Ultrafiltration and Alumina Adsorption of Micelles for the Preconcentration of Copper(II) in Water

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Micellar-enhanced ultrafiltration was considered from the viewpoint of trace analysis, by taking copper(II) as an example. Copper(II) cations were collected electrostatically on micelles of sodium dodecyl sulfate, and separated from the mother liquor by ultrafiltration. However, the final solution contained a large amount of surfactant, which caused serious interference in the determination. This problem was overcome by using alumina adsorption, where negatively charged micelles were adsorbed on positively charged alumina particles and then recovered by conventional filtration. The copper was leached from the micelles with 4 mol l⁻¹ nitric acid, leaving the surfactant on the alumina. The proposed method was successfully applied to an analysis of certified reference water samples.

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Introduction

Although modern instrumental methods for trace analysis are highly sensitive and selective, preconcentration techniques are often required to improve the accuracy and precision of the analytical results.^{1,2} Micellar-enhanced ultrafiltration (MEUF) offers a simple separation method, where a surfactant is added to an aqueous solution and forms aggregates, called micelles, into which the desired substance solubilizes. The aqueous solution is then forced through an ultrafiltration membrane with pore sizes small enough to reject the micelles containing the desired substance. This process has been studied for the removal of organic pollutants and heavy metal ions from water.³⁻⁷ To the best of our knowledge, however, MEUF has not been used for the preconcentration of trace metals at ng ml⁻¹ levels before the instrumental determination steps.

The present communication describes the limitations of MEUF for the use of preconcentrating trace elements. For example, a relatively large concentration of surfactant seriously disturbed the determination of copper. As an alternative to ultrafiltration, we proposed alumina adsorption, which facilitated a rapid separation of micelles from the mother liquor and eliminated interference from the surfactant. Further, copper was preliminarily converted into the water-insoluble complex with the aid of ammonium pyrrolidinedithiocarbamate (APDC) to widen the scope of the applicability. The proposed method was combined with graphite-furnace atomic absorption spectrometry (GFAAS), which allowed a rapid and reliable determination of traces of copper in river and seawater.

Experimental

Apparatus and reagents

A Seiko SAS-760 atomic absorption spectrometer equipped with an SAS-715 graphite-furnace atomizer was employed for the determination of copper under the following furnace operating conditions. The graphite tube was gradually warmed during 20 s to 150°C and held for 15 s. The tube was then heated during 5 s to 800°C and held for 10 s; it was further heated to a final atomization temperature of 2400°C for 2 s. The clean-up step was performed at 2550°C for 3 s to eliminate the memory effect. The wavelength and hollow-cathode lamp current used were 324.8 nm and 10 mA, respectively. A Hitachi ECV-843 BY clean bench was used for preconcentration procedures.

An Advantec UHP-43 batch-stirred cell (capacity 70 ml) was used for ultrafiltration experiments. The membrane filters (43 mm diam.) used were Advantec UK-10 (10000 Da molecular weight cut-off), Diaflo YM-1 (1000 Da) and Diaflo YM-05 (500 Da). An SDS solution (40 mg ml⁻¹) was prepared by dissolving sodium dodecyl sulfate (special grade for water analysis, Nacalai Tesque) in water. An APDC solution (2.0 mg ml⁻¹) was prepared by dissolving ammonium pyrrolidinedithiocarbamate (special grade for AAS, Nacalai Tesque) in water. Alumina particles (*ca.* 50 µm, gamma-type, chromatographic grade, Katayama Chemicals) were washed with 4 mol l⁻¹ nitric acid for 10 min in a Branson ultrasonic cleaning bath (42 kHz, 120 W) and then rinsed thoroughly with water. Certified reference water samples (SLRS-3, CASS-3 and NASS-5) were obtained from National Research Council of Canada. All reagents used were of analytical grade (Nacalai Tesque), unless stated otherwise. Water was purified by distillation and ion exchange and then passed through a Millipore Milli-Q purification system.

Recommended procedure

To 100 ml of water sample (preliminarily adjusted to pH 2)

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Fig. 1 Effect of the concentration of SDS on ultrafiltration with a 10000-Da (○), 1000-Da (▲), or 500-Da (■) membrane filter.

was added 2 ml of an APDC solution to form a copper-APDC complex. After adding 10 ml of an SDS solution, the mixture was stirred for 15 min to collect the hydrophobic complex in SDS micelles. After adding 3 g of alumina, the suspension was stirred for 5 min and then poured into an empty polypropylene column (with a porous polyethylene disk of 36 μm pore, 7 mm in diam.) to separate the micelle-alumina particles from the mother liquor. The copper was desorbed from the micelles with 1 ml of 4 mol l^{-1} nitric acid and collected in a 5-ml volumetric flask by suction. The desorption was repeated twice more with 1 ml each of 4 mol l^{-1} nitric acid. The combined eluents were diluted to the mark with water. A 10- μl aliquot of the solution was injected into a graphite cuvette and analyzed by GFAAS. A calibration graph was prepared by taking nanogram quantities of copper and 3 ml of 4 mol l^{-1} nitric acid in a 5-ml volumetric flask and diluting to the mark with water.

