Extraction of Metal-APDC Chelates into Admicelles Followed by Flotation for Water Analysis

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Abstract

A rapid and efficient preconcentration method was developed for the determination of trace metals in water. Trace metals [e.g., Ni(II), Cu(II), Ga(III), Cd(II), Pb(II), and Bi(III)] in 1 dm³ of sample solution were converted into the hydrophobic chelates with ammonium pyrrolidinedithiocarbamate. The resulting metal chelates were extracted into admicelles (silica particles covered with cetyltrimethylammonium chloride), which were floated with numerous tiny bubbles to the solution surface. The floated admicelles were collected in a small sampling vessel by suction and the metals were eluted from the admicelles with dilute nitric acid. A 200-fold multielement preconcentration and subsequent determination by inductively coupled plasma-mass spectrometry were achieved within 30 min. The proposed method was applied to the analysis of river water.

Key words: admicelle, flotation, preconcentration, cetyltrimethylammonium chloride, silica gel, ammonium pyrrolidinedithiocarbamate, water analysis

1 Introduction

The determination of trace metals in natural water is of great importance for the assessment of environmental pollution and a better understanding of their geochemical behavior. In spite of widespread use of modern analytical instruments with high sensitivity, preconcentration steps are still often necessary to determine trace metals in natural waters with satisfactory accuracy and precision [1,2]. Although a variety of techniques, including liquid-liquid extraction, solid-phase extraction, ion-exchange, coprecipitation, electrodeposition, and volatilization, have been employed for this purpose, limited techniques are available for rapid preconcentration of trace metals from large-volume samples.

In our laboratory, admicelles have been studied as separation and preconcentration vehicles in trace analysis [3-8]. They are surfactant aggregates formed on solid surfaces (e.g., alumina [9,10] and silica [11-13]) and capable of extracting hydrophobic compounds from aqueous solutions [5,10]. Because the surfactant aggregates are supported on a solid material, the admicellar extraction is free from difficulties encountered in other micelle-mediated techniques (e.g., micellar-enhanced ultrafiltration and cloud-point extraction).

Another feature of admicelles is their property of adhering to air bubbles. The adsorption of surfactant ions onto the oppositely-charged solid supports makes the particle surfaces hydrophobic, hence the resulting admicelles are readily adsorbed on gas-water interfaces and floated with bubbles rapidly. Therefore, the combined use of the admicellar extraction and flotation is promising for the rapid preconcentration of trace
constituents in water, as demonstrated in our recent studies [7,8]. For example, trace metals in 1 dm$^3$ of sample solution were readily preconcentrated 100-fold by the admicelle-flotation scheme [8], where a hydrophobic chelating agent, dithizone, was incorporated into the admicelles prior to the extraction. The dithizone-incorporated admicelles, however, contained some metal contaminants (e.g., Ni, Cu, and Pb) at 20- to 60-ng levels, which hindered the sensitive determination of trace metals.

An alternative approach to the dithizone-admicellar extraction of trace metals is that they are preliminarily converted into the hydrophobic chelates and then extracted into admicelles by hydrophobic interaction [4]. In this approach, no chelating agent is present during the preparation of admicelles, hence contamination can be effectively controlled. In the present study, this approach was adopted for the admicelle-flotation scheme using a water-soluble chelating agent, ammonium pyrrolidinedithiocarbamate (APDC). This reagent is characterized by its wide reactivity with various metals to form hydrophobic chelates [1,2,14]. The metal-APDC chelates were extracted into admicelles composed of silica and a cationic surfactant, cetyltrimethylammonium chloride (CTAC). After recovering the admicelles by flotation, the extracted metals were eluted with dilute nitric acid. Compared with the dithizone-admicellar method [8], the proposed method provided lower blanks and a higher preconcentration factor of 200. In addition, the elution procedure was further simplified. The proposed method was combined with inductively coupled plasma-mass spectrometry (ICP-MS) for the analysis of river water.

2 Experimental

2.1 Apparatus

The flotation apparatus used (Fig. 1) was constructed as reported previously [8]. A 1-dm$^3$ graduated cylinder was used as a flotation cell. The bubbler was equipped with a sintered-glass disk (5-10 μm pore size), through which nitrogen gas was introduced into the sample solution at a flow rate of 25 cm$^3$ min$^{-1}$. The solution was stirred with a magnetic stirrer to disperse the bubbles and admicelles in the solution. The sampling vessel was a Millipore filter holder (15 mm i.d. x 100 mm high) equipped with an Omnipore hydrophilic PTFE membrane filter (10 μm pore size). A silicone-rubber stopper with a tapered bent glass tube was fitted on the top of the sampling vessel. The lower end of the sampling vessel was inserted into a suction bottle.

