A Novel Separation and Preconcentration Method for Traces of Manganese, Cobalt, Zinc and Cadmium Using Coagulation of Colloidal Silica

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A separation and preconcentration method has been developed for traces of heavy metals using coagulation of colloidal silica. An appropriate amount of colloidal silica was added to a sample solution, the pH was adjusted to 11 with tetramethylammonium hydroxide solution and calcium chloride solution was then added to coagulate the silica. The coagulated silica and solution were separated by centrifugation, and the silica was then treated with hydrofluoric and perchloric acids. The residue was taken up in dilute nitric acid and subjected to ICP-AES to determine manganese, cobalt, zinc and cadmium. The proposed method was successfully applied to analysis of river-water.

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The importance of trace elements has been recognized in various fields, especially in environmental chemistry, medical science and the electronic industry. Therefore, trace elements in diverse samples are routinely determined. In such a case, it is often required to separate an analyte from matrix components and to preconcentrate it to eliminate the potential interferences and improve the sensitivity. Hence, various separation and preconcentration methods have so far been developed and reviewed in detail by Alfassi et al.1 Among these are solvent extraction and coprecipitation, which are simple, useful and versatile for various samples, and have been extensively used for trace element analysis. However, both of them have some drawbacks; namely, organic solvents used in solvent extraction are toxic and the formation of precipitates is usually time-consuming.

Thus, in order to overcome these drawbacks, a solid phase extraction technique has recently aroused interest widely; solid phase extraction of trace elements has been reviewed by Camel.2 The present authors have also employed solid phase extraction and coprecipitation, which are simple, useful and versatile for various samples, and have been extensively used for trace element analysis. However, both of them have some drawbacks; namely, organic solvents used in solvent extraction are toxic and the formation of precipitates is usually time-consuming.

Various types of silica are easily available and exhibit characteristic properties. Silica gel is used for separation and preconcentration of metal ions and chemically modified silica gels have also been developed for improvement of selectivity for metal ions.6 On the other hand, colloidal silica seems to be attributable to hydration. If the pH of colloidal silica solution is increased to more than 8 and any electrolytes are added to it, the most silanol groups of the silica dissociate and metal cations are adsorbed on the surface of the silica by ion exchange, resulting in dehydration of the surface of the silica. This dehydration leads to coagulation of the colloidal silica.13

However, the adsorption of metals on colloidal silica and the stability of colloidal silica in the presence of electrolytes have been studied by many investigators.7–15 Enhanced stability of colloidal silica seems to be attributable to hydration. If the pH of colloidal silica solution is increased to more than 8 and any electrolytes are added to it, the most silanol groups of the silica dissociate and metal cations are adsorbed on the surface of the silica by ion exchange, resulting in dehydration of the surface of the silica. This dehydration leads to coagulation of the colloidal silica.

In this work, a rapid preconcentration method of manganese, cobalt, zinc and cadmium was developed using coagulation of colloidal silica by addition of calcium chloride. The metals collected by the silica were determined by ICP-AES after treatment of the silica with hydrofluoric and perchloric acids. The coagulation of colloidal silica is faster as compared with the time needed for conventional precipitate formation. The proposed method has yielded reproducible results for determination of manganese, cobalt, zinc and cadmium in river-water. The selectivity of colloidal silica for the metals tested was found to be Zn²⁺ > Cd²⁺ > Mn²⁺ > Co³⁺.

Experimental

Reagents and samples

All reagents used were of analytical reagent grade. Distilled and deionized water was further purified via passage through a Milli-Q® Ultrapure water purification system (Millipore, Bedford, USA).

The 1000 mg l⁻¹ stock solutions were prepared by dissolving their metal, chloride, or sulfate in a suitable dilute mineral acid. Working standard solutions were daily prepared from each stock standard solution.

A 10% (m/m) colloidal silica solution was prepared by diluting 20 g of high purity colloidal silica, Quartron PL-3 (silica concentration, 20% (m/m); average particle size, 35 nm;
Fuso Chemicals, Osaka), to 40 g with water. A 5 mol l\(^{-1}\) calcium chloride (Kanto Chemicals, Tokyo) solution was used for coagulation of colloidal silica, and hydrofluoric and perchloric acids (Kanto Chemicals) were used for digestion of coagulated silica. A 10% tetramethylammonium hydroxide solution (Tokuyama, Tokyo) was used for pH adjustment.

