

# 'One-pot' Electrochemical Determination of Copper and Formaldehyde in Electroless Copper Plating Baths

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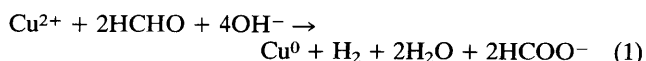
A simple electrochemical method has been developed for the determination of copper and formaldehyde concentrations in electroless copper plating baths. This method uses dc amperometry and anodic stripping voltammetry for the determination of formaldehyde and copper concentrations, respectively. The analyses are done sequentially using a single gold electrode in the same sample solution. The advantages of this 'one-pot' technique are simplicity and speed of analysis, important advantages over alternative methods of analysis which are either more time consuming, involve multiple samples, or use more elaborate instrumentation. A commercial plating bath was analysed using the described technique, yielding results which had a precision of within 5% for formaldehyde and copper. While not rigorously precise, this method can be used in process control to indicate when bath replenishment or replacement is necessary. The method can easily be implemented in plating facilities by operators using portable equipment, and an automated, on-line procedure is also possible.

**Keywords:** Electroless plating; copper; formaldehyde; electroanalysis; amperometry; stripping voltammetry

## Introduction

Electroless plating baths<sup>1,2</sup> are extensively used in such areas as electronics manufacturing, jewellery making, and other applications where appropriate conductivity, corrosion protection, or other surface properties are desired. The use of electroless deposition largely avoids the problems of dendrite formation and uneven deposits which are often produced using electrolytic deposition, where non-uniform current densities can occur. For this reason electroless deposition is particularly useful for plating through holes in printed wiring boards,<sup>3</sup> and in other areas where the throwing power of electrolytic baths is an issue. Since no electrical connection to the substrate is required, plating may even be accomplished on appropriately sensitized non-conductive substrates.

One of the most common electroless plating baths is based on the copper-formaldehyde system.<sup>4,5</sup> The reduction of Cu<sup>2+</sup> by formaldehyde at the plating surface is given as:



It should be emphasized that this simplified equation is representative of the overall stoichiometry only and the actual oxidative process involves the H<sub>2</sub>C(OH)O<sup>-</sup> anion.<sup>6,7</sup>

In order for the bath to function effectively, the concentrations of copper ions and formaldehyde must be maintained within a specified range. If the values fall outside the set levels, the coatings produced may be off-colour, too thin or brittle, or uneven or 'spotty' coverage may result. Also, plating times may be inconveniently long if the components become

depleted. Quality control mandates that the copper and formaldehyde concentrations be frequently determined to ensure good, consistent plating results.

Currently, copper/formaldehyde baths are analysed by wet chemical or spectroscopic means,<sup>8</sup> a procedure usually done in remote analytical labs and which can require a considerable amount of time and effort (if just from sample turnaround times). Because the concentrations of copper and formaldehyde change continuously during the lifetime of a bath, it would be desirable to have a rapid means of analysis which can be implemented in the plating facility, or on-line using portable equipment. In fact, electrochemical techniques based on stripping voltammetry using mercury<sup>9-11</sup> and platinum<sup>12</sup> electrodes have been developed for just this purpose. The use of a mercury electrode offers the advantage of being able to analyse for many plating bath components in a single analysis.<sup>9-11</sup>

Our results show that the analysis can be simplified even further, especially avoiding the potential complications arising from the use of a mercury electrode. As plating bath compositions must fall within a supplier-specified window which is often somewhat generous, extreme accuracy and precision are not required. As an example, the manufacturer of the electroless copper plating bath analysed in this work (see Experimental section) specifies a range of 2.5 to 3.5 ppt copper and 6 to 9 ppt formaldehyde. The important aspect is that the results be reliable (in a process control sense) and be obtained quickly and easily by shop analysts. To this end, we have developed a convenient, 'one-pot' electrochemical technique for the determination of both copper and formaldehyde concentrations in electroless plating baths. The method described in this article is sufficient to establish if a plating bath has exceeded its useful lifetime or requires replenishment. This method is easily implemented using commercially available instrumentation. In addition, compact, user-friendly systems are under development which will make implementation even easier.

## Experimental

All chemicals used were of analytical-reagent grade. Distilled water was further purified by passage through a Corning Mega Pure water purification system (Corning, NY, USA). Copper standards and standard additions were performed by appropriate dilution of a 1000 ppm Cu atomic absorption standard (Aldrich, Milwaukee, WI, USA). Formaldehyde standards and standard additions were performed by dilution of a 37% HCHO reagent solution (J. T. Baker, Phillipsburgh, NJ, USA). All solutions were prepared fresh each day.