A Seiko SPQ-6500 ICP-mass spectrometer was used for the determination of trace metals under the following plasma conditions: RF power, 1.2 kW; sampling depth, 12 mm; argon flow rates (in dm$^3$ min$^{-1}$), 18 for outer, 0.8 for intermediate, and 1.0 for carrier. The determination was performed at the following m/z values: 60 for Ni$^+$, 63 for Cu$^+$, 71 for Ga$^+$, 114 for Cd$^+$, 208 for Pb$^+$, and 209 for Bi$. A Tokyo Rika NTS-1300 mechanical shaker was used for the preparation of admicelles at a shaking rate of 70-80 strokes mim$^{-1}$. A Tokyo Rika AU-60C ultrasonic cleaning-bath (28 kHz, 210 W) was used for the purification of silica.

2.2 Reagents
Silica gel (chromatographic grade, 40-50 μm in particle size, Kanto Kagaku) was ultrasonically washed with 5 \( M = \text{mol dm}^{-3} \) nitric acid for 5 min and rinsed thoroughly with water. A CTAC solution (7.5 mg cm\(^{-3} \)) was prepared by dissolving cetyltrimethylammonium chloride (extra-pure grade, Kanto Kagaku) in 0.1 \( M \) aqueous ammonia. An APDC solution (5.0 mg cm\(^{-3} \)) was prepared by dissolving ammonium pyrrolidinedithiocarbamate (special grade for atomic absorption spectrometry, Nacalai Tesque) in water.

Standard solutions of metals (1.0 \( \mu \text{g cm}^{-3} \) in 0.1 \( M \) nitric acid) were prepared from commercial standard solutions (Nacalai Tesque). A humic acid solution (0.3 \( \mu \text{g cm}^{-3} \)) was prepared by dissolving humic acid (extracted from peat soil, Nacalai Tesque) in 0.1 M potassium hydroxide solution and passing through Nuclepore polycarbonate membrane filters (0.4 μm pore size). Artificial river water was prepared as follows. Fifty milligrams of sodium chloride, 100 mg of sodium sulfate, 20 mg of potassium chloride, 200 mg of calcium nitrate tetrahydrate, and 150 mg of magnesium chloride hexahydrate were dissolved in 100 cm\(^3\) of water. A 10-cm\(^3\) aliquot of the solution was mixed with 3.4 cm\(^3\) of humic solution, while adjusting the volume to 1.00 dm\(^3\) with water (Na 5.2, K 1.0, Mg 1.8, Ca 4.6, Cl 9.2, SO\(_4\) 6.8, NO\(_3\) 7.1, and humic acid 1.0 mg dm\(^{-3}\) ). The pH buffers used were as follows: formic acid-tetramethylammonium hydroxide (TMAH) for pH 3.7-4.3, acetic acid-TMAH for pH 4.3-5.5, 2-morpholinoethanesulfonic acid (MES)-TMAH for pH 5.5-6.5, 3-morpholinopropanesulfonic acid (MOPS)-TMAH for pH 6.5-7.5, tris(hydroxymethyl)aminomethane (Tris)-nitric acid for pH 7.5-8.5, and N-cyclohexyl-2-aminoethanesulfonic acid (CHES)-TMAH for pH 8.5-9.5.

All reagents used were of analytical reagent grade, unless otherwise stated. Water was purified with a Millipore Milli-Q Gradient A-10 system.

### 2.3 Preparation of admicelles

To 0.50 g of silica particles placed in a 50-cm\(^3\) centrifuge tube was added 20 cm\(^3\) of CTAC solution and gently shaken for 5 min to form CTAC-silica admicelles. The solution was removed by centrifugation at 3000 rpm for 5 min. The remaining particles of admicelles were rinsed twice with 7.0 cm\(^3\) each of water before use.

### 2.4 Small-scale batch extraction of metals

A series of sample solutions (containing 25 \( \mu \text{g dm}^{-3} \) each of metals of interest and 5.0 mM of an appropriate pH buffer) was prepared at different pH’s. A 40-cm\(^3\) aliquot of the solution was taken and mixed with 0.20 cm\(^3\) of APDC solution to form hydrophobic metal-APDC chelates. The solution was poured into a 50-cm\(^3\) polypropylene centrifuge tube in which 0.25 g (as silica) of admicelles had been placed. After gently shaking for 30 min, the solution was separated by centrifugation at 3000 rpm for 5 min and reserved for ICP-MS. The sedimented admicelles were removed and the inner wall of the centrifuge tube was washed with a small amount of pure water followed by 5 \( M \) nitric acid. The reserved supernatant solution was combined with the nitric acid and analyzed by ICP-MS to determine the extraction yields.

