# Determination of Gold Ion in Gold-Plating Baths

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Gold ion can be determined by differential pulse stripping voltammetry, using a hanging mercury drop electrode. Pre-concentration potential was -1000 mV vs. Ag/ AgCl for a 10-min pre-concentration period. A 0.9 mol/ dm<sup>3</sup> KCN solution containing 0.1mol/dm<sup>3</sup> NaOH was used as the supporting electrolyte. Concentration of 27.5 to 100 mg/dm<sup>3</sup> gold ion in the solution can be determined with relative standard deviation of 10 percent. Results are reported for electro- and electroless gold plating bath samples.

All types of gold and gold alloy plating are used for many different applications by many different industries. Usually, determination of gold in plating baths has been by gravimetric analysis (see ref.). This method is tedious, however, and requires prolonged time for the analysis. Determination of Au ion by using stripping voltammetry has not been reported. In this effort, a method of determining gold ion in a gold plating bath was studied by using stripping voltammetry and determination of gold ion was attempted in an actual gold plating bath.

#### Experimental Procedure

A lab system consisting of a polarographic analyzer and stand with a hanging mercury drop electrode, a platinum auxiliary electrode, and an Ag/AgCl reference electrode was used. Anodic stripping voltammetry was employed in the differential-pulse mode. Conditions were controlled by personal computer, and metal ions were determined from potentialcurrent curves.

Au(III) ion standard stock solution was prepared by dissolving 1 g HAuCl<sub>4</sub>·4H<sub>2</sub>O in 100 cm<sup>3</sup> of distilled water. The test electrolyte was diluted with water to the specified concentration range, which for Au was 250 to 500 mg/dm<sup>3</sup>. One cm<sup>3</sup> of test solution and one cm<sup>3</sup> of Au(III) standard solution were transferred by pipette into a 10-cm<sup>3</sup> measuring flask. Five cm<sup>3</sup> of 1.8 mol/dm<sup>3</sup> KCN, containing 0.2 mol/dm<sup>3</sup> NaOH, 0.4 cm<sup>3</sup> of 0.2 mol/dm<sup>3</sup> KI and 1 cm<sup>3</sup> of 1 mol/dm<sup>3</sup>



Fig. 1—Peaks of Au and Ni ions. Au: 47.8 mg/dm<sup>3</sup>, Ni: 0.11 mg/dm<sup>3</sup>; measurement conditions as in Table 1.

 $Na_2S_2O_3$  were added and made up to 10 cm<sup>3</sup> with distilled water. This solution was transferred into the measurement cell, and was purged with  $N_2$  gas for 10 min. The preconcentration potential (-1000 mV vs. Ag/AgCl) was applied to a fresh mercury drop while the solution was stirred for 10 min. Following the pre-concentration period, stirring was stopped and after 10 sec, the voltammogram was recorded by applying a negative-going differential pulse scan (scan rate of 5 mV/sec and amplitude of 50 mV). The scan was terminated at -1700 mV vs. Ag/AgCl.

The peak was not dependent on the Au(I) ion. In the polarographic system, the values of slope and peak were linear and dependent on the Au(I) ion concentration. In this study, the calibration curves reflected the values of the slope of the peak.

### Results and Discussion

The concentration of Au(III) ion was constant at 47.8 mg/ dm<sup>3</sup>. One peak was observed in the forward scan at about 1500 mV. A reduction peak of Au(I) ion to Au(0) is shown in Fig. 1. A reduction peak for Au(III) ion to Au(I) was not observed. A reducing agent was needed for the determination; potassium iodide, L-ascorbic acid and hydroxyl ammonium chloride were considered.

The most suitable reducing agent was potassium iodide; however, free iodine interfered with the peak of Au(I) ion. This interference was eliminated by addition of sodium thiosulfate. All gold ion was monovalent, obviating the need for a reducing agent.

Measurement error was decreased with increase of deaeration time and enough reproducible data were obtained with a de-aeration time greater than 10 min. A solution of KCN was used as the supporting electrolyte. The effect of KCN concentration containing 0.1 mol/dm<sup>3</sup> NaOH on the slope of the peak is shown in Fig. 2. The slope of the peak was greater with increase of KCN concentration above 0.8 mol/ dm<sup>3</sup>, and was maximized at 0.9 mol/dm<sup>3</sup>, decreasing thereafter. KCN concentration was fixed at 0.9 mol/dm<sup>3</sup>.



Fig. 2—Effect of KCN concentration containing 0.1 mol/dm<sup>3</sup> NaOH on the slope of the peak. Au: 47.8 mg/dm<sup>3</sup>; measurement conditions as in Table 1.



Fig. 3—Effect of NaOH concentration containing 0.9 mol/dm<sup>3</sup> KCN on the slope of the peak. Au: 47.8 mg/dm<sup>3</sup>; measurement conditions as in Table 1.

The effect of NaOH concentration containing 0.9 mol/dm<sup>3</sup> KCN on the slope of the peak is shown in Fig. 3. The reproducible data were obtained at NaOH concentrations above 0.05 mol/dm<sup>3</sup>. It was concluded that Au(I) ion was made stable in the form of an AuCN<sub>2</sub><sup>-</sup> complex ion with KCN above 0.05 mol/dm<sup>3</sup> NaOH. NaOH concentration was fixed at 0.1 mol/dm<sup>3</sup>. Pre-concentration potential was determined in the range of -800 to -1200 mV vs. Ag/AgCl. The slope of the peak was not altered. The pre-concentration potential was fixed at -1000 mV vs. Ag/AgCl. The effect of pre-concentration time on the slope of the peak is shown in Fig. 4. The slope of the sensitivity limit of determination was increased. Pre-concentration time, however, was fixed as 10 min for determination of concentration of Au ion in a plating bath.

