Flow Injection Spectrophotometric Determination of Sub-mg dm⁻³ Silver(I) in a Strongly Acidic Solution Containing Concentrated Copper(II) Using a Pyridylazo Reagent

Kazuyoshi FUJIMURA,^{*,†} Tamao ODAKE,^{**} Hiromi TAKIGUCHI,^{**} Noriyuki WATANABE,^{*} and Tsuguo SAWADA^{*}

**Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan*

***Safety and Health Office, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan*

A novel spectrophotometric flow injection method for determination of silver(I) in a strongly acidic solution containing concentrated copper(II) was developed using a coloring ligand, 4-(3,5-dibromo-2-pyridylazo)-*N*-ethyl-*N*-(3-sulfopropyl)-aniline (3,5-diBr-PAESA). The method was first investigated by batch method. The interference from copper(II) chelate could be eliminated by the masking effect of EDTA. By utilizing the large formation constant ($K = 12.3$) of AgBr, one could determine silver(I) as a decrease of absorption by silver(I) chelate due to formation of AgBr by addition of KBr. Based on the results of batch experiments, two types of flow injection analysis (FIA) systems were constructed. Sub-mg dm⁻³ determination of silver(I) was attained without interference from excess copper(II). The proposed method was successfully applied to determination of silver in a copper plating solution used in a plant to manufacture copper printed circuit boards, where the concentration of silver was critically important in the process control.

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Introduction

The reliability of industrial material often depends on the precise control of the contents of minor elements, which exist in minute amounts compared with the major components. The minor components might be undesirable impurities or indispensable components, or sometimes accidental ingredients with a positive role. Carbon or oxygen in steel, and various elements in silicon, are well-known examples where the minor components have important effects on the performance of the materials. The determination of the minor elements is not always easy; it is especially difficult in the cases when minor and major elements are similar, such as cobalt in iron or silver in copper. We previously reported the determination of a very small quantity of cobalt(II) in high concentration copper(II) acidic solutions.¹

Analysis of a small quantity of silver(I) in strongly acidic solutions containing concentrated copper(II) is in fact the situation encountered in the process control of printed circuit board manufacturing. The presence of silver(I) in the solution influences the quality of the product. Hence, silver(I) determination in the process sometimes becomes crucially important. Sladkov and Osipova used stripping voltammetry for

the determination of silver(I) in the presence of copper(II).² They utilized a water-soluble complexing polymer, polyethylenimine, to avoid the interference from intermetallic interaction with a large excess of copper(II). However, their method was not applicable for the cases where copper(II) existed over 1000 times more than silver(I).² Flameless atomic absorption spectroscopy (AAS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) are useful for determination of silver(I) in high concentration of copper(II) solution with sufficient sensitivity and selectivity. However, when these instruments are used for on-site analysis of the strongly acidic solution at the circuit board plant to control quality, a scavenger system or a chemical hood is needed to eliminate mist and vapor containing metallic oxides, nitrogen oxides, and strong acids such as sulfuric acid and nitric acid from the atmosphere, which affect the copper thin film on the printed-circuit board.

Flow injection analysis (FIA) is also attractive because an FIA system is relatively inexpensive and easy to handle, and needs neither scavenger system nor chemical hood. Several researchers reported on FIA methods for determination of silver(I). The decrease of UV absorption resulting from metal ion exchange reaction between nickelocyanide and silver(I) was used for determination of silver(I).³ Catalytic actions of silver(I) on various chemical reactions have been utilized in FIA detection. For example, there were fluorometric detection methods coupled to the reduction of safranin with iodide⁴ and visible absorption detections due to oxidation of Janus green⁵ or thionine⁶ with peroxodisulfate in the presence of *o*-phenanthroline as an activator. The catalytic effect of silver(I) on a metal exchange

[†] To whom correspondence should be addressed.