### 2.5 Analytical procedure

To 1.00 dm\(^3\) of water sample placed in a flotation cell was added 0.50 \( M \) Tris-HNO\(_3\) buffer solution to adjust the pH to 8-8.5. After adding 10 cm\(^3\) of APDC solution, 0.50 g (as silica) of admicelles was added to the sample solution and dispersed uniformly for 15 min to extract hydrophobic metal-APDC chelates. A 1.0-cm\(^3\) portion of ethanol was added to the solution, into which nitrogen gas was introduced to float the admicelles completely. The floated admicelles were collected into a sampling vessel by suction. From the sampling vessel, the silicone-rubber stopper was removed and the admicelles were rinsed with 5.0 cm of water. After removing the suction bottle, the sampling vessel was fitted on a bell jar for suction filtration. To elute the extracted metals, 0.50 cm\(^3\) of 5.0 \( M \) nitric acid was added to the admicelles, left to stand for 5 min, and sucked into a 5-cm\(^3\) volumetric flask. The admicelles were washed with 1.0 cm\(^3\) each of 1.0 \( M \) nitric acid and water. The combined
solution was diluted to the mark with water and analyzed by ICP-MS for trace metals. Calibration graphs were constructed using 0.70 M nitric acid containing metals of interest at pg cm$^{-3}$ to ng cm$^{-3}$ levels.

3 Results and Discussion

3.1 Extraction behavior of trace metals

The admicelles used were prepared on the basis of a previous study [8], where silica particles were simply mixed with an ammoniacal CTAC solution. The cationic surfactant, CTAC, was strongly adsorbed on the negatively-charged silica surfaces (the isoelectric point, $pI = ca. 2$ [15]). The resulting admicelles were stable over a wide pH range of 4-10. The CTAC loaded on the particles was 300 mg g$^{-1}$.

Figure 2 shows the extraction behavior of trace metals with APDC, which was investigated by batch extraction experiments on a small scale. Over pH 5-9, Ga(III), Cd(II), Pb(II), and Bi(III) were simultaneously extracted in greater than 90% yields. On the other hand, the complete extraction of Ni(II) and Cu(II) required adjusting the pH to around 8. This behavior of Ni(II) and Cu(II) is different from the conventional liquid-liquid extraction with APDC [14] and the sodium dodecylsulfate-alumina admicellar extraction with APDC [4]; the reason is not clear at present. In the present study, the sample pH was adjusted to 8-8.5 to ensure the simultaneous collection of trace metals.

3.2 Collection of trace metals by the admicelle-flotation

The experimental conditions for the admicelle-flotation were optimized previously [8]. For artificial river water, complete flotation was achieved within 1 min. The CTAC admicelles were rapidly floated with numerous tiny bubbles and supported on the solution surface by a stable foam layer, hence they were readily collected in a small sampling vessel by suction. However, the flotability of the CTAC admicelles was sensitive to ionic strength. For example, part of the admicelles were not floated even by bubbling for 20 min and remained in the solution at the salinity of seawater (Na 12, Mg 1.3, and Cl 23 g dm$^{-3}$). Further loading of CTAC (300-500 mg g$^{-1}$) was ineffective in improving the flotability. Therefore, we focused our attention on the preconcentration of trace metals in fresh-water samples.

Table 1 shows the percentages of trace metals collected from 1.00 dm$^3$ of artificial river water, into which 5.0 cm$^3$ of APDC solution was added for the chelation. The nearly complete and simultaneous collection of Ni(II), Cu(II), Ga(III), Cd(II), Pb(II), and Bi(III) was achieved with 0.50 g (as silica) of admicelles. This amount

<table>
<thead>
<tr>
<th>Admicelles added / g (as SiO$_2$)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Ga(III)</th>
<th>Cd(II)</th>
<th>Pb(II)</th>
<th>Bi(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>73, 80</td>
<td>73, 79</td>
<td>63, 69</td>
<td>85, 89</td>
<td>81, 84</td>
<td>83, 85</td>
</tr>
<tr>
<td>0.50</td>
<td>95, 95</td>
<td>91, 98</td>
<td>88, 93</td>
<td>99, 100</td>
<td>92, 96</td>
<td>91, 97</td>
</tr>
</tbody>
</table>

$^a$ Concentrations (in mg dm$^{-3}$): Na 5.2, K 1.0, Mg 1.8, Ca 4.6, Cl 9.2, SO$_4$ 6.8, NO$_3$ 7.1, humic acid 1.0.

