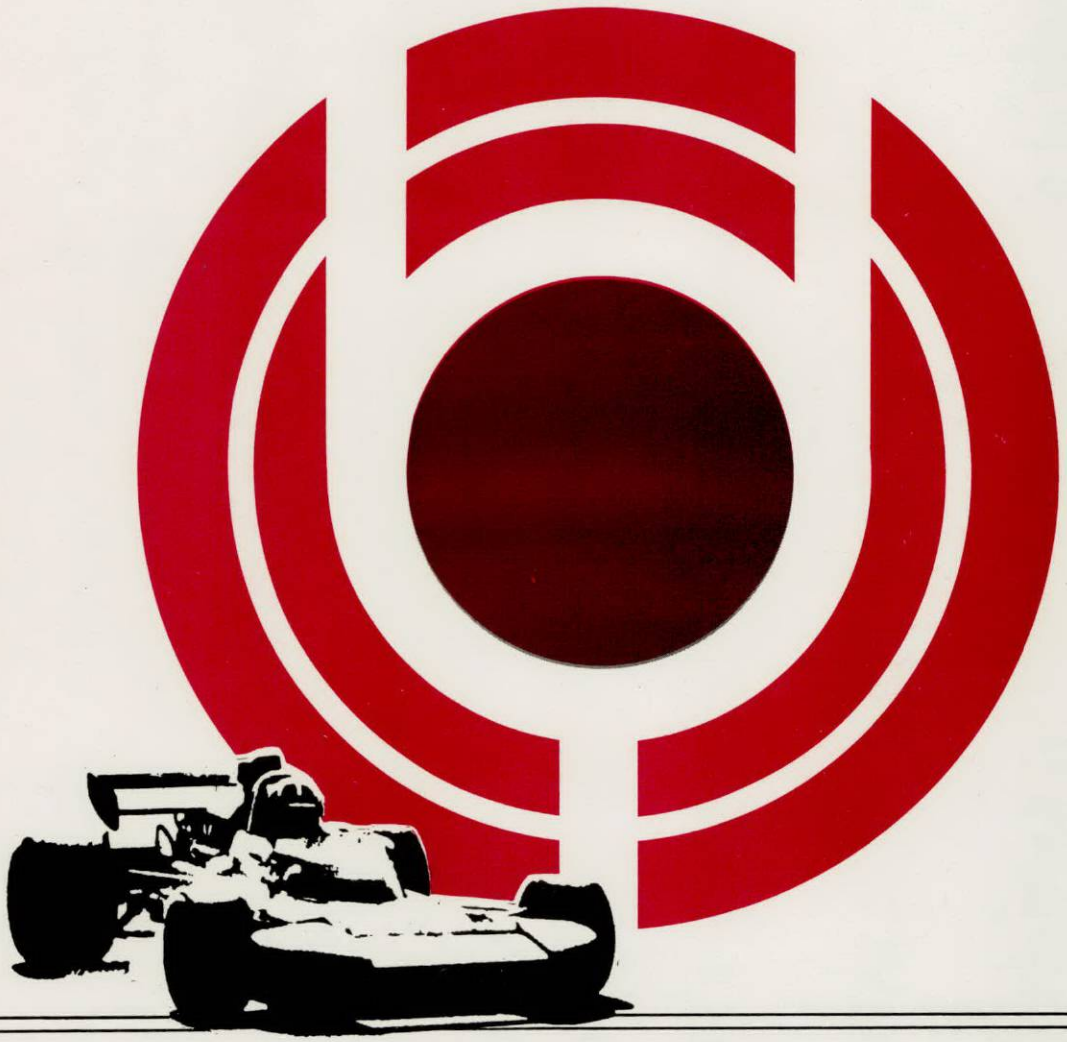
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American Electroplaters' Society
SUR/FIN '83

70th Annual Technical Conference



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Session F - Electronics II

AMERICAN ELECTROPLATERS' SOCIETY, INC.

70TH ANNUAL TECHNICAL CONFERENCE - INDIANAPOLIS, IN

ELECTRONICS II

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Session F

A New Process for Recovering Gold as Potassium Gold Cyanide

Dr. Henry H. Law and N. E. Gabriel
Bell Labs.
Murray Hill, NJ

A New Process for Recovering Gold as Potassium Gold Cyanide

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Introduction

Potassium gold cyanide is the common gold compound used in the electroplating industry. Thus, in the spent gold plating bath, the plating dragout solution, and the parts rinse water, gold exists as $Au(CN)_2^-$ ion. The present approach to recovering gold, as illustrated in Fig. 1, is to convert the $Au(CN)_2^-$ ion to metallic gold and then change the reclaimed gold back to potassium gold cyanide. With the more concentrated solutions, most of the gold is separated first either by electroplating or by precipitation with zinc. The more dilute solutions are passed through an ion exchange column for complete recovery (<1 ppm). The resins are then incinerated and the gold is recovered from the ashes. Although in principle all the gold is recovered, there are too many steps involved and it is time consuming. With the high price of gold, the longer the turn-around time, the higher is the inventory cost. A process that would directly recover gold as potassium gold cyanide would have significant cost advantages and is desirable.

One approach to recover gold as potassium gold cyanide is the use of anion exchange resins. Strong basic anion exchange resins are capable of absorbing $Au(CN)_2^-$ ion

quantitatively. AMBERLITE* IRA-400 resin has a capacity of 0.66 gram of Au/gram of dry resin.[1] Recently, we showed that a thiocyanate organic/water solution can elute the $Au(CN)_2^-$ from resins rapidly.[2,3] Thus, instead of removing the gold by electroplating or by precipitation, anion exchange resins could be used to collect all the $Au(CN)_2^-$ and a method of separating $Au(CN)_2^-$ from the eluent as $KAu(CN)_2$ would yield the desired process. Crystallization appears to be a simple way to obtain $KAu(CN)_2$ if the eluent can be supersaturated. Since the solubility of pure $KAu(CN)_2$ in water is