E-mail: fujimura@appchem.t.u-tokyo.ac.jp

N. W. present address: Laboratory of Research and Development, BAS Inc., 1-28-12 Mukoujima, Sumida, Tokyo 131-0033, Japan.
T. S. present address: Japan Science and Technology Agency, 5 Sanbancho, Chiyoda, Tokyo 102-0075, Japan.

reaction based on the principle of Hard and Soft Acids and Bases was applied to an FIA of silver(I).⁷ The method employed mercury(II) and copper(II) as Soft and Hard ion, respectively. The sensitivity and throughput of the method coupled to the decrease in the absorbance of copper(II)-diethyl-dithio-carbamate complex seemed fairly good. However, the consumption of Hg(II)-EDTA and chloroform as a solvent for extraction is a drawback from the view-point of environmental considerations. In addition to that, interference from other metal ions seems to occur. Liu *et al.* proposed amido-thiourea immobilized glass beads packing for separation and preconcentration of silver(I) in FIA, which was coupled with AAS.⁸ There were also potentiometric detections by silver(I) selective electrodes using 2-mercaptobenzothiazole⁹ as an ionophore and using calyx[4]-arene as a carrier.¹⁰ However, none of these FIA methods were applicable to practical analyses of silver(I) in coexistence with excess amounts of other metal ions such as copper(II).

Sensitive spectrophotometric analysis of silver(I) is unusual due to the lack of appropriate coloring reagents. Water-soluble 4-(3,5-dibromo-2-pyridylazo)-*N*-ethyl-*N*-(3-sulfopropyl)aniline (3,5-diBr-PAESA) proposed by Ohshita *et al.* for silver(I) determination in water in the case of absence of other interfering ions^{11,12} is one of a few candidates. In this paper, a spectrometric method for determination of small quantities (down to sub-mg dm⁻³, several hundreds µg dm⁻³) of silver(I) in a strong acidic solution containing high concentrations (4%) of copper(II) using FIA system was proposed. With the batch method being initially used, a basic determination method using 3,5-diBr-PAESA and elimination of the interference from copper(II) by masking with EDTA was investigated. Furthermore, an addition of bromide ions was examined to improve the precision on determination of small amounts of silver(I). Based on the results of batch experiments, two types of FIA systems were constructed and evaluated in regard to determination of small amounts of silver(I) in a strongly acidic solution containing high concentrations of copper(II).

Experimental

Reagents and chemicals

3,5-diBr-PAESA (Fig. 1) was purchased from Dojin Chemical Co. (Kumamoto, Japan). All reagents were of analytical grade. Silver(I) standard solution (1000 mg dm⁻³) was prepared by dissolving 0.1576 g of silver nitrate in water, and this mixture was diluted to 100 cm³ with nitric acid diluted with 160-fold volume of water. The silver(I) solution for standard addition or calibration was obtained by appropriate dilution of the 1000 mg dm⁻³ solution with nitric acid diluted with 160-fold volume of water.

The solution of 3,5-diBr-PAESA (10⁻³ mol dm⁻³) was prepared by dissolving 10.9 mg of the reagent in 20 cm³ water.

The EDTA-SDS buffer solution was prepared by mixing 100 cm³ of 20% sodium acetate, 450 cm³ of 0.2 mol dm⁻³ EDTA-2Na and 250 cm³ of water, followed by warming the solution above 23°C, then dissolving 1.2 g of SDS (Kanto Chemical, Tokyo, Japan) into it.

The standard sample solution in this paper was 1 to 3 mol dm⁻³ sulfuric acid solution containing 4% copper(II) and sub-mg dm⁻³ silver(I). As real samples, two kinds of metallic copper were used for determination of silver by batch method, and a copper plating solution provided by a plant for copper printed circuit boards was used in FIA method.

Water used in this paper was ion-exchange water, because it was confirmed in advance that silver was not detected in the

Fig. 1 Scheme of 4-(3,5-dibromo-2-pyridylazo)-*N*-ethyl-*N*-(3-sulfopropyl)aniline (3,5-diBr-PAESA).

ion-exchange water by ICP-AES and the ion-exchange water did not include silver more than µg dm⁻³ level.