$^b$ Stirring time: 15 min.
is 4 times less than that required in the previously-reported dithizone method [8]. As shown in Fig. 3, a 15-min stirring was sufficient to collect 6 metals nearly completely.

The results given in Table 1 also indicate that major inorganic ions (e.g., Na, K, and Mg) and humic acid at the natural abundance levels in river water caused no interference in the metal-collection. In natural waters, some minor metals, such as Al(III), Mn(II), Fe(III), and Zn(II), are also often found at relatively high concentrations, hence their potential interference was examined. In the presence of 100 µg dm⁻³ each of these metals, the collection yields of trace metals at the 1.0-µg dm⁻³ level decreased to 74% (Ni), 52% (Cu), 86% (Ga), 56% (Cd), 76% (Pb), and 60% (Bi). The collection yields, however, improved to 88% or better for all metals when using 10 cm³ of APDC solution.

3.3 Elution of trace metals

In the previously-reported dithizone method [8], 2.0 g (as silica) of admicelles was necessary to collect trace metals completely, hence the elution required treating them twice with 1.0 cm³ each of 5.0 M nitric acid. In the proposed APDC method, the adequate amount of admicelles was reduced to one-fourth, hence satisfactory elution was achieved more easily. As shown in Table 2, the simple treatment with 0.50 cm³ of 5.0 M nitric acid was sufficient for the nearly complete and simultaneous elution of the desired metals, though the elution yields considerably decreased with 1.0 and 3.0 M nitric acid. To minimize the potential damage to the ICP-mass spectrometer, the final solution was made up to 5.0 cm³ with water, which corresponds to a 200-fold preconcentration. Unfortunately, repeated use of the admicelles was difficult due to the deterioration in the flotability.

Table 2 Elution of trace metals with 0.50 cm³ of dilute nitric acid

<table>
<thead>
<tr>
<th>Acidity / M</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Ga(III)</th>
<th>Cd(II)</th>
<th>Pb(II)</th>
<th>Bi(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5</td>
<td>0</td>
<td>55</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.0</td>
<td>0</td>
<td>0</td>
<td>87</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>5.0</td>
<td>93</td>
<td>94</td>
<td>96</td>
<td>104</td>
<td>101</td>
<td>102</td>
</tr>
</tbody>
</table>

3.4 Application to river water analysis

A riverine water sample was filtered with 0.45-µm Millipore membrane filters to remove suspended solids. A 1.00-dm³ aliquot of the filtrate was taken and treated as described in Section 2.5. The results are summarized in Table 3. The metals previously added to the filtered sample (Nos. 5, 6) were successfully recovered. The blank values through the whole procedure were 0.010 ± 0.003 µg for Ni and 0.007 ± 0.002 µg for Pb (mean ± standard deviation, n = 4). For the other metals, the blanks were not detectable (<0.005 µg for Cu; <0.0005 µg for Ga, Cd, and Bi). The time required for a determination (including admicellar extraction, flotation, elution, and ICP-MS for 6 metals) was about 30 min.
Table 3  Determination of trace metals in a riverine water sample $^a$

<table>
<thead>
<tr>
<th>Metal</th>
<th>Found / $\mu$g</th>
<th>Concentration in sample $^c$ / $\mu$g dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. 1</td>
<td>No. 2</td>
</tr>
<tr>
<td>Ni</td>
<td>1.08</td>
<td>1.05</td>
</tr>
<tr>
<td>Cu</td>
<td>0.52</td>
<td>0.55</td>
</tr>
<tr>
<td>Ga</td>
<td>0.010</td>
<td>0.008</td>
</tr>
<tr>
<td>Cd</td>
<td>0.015</td>
<td>0.013</td>
</tr>
<tr>
<td>Pb</td>
<td>0.022</td>
<td>0.034</td>
</tr>
<tr>
<td>Bi</td>
<td>0.004</td>
<td>&lt; 0.001</td>
</tr>
</tbody>
</table>

$^a$ Filtered with 0.45-$\mu$m Millipore membrane filters.
$^b$ 0.50 $\mu$g each of Ni(II) and Cu(II) and 0.025 $\mu$g each of Ga(III), Cd(II), Pb(II), and Bi(III) were simultaneously added.
$^c$ Mean ± standard deviation.

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References