An artificial river-water sample that contained 5 mg l\(^{-1}\) of Na\(^+\), 1 mg l\(^{-1}\) of K\(^+\) and 3 mg l\(^{-1}\) of Mg\(^{2+}\) was prepared from each 1000 mg l\(^{-1}\) stock standard solution according to the literature.\(^{16}\)

A river-water sample was collected at Yoro River (Chiba, Japan), filtered through a 0.45-µm membrane filter (Millipore) and acidified with nitric acid.

**Instrumentation**

A Seiko Instruments Plasma Spectrometer SPS 1700HVR (Seiko Instruments, Chiba) was used through the experiments. The optimized operating parameters are listed in Table 1.

A pH meter F-13 (Horiba, Kyoto) was used for the measurement of pH and a centrifugal machine H-103N (Kokusan, Tokyo) was used for separation of colloidal silica after coagulation.

**General procedure**

About 100 g of sample solution was taken in a polypropylene centrifuge tube and mixed with 300 µl of 10% colloidal silica solution. The pH of the solution was adjusted to about 11 with 10% tetramethylammonium hydroxide solution; 10 µl of 5 mol l\(^{-1}\) calcium chloride solution was then added to coagulate the silica. The coagulated silica was immediately centrifuged at 3000 rpm for 3 min and the supernatant was discarded. The silica was transferred to a 7-ml perfluoroalkoxylalkane (PFA) jar with 3 ml of hydrofluoric acid, and 1 ml of 4.5 mol l\(^{-1}\) perchloric acid was added to it, followed by evaporation nearly to dryness on a hot plate. The residue was then diluted to 5 ml with 0.1 mol l\(^{-1}\) nitric acid. The solution prepared as above was subjected to the determination of metals by ICP-AES.

**Results and Discussion**

*Choice of alkali and electrolyte for coagulation of colloidal silica*

Some alkali is required to adjust the pH of a sample solution at higher than 8 to coagulate colloidal silica. Highly purified sodium or potassium hydroxide is not commercially available. Ammonia water is not suitable to adjust the pH of a sample solution at higher than 10 because of its irritating smell. On the other hand, highly purified tetramethylammonium hydroxide is now commercially available at a reasonable cost. Therefore, tetramethylammonium hydroxide was used as alkali to adjust the pH of sample solutions.

*Milonich et al.\(^{13}\) studied the effect of presence of chlorides and sulfates of alkali-earth elements on coagulation of colloidal silica and found that calcium, strontium and barium were equally efficient and magnesium was less efficient. Accordingly, we chose calcium chloride as an electrolyte to coagulate colloidal silica.*

*Effect of the colloidal silica concentration on preconcentration of single elements*

The effect of the colloidal silica concentration on the recoveries of 1 µg of cobalt or zinc in 100 ml of Milli-Q water was studied over the range of 0.001 to 0.03%. The results obtained are shown in Fig. 1. The recoveries of zinc and cobalt were almost constant at higher than 0.003% and 0.005%, respectively. Therefore, the colloidal silica concentration of 0.01% was adopted for preliminary experiments for single element preconcentration.

*Effect of the calcium chloride concentration*

The effect of the colloidal silica concentration on the recoveries of 1 µg of cobalt or zinc in 100 ml of Milli-Q water was studied over the range of 0 to 3 mmol l\(^{-1}\). The results obtained are shown in Fig. 2. The colloidal silica did not coagulate without calcium chloride and so the recovery of zinc was 0%. At 0.3 mmol l\(^{-1}\), the particle concentration of the calcium solution was adopted for the experiments.

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**Table 1: Operating condition of ICP-AES**

<table>
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<th>Plasma conditions</th>
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<tr>
<td>Incident RF power/kW</td>
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<tr>
<td>Plasma gas/l min(^{-1})</td>
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<tr>
<td>Auxiliary gas/l min(^{-1})</td>
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<td>Carrier gas/l min(^{-1})</td>
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<table>
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<tr>
<th>Sampling conditions</th>
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<tbody>
<tr>
<td>Observation height/mm</td>
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<tr>
<td>Sample flow rate/ml min(^{-1})</td>
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<tr>
<td>Wavelength/nm</td>
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<tr>
<td>Mn: 257.687</td>
<td>Co: 228.687</td>
</tr>
<tr>
<td>Zn: 213.924</td>
<td>Cd: 214.506</td>
</tr>
</tbody>
</table>

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*a. Seiko Instruments Plasma Spectrometer SPS 1700HVR.*

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Fig. 1 Effect of concentration of colloidal silica on recoveries of cobalt and zinc. Sample solution, 1 µg of cobalt (○) or zinc (●) in 100 ml; colloidal silica, 3 mmol l\(^{-1}\).