The copper plating bath solutions were made fresh each day by mixing commercial solutions (MacDermid, Waterbury, CT, USA) 22A and 22B. This product is a two-component formulation with one solution containing copper(II) ions and

formaldehyde, the other containing sodium hydroxide. The components 22A and 22B and de-ionized water were mixed in the ratio 1:1:8. A plating bath solution mixed as directed initially contains 3.1 ppt of  $\text{Cu}^{2+}$ , 7.5 ppt of HCHO and 11.5 ppt of NaOH. A complexing agent such as EDTA is also present to prevent precipitation of copper hydroxide.<sup>4,5</sup>

Electrochemical measurements were performed using a Bioanalytical Systems (West Lafayette, IN, USA) Model 100W electrochemical analyser. Before use, conventionally sized disk electrodes (1.6 mm diameter) and microelectrodes (10  $\mu\text{m}$  diameter) were polished using 0.05  $\mu\text{m}$  alumina powder slurries. A platinum wire coil was used as the counter electrode. All potentials given are *versus* an Ag/AgCl reference electrode. The solutions were not deoxygenated before analysis, and all measurements were performed at room temperature. Other electrochemical parameters are given in the figure captions.

## Results and Discussion

### General Considerations

Although mercury film and hanging mercury drop electrodes have previously been used for both anodic stripping voltammetry of copper<sup>9–11,13</sup> and fundamental studies of the electrochemical reduction<sup>9–11,14,15</sup> and oxidation<sup>16</sup> of formaldehyde, a solid electrode would be easier to use and more acceptable considering the potential contamination aspects. This would be especially true for monitors used directly in plating baths.

Many studies have been done on the electrochemistry of formaldehyde at solid electrodes such as platinum<sup>6,17–20</sup> and gold.<sup>7,21–24</sup> A good review of the oxidation reactions is provided in ref. 23. The reaction mechanisms are dependent on the electrode used and both oxidized products ( $\text{HCOO}^-$ ,  $\text{CO}_2$ ) and reduced products [ $\text{CH}_3\text{OH}$ ,  $(\text{CH}_2\text{OH})_2$ ] are possible.

In an actual electroless copper plating bath, the potentials required for the reduction of formaldehyde at electrodes other than mercury resulted in the plating of copper<sup>24,25</sup> onto the electrode surface. For this reason, an analytical technique based on the oxidation reactions of formaldehyde<sup>6,7,17–23</sup> was the obvious choice. In fact, oxidative processes at platinum electrodes have been used specifically for determining formaldehyde concentrations in electroless copper plating baths<sup>12</sup> and in chromatography.<sup>26</sup>

The use of anodic stripping voltammetry (ASV)<sup>13</sup> has proved valuable for the analysis of copper in plating baths<sup>9–11</sup> and was thus chosen to measure copper concentrations in the present work. Since the copper ion concentration in the copper plating bath studied (see Experimental) is high relative to the concentrations usually determined by ASV, no deoxygenation of the solution was necessary and solid (non-mercury-based) electrodes worked well. After examining several electrode materials (Pt, Ag, Cu, Au, C) with both copper and formaldehyde determinations in mind, it was found that a gold electrode worked best.

While it may be desirable to perform the analysis directly in the plating bath itself, there are certain problems with this approach. The concentrations of copper and formaldehyde in a typical plating bath are large enough so that the range of linear response can be exceeded using conventional electrochemical parameters (deposition time, scan rates, *etc.*). More importantly, the presence of any metal electrode such as gold or platinum, which provides a catalytic surface for reaction (1) to occur, resulted in the plating out of copper on the electrode surface. Therefore, a copper electrode surface was formed after a short immersion time, a result which made an accurate

determination of the copper and formaldehyde concentrations difficult. Although the use of carbon-based (graphite or glassy carbon) electrodes did not result in the spontaneous plating out of copper, formaldehyde exhibited no electrochemical oxidation at these electrodes.

