Notes

Immobilization of Dithizone on Surfactant-Coated Alumina for Preconcentration of Metal Ions

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In spite of the existence of powerful instrumental determination methods, most trace metal analyses performed to date have required some pretreatment of samples, not only to concentrate the desired trace metals but also to avoid the interferences provided by coexisting elements.¹⁻³

Ionic or nonionic surfactant molecules form self-aggregates called "micelles" above a certain concentration, known as the critical micelle concentration (CMC). The hydrocarbon cores of the micelles give them the unique ability to solubilize many hydrophobic compounds which are otherwise only slightly soluble or insoluble in water. Surfactants can also form aggregates on solid surfaces, which are known as "hemi-micelles" or "ad-micelles" and have solubilization capacities similar to the micelles. For example, surfactant-coated hydrated iron(III) oxide⁴ or alumina⁵ have been used for removal of sparingly soluble chemicals (e.g., toluene, *p*-xylene, trichloroethylene and pentachlorophenol) from aqueous solutions. The literature survey, however, shows that there is no study on the use of these hemi-micelles or ad-micelles for the preconcentration of traces of metal ions.

In the present work, a new type of chelate-forming sorbent has been prepared in an aqueous media, based on immobilization of dithizone on surfactant-coated alumina. The sorption and desorption properties were examined to evaluate the sorbent. Copper(II) ions are taken for an example.

Experimental

Apparatus

A Seiko SPS 1100H inductively coupled plasma-atomic emission spectrometer was used for the determination of copper. A Tokyo Rika NTS-1300 S water bath shaker was used for shaking sample mixtures at the shaking rate of 160 min⁻¹. An Iwaki AP-220ZN

air pump was used for suction through the sorbent column.

Reagents

Alumina powder. Alumina (10–50 µm in particle size, chromatographic grade, Katayama Chemicals, Japan) was purified prior to use by shaking with 5 mol l⁻¹ nitric acid, and washing three times with water.

Sodium dodecyl sulfate (SDS). Analytical grade reagent (Katayama Chemicals) was used without further purification.

Dithizone-SDS solution. To 50 ml of 0.1 mol l⁻¹ aqueous ammonia were added 15.0 mg of dithizone (analytical grade, Katayama Chemicals) and 1.0 g of SDS. The solution was mixed for 2 min by ultrasonic irradiation and diluted to 100 ml with water.

Dithizone-coated alumina. Alumina particles coated with dithizone were prepared immediately before use. To a 100-ml Erlenmeyer flask were added 1.5 g of alumina, 10 ml of dithizone-SDS solution and 40 ml of water. The solution was acidified to pH 2 with 4 mol l⁻¹ hydrochloric acid and shaken mechanically for 15 min. After the supernatant solution was discarded, the dithizone-coated alumina was packed into a column (15 mm in diam. × 7 mm height).

Concentration of copper(II) ions

A water sample containing copper(II) was acidified to pH 2 with 4 mol l⁻¹ hydrochloric acid and passed through the dithizone-coated alumina column at a flow rate of 4 ml min⁻¹ with the aid of a suction pump. To the column was added 2.5 ml of 4 mol l⁻¹ nitric acid to decompose the copper(II)-dithizone complex. The nitric acid solution was collected by suction and analyzed for copper by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Determination of SDS by toluidine blue method

To 5 ml of sample (containing less than 0.5 mg of SDS) was added sodium hydrogencarbonate until saturation, to adjust the pH to 8–8.5. After adding 5 ml of chloroform and swirling thoroughly with a magnetic

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stirrer, we added one drop of toluidine blue indicator. Then titration was carried out with a cationic surfactant solution (alkyldimethylbenzylammonium chloride, 0.1 mg ml^{-1}) until the color of chloroform layer changed from blue to pink-red. The SDS concentration was calculated using a calibration graph (standard SDS solution vs. the cationic surfactant solution).

Results and Discussion

Immobilization of dithizone on alumina

Direct interaction was first examined by mixing dithizone powder and an alumina suspension at less than pH 3. Even after mixing for 4 h, the components remained separate, indicating no adsorption of dithizone on alumina. In alkaline solutions (e.g., in 1 mol l^{-1} aqueous ammonia), although dithizone existed in soluble form, still no adsorption on alumina was observed.

