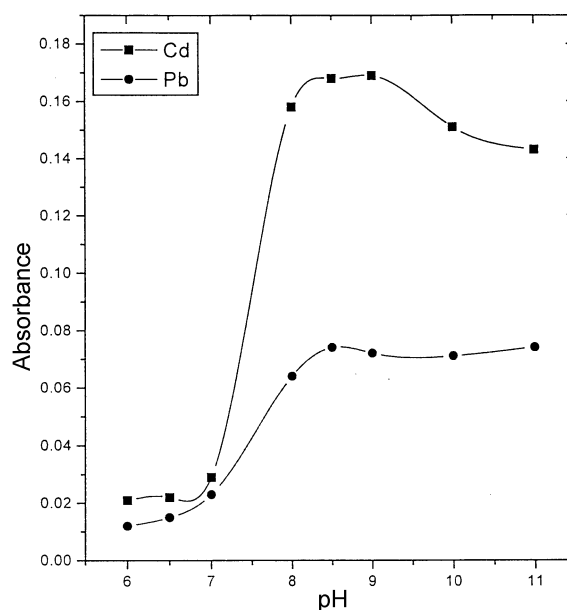
Figure 2. Precipitation of analytes with 8-hydroxyquinoline for an efficient flotation as a function of solution pH. Cd(II): 30 ng/mL; Pb(II): 100 ng/mL.

precipitation of trace Cd(II) and Pb(II) with the precipitation of La(III) 8-hydroxyquinolinate was investigated by adjusting the solution pH from 6 to 11 with ammonia (Figure 2).

The best efficiency was showed up around pH 9.0. The absorbance of Cd(II) was decreased above pH 9.5 because the 8-hydroxyquinolinate precipitation competes with ammine complexation with ammonia as the following reaction:

$$Cd^{2+}(aq) + 4NH_3(aq) = Cd(NH_3)_4^{2+}(aq) \ (\ \log K = 7.0 \ )$$
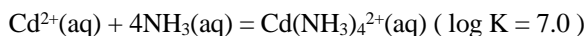
On the other hand, because 8-hydroxyquinoline is a weak acid, it can not form the insoluble complex with most metal ions in the acidic solution. Such a phenomenon can be known from the reaction as a following:

And the co-precipitation of Cd(II) and Pb(II) was drasti-

$$M^{n+} = Cd(II), Pb(II), La(III).$$
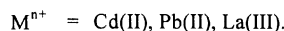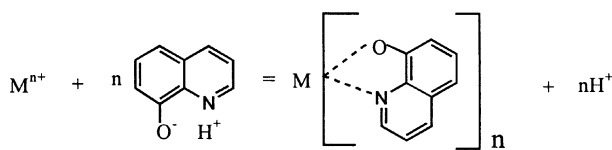
cally increased between pH 7 and 8 because 8-hydroxyquinoline had an iso-electric point at the pH 7.4.[21] Thus, their precipitation of 8-hydroxyquinoline was started at this pH range. From this result, the pH of the sample solution was adjusted to pH 9.0 with ammonium hydroxide.

Surfactant. Usually, metal 8-hydroxyquinolinate precipitates have a hydrophobic property so that they can be floated only by bubbling nitrogen gas without any surfactant. But the precipitates floated are so unstable on the solution surface that parts of them are sometimes re-dispersed into the solution. Thus, the use of a surfactant is recommendable to form a stable foam layer because such foams can support the precipitates on the surface.

Several kinds of surfactants were investigated (Figure 3): cetyltrimethyl ammonium chloride as a cationic surfactant, sodium lauryl sulfate and sodium oleate as anionic surfactants, and Span 20 and Tween 20 as nonionic surfactants. As shown in Figure 3, the flotation efficiency was slightly more improved by using a surfactant than without any surfactant. In a usual case of inorganic precipitate flotation, a surfactant has been used to change the surfaces of precipitates from hydrophilic to hydrophobic because the surfaces were covered with the hydrophobic site of a surfactant by the formation of stable foam layers.[23,24] But most of surfactants showed the similar effects on the flotation regardless of their positive, neutral or negative charge in the present study because they have a function to make a foam layer stable.