In order to circumvent the problems mentioned above, the analysis for both copper and formaldehyde is performed by injecting a small aliquot of the plating bath solution into a 1 mol  $\text{l}^{-1}$  NaOH solution. Conditions of very high pH were used in order to shift the formaldehyde speciation equilibrium towards the most readily oxidized species,  $\text{H}_2\text{C}(\text{OH})\text{O}^-$ .<sup>6,7,22</sup> Typical dilutions were on the order of 1:20 to 1:100, the latter dilution factor being used for fresh plating baths. This dilution has the desirable effect of minimizing the spontaneous plating of copper onto the electrode surface, while still maintaining copper and formaldehyde concentrations at levels convenient for the sensitivity of the electroanalytical techniques used. Of course, an added benefit of this procedure is that the electrolyte is well defined from one analysis to the next.

### Electrochemical Response of a Gold Electrode in Formaldehyde–NaOH Solutions

The voltammetric response of a conventionally sized (1.6 mm diameter) gold disk electrode in 1 mol  $\text{l}^{-1}$  NaOH is shown in Fig. 1. Scanning anodically from  $-1.0$  V, the voltammogram exhibits a small wave beginning at  $-0.15$  V, followed by a peak at  $0.35$  V. On the return scan, a sharp peak occurring at  $0$  V and a smaller broad peak with a maximum at  $-0.3$  V can be seen. These features have been noted by other researchers,<sup>18,21</sup> and are attributed to the formation (forward scan) and reduction (reverse scan) of gold oxide(s).

The solid trace in Fig. 1 represents the voltammogram obtained in a 1 mol  $\text{l}^{-1}$  NaOH solution in which 0.73 ppt formaldehyde is also present. An anodic scan starting from  $-1.0$  V exhibits a peak at  $-0.45$  V followed by another anodic process occurring at about  $0$  V. Overlap of the decreasing portion of the peak at  $-0.45$  V with the broad peak at  $0$  V results in a step-wise form of the  $I$ - $E$  curve. These peaks are due to the oxidation of formaldehyde,<sup>6,7,20–22</sup> and increased in magnitude with the addition of more formaldehyde. Further increases in potential (positive of  $0.2$  V) result in a decrease of the current to almost zero. Because this latter potential is the potential at which the oxidation of the gold electrode itself occurs (see Fig. 1, B), it is reasonable to relate the inhibition of the formaldehyde oxidation to the formation of a gold oxide surface layer. As noted by previous researchers,<sup>6,20,26</sup> the presence of a gold oxide layer on the electrode surface is sufficient to completely block the oxidation of formaldehyde.

On the return scan, the reduction of the gold oxide layer (beginning at  $0.1$  V) is sufficient to cause the resumption of

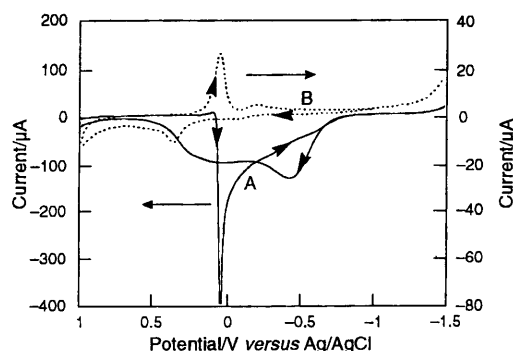


Fig. 1 Voltammetric response of a gold disk electrode in 1 mol  $\text{l}^{-1}$  NaOH A, with and B, without 0.73 ppt HCHO. The initial potential was  $-1.0$  V and the scan rate was  $0.1$  V  $\text{s}^{-1}$ .

formaldehyde oxidation, a phenomena which is indicated by the sudden anodic current spike seen in Fig. 1. It is possible that the adsorption of reaction intermediates on the electrode surface is also responsible for this inhibition effect, as has been proposed with platinum electrodes.<sup>17,18,23</sup> Alternatively, the spike at 0 V may also be due to the oxidation of adsorbed reactants at the electrode surface.<sup>7,23</sup> It is beyond the scope of this work to explain fully the above observations as previous research has discussed the complexity of the formaldehyde oxidation reaction.<sup>6,7,17–23</sup>

### Formaldehyde Analysis

Owing to the complications arising from the plating of copper onto the electrode surface and the resulting inhibition of formaldehyde oxidation, it was felt that voltammetric techniques for the determination of formaldehyde at a gold electrode were not adequate. However, an amperometric experiment at a carefully chosen potential proved to give reasonable results. The electrode was potentiostated at 0.1 V and the current due to the oxidation of added formaldehyde was measured as the solution was stirred. The stirring insured solution homogeneity and established plateau currents which are easier to measure.

