On-Line Hydroxide Precipitation-Dissolution of Cu in Atomic Spectrometry

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Precipitation preconcentration is one of the most commonly used techniques to preconcentrate inorganic ions both in batch type[1-3] and in more recently developed flow injection on-line type.[4-10] On-line preconcentration by precipitation is simple, fast, yet efficient for the preconcentration of trace elements. Particularly, it is non-selective and multi-element preconcentration. Most of researches have focused on the utilization of coprecipitation because it is more efficient in collecting trace elements quantitatively. Direct precipitation has advantage of collecting large amount of sample and give higher enrichment factor consequently. It also can be selective by choosing a proper precipitant while co-precipitation is non-selective. Various inorganic as well as organic precipitants can be chosen for a desirable selectivity.

Only a few studies have been performed so far using direct precipitation. Valcarcel[9] has shown that trace amount of Pb in a rock sample can be effectively analyzed by continuous precipitation using ammonia. Our group[10,11] has recently shown that sulfide precipitation can be utilized in the analysis of tin group elements. Hydroxide precipitation for Cd[11] was studied to give more than 90 times of enrichment factor. In this research, direct precipitation preconcentration by forming hydroxide precipitation for Cu was studied because it can form hydroxide precipitation at a very low concentration level. Unlike the use of organic precipitant (rubeanic acid) by Valcarcel,[9] a simple hydroxide precipitate was employed so that it could be applied to Flame AA and ICP or to other techniques conveniently. Quantitative preconcentration of Cu was easily accomplished and applied in the analysis of standard material (NIST-SRM). The results were in good agreement with the certified values. Other elements that can form hydroxide precipitation such as Fe, Co, V and U can also be used.

Experimental

Doubly deionized 18 MΩ cm water (Millipore Q system) was used in the study. Copper stock solution was prepared from elemental 99.999% Cu (Spex, NJ, U.S.A.). NIST (National Institute of Science and Technology) reference SRM (Standard Reference Material) 1566 (oyster), 1567 (wheat), and 1571 (orchard leaves) were dissolved in nitric acid and diluted to the volume. For SRM 1566, it was not dissolved completely in nitric acid alone. After cooling, H_2O_2 was added and slowly heated to dissolve completely.

Copper was analyzed by Flame Atomic Absorption Spectrometer (model 9100 A, Sunil, Korea) and ICP (model P1000, Perkin Elmer, CT, U.S.A). The basic experimental system is the same as the one used in other studies[11,12] and the details will not be discussed here.

Result and Discussion

Precipitant. Two types of precipitants were used of which the first type was strong base of NaOH. Secondly, a buffer solution was used to provide more stable pH condition throughout the reaction process. Bicarbonate-carbonate and ammonia-ammonium buffers were examined. Both strong bases and buffers should have enough ionic strength so that the final pH could maintain proper pH. The concentration of NaOH was controlled so that the pH of the solution after the reaction became 10.

Interestingly, hydroxide precipitate of Cu showed very different behavior for different precipitating agents. In Figure 1-a, it could be observed that all the sample was precipitated and dissolved out as expected when NaOH was used as a precipitant. When carbonate buffer was used(1-b), not all of Cu were precipitated and/or collected. Ammonia buffer showed a similar behavior. The first broad peak was from Cu not reacted and/or not filtered. The second sharp one was from filtered and dissolved Cu. This is quite different from the previous study[11] of Cd where buffers showed similar behaviour to NaOH in terms of recovery which is defined as the ratio of the second peak area to the total area.

The precision showed a very different behavior also compared to the previous study. In Cd, the precision was better for buffer than NaOH in peak area measurement. However in Cu, the opposite was true and NaOH was chosen as a precipitant. Changes of precision could be from the change of precipitate shape and/or the degree of coagulation. It was observed in the previouse study that shapes of precipitate changed with precipitants. Obviously, like in this study, different shapes of precipitates are formed with different metal ions also.

Reaction Time. The reaction time could be controlled either by the pumping rate or the reaction coil length. Since the flow should satisfy the requirement of nebulization flow, coil length was changed preferably. The relationship between reaction time and the recovery is shown in Figure 2. For Cu, signal was increasing until 4.5 m or 80 s and stayed in constant after 4.5 m, which is considerably longer than Cd of 25 s. The reaction time of copper hydroxide is shorter than cadmium hydroxide.

