Use of Surfactant Aggregates Formed on Alumina for the Preparation of Chelating Sorbents

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To 1.5 g of γ -alumina particles in 40 ml of water was added 10 ml of ammoniacal solution containing 1.5 mg of dithizone and 100 mg of sodium dodecyl sulfate. The solution was acidified to pH 2 to form the surfactant aggregates on the alumina surfaces, into which dithizone was trapped. Traces of copper(II) and silver(I) in water were completely collected on the dithizone-coated alumina over a wide range of pH 1–7; cadmium(II), cobalt(II), nickel(II), lead(II) and zinc(II) were simultaneously recovered at pH 3–7. The chelating sorbent functioned well even in aqueous solutions containing a large amount of matrix element. The proposed sorption method has been successfully applied to the determination of traces of copper in lead metal.

Keywords Sorption, surfactant micelle, sodium dodecyl sulfate, dithizone, trace metal

Surfactant molecules in aqueous solutions form self-aggregates called "micelles" above the critical micelle concentration. The hydrocarbon cores of the micelles give them the unique ability to solubilize hydrophobic organic compounds which are otherwise insoluble or sparingly soluble in water. Recently, similar interactions were observed on the surfactant aggregates formed on solid surfaces, so-called "hemi-micelles" and "ad-micelles". Valsaraj, for example, reported the partitioning of several hydrophobic organic compounds (e.g., chloroform, benzene, dichlorobenzene and pentachlorophenol) between the aqueous solution and the surfactant aggregates on alumina.^{1,2} Holsen *et al.* tried to remove toluene, *p*-xylene and trichloroethylene by using surfactant aggregates formed on hydrated iron(III) oxide.³

Previously, we proposed a new preparation technique of chelating sorbents, where a water-insoluble chelating agent was rapidly introduced into the aggregates of sodium dodecyl sulfate (SDS) on alumina particles.⁴ The idea is illustrated in Fig. 1. Although the surfactant-coated alumina was useful for the preconcentration of traces of copper(II) in pure water, the work was only preliminary to show the potential of our idea. Therefore, more systematic study is essential for a better understanding of the unique properties and limitations of the method.

In the present work, the interactions between SDS and α - and γ -alumina particles were first studied at different solution pH's. Second, the sorption behavior on the dithizone-coated alumina was studied for eight trace elements as a function of the pH of the solution. Third, the effect of a matrix element on the sorption was examined, by taking copper(II) in lead nitrate solutions

Fig. 1 Schematic of incorporation of a chelating agent in SDS aggregates on alumina.

as an example. Finally, the sorption method was applied to the determination of traces of copper in lead metal. Compared with the conventional extraction method with dithizone-chloroform or -carbon tetrachloride, the proposed method can be successfully combined with inductively coupled plasma-atomic emis-

sion spectrometry (ICP-AES), because the desorption is easily achieved with diluted nitric acid. In addition, sorption and desorption, as well as preparation of the sorbent do not require any toxic organic solvents, which is another advantage from the viewpoint of environmental protection.

Experimental

Apparatus

A Seiko SPS 1100H sequential type ICP-atomic emission spectrometer was used under the following operating conditions: wavelengths(nm) 328.07 for Ag, 226.50 for Cd, 228.62 for Co, 324.76 for Cu, 257.61 for Mn, 221.65 for Ni, 220.36 for Pb and 213.85 for Zn; RF power 1.2 kW; argon flow rates($l\ min^{-1}$) 16 for outer, 0.7 for intermediate and 0.7 for carrier; observation height 17–24 mm above load coil.

A Tokyo Rika NTS-1300S shaker was employed for preparing sorbents at the shaking rate of $160\ min^{-1}$. A Branson ultrasonic cleaning bath (47 kHz, 120 W) was used for purification of alumina particles. All separation procedures (except for centrifugation) were carried out in a Hitachi ECV-843 BY clean bench.

Reagents

Alumina particles (10–50 μm , γ -type, chromatographic grade, Katayama Chemicals) were ultrasonically washed in $5\ mol\ l^{-1}$ nitric acid for 3 min and rinsed thoroughly with water three times. Alpha-alumina particles (Kanto Chemicals) were also used for the comparison.

A dithizone-SDS solution was prepared by dissolving 15.0 mg of dithizone ("pro analysi", Merck) and 1.0 g of SDS (Nacalai Tesque) in 50 ml of $0.1\ mol\ l^{-1}$ aqueous ammonia and diluting to 100 ml with water. A volume of 10 ml of the solution was added to 1.5 g of alumina particles in 40 ml of water. The suspension was acidified to pH 2 with $4\ mol\ l^{-1}$ hydrochloric acid and mixed for 15 min with a mechanical shaker. After the supernatant solution was discarded, the dithizone-coated alumina was packed into a column (15 mm in diam. $\times$ 7 mm height).