Of them, sodium lauryl sulfate showed the best efficiency in both cases of Cd(II) and Pb(II) because it could form a tiny and stable foam layer and support precipitates on the solution. And the amount of the surfactant needed for the most effective foam layer was investigated by adding 0.3 to 3.0 mL of 0.1% sodium lauryl sulfate solution to the artificial sample solution. But the absorbances of Cd(II) and Pb(II) were not almost changed regardless of its amounts in this range. Therefore, only small amount of the surfactant
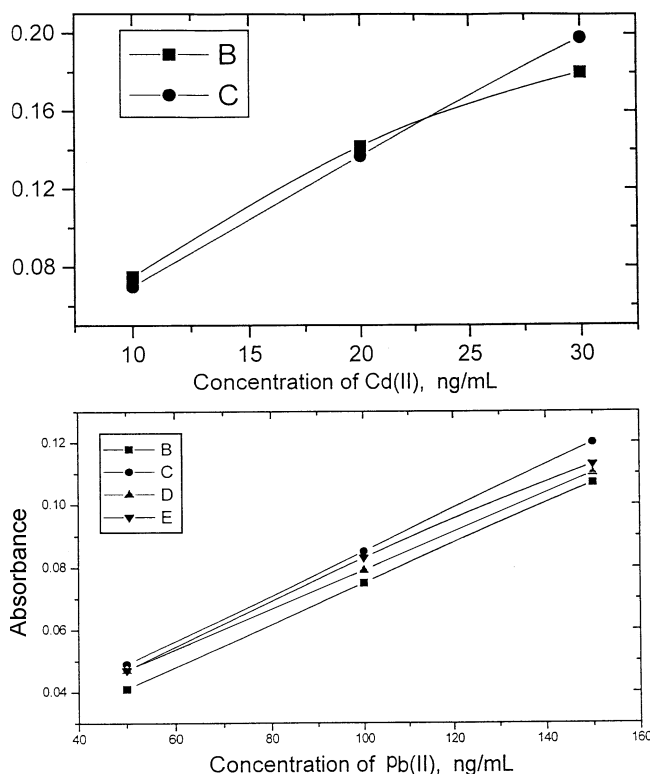

Figure 3. Effect of surfactants on the flotation of M(II)-8-hydroyquinolinate precipitates. B: without any surfactant; C: sodium lauryl sulfate; D: cetyltrimethylammonium bromide; E: Span 20.

was used to flee from difficulties by the formation of an excess foam in the separation and dissolution of floated precipitates. From the result, 1 mL of 0.1% sodium lauryl sulfate was decided to be added to the sample solution.

Stirring time. The mechanical stirring of sample solution is necessary to co-precipitate Cd(II) and Pb(II) on La(III) 8-hydroxyquinolinate, effectively and to make them flocculent for an efficient flotation. An experiment was carried out changing the stirring time to optimize it. But the absorbances for Cd(II) and Pb(II) were almost not changed by stirring more than 2 minutes. That meant that Cd(II) and Pb(II) were rapidly gathered on La(III) 8-hydroxyquinolinate and the precipitates were flocculent. In this study, the precipitates were floated after stirring the solution for 5 minutes.

Bubbling of nitrogen gas. A lot of tiny nitrogen gas bubbles have an important function to float the precipitates to the surface from a bulk solution.[6] That is, the flotation of precipitates is influenced by the bubbling rate and bubble size of nitrogen gas. Usually, the gas is bubbled through a sintered glass disk from the bottom of flotation cell. And the size of the bubble decreases with decreasing the pore size of the disc and also the size is optimized at a proper bubbling rate.

In this work, the glass disc of No. 4 porosity (5-10 μm pore size) was used, and the influence of the bubbling rate was investigated by changing the flow-rate from 20 to 80 mL/min (Figure 4). Figure 4 showed nearly similar and good efficiencies up to 40 mL/min, but if the rate was over 50 mL/
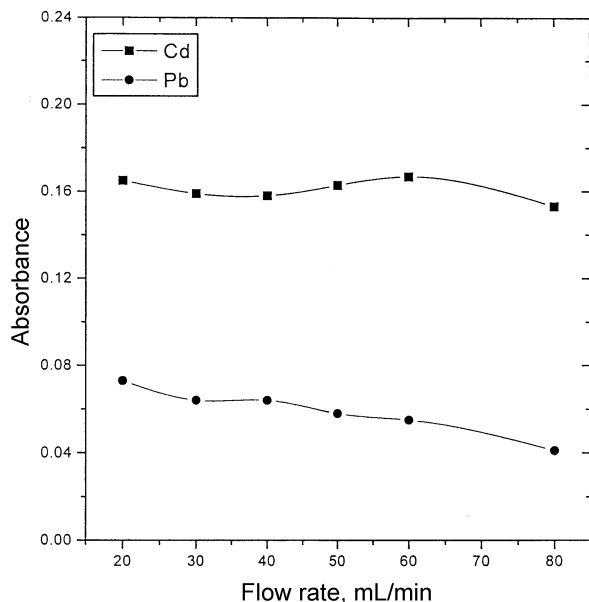
Figure 4. Dependency of nitrogen flow rate on the flotation efficiencies of M(II)-8-hydroxyquinolinate precipitates. Cd(II): 30 ng/mL; Pb(II): 100 ng/mL.