The choice of electrode potential was not arbitrary. It was chosen to be negative enough to avoid electrode passivation due to gold oxide formation; amperometric experiments at potentials positive of 0.1 V showed less current and more fluctuations. These decreases were no doubt due to the formation of gold oxide at the electrode surface. On the other hand, the optimum potential was positive enough to show a significant rate of oxidation of formaldehyde and to avoid complications arising from copper plating onto the electrode surface. At this potential, any copper metal which plated out onto the electrode surface by electroless deposition is immediately re-oxidized. It has been verified that an addition of  $\text{Cu}^{2+}$  ions to the solution had no effect on the oxidation of formaldehyde at that potential.

Fig. 2 shows the amperometric response of a conventionally sized (1.6 mm diameter) gold disk electrode potentiostated at 0.1 V in a 1 mol  $\text{l}^{-1}$  NaOH solution to which formaldehyde has been added in four steps to give total concentrations of 185, 370, 555, and 740 ppm. The noise observed in the plateau regions is probably due to stirring irregularities, while the slight decrease in current with time immediately after each injection may be due to fouling of the electrode surface by

reaction intermediates.<sup>6,21,23</sup> Repolishing the electrode after each step restored the response to its former value. However, for the purposes of this analytical technique, sufficient precision was obtained by measuring the current at a consistent time after the injection. This point was chosen by visually inspecting the current steps and choosing the first point after the maximum current for each step was reached, allowing for noise fluctuations.

For each injection (chosen to yield equal concentration increases), the increase in current was approximately 23  $\mu\text{A}$ . Additional experiments showed that this linearity was valid over a concentration range of at least 10 to 2000 ppm. In the absence of formaldehyde, the measured current was negligible compared to the large current obtained for the oxidation of formaldehyde (see Fig 1). This small background current is no doubt due to the oxidation of the gold electrode. The observation that the current for the oxidation of formaldehyde at gold was linear with respect to reactant concentration has been noted by other researchers.<sup>7</sup> Although a stirred solution does not provide the well defined hydrodynamics of a rotating disk electrode, the nearly plateau current shapes observed are sufficient to provide reasonable results.

The analysis of a plating bath was performed in a similar fashion. The current was monitored as an aliquot of a freshly prepared plating bath solution was injected into the stirred 1 mol  $\text{l}^{-1}$  NaOH solution, followed by the injection of a formaldehyde standard addition. The current response for the two injections is shown in Fig. 2. The standard addition equation [eqn (2)] yields the concentration of the unknown,  $c_u$ , given the known values of  $V$  (initial solution volume),  $i_u$  (current of unknown),  $c_s$  (concentration of spike),  $v$  (volume of spike) and  $i_{\text{tot}}$  (total current of unknown and standard addition).<sup>27</sup>

$$c_u = \frac{-vc_s i_u}{i_u V - i_{\text{tot}}(V + v)} \quad (2)$$

From this equation, a value of 7.3 ppt for the concentration of formaldehyde in the original plating bath solution can be calculated. This compares well with the 7.5 ppt value given in the product specifications and is within the specified range of 6 to 9 ppt.

### Copper Analysis

Although the analysis of metal ions by anodic stripping voltammetry is usually performed in acidic media,<sup>13</sup> the concentration of copper in most plating bath solutions is sufficient to yield a response in 1 mol  $\text{l}^{-1}$  NaOH. Since the copper and formaldehyde determinations in this method are performed in different potential regions, and the dilution factor is the same, it is possible to perform the analysis for copper in the same solution in which the formaldehyde analysis was performed. This greatly simplifies the procedure.

Fig. 3 shows the currents observed for an anodic stripping experiment in which increasing amounts of copper were added to a 1 mol  $\text{l}^{-1}$  NaOH solution, deposited on the gold disk electrode at  $-0.6$  V for 10 s, then stripped using an anodic scan. The magnitude of the peak at  $-0.2$  V varies linearly with copper concentration throughout the range given ( $\Delta i/\Delta c = 0.034 \pm 0.006 \mu\text{A}$  per ppm Cu), but deviated from linearity at higher concentrations or longer deposition times. The deposition times were thus chosen so that linear response conditions would be obtained. Another, much smaller peak is observed at about  $-0.45$  V, but the height of this peak did not correlate linearly with bulk copper ion concentration. A small shoulder at about  $-0.1$  V was seen at the tail end of the larger copper stripping peak. This feature was also seen in a blank and did not depend on deposition time or potential. The shoulder is