The certified reference material for lead (BCR No. 287, chips) was obtained from the Community Bureau of Reference in Brussels. Metal standard solutions ($1\ \mu g\ ml^{-1}$, in $0.1\ mol\ l^{-1}$ nitric acid) were prepared from commercial standard solutions and diluted to appropriate concentrations with $0.1\ mol\ l^{-1}$ nitric acid immediately before use.

A buffer solution for the toluidine blue method was a (1+4) mixture of $1\ mol\ l^{-1}$ aqueous ammonia and $1\ mol\ l^{-1}$ ammonium chloride solution. Water was purified by distillation and ion-exchange, and then passed through a Millipore Milli-Q purification system.

Determination of SDS by toluidine blue method⁵

To 5 ml of a sample (containing $<1\ mg$ of SDS,

previously adjusted to pH 7–8) were added 0.05 ml of buffer solution and 5 ml of chloroform. After adding a drop (*ca.* 0.07 ml) of toluidine blue indicator (Wako Chemicals), SDS in the solution was titrated with a standard solution of cationic surfactant (alkyldimethylbenzylammonium chloride) until the color of chloroform layer changed from blue to pink-red.

Determination of traces of copper in lead metal

A 5- or 10-g lead sample was dissolved in 25 or 50 ml of $5\ mol\ l^{-1}$ nitric acid and diluted to 100 ml with water. An aliquot of the solution (0.5 or 1 g as Pb) was further diluted to 50 ml, while adjusting the pH to 1. The solution was introduced onto the dithizone-coated alumina column to sorb copper at a flow rate of 2–3 $ml\ min^{-1}$. After washing the column with 30 ml of $0.01\ mol\ l^{-1}$ nitric acid, the copper was desorbed with 3 ml of $4\ mol\ l^{-1}$ nitric acid. The solution was diluted to 10 ml with water and this sample was analyzed by ICP-AES for copper.

Results and Discussion

Sorption of SDS on alumina particles

Molecules of an anionic surfactant SDS were effectively sorbed on the positively charged alumina surfaces from slightly acidic solutions.^{2,4} The difference of sorption on γ - and α -alumina was studied as follows. To 50 ml of water was added 1.5 g of alumina, and the pH was adjusted to different values with hydrochloric acid or aqueous ammonia (0.1 and $4\ mol\ l^{-1}$). After adding 100 mg of SDS, the pH of the solution was measured once more and recorded. The suspension was shaken for 15 min and, after centrifugation, a 5-ml aliquot of the supernatant solution was taken for the analysis by the toluidine blue method. Because the color change from blue to red at the end point was quite sharp, it allowed us to detect as little as $10\ \mu g$ of SDS.

Figure 2 shows the clear difference between two types of alumina particles. The complete sorption of SDS occurred on the γ -alumina over a wide range of pH 1–6. The α -type, however, sorbed very little SDS, probably because of the chemically inert surfaces.⁶ The use of γ -alumina is essential for the preparation of chelating sorbents.

Various amounts of SDS were mixed with 1.5 g of γ -alumina at pH 2 to measure the sorption capacity of alumina. The SDS was added as powder or different volumes of dithizone-SDS solution (containing $0.15\ mg\ ml^{-1}$ of dithizone and $10\ mg\ ml^{-1}$ of SDS), and the SDS sorbed was determined by the toluidine blue method. As shown in Fig. 3, the SDS up to *ca.* 250 mg was completely sorbed on the alumina. Hemi-micelles or ad-micelles incorporating dithizone would be formed on the surfaces of alumina. The supernatant solution was colorless and transparent, which indicates that the dithizone was almost completely captured on the SDS-alumina. However, when $>300\ mg$ of SDS was added,

Fig. 2 Sorption of 100 mg of SDS on 1.5 g of γ -alumina (○) or α -alumina (●) at different pH's.

Fig. 3 Sorption of SDS on 1.5 g of γ -alumina at pH 2. Different amounts of SDS were added as powder (○) or dithizone-SDS solution (●).

the supernatant solution became dark violet. This could be caused by the excess of SDS, which forms micelles in the solution and also traps the dithizone.

We recommend to use 1.5 g of alumina, 100 mg of SDS and 1.5 mg of dithizone, because the SDS and dithizone are completely retained on the alumina and the resulting sorbent has enough capacity for collecting trace elements.