Filter Type. Several different types of filters were used and the results are shown in Table 1. Paper filters were rugged but showed some leaks while membrane filter (HA type 0.45 µm) and stainless steel filters (0.5 µm) showed almost 100% recovery of precipitates. Membrane filters gave slightly better precision but should be replaced after 10 runs. Because of high back pressure at the filter, membrane filters could be easily deformed. Thus, stainless filter was used for the matter of convenience. One of the
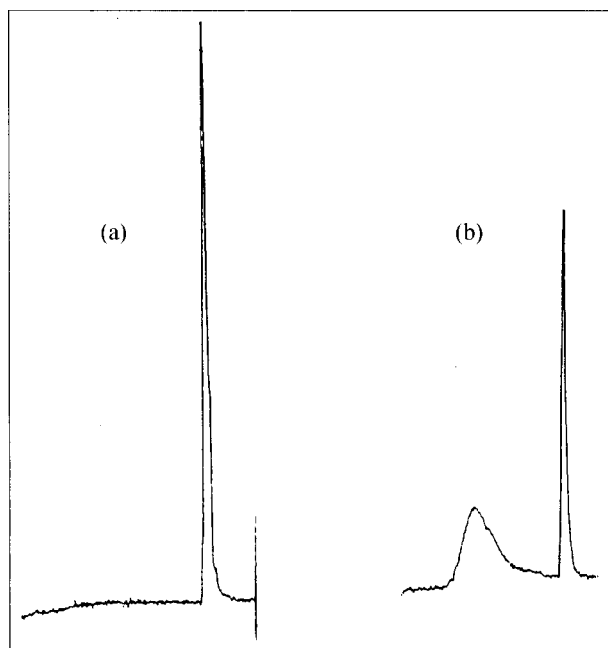
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Notes

Figure 1. Different behaviors of continuous copper hydroxide precipitation when (a) NaOH was used and (b) carbonate was used as a precipitant.
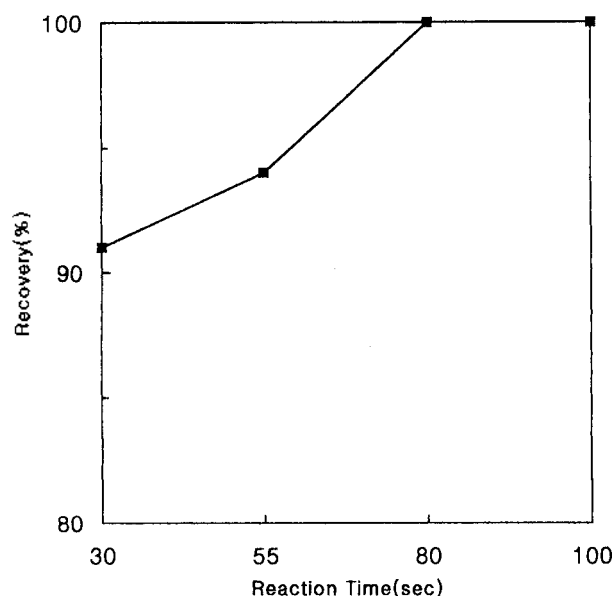

Figure 2. The relation between reaction time and the recovery of precipitate (%).

difference noticed from the previous precipitation study[11] was that there was a large increase in recovery when an additional membrane filter was added in copper hydroxide precipitate. It suggests that hydroxide precipitates of copper are consisted of fine particles.

Dissolving Acid. Several acids, nitric acid, sulfuric acid, and hydrochloric acid were examined as a dissolution agent. Signal intensity and area were the same regardless of the type of acid used. Precisions were also similar with each other (5.0-6.4% RSD) and 0.5 M nitric acid showed a shoghtly better value. The effluent flow from the system must be matched with FAAS. Currently, the effluent flow is

Table 1. The Recovery Rate of Copper Hydroxide Precipitate with Different Filters

Filter Type	Recovery Rate (%)
1 paper filter (10 μm)	45%
2 paper filters (10 μm)	60%
0.5 μm membrane + 1 paper filter	85%
2×(0.5 μm membrane + paper filter)	100%
0.5 μm stainless steel filter	98%

Table 2. Operating Conditions of Flame AA and ICP

Flame AA		
	wavelength	324.7 nm
	Slit	0.2 mm
	Lamp current	2.0 mA
	Air Flow Rate	6.5 L min^{-1}
	Acetylene Flow Rate	1.0 L min^{-1}
	Flame	lean flame
ICP		
	Power	1.0 kW
	Observation Height	15 mm
	Wavelength	217.0 nm
	Nebulizer Gas flow	1.3 L min^{-1}
	Auxiliary Gas Flow	1.0 L min^{-1}
	Tangential Gas Flow	15.0 L min^{-1}

2 mL/min which is a little slower than the recommended flow of 3.0 mL/min in AA. The flow can be increased by increasing the reaction coil length to keep the reaction time constant.