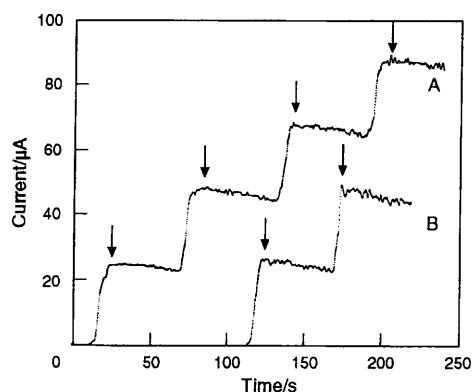


Fig. 2 Current–time behaviour of a gold disk electrode held at 0.1 V in 10 ml of 1 mol  $\text{l}^{-1}$  NaOH. A, with the addition of four equal amounts of HCHO to yield concentrations after addition of 185, 370, 555 and 740 ppm; B, (offset 100 s for clarity) with the addition of 25  $\mu\text{l}$  of a freshly prepared plating bath (see Experimental), followed by a standard addition of HCHO (50  $\mu\text{l}$  of 3.7% HCHO). The arrows indicate times of current measurement.



likely to be indicative of the oxidation of the gold electrode surface.

To perform the analysis for copper, an anodic stripping experiment was done with the solution used for the formaldehyde analysis above. Again, standard addition can be used to provide quantitative results. Fig. 4 shows the stripping response for copper using the parameters given in the figure caption. From eqn (2), a value of 3.3 ppt copper in the original plating bath can be calculated. This value is in reasonable agreement with the value of 3.1 ppt given in the product specifications, and within the specified range of 2.5 to 3.5 ppt.

The presence of components other than copper in the plating bath solution did not substantially affect the anodic stripping response for copper, as shown in Fig. 3. The two experiments were identical, except that in one case an aliquot of an old plating bath solution was added. It was assumed that the old plating bath solution provides essentially the same matrix as a new one, except for the presence of copper ions and formaldehyde. The only significant difference observed in the two responses was due to dilution effects, and thus the presence of complexing agents, stabilizers, or other proprietary ingredients in the bath does not significantly affect the analytical method.

#### Recommended Procedures for Determination of Copper and Formaldehyde

The analytical procedure can be summarized as follows: (1) The working electrode may be lightly polished with 0.05  $\mu\text{m}$  alumina slurry before use. (2) The current at a gold electrode potentiostated at 0.1 V in a small volume (10 ml) of 1 mol  $\text{l}^{-1}$  NaOH is continuously measured. (3) An aliquot (typically 100–250  $\mu\text{l}$ ) of the plating bath solution is injected into the stirred solution, followed by a known aliquot of a HCHO standard addition. (4) From the relative magnitude of the two current plateaus, a concentration of HCHO in the original bath is calculated [see eqn (2)]. (5) The electrode potential is then set at  $-0.6$  V for a fixed period (5–30 s), and then scanned to 0.2 V as the current is monitored. Stirring may be required during the deposition step. (6) A known aliquot of a copper standard is added, and step (4) is repeated. (7) From the relative magnitude of the two dominant stripping peaks (at  $-0.2$  V) observed in steps (5) and (6), a concentration of copper in the original bath is calculated, again using the standard addition expression [eqn (2)].

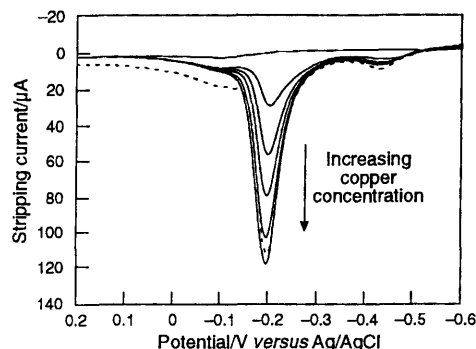
The above procedure was found to give good results with plating bath solutions which were relatively new. The analysis

of solutions much lower in copper or formaldehyde concentration (such as those present in old baths or rinse tanks) requires some modifications. Larger amounts of the plating bath aliquot, or longer deposition times for the copper stripping experiment, may be needed. We analysed older plating bath solutions with much less copper and formaldehyde and found that the method described above gave good results.