Results and Discussion

Ultrafiltration of micelles collecting copper(II)

The ultrafiltration cell was initially filled with 20 ml of water containing different amounts of SDS. The permeate solution was analyzed for SDS by the toluidine blue titration method.⁸ Figure 1 shows that the recovery of SDS (the fraction retained on the membrane) increased abruptly above the critical micelle concentration (2.3 mg ml^{-1}) and reached values of 80–90%. Most of the permeable fraction may correspond to monomeric or unassociated surfactant. Among the different membrane filters used here, a 10000-Da cut-off membrane filter was most convenient because filtration was completed within 30 min. With a membrane filter having a 500 or 1000 Da molecular weight cut-off, the filtration required more than 2 h to treat 20 ml of the sample solution.

The collection efficiency was examined using 20 ml of water containing 1 μg of copper(II). After adding 400 mg of SDS, ultrafiltration was carried out with a 10000-Da cut-off membrane filter, and the permeate solution was analyzed by GFAAS. As is shown in Table 1, more than 96% of the copper(II) were adsorbed electrostatically at pH 2 onto, or near, the micellar surface, which had a highly negative charge density. The recovery decreased with increasing the pH of the

Table 1 Collection of 1 μg of copper(II) in 20 ml of water by ultrafiltration^a

SDS added/mg	Cu recovered, %		
	pH 2	pH 5	pH 7
400	96, 99, 100	71, 75, 79	57
0	3, 5	3, 10	47, 58

a. With a 10000-Da membrane filter.

solution, probably due to a decrease in the positive charge by the formation of hydroxocomplex or hydroxide. Direct ultrafiltration without SDS was also carried out for a comparison. In the absence of SDS, nearly all of the copper(II) passed through the membrane filter over the pH range of 2–5. About half of the copper(II), however, was retained at pH 7, probably due to the formation of colloidal copper(II) hydroxide.

The remaining solution on the membrane filter was viscous and contained large amounts of SDS. When a 10- μl aliquot of the solution was injected into a graphite cuvette, large background absorption (absorbance of *ca.* 0.9) occurred. Ashing at 900–1000°C decreased the signal intensity of copper without any reduction of the background. At higher temperatures, both the signal and the background decreased.

In addition to interference from the surfactants, the concentration factor obtained by MEUF was rather poor and the ultrafiltration membrane filter was expensive. Therefore, we proposed an alternative separation method of micelles, as described below.

Adsorption of micelles on alumina particles

Because the surfaces of alumina particles are positively charged in acidic solutions, they strongly adsorb anionic surfactants.^{9,10} This phenomenon was used for the separation of micelles from the mother liquor. In this experiment, copper(II) was preliminarily converted into the hydrophobic complex with APDC, because the collection based on electrostatic attraction was seriously affected by the solution pH and coexisting ions. The copper-APDC complex was trapped in the hydrophobic core of micelles and adsorbed on alumina by stirring. The separation of alumina particles from the solution was rapidly carried out by using a conventional porous disk (*e.g.*, 36 μm pore); hence, the sample volume could easily be increased.

Nanogram quantities of copper(II) in 100 ml of water were completely recovered with 400 mg of SDS and 3 g of alumina. The desorption of copper from the micelles was achieved with 4 mol l^{-1} nitric acid, leaving SDS on alumina. The SDS accompanying copper was determined by the toluidine blue method and found to be less than 1 mg, which did not interfere with the determination at all.

Application to water analysis

The proposed method was applied to the determination of copper in certified reference water samples. To a 100-ml aliquot of the sample was added 2 ml of an APDC solution at pH 2. The preconcentration and determination were carried out as described in the *Recommended procedure*. As shown in Table 2, the analytical results were in good agreement with the certified values. The time required for a determination (including preconcentration and GFAAS) was less than 1 h. Because APDC reacts with various heavy metals,^{11,12} combining the proposed preconcentration method with ICP-MS or ICP-AES allows rapid and simple multielement determinations,

Table 2 Determination of copper in reference water samples

Sample ^a	Cu found/ng ml ⁻¹	
	Certified value	Analytical result (<i>n</i> = 4)
River water (SLRS-3)	1.35 ± 0.07	1.42 ± 0.05
Seawater (CASS-3)	0.517 ± 0.062	0.549 ± 0.070
Seawater (NASS-5)	0.297 ± 0.046	0.304 ± 0.011

a. Salinity: 30.2‰ for CASS-3 and 30.5‰ for NASS-5.

which may provide useful and valuable information for environmental science and aquatic chemistry.

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