When the potential scanning rate was changed, the slope of the peak was not different; however, detection sensitivity of the peak had a tendency to be low. The potential scanning rate was made 5 mV/sec. The pulse width was made 50 mV and pulse time 40 msec. The determination was not affected whether both values were increased or decreased.

Optimum measurement conditions are shown in Table 1. The calibration curve of Au(I) ion is shown in Fig. 5. The determination range was from 27.5 to 100 mg/dm<sup>3</sup>. The relative standard deviation was 10 percent.

There are many different applications for gold and gold alloy plating baths—decorative (jewelry, watch attachments and other items of personal use and adornment), electrical and electronics (semiconductors, printed/etched circuits and contacts/connectors). Many metals and materials have been



Fig. 4—Effect of pre-concentration time on the slope of the peak. Au: 47.8 mg/dm<sup>3</sup>; measurement conditions as in Table 1.



Fig. 5—Calibration curve of Au(I) ion; measurement conditions as in Table 1.

added as alloys for the purpose of color and hardness. Many metal ions were dissolved in our bath from various materials. For example, the hard gold plating bath contained cobalt ions, the Au-alloy plating bath contained Cd and Cu ions. The materials used were Cu, Cu/Zn alloy, Ni and stainless steels, and those ions were dissolved in the bath.

The effects of coexistent ions are shown in Table 2. Possible interferences from concomitant metal ions were evaluated for measurement of 47.8 mg/dm<sup>3</sup> of Au(III) ion. Ninety-seven mg/cm<sup>3</sup> of Ag(I), 5 g/cm<sup>3</sup> of H<sub>3</sub>PO<sub>4</sub><sup>-3</sup>, 378 mg/ cm<sup>3</sup> of EDTA<sup>-2</sup>, 100 mg/cm<sup>3</sup> of Cu(II), 96 mg/cm<sup>3</sup> of Zn(II) and 40.8 mg/cm<sup>3</sup> of Pb(II) did not interfere. Small amounts of Co, Ni, Cr and Fe ions did produce interference. These interferences were removed, however, by means of mercury cathode electrolysis. Controlled-potential electrolysis and masking techniques were not successful. Nickel ion, for which the maximum permissible amount was small for gold, was examined. Its amount was about 1/450 of the Au concentration. The peaks of Au and Ni ion are shown in Fig. 1. The peak of Ni was near the peak of Au. If the interference of Ni was removed, that of other metals was removed as well. Addition of Au standard solution was required to overcome interference from the nickel. For particular samples, determination of Ni was necessary at first. Next, Au standard solution was added above 450 times the concentration of Ni ion. Usually, the amount of Au standard solution needed was about 30 to 50 mg/dm<sup>3</sup>.

The composition of the gold electroplating bath used was 3 to 7 g/dm<sup>3</sup> Au, 0 to 0.1 mg/dm<sup>3</sup> Pb, 0 to 0.1 mg/dm<sup>3</sup> CN<sup>\*</sup>. Five cm<sup>3</sup> of plating solution were transferred by pipette into a 100-cm<sup>3</sup> measuring flask and made up to 100 cm<sup>3</sup> with distilled water. One cm<sup>3</sup> of this solution was prepared as test solution. Gold ion concentration in the gold electroplating bath was 7.2 g/dm<sup>3</sup>. The relative standard deviation was 10 percent. The error was  $\pm 10$  percent compared with a gravimetric analysis.

Table 1 Optimum Measurement Conditions		
Deaeration time, min	10	
KCN conc., mol/dm <sup>3</sup>	0.9	
NaOH conc., mol/dm <sup>3</sup>	0.1	
Pre-conc. potential, mV vs. Ag/AgCl	-1000	
Pre-conc. time, min	10	
Scan rate, mV/sec	-5	
Pulse amplitude, mV	50	
Pulse duration, msec	40	

## Table 2 Effect of Coexistent Ions

Ion	Quantity	Error
	mg/dm <sup>3</sup>	%
Ag(I)	97	-1.0
Co(II)	0.58	2.0
	1.16	-95.0
Cr(VI)	7.56	-2.5
	8.70	-100
Cu(II)	100	-4.0
Fe(III)	5	-4.0
	15	-13.0
Ni(II)	0.11	0
	0.35	-72.0
Pb(II)	40.8	0
Zn(II)	96	3.0
PO <sub>4</sub> -3	5000	0
EDTA-4	378	0
Au: 47.8 mg/dm <sup>3</sup>		

An electroless gold plating bath was tried; composition 2 to 5 g/dm<sup>3</sup> Au, 0 to 0.1 mg/dm<sup>3</sup> Pb, 0 to 0.1 mg/dm<sup>3</sup> Ni\*. Ten cm<sup>3</sup> of plating solution was transferred by pipette into a 100-cm<sup>3</sup> measuring flask, and made up to 100 cm<sup>3</sup> with distilled water. One cm<sup>3</sup> of this solution was prepared as test solution. Gold ion concentration in the electroless gold plating bath was 2.8 g/dm<sup>3</sup>. The relative standard deviation was 10 percent. The error was  $\pm 10$  percent, compared with gravimetric analysis. If nickel or cobalt ions are abundant, the dilution rate of the electrolyte and the amount of the Au standard must increase.

\* Manufacturer's estimated amount, using atomic absorption spectrometry.

Editor's note: Manuscript received, August 1996.

Reference

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