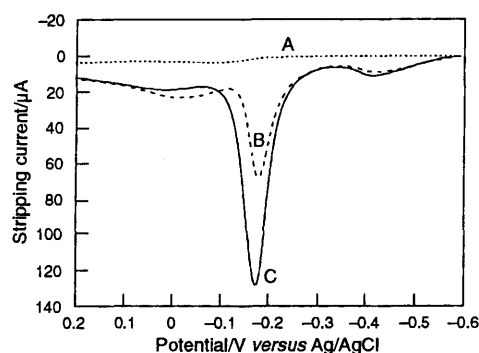
As noted earlier, copper will plate out onto the electrode surface if the electrode is left unpotentiostated in a plating bath solution. Fortunately, the dilution of the reactants in the above analytical procedure decreased this plating rate considerably. As evidence of this, no significant copper stripping peak was observed for an unpotentiostated electrode immersed in a dilute solution for the time required for an analysis. Although metallic copper plated out on the platinum counter electrode after a period of time, this did not appear to have an effect on the calculated results. However, if prolonged contact with the diluted plating solution were allowed prior to analysis, the amount of copper lost may be sufficient to lead to erroneously low copper values.

In general, the formaldehyde analysis yielded better precision than the copper analysis. Despite repeated attempts, the stripping peaks for copper were only good to about 5% precision. Many concentration ranges and conditions were tried, but no source of error could be identified. Note that a plating bath contains components other than copper and formaldehyde, including complexing agents, stabilizers, and other proprietary ingredients. Owing to the uncertainty of the exact matrix, electroanalysis will not be as 'clean' as in a one- or two-component medium. In addition, anodic stripping voltammetry of copper in basic solutions at bare electrodes is not the accepted quantitative method reported in the literature.<sup>13</sup>

The above results were obtained using a conventionally-sized disk electrode. A substantial advantage could be realized if the procedure were based on a gold microelectrode since plateau rather than peak currents are observed<sup>28</sup> in quiescent solutions. Enhanced signals have also been noted in ASV using microelectrodes without stirring.<sup>29–31</sup> In addition, the obviation of the requirement for a stirring apparatus would offer true advances in simplifying this entire method. Unfortunately, the current response obtained using a gold microelectrode under the same conditions as detailed above produced a signal which was noisy and did not give a steady-state response. For this reason, it was not possible to use the gold microelectrodes for quantitative analysis of either formaldehyde or copper. Possible reasons for these microelectrode results, such as surface fouling, are being investigated.



**Fig. 3** Linear-scan stripping-voltammetry at a gold disk electrode in 10 ml of 1 mol  $\text{l}^{-1}$  NaOH. Copper concentrations were 0, 32, 64, 96, 128 and 160 ppm (solid lines). The dashed line is the same solution with a copper concentration of 160 ppm but with the addition of 250  $\mu\text{l}$  of an old plating bath. A 10 s deposition time at  $-0.6$  V with stirring and a 10 s standing time prior to scan initiation were used. The scan rate was 0.1 V  $\text{s}^{-1}$ .



**Fig. 4** Linear-scan stripping-voltammetry at a gold disk electrode in A, 1 mol  $\text{l}^{-1}$  NaOH; B, with addition of 250  $\mu\text{l}$  of freshly prepared plating bath; C, with plating bath addition and standard addition of 250  $\mu\text{l}$  of 3.2 ppt Cu (additional concentration of Cu was 80 ppm). A 10 s deposition time at  $-0.6$  V with stirring and a 10 s standing time prior to the scan initiation were used. The scan rate was 0.1 V  $\text{s}^{-1}$ .

### Conclusions

We have demonstrated the validity of an electrochemical method which can be used for the determination of copper and formaldehyde concentrations in electroless copper plating baths. Only one solution and minimal effort and instrumentation are required. The method could be performed using portable equipment and automated for on-line control.

For the purpose of deciding whether a plating bath needs to be replenished or replaced, extremely accurate or precise numbers are generally not required. The described method for the determination of copper and formaldehyde provides precision and accuracy sufficient for such a decision. The advantages of speed and simplicity far outweigh the small loss of precision or accuracy.