Effect of pH on sorption of trace elements

In order to survey the recovery of eight trace elements, 50 ml of samples were introduced onto the dithizone-coated alumina column at different pH's. Then the effluent was analyzed by ICP-AES. Figure 4 shows that silver and copper are completely sorbed over pH 1–7. Other trace metals (*i.e.*, Cd, Co, Ni, Zn and Pb) can also be collected simultaneously at pH 3–7, though the recovery of manganese is less than 30%.

Trace metals at higher concentrations were examined

Fig. 4 Sorption of 10 μ g each of Ag(I), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Zn(II) and 100 μ g of Pb(II) in 50 ml of water.

for the sorption. The optimal pH range was little effected for most metals (*i.e.*, Ag, Cd, Co, Cu and Pb), but it was shifted to higher pH's for nickel and zinc (see Fig. 5).

The sorption behavior can be expected from the conventional liquid-liquid extraction with dithizone-chloroform and -carbon tetrachloride.^{7,8} Compared with those extraction techniques, the proposed sorption method has an advantage: trace metals are desorbed from the column with diluted nitric acid, which is directly introduced into ICP.

Separation of copper from lead matrix

The effect of the matrix element on the sorption was studied by taking copper(II) in lead nitrate solutions as an example. The sorption was carried out at pH 1, because the recovery of the two elements was very different from each other (see Figs. 4, 5). More than 99% of copper was desorbed along with the dithizone by using 3 ml of 4 mol l⁻¹ nitric acid.

Table 1 shows that the dithizone-coated alumina is useful and stable even in the presence of 5.0 g of lead. The lead accompanying the copper was determined by ICP-AES for obtaining the separation factor (*S*): $S =$

Fig. 5 Sorption of 25 µg each of Ag(I), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Zn(II) and 250 µg of Pb(II) in 50 ml of water.

Table 1 Effect of lead matrix on the recovery of copper

Lead in 50 ml of sample solution ^a /g	Cu sorbed and desorbed ^b , %	Separation factor
0	99, 99, 101	—
0.5	100	8.6×10^{-4}
1.0	98, 100, 101	4.4×10^{-4}
2.0	99	3.3×10^{-4}
3.0	99	2.2×10^{-4}
5.0	99	1.6×10^{-4}

a. 1.0 µg of Cu(II) was added.

b. Sorbed at pH 1 and desorbed with 3 ml of 4 mol l⁻¹ HNO₃.

$(Q_T^0/Q_M^0)/(Q_T/Q_M)$, where Q_T^0 is the quantity of the trace element in the sample, Q_M^0 the quantity of the matrix element in the sample, and Q_T and Q_M are the corresponding quantities after the separation. The excellent separation factors were obtained: $(1.6 - 8.6) \times 10^{-4}$. Further, the SDS was not desorbed from the column. Therefore, no interference occurred in the determination by ICP-AES.

Table 2 Determination of copper in lead metal samples

Sample taken/ g	Aliquot taken	Cu found/ µg	Cu in sample, ppm
Certified reference material (BCR No. 287) ^a			
10.0	1/10	0.96	0.96
	1/10	0.97	0.97
	1/10	0.97	0.97
	1/10	1.02	1.02
	1/10	1.02	1.02
			Av. 0.99
Reagent grade lead			
5.29	1/5	8.29	7.82
	1/5	8.45	7.97
	1/5 ^b	8.79	7.82
	1/5 ^b	8.90	7.92
			Av. 7.88
10.20	1/10	8.85	8.68
	1/10	8.86	8.69
	1/10 ^c	9.85	8.68
	1/10 ^c	9.90	8.73
	1/10 ^c	9.95	8.77
			Av. 8.71
High-purity lead (99.999%)			
10.0	1/20 ^c	1.11	0.22
	1/10	0.22	0.22
	1/10	0.23	0.23
	1/10	0.23	0.23
	1/10	0.23	0.23
	1/10 ^c	1.20	0.20
	1/10 ^c	1.23	0.23
			Av. 0.22

a. Certified value $0.98 \pm 0.05 \mu\text{g g}^{-1}$.

b. 0.50 µg of Cu was added.

c. 1.00 µg of Cu was added.

Determination of traces of copper in lead metal

The validity of the proposed sorption method was evaluated by the analysis of certified reference material. The blank value through the whole procedure was less than the detection limit ($<0.03 \mu\text{g}$ for copper). As shown in Table 2, accurate and reproducible results were obtained with the relative standard deviation of 3.0% ($n=5$).

Table 2 also shows the results obtained for reagent grade (granular, Katayama Chemicals) and high-purity lead metal samples (99.999% purity, granular, Katayama Chemicals). The copper added to the sample was quantitatively recovered and successfully determined. A slight difference (i.e., 7.88 and 8.71 ppm) for the reagent grade samples probably comes from the inhomogeneous distribution of copper.

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