min, the convection of the solution occurred so violently that the foam layer was broken up and a portion of the precipitate was re-dispersed into the bulk solution. Furthermore, lots of large bubbles were formed above 60 mL/min rate so that the precipitates were broken by the insertion of bubbles into the interstices of flocculent precipitates. Therefore, nitrogen gas was bubbled at 20 mL/min rate to float and maintain the precipitates onto the surface of solution.

Interferences of concomitant ions. In the proposed procedure, interferences of various concomitant ions were investigated on the flotation and determination of Cd(II) and Pb(II). The ions that could be precipitated with 8-hydroxyquinoline above pH 7.5 were chosen for the investigation of interfering effects because other ions precipitated below pH 7.5 were eliminated through the flotation process. Al(III), Cu(II), Fe(III), Mg(II), Mn(II), Zn(II), and so on were known to precipitate with 8-hydroxyquinoline above pH 7.5.[21,22]

Their interferences were investigated by changing the amounts of concomitant elements added to the sample solution. Al(III), Fe(III) and Mg(II) did not interfere with the determination of Cd(II) and Pb(II) up to about 10 mg/L in sample solutions and other ions also did not interfere with up to 5 mg/L. And the others were usually existed at very low concentration in water samples so that their interferences can be tolerated. Therefore, it was considered that interference effects of concomitant elements could be ignored in this method.

Analysis of real samples and recovery test. In order to evaluate this method for the practical applications, this procedure was applied to the determination of trace Cd(II) and Pb(II) in waste water of our campus and the recoveries of Cd(II) and Pb(II) spiked with given amounts were obtained. The absorbances measured on the concentrated base of a

Table 1. Analytical results of Cd(II) and Pb(II) in waste water of Seochang Campus, Korea University by this organic precipitate flotation method

Element	Spiked (ng/mL)	Found (ng/mL)	Average	RSD (%)	Recovered[*] (ng/mL)	Recovery (%)[*]
Cd(II)	0.0	0.3 0.3 0.2 0.3	0.3	19.2		
	5.0	4.9 4.7 4.9 4.9	4.9	2.4	4.6	92.0
Pb(II)	0.0	27.4 23.1 24.2 24.2	24.7	7.5		
	25.0	47.8 48.9 47.8 48.9	48.4	1.3	23.7	94.8

[*]refer the description in a section of "Analysis of real samples and recovery test".

standard solution were plotted against the concentrations of Cd(II) and Pb(II) in original solutions to make calibration curves. In this case, the standard solution was prepared by diluting the stock solutions with a deionized water. Both calibration curves were linear with linearities of R = 1 (SD = 4.215E-17) and 0.99502 (SD = 0.0034) up to 20 ng/mL and 120 ng/mL for Cd(II) and Pb(II), respectively.

Table 1 indicates analytical results and recoveries of Cd(II) and Pb(II) in real sample. For the results, the concentrations are 0.3 ng/mL for Cd(II) and 24.7 ng/mL for Pb(II) in a waste water, and their recoveries are 92.0% and 94.8%, respectively. But the recovery values are calculated with a following equation:

$$\text{Recovery (\%)} = \frac{\text{Recovered value}}{\text{Spiked value}} \times 100$$

where, the recovered value mean the value which are obtained by subtracting the analytical value of an original sample from the found value of a spiked sample. Here, the spiked sample is the sample in which a given amount of analytes are added. And relative standard deviations of less than 20% for the data means that this method is relatively reproducible in the trace analysis of ng/mL levels. Along the lines, it can be concluded that this simple and rapid method is applicable to the preconcentration and determination of trace Cd(II) and Pb(II) from a large volume of water solution.

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