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### References

- 1 *Electroless Plating: Fundamentals and Applications*, eds. Mallory, G. O., and Hajdu, J. B., American Electroplaters and Surface Finishers Society, Orlando, 1990.
- 2 *Modern Electroplating*, ed. Lowenheim, F. A., Wiley, New York, 1974.
- 3 Stone, F. E., in *Electroless Plating: Fundamentals and Applications*, eds. Mallory, G. O., and Hajdu, J. B., American Electroplaters and Surface Finishers Society, Orlando, 1990, ch. 13.
- 4 Bindra, P., and White, J. R., in *Electroless Plating: Fundamentals and Applications*, eds. Mallory, G. O., and Hajdu, J. B., American Electroplaters and Surface Finishers Society, Orlando, 1990, ch. 12.
- 5 Pearlstein, F., in *Modern Electroplating*, ed. Lowenheim, F. A., Wiley, New York, 1974, ch. 31.
- 6 Adzic, R. R., Avramov-Ivic, M. L., and Tripkovic, A. V., *Electrochim. Acta*, 1984, **29**, 1353.
- 7 Beltowska-Brzezinska, M., *Electrochim. Acta*, 1985, **30**, 1193.
- 8 Parthasaradhy, J. V., *J. Sci. Ind. Res.*, 1988, **47**, 639.
- 9 Okinaka, Y., *Plat. Surf. Finish*, 1985, **72**, 34.
- 10 Rothstein, R. L., *Plat. Surf. Finish*, 1984, **71**, 36.
- 11 Rothstein, R. L., *Met. Finish*, 1984, **82**, 35.
- 12 Tam, T. M., *J. Electrochem. Soc.*, 1985, **132**, 806.
- 13 Wang, J., *Stripping Analysis: Principles, Instrumentation and Applications*, VCH, Deerfield Beach, FL, 1985.
- 14 Montenegro, M. I., Pletcher, D., Liolios, E. A., Mazur, D. J., and Zawodzinski, C., *J. Appl. Electrochem.*, 1990, **20**, 54.
- 15 Barnes, D., and Zuman, P., *J. Electroanal. Chem.*, 1973, **46**, 323.
- 16 Vaskelis, A., and Norkus, E., *J. Electroanal. Chem.*, 1991, **318**, 373.
- 17 Olivi, P., Bulhoes, L. O. S., Beden, B., Hahn, F., Léger, J.-M., and Lamy, C., *J. Electroanal. Chem.*, 1992, **330**, 583.
- 18 Bagotzky, V. S., and Vasilyev, Y. B., *Electrochim. Acta*, 1964, **9**, 869.
- 19 Liang, C., and Franklin, T. C., *Electrochim. Acta*, 1964, **9**, 517.
- 20 Sibille, S., Moiroux, J., and Marot, J.-C., *J. Electroanal. Chem.*, 1978, **88**, 105.
- 21 Enyo, M., *J. Electroanal. Chem.*, 1985, **186**, 155.
- 22 Van Den Meerakker, J. E. A. M., *J. Appl. Electrochem.*, 1981, **11**, 387.
- 23 Parsons, R., and VanderNoot, T., *J. Electroanal. Chem.*, 1988, **257**, 9.
- 24 MacDonald, D. D., *J. Electrochem. Soc.*, 1974, **121**, 651.
- 25 Fletcher, S., Barrada, R. G., and Porter, J. D., *J. Electrochem. Soc.*, 1978, **127**, 1960.
- 26 Rocklin, R. D., in *Formaldehyde: Analytical Chemistry and Toxicology*, ed. Turoska, V., American Chemical Society, Washington, *Advances in Chemistry*, vol. 210, 1985, ch. 2.
- 27 Willard, H. H., Merritt, L. L., Jr., Dean, J. A., and Settle, F. A., Jr., *Instrumental Methods of Analysis*, Wadsworth, Belmont, CA, 1981, 6th edn., Pp. 719.
- 28 Fleischmann, M., Pons, S., Rolison, D. R., and Schmidt, P. P., *Ultramicroelectrodes*, Datatech Systems, Morgantown, NC, 1987.
- 29 Wang, J., Angnes, L., Tobias, H., Roesner, R. A., Hong, K. C., Glass, R. S., Kong, F. M., and Pekala, R. W., *Anal. Chem.*, 1993, **65**, 2300.
- 30 Wang, J., Brennsteiner, A., Angnes, L., Sylwester, A., LaGasse, R. R., and Bitsch, N., *Anal. Chem.*, 1992, **64**, 151.
- 31 Wehmeyer, K. R., Wightman, R. M., *Anal. Chem.*, 1985, **57**, 1989.

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