The experimental conditions used for the analysis of Cu with Flame AA and ICP were typical conditions used in other experiments and listed in Table 2. Optimum experimental conditions were obtained with Flame AA, which are listed in Table 3.

Analysis of NIST SRM. To test the accuracy of this on-line direct precipitation preconcentration technique, several NIST samples were analysed. NIST-SRM 1566, 1567, and SRM 1571 were analysed for Cu. After being dissolved, they were analysed by the calibration method. ICP was used because of its high sensitivity and low

Table 3. Optimum Experimental Condition of Continuous Preconcentration of Cu by the Direct Hydroxide Precipitation Technique

Reaction Coil Length	5 m
Precipitant	0.01 M NaOH
Flow Rate of Precipitant	1.0 mL min^{-1}
Dissolving Reagent	1.0 M HNO₃
Filter Type	Stainless + membrane filter
Total Flow Rate	2.0 mL min^{-1}

Table 4. Concentrations of Cu Determined in NIST-SRM Samples

unit; ppb

Samples	Found	Certified
RM 1566 (Oyster)	1.9±0.2	2.0±0.1
SRM 1567 (Wheat Flour)	1.9±0.2	2.0±0.1
SRM 1571 (Orchard Leaves)	2.3±0.3	2.0±0.2

interferences. First, a calibration curve was obtained with standard solutions, which were prepared from the stock solution. It showed a good linearity for the range of interests. However, when concentrations were determined from the calibration curve, the result disagreed from the true values more than 20%. This was probably due to the interferences from the matrix of SRM. Thus, standard addition method was chosen and the results showed good agreement with the reference values (Table 4).

To increase the enrichment factor, sample volume should be increased. Currently, 1.0 mL of sample loop is used and the enrichment factor is 8 with the sampling speed of 15/hr. If it is increased to 10.0 mL, it could be increased more than 80 times. However, the sampling speed is reduced to 2/hr.

In conclusion, on-line precipitation preconcentration is a very simple and accurate technique to enhance the analytical capability of the existing instrument. Enrichment of 8 fold with accurate result could be done very comfortably. If time is sacrificed, further enrichment is possible and can be extended to various other elements.

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Thiophene-Fused Tetrathiafulvalenes as a New Molecular Donor

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As a potential π-electron donor, tetrathiafulvalene (TTF) and its derivatives have been intensively studied and synthesized by coupling and noncoupling methods.[1-6] Recent examples include new TTF derivatives fused with some heterocycles such as pyrrole, pyrazine, selenophene and thiophene.[4] These heterocycle-fused TTFs exhibit either lower or higher oxidation potentials than those of TTF depending on the electron withdrawing ability of hetero-cycles. As the precursors of recently developed TTF derivatives, a number of 2-thioxo-1,3-dithiole derivatives were developed by utilizing dmit moiety.[1-3] One of the useful synthetic routes is to use Lawesson's reagent (LR), in which heterocycles such as dithiin or thiophene are made by the unusual cyclization.[5]

Here, we report unexpected desulfurization of dicarbonyl dmit **4** accompanied with *in situ* cyclization to give thiophene-fused 2-thioxo-1,3-dithiole **1** along with the synthesis and electrochemical properties of its coupled products, bis (diphenylthiophene)-TTF **3** and diphenylthiophene-fused bis (methylthio)TTF **7**. The synthesis and the electrical property of charge-transfer salt of **7** with F4-TCNQ (tetrafluorotetracyano-*p*-quinodimethane) are also described.

Experimental

Instrumentations such as NMR, FT-IR, UV, Mass spectrometer were described in the previous publication.[7] Elemental analysis was carried out at Korea Basic Science Institute (KBSI).

1,8-diketone (4). To a purple ethanol solution (40 mL) of disodium salt **6** (10 mmol) was added two mole ratio of desylchloride **5** (20 mmol, 4.61 g) dissolved in ethanol (100 mL). After stirring for 1h, the yellow precipitate was collected from filtrate and washed with ethanol. yield ~100 %; mp. 157-158 °C; ^{1}H NMR (250 MHz, CDCl$_3$)

TTF   F4-TCNQ