## Simultaneous Analysis of Silver Plating Bath Comprising Silver Cyanide, Phosphate & Mercaptobenzothiazole Derivatives Using a Capillary Ion Analyzer

By K. Hwang, S.A. Choi & C. Cho

PSC (potassium silver cyanide), anionic surfactant and  $HPO_4^{-2}$  components consisting of Ag plating solutions were simultaneously analyzed with a capillary ion analyzer, using a phthalate buffer at pH 5.6. Detection of each ion was achieved using on-column indirect photometry at 254 nm. Quantities of PSC,  $HPO_4^{-2}$  and mercaptobenzo-thiazole derivatives were found to be about 1.6 g/L, 0.6 g/L and 0.2 (v/v) percent, respectively, in the artificial silver plating solution ,compared with a standard solution. The three components were analyzed without affecting other components, such as surfactants and cyanide. This simultaneous analysis method for silver plating solutions is a very powerful technique for process control systems.

Generally, metal plating baths comprise various components, such as metal complexes, electrolytes, surfactants, brighteners and organics, so that operators need to control the bath to obtain a good-quality product. Bath composition analysis is thus one of the most important factors in the development of electroplating technology. For these reasons, monitoring of Ag content, surfactants and organic acids is important.<sup>1.2</sup> The classical analytical method of PSC (potassium silver cyanide) and surfactant etc. are reported.<sup>3-5</sup>

Current methods for monitoring these organic acids include ion chromatography (IC), employing a gradient separation that can be very time consuming. Analyses are carried out using a capillary electrophoretic technique that has been developed for rapid analysis of low-molecular-weight inorganic and organic ions.<sup>6</sup> The results have been shown to provide results comparable to conventional IC, as well as offering the advantage of speed, ease of use and fast changeover from one analysis to another.<sup>7,8</sup> The main barrier is the development of simultaneous analysis for all the system components.

In this paper, we report analysis of plating bath composition with capillary ion analyzer for use in an on-line system.



Fig. 1—Capillary ion analyzer chromatogram of Ag plating solution diluted 100 times.

## Experimental Procedure

Potassium silver cyanide (PSC, 99.62%) and potassium cyanide (95%) were used, as well as potassium hydrogen phosphate ( $K_2HPO_4$ , 99.99%), mercaptobenzothiazole, thiopropane sulfonic acid, sodium salt ( $NaC_{10}H_{10}NO_3S_3$ , denoted as R2).

Aqueous solutions were prepared with ultrapure water. A capillary ion analyzer (CIA) was used for waters chromatography, and the detector was UV at 254 nm (Hg lamp). CIA operation conditions were as follows: Detection polarity negative, capillary fused silica 60 cm x 75  $\mu$ m, chamber temperature 25 °C, applied voltage 20 kV, hydrostatic injection 9.8 cm height for 10 sec (10  $\mu$ L), and purge time 2 min.

Buffer was applied phthalate with CIA-pak OFM Anion BT solution. An osmotic flow modifier, OFM, was added to the electrolyte as an additive that reverses the normally cathodic direction of the electro-osmotic flow (EOF) found in fused silica capillaries. This creates a co-electro-osmotic condition that augments the mobility of the analytes.

## Results & Discussion

A silver plating solution was analyzed using a phthalate buffer at pH 5.6. When negative high voltage is applied to a vial of the electrolyte on the sample side, and the electrolyte of the receiving side has positive high voltage applied, the negatively charged components migrate toward the electrolyte of the receiving side. Absorption by the buffer is measured for low and high values when the analyzed species moves to the detector. The main species in the plating solution are PSC,  $HPO_4^{-2}$  and an anionic surfactant. Because these components act as plating, pH control and wetting agents, it is a very powerful technique in process control systems, inasmuch as the components are analyzed at the same time.

Figure 1 shows a CIA chromatogram when the silverplating solution is diluted 100 times. The three components were separated quite well. Here, the first peak is PSC and the

second is  $H_2PO_4^{-1}$  (denoted as  $HPO_4^{-2}$  in CIA chromatograms;  $HPO_4^{-2}$  exists in the silver plating solution). The third peak is boric acid. The negative peak is R2. The strongly charged species are detected later, because of reaction by the additive OFM.<sup>9</sup> PSC did not decompose in the buffer pH 5.6 of the additive OFM;<sup>10,11</sup> therefore, the pH of the buffer did not need to be changed, and peaks of PSC and  $HPO_4^{-2}$  did not perfectly separate when the pH is more than 5.6. To quantify the components, ratios of PSC:HPO\_4^{-2}:R2 = 100 (wt/vol)pct:40 (wt/vol)pct:2(vol/vol)pct mixed solutions were prepared. The solution was diluted



*Fig.* 2—*Capillary ion analyzer chromatogram of laboratory Ag plating solution diluted 100 times.* 

by 100 times (Fig. 2). Peak intensity shows very reasonable values in the CIA chromatogram.