Apparatus

Absorption spectra were obtained using a spectrometer V530 (JASCO Co., Tokyo, Japan). A UV-Visible detector 870UV (JASCO Co., Japan) was used as a flow detector. Double plunger pumps SNK RX703T and SR 300T (Sanuki Inc., Tokyo, Japan) were used as flow pumps. Reaction coil and all flow tubes in the FIA systems were made of Teflon tubing of 0.5 mm inner diameter. Injection valves Rheodyne7125 were used as a silver standard solution injector, a KBr injector, and a sample injector, with a sample loop of appropriate length. For comparison, the concentration of Ag(I) was also determined by an ICP-AES (Hitachi P-4010, Japan) at 328.068 and 338.289 nm, by averaging the values obtained at the two wavelengths.

Procedure of batch method

Batch experiment for determination of silver(I) was performed according to the following procedure.

1) In a 30-cm³ beaker, 1 cm³ of the sample solution containing less than 10 µg of silver ion was placed by using a micropipette, and 8 cm³ of EDTA-SDS buffer solution was added. Then the solution was stirred vigorously for a moment. Here, copper(II) in the sample solution reacts with EDTA to form Cu-EDTA as follows:

2) In an optical cell, 2 cm³ of the above solution was placed by using a micropipette. Then the absorbance at 560 nm was measured.

3) In the solution obtained by the procedure 2), 50 mm³ of 10⁻³ mol dm⁻³ 3,5-diBr-PAESA solution was added by using a micropipette followed by stirring. Here, silver(I) reacts with 3,5-diBr-PAESA (L) to form silver(I) chelate as follows:

Then after 2 min the absorbance at 560 nm was measured.

4) Further 22 mm³ of 10% KBr solution was added to the solution in the above optical cell by using a micropipette, followed by stirring. Here, silver(I) chelate is converted to AgBr as follows:

Then after 2 min the absorbance at 560 nm was measured.

Silver determination by standard addition method was performed by adding 0, 2.5, 5.0, 7.5, and 10 mm³ of 100 mg dm⁻³ silver solution respectively in the above procedure 1). The calibration curve for silver determination was obtained by the procedure of the above batch method.

Fig. 2 Flow diagrams of two types (a, method A; b, method B) of FIA systems for determination of silver(I) in a strongly acidic solution containing concentrated copper(II). R, Reagent (2.5×10^{-4} mol dm $^{-3}$ 3,5-diBr PAESA); C, carrier H $_2$ O; S, sample; B1, EDTA-SDS buffer; B2, 10-fold diluted EDTA-SDS buffer; AI, Ag injector (500 mm 3); KI, KBr injector (50 mm 3); SI, sample injector (8 cm 3); P1 – P5, double plunger pumps, P1, P2, P4, 0.1 cm 3 min $^{-1}$, P3, 0.8 cm 3 min $^{-1}$, P5, 1.0 cm 3 min $^{-1}$; MC, mixing coil (5 m); RC1, reaction coil (10 m, 45°C); RC2, reaction coil (5 m, 45°C); D, absorbance detector; W, waste.

Silver content in metallic copper was determined according to the following procedure. First, 2 or 5 g of metallic copper was dissolved in 20 cm 3 of nitric acid diluted with water of the same volume in a beaker by heating. The wall of the beaker was washed by a small amount of water; the solution in the beaker was reheated to remove nitrogen oxides and was then allowed to cool down to ambient temperature. The solution was diluted to 100 cm 3 with water. In an optical cell, 0.5 cm 3 of the copper sample solution and 2 cm 3 of EDTA-SDS buffer solution were mixed with a stirrer. The temperature of the mixed solution was kept above 20°C in order to avoid deposition of SDS. In the optical cell, 50 mm 3 of 10^{-3} mol dm $^{-3}$ 3,5-diBr-PAESA solution was added; the solution was mixed by a stirrer, and the absorbance at 560 nm was measured (absorbance R). Then 22 mm 3 of 10% KBr solution was added in the optical cell, and the absorbance at 560 nm was measured (absorbance B). The silver content was determined by the difference of the absorbance (absorbance R – absorbance B).