Therefore, we tried to coat alumina surfaces with SDS, into which dithizone could be subsequently trapped. The extent of SDS adsorption on alumina at different pH's was studied by shaking 50 ml of water (containing 1.5 g of alumina and 100 mg of SDS) for 15 min. The SDS concentration was fixed at 2 mg ml^{-1} , which is below the CMC of SDS ($8 \times 10^{-3} \text{ mol l}^{-1}$).⁵ This was done since above CMC the excess SDS would form micelles in the aqueous solution which is not adsorbed on the alumina surfaces.^{6,7} As shown in Fig. 1, the adsorption of SDS is highly dependent on the solution pH. Negatively charged SDS was more effectively adsorbed on the positively charged alumina surfaces at lower pH's; nearly complete adsorption was achieved at pH 1–4 by shaking for 15 min. About 99% of SDS was adsorbed even in 1 mol l^{-1} nitric acid, but the value was decreased to 85% in 4 mol l^{-1} nitric acid.

Water (50 ml) containing 1.5 g of alumina and 100 mg of SDS was shaken for 15 min at pH 2 to prepare the SDS-coated alumina. To the suspension was directly added 1.5 mg of dithizone powder, and the solution was

stirred for 30 min. One could see, however, that a considerable amount of dithizone powder still remained unadsorbed.

Therefore, we dissolved dithizone in an ammoniacal SDS solution, which was shaken with alumina for 15 min as described in *Reagents*. Due to such acidifying of the ammoniacal dithizone-SDS solution, dithizone became insoluble in aqueous solution, while SDS would form hemi-micelles or ad-micelles on alumina by strong adsorption. The micelles could trap dithizone molecules homogeneously, which would cause alumina to change color from white to gray-blue. Maximum dithizone adsorption was examined by varying amounts of dithizone at pH 2. The visual observations showed that up to 1.5 mg of dithizone could be adsorbed on 1.5 g of alumina, while with more than 4 mg, the excess dithizone formed a black precipitate along with the gray-blue alumina particles.

Concentration of copper(II) ions by dithizone-coated alumina

Adsorption efficiency of the prepared dithizone-coated alumina was studied by using copper(II) ions as an example. Microgram quantities of copper(II) in 50–1000 ml of water were adsorbed at pH 2 on the alumina column at a flow rate of 4 ml min^{-1} and the effluent was directly analyzed by ICP-AES for copper. Some experiments were also carried out in batch wise operation, where the sample (pH 2) was mechanically shaken for 30 min with 1.5 g of dithizone-coated alumina and, after filtration through a $0.45\text{-}\mu\text{m}$ Millipore membrane filter, the filtrate was analyzed by ICP-AES. Each experiment was carried out in three sets to check the reproducibility. Table 1 shows that nearly all copper(II) is collected on dithizone-coated alumina in batch and column operations, with good reproducibility.

When 2 l of sample (pH 2, $50 \mu\text{g Cu l}^{-1}$) was passed through the alumina column to determine the copper(II) in the effluent at each 200-ml interval, it was found that quantitative adsorption ($>99\%$) was always achieved up to 1 l of sample. At 1.2 l, however, the breakthrough point was reached with an adsorption recovery of 80%.

Desorption of the copper(II) from the alumina column was studied by using 2.5 ml of different eluants (e.g., with $0.1\text{--}4 \text{ mol l}^{-1}$ nitric acid, hydrochloric acid, or aqueous ammonia). It was found that 4 mol l^{-1} nitric acid was the most effective eluant for quantitative desorption (96–

Fig. 1 Effect of pH on adsorption of SDS on alumina. SDS, 100 mg, and 1.5 g of alumina in 50 ml of water were mixed for 15 min.

Table 1 Adsorption of copper(II) on dithizone-coated alumina at pH 2

Sample volume/ml	Cu ^{II} added/ μg	Cu ^{II} adsorbed, %	
		Column	Batch
50	2.5	101, 101, 102	98, 101, 101
50	4.0	100, 101, 102	100, 101, 102
50	10.0	100, 100, 101	96, 96, 97
500	25.0	100, 101, 102	—
1000	50.0	96, 96, 98	—

100%); the column immediately lost its color, indicating the destruction of dithizone-copper complex. About 1 mg of SDS was found in the column effluent; this did not interfere with the determination by ICP-AES.

The proposed immobilization method is simple and rapid. Considering the well-established dithizone chemistry, we hope that the dithizone-coated alumina could easily be used for separation and preconcentration of traces of metal ions in a wide range of applications. Other water-insoluble chelating agents are expected to be readily immobilized on alumina by the proposed method.

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