As shown in the CIA chromatogram of Fig. 2, R2, independently separated, has been linear for all dilution factors. Figure 3 shows dynamic range of good linearity for R2, which can be analyzed to 0.2 (vol/vol) pct. All integration methods used valley-to-valley boundaries. On the other hand, for PSC and HPO<sub>4</sub><sup>-2</sup> peaks not separating perfectly in the chromatogram, the poor separation may be ascribed to simul-



Fig. 3—Peak area vs. R2 concentration in laboratory Ag plating solution.



Fig. 4—Peak area vs. PSC concentration in  $HPO_{4}^{-2}$  0.4 g/L fixed.

taneous reaction of the two species with OFM, simultaneous sensitivity of two species in the UV detector, or asymmetry of the PSC peak.

To see the integration relationship between PSC and HPO<sub>4</sub><sup>-2</sup>, we carried out experiments for variable PSC concentration in fixed HPO<sub>4</sub><sup>-2</sup>, 0.4 g/L (40 g diluted 100 times), and for variable HPO<sub>4</sub><sup>-2</sup> concentration in fixed PSC, 1.0 g/L (100 g/L diluted 100 times). Figure 4 shows the integration value vs. concentration of PSC in fixed HPO<sub>4</sub><sup>-2</sup>, 0.4 g/ L. PSC can be quantified with 1.6 g/L concentration (160 g/L diluted 100 times). Also, Fig. 5 shows integration value vs. concentration of HPO<sub>4</sub><sup>-2</sup> in fixed PSC, 1.0 g/L. HPO<sub>4</sub><sup>-2</sup> can be measured at 0.6 g/L concentration

(60 g/L diluted 100 times). The integration value of PSC and HPO<sub>4</sub><sup>-2</sup> concentrations were constant (Figs. 4 and 5). These facts suggest that not only can a silver plating solution with a concentration variety of PSC and HPO<sub>4</sub><sup>2-</sup> be analyzed, but a silver strike solution can be analyzed as well. Otherwise, the maximum value of the analysis, despite variable PSC and  $HPO_4^{-2}$ , determines PSC at 1.6 g/L and  $HPO_4^{-2}$  at 0.6 g/L. At less than maximum value of analysis of PSC and HPO $_{4}^{-2}$ , the integration values are not affected by each other for variable concentration of PSC and  $HPO_{4}^{-2}$ . The dynamic range by dilution factor was narrow—PSC:HPO<sub>4</sub><sup>-2</sup> = 5:2 (wt/vol) pct ratio concentration, but was slightly wider in one fixed concentration. The reasons are the not-perfectly-separated broad PSC and HPO<sub>4</sub><sup>-2</sup> peaks. In greater than maximum value of analysis of PSC and  $HPO_4^{2-}$ , the integration values can affect each other for a variety of concentrations of PSC and HPO<sub>4</sub><sup>-2</sup>, so the contents can be quantified for under maximum value of analysis although PSC and HPO<sub>4</sub><sup>2</sup> peaks are not perfectly separated.

PSC, R2 and  $\text{HPO}_4^{-2}$  peak areas were not changed when KCN of the silver plating solution was added. Each PSC, R2 and  $\text{HPO}_4^{-2}$  standard solution had good linearity because of PSC 2 g/L, R2 0.08 (vol/vol) pct, and  $\text{HPO}_4^{-2}$  0.8 g/L. The silver plating solution is very sensitively measured when each material is analyzed from each standard solution. The advantage of the technique is that three components can be analyzed at the same time, and this analysis method can be usefully applied on a line control system.



Fig. 5—Peak area vs. HPO<sub>4</sub><sup>-2</sup> concentration in PSC 1 g/L fixed.

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After multiplication of Eq. (A8) by 2 and addition with Eqs. (A5)-(A7), we obtain:

$$\partial C_{\rm Cr(VI)} / \partial t = D \partial^2 C_{\rm Cr(VI)} / \partial x^2$$
 (A11)

where  $C_{Cr(VI)}$  is the total concentration of species containing Cr(VI) and may be expressed by the relationship:

$$C_{\rm Cr(VI)} = [H_2 \text{CrO}_4] + [H \text{CrO}_4^{-}] + [CrO_4^{-2}] + 2[Cr_2O_7^{-2}] (A12)$$

Further, after multiplication of Eqs. (A5), (A8) and (A10) by 2, 2 and -1, respectively, and addition with Eqs. (A6) and (A9), we obtain:

$$\partial C_{\rm H} + /\partial t = D \partial^2 C_{\rm H} / \partial x^2 \tag{A13}$$

where  $C_{\rm H}^{+}$  is the total concentration of donors and acceptors of protons and may be expressed by the relationship:

$$C_{\rm H}^{+} = 2[H_2 {\rm CrO}_4] + [{\rm HCrO}_4^{-}] + 2[{\rm Cr}_2 {\rm O}_7^{-2}] + [{\rm H}^+] - [{\rm OH}^-]$$
(A14)

It can be seen from Eq. (A14) that a  $Cr_2O_7^{-2}$  anion is also the donor of protons. When reacting with water [see (A3)], it produces two species of HCrO<sub>4</sub><sup>-</sup>. The concentration of acceptors of protons (OH<sup>-</sup> ions) has a negative sign.

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