Flow injection analysis method

Two types of FIA systems (method A and method B) were examined. The FIA system of method A was constructed with three double plunger pumps, a silver standard solution injector, a KBr solution injector, a mixing coil (5 m), a reaction coil (10 m) and an absorbance detector set at 560 nm, as shown in Fig. 2a. Since raising the temperature of the 10 m reaction coil up to 80°C did not improve the sensitivity remarkably,

Fig. 3 Absorption spectra of 3,5-diBr-PAESA (5×10^{-6} mol dm $^{-3}$) and its silver(I) (2.5×10^{-6} mol dm $^{-3}$) and copper(II) (2.5×10^{-6} mol dm $^{-3}$) chelates. 1, 3,5-diBr-PAESA in 0.1% SDS solution; 2, silver chelate in 0.1% SDS solution; 3, copper chelate in 0.1% SDS solution.

the temperature of the reaction coil was maintained at 45°C.

The FIA system of method B was constructed with two double plunger pumps, a sample injector, a KBr solution injector, a reaction coil (5 m) maintained at 45°C and an absorbance detector set at 560 nm, as shown in Fig. 2b.

Results and Discussion

Absorbance spectra and choice of measuring wavelength

Bidentate ligand 3,5-diBr-PAESA reacts with silver(I) and copper(II) to form a metal chelate. In aqueous solution or in dilute SDS solution, the metal chelate forms ML, which has low molar absorptivity. In the presence of an anionic surfactant such as SDS with an appropriate concentration, however, the metal chelate forms ML $_2$, which has a much higher molar absorptivity than ML.¹² It is said that the bidentate 3,5-diBr-PAESA can easily form an ML $_2$ chelate because the ligand is concentrated locally in the SDS micelle.¹¹ The coordination sites to metal ion are considered to be the pyridine nitrogen and nitrogen in the azo group of 3,5-diBr-PAESA. Two molecules of 3,5-diBr-PAESA are considered to coordinate with each metal ion in a tetrahedral structure.¹¹

In a solution containing more than 0.08% of SDS, the metal chelate forms ML $_2$. The absorption spectrum of ML $_2$ was stable and unchanged in the solution containing 0.08 to 0.15% SDS. The SDS concentration was chosen to be 0.1% in measuring absorbance spectra. The absorbance spectra of 3,5-diBr-PAESA and its silver(I) and copper(II) chelate in 0.1% SDS solution are shown in Fig. 3. The results of Fig. 3 agreed well with the reference: the molar absorptivity of silver(I) chelate (AgL $_2$) was 80000 dm 3 mol $^{-1}$ cm $^{-1}$ at 590 nm in 0.1% SDS solution, and that of copper(II) chelate (CuL $_2$) was 124000 dm 3 mol $^{-1}$ cm $^{-1}$ at 638 nm.¹¹ The large absorption by excess copper(II) chelate hinders the absorption by silver(I) chelate. Due to the addition of EDTA, however, copper(II) chelate is completely converted to Cu-EDTA complex. And because the stability constant of Cu-EDTA ($K = 6 \times 10^{18}$) is much larger than that of Ag-EDTA ($K = 2 \times 10^7$), we concluded that the added EDTA formed a chelate complex with copper(II) but not with silver(I), and that it was effective to add EDTA in the analyte solution to eliminate the interference from concentrated copper(II).

As shown in Fig. 3, measurements at the wavelengths ranging from 560 to 600 nm seemed to be appropriate in terms of the

Fig. 4 Absorption spectra of copper(II) (0.2 mol dm^{-3}) and Cu-EDTA (0.2 mol dm^{-3}). 1, Copper(II) in acidic solution; 2, Cu-EDTA in acidic solution.

difference of absorbance between 3,5-diBr-PAESA and its silver(I) chelate; Ohshita *et al.* selected 600 nm to detect the silver(I) chelate.¹² Indeed, Cu-EDTA has considerable absorptivity at 600 nm, as shown in Fig. 4. Because in this paper a high concentration of copper(II) was included in the sample, 560 nm was chosen as a measuring wavelength of the detector to reduce the background absorption by Cu-EDTA.