Fig. 2 Effect of concentration of calcium chloride on recovery of zinc. Sample solution, 1 µg of zinc in 100 ml; colloidal silica, 0.01%.

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The recoveries of these ions at 0.03% were almost same as that in Milli-Q water. The calcium chloride of 0.5 mmol l$^{-1}$ was used hereinafter, since use of any higher concentration of calcium might result in contamination due to its impurities.

**Adsorption behavior of manganese, cobalt, zinc and cadmium on colloidal silica**

In order to investigate adsorption behavior of manganese, cobalt, zinc or cadmium on colloidal silica, we determined the recoveries of 1 or 10 µg of each element in 100 ml of Milli-Q water. The results obtained are shown in Table 2. Manganese and cobalt were about 92% adsorbed and zinc and cadmium were about 95% adsorbed. The relative standard deviations of the recovery of these ions were about 1%.

The recoveries of 1 µg each of manganese, cobalt, zinc and cadmium in 100 ml of Milli-Q water by simultaneous preconcentration of them were 88.3, 87.2, 95.8 and 92.8%, respectively. Therefore, the order of ion selectivity series of colloidal silica is guessed as Zn$^{2+}$ > Cd$^{2+}$ > Mn$^{2+}$ > Co$^{2+}$. This order is similar to that on hydrated silica reported by Dushina et al.$^{17}$

**Effect of the colloidal silica concentration by simultaneous preconcentration of multi elements**

The effects of the colloidal silica concentration on recoveries of manganese, cobalt, zinc and cadmium by simultaneous preconcentration of them were reinvestigated over the concentration range of 0.01 to 0.03% because the recoveries of manganese, cobalt and cadmium were lower than those for each preconcentration of these ions. The results are shown in Fig. 3. The recoveries of these ions at 0.03% were almost same as that for each preconcentration at 0.01%. Therefore, the colloidal silica concentration of 0.03% was adopted for simultaneous preconcentration of multi elements.

**Analysis of river-water sample**

The applicability of the proposed method to real samples was evaluated by examining the recoveries of manganese, cobalt, zinc and cadmium from artificial river-water and actual river-water samples. The results are summarized in Tables 3 and 4. The recoveries of manganese, zinc and cadmium in the artificial river-water were close to that in Milli-Q water, while the recovery of cobalt in the artificial river-water was lower than that in Milli-Q water. Sodium, potassium and magnesium ions might interfere with the adsorption of cobalt on silica.

The concentrations of zinc and manganese in the sample collected at Yoro River were found to be 0.6 ± 0.03 ng g$^{-1}$ and more than 10 ng g$^{-1}$, respectively. The concentration of manganese in the sample was so high that its accurate concentration was not obtained. Cobalt and cadmium could not be detected. The recoveries for the additions of 1 µg of cobalt, zinc and cadmium to 100 g of river-water sample were 81.8, 95.6 and 90.0%, respectively. The recoveries of cobalt and cadmium in the river-water sample were lower than those in the case of Milli-Q water. The lower recoveries of cobalt and cadmium in the river-water sample might be due to the presence of some interfering substances (e.g., natural organic matter) in the sample which reduced the free concentration of cobalt and cadmium through complexation. On the other hand, the recovery of zinc in river-water is almost the same as those in Milli-Q water and in the artificial river-water. Therefore, these recoveries are summarized in Tables 3 and 4.
results obtained for zinc indicate the applicability of the present method to the determination of zinc in river-water. For seawater, the effect of high concentration of salts on adsorption of zinc must previously be investigated before the application of the present method.

The overall reagent blank value of zinc was found to be 16 ng (average of three runs). Those of manganese, cobalt, and cadmium were less than their lower limits of determination (Mn: 0.0010 µg ml\(^{-1}\), Co: 0.0025 µg ml\(^{-1}\), and Cd: 0.0015 µg ml\(^{-1}\)).

The present method is simple and rapid as compared with the coprecipitation methods since the coagulation of silica occurs within a few minutes after the addition of calcium chloride. Furthermore, this method is reproducible, as can be seen from the standard deviations, and the cost is lower because high pure colloidal silica is inexpensive and the consumption of the required reagents is relatively low.

References