The batch method and effective addition of bromide ion

In the batch method, as the sample solution prepared for the measurement of absorption was viscous, it was necessary to wipe off the outer wall of the optical cell that was smeared with the sample solution: first with wet tissues, then with dry tissues. Otherwise increased error variance was obtained. So, as a reference, a blank cell was chosen instead of a cell filled with EDTA-SDS solution.

As the absorption of Cu-EDTA and 3,5-diBr-PAESA was still considerable even at 560 nm, the precise control of the sampling amount of the strongly acidic solution involving high concentration of copper(II) and 3,5-diBr-PAESA solution was extremely important. The measurement of absorbance decrease due to addition of KBr solution was expected to overcome the difficulty and to improve the reproducibility and operability of the method. Silver(I) chelate was thoroughly converted to AgBr due to the large formation constant ($K = 12.3$) of AgBr. AgBr was dissolved at this concentration and the AgBr solution itself is optically transparent.

The solution of 3,5-diBr-PAESA was stable under visible light irradiation or moderate thermal treatment, but gradually faded in the strongly acidic condition. Therefore, the 3,5-diBr-PAESA solution was added to the sample solution of 1 to 3 mol dm^{-3} sulfuric acid after the sample solution was neutralized by addition of the EDTA-SDS buffer solution. Since 3,5-diBr-PAESA in the EDTA-SDS solution was stable, the use of the pre-mixed solution was advantageous for KBr addition in terms of error variance. Dependency of absorbance on temperature was examined at a temperature ranging from 25 to 80°C. It was found that absorbance of the sample solution slightly increased depending on the temperature ($0.004 \text{ AU/}^\circ\text{C}$). So the temperature was controlled at 25°C.

A calibration curve of silver(I) obtained after procedure 4) described in the section of *Procedure of batch method* was linear up to 1 mg dm^{-3} , but the slope gradually diminished near 10 mg dm^{-3} .

Silver content determination in metallic copper using the batch method

Metallic copper includes silver at the mg dm^{-3} level. Two kinds of metallic copper were used as real samples, and their silver content was determined by the batch method using KBr addition. The same sample solutions were analyzed by the ICP-AES. The results obtained by the KBr addition batch method and ICP-AES are shown in Table 1. Silver concentrations in the sample solutions obtained by the batch method and those obtained by ICP-AES were very similar. The KBr addition batch method proved to be applicable to determination of silver content in metallic copper, though the limit of determination of both methods on this condition was sub-mg dm^{-3} level.

FIA

Based on the above results of the batch experiments, two types of FIA systems: method A and method B, were constructed. The FIA method A was first constructed to verify the usefulness of the flow system in determination of silver(I) in strongly acidic solutions containing concentrated copper(II). In the FIA method A shown in Fig. 2a, a known amount of silver ion was injected intermittently onto the analyte solution flowing continuously at a flow rate of $0.1 \text{ cm}^3 \text{ min}^{-1}$. The baseline level corresponded to the original content of silver(I) in the analyte solution, and the baseline shifted positively depending upon the injected amount of silver(I) (see signal A in Fig. 5a). Because the magnitude of the shift corresponded to the concentration of injected silver(I), by injecting silver(I) of several concentrations, one could determine silver(I) in the analyte solution by the standard addition method. The positive shift of baseline was kept for about 5 min, which corresponded to the injection volume of 500 mm^3 and the flow rate of carrier water of $0.1 \text{ cm}^3 \text{ min}^{-1}$. After the baseline recovered, KBr solution of an excess amount compared to the amount of silver(I) supposed to be present in the analyte solution was injected, and the baseline shifted negatively (see signal B in Fig. 5a), because bromide ions took Ag(I) from silver(I) chelate to form AgBr. The slope of the calibration curve obtained by KBr addition was identical to the one obtained without KBr addition. The silver(I) content in the real sample could be determined by comparison with the reference value of signal A in Fig. 5a. Chloride ion was not so useful in taking Ag(I) from silver(I) chelate to form silver salt as bromide ion.

The standard deviation of the magnitude of baseline fluctuation was $s = 0.0020$ ($n = 4$) for addition of 0.5 mg dm^{-3} Ag without KBr addition. The same factor for the case with KBr addition, however, was less than 0.0020 within the linear range of calibration curve. The coefficient of variance was about 10% for both schemes.

The FIA method B was designed and constructed to simplify the flow system of the FIA method A. In the FIA method B shown in Fig. 2b, 8 cm^3 of the analyte solution was prepared by adding 225 mm^3 of $10^{-3} \text{ mol dm}^{-3}$ 3,5-diBr-PAESA (L) to the solution obtained by procedure 1) described in the section of *Procedure of batch method*. The reactions in the solution are as follows:

The analyte solution was injected intermittently on the flow of buffer solution. Since the flow rate of buffer solution was $1 \text{ cm}^3 \text{ min}^{-1}$, a trapezoidal transition of the baseline lasted for about 8 min, as shown in Fig. 5b. During the flat transient,

Table 1 Silver content in the metallic copper samples determined by the KBr addition batch method and ICP-AES

Sample configuration	Sample amount/ g	Silver concentration in the copper sample solution (metallic copper 2 or 5 g/100 cm ³)/mg dm ⁻³		Silver content in the metallic copper/ mg dm ⁻³
		ICP-AES	Batch method (KBr addition)	
Granule (8 - 16 mesh 99.99%)	5.0525	0.2	0.2	4
Strip (3 × 5 × 5 mm)	2.0331	0.4	0.4	20

Fig. 5 Absorbance monitor of FIA. a, Method A; b, method B. A, Transient caused by Ag⁺ addition; B and C, transient caused by KBr addition.

50 mm³ of 2.5% KBr solution was injected on a separate stream of water, which joined the main stream of buffer solution just behind the sample injector. When the part of the analyte solution encountered the plug of KBr solution, silver(I) chelate was consumed, due to formation of AgBr as follows:

AgBr is optically transparent and was present in a dissolved state. The total depletion of silver(I) chelate by bromide ion took about 2 min, which corresponded to a small trapezoidal dip on the flat transient. The magnitude of the dip corresponded to the amount of silver(I) contained in the analyte solution. The presence of 0 to 4% copper(II) did not affect the quantitation of silver(I).

A copper plating solution provided by a plant for copper printed circuit boards was used as a real sample. The plating solution contained 4% cupric ion and 1 mol dm⁻³ sulfuric acid. Using the FIA method B, the calibration curve of the standard addition method for determination of silver(I) in the plating solution was obtained; the concentration of silver(I) in the plating solution was determined to be 0.26 mg dm⁻³, which agreed quite well with the result determined by ICP-AES. The FIA method B was more advantageous than the FIA method A in terms of low cost due to less consumption of expensive

3,5-diBr-PAESA reagent. To perform a series of experimentations to get a calibration curve and to analyze samples, we needed at least 100 cm³ of the 2.5 × 10⁻⁴ mol dm⁻³ 3,5-diBr-PAESA reagent solution in method A, which corresponds to 2.5 × 10⁻⁵ mol of 3,5-diBr-PAESA. However, in method B, 1.5 cm³ of the 10⁻³ mol dm⁻³ 3,5-diBr-PAESA solution (1.5 × 10⁻⁶ mol of 3,5-diBr-PAESA) was sufficient, which was less than one-tenth of that needed in method A.

Conclusions

A spectrophotometric detection method using a pyridylazo reagent, 3,5-diBr-PAESA, was developed to determine sub-mg dm⁻³ silver(I) in a strongly acidic solution containing a high concentration of copper(II). First the method was verified by the batch experiment, and then FIA systems were constructed. It was found that the method was quite reliable for the quantitation of silver(I) in sub-mg dm⁻³ level. The method was applicable to determination of silver(I) in the plating solution used in the plant for copper printed circuit boards, where monitoring the concentration of contaminants or impurities was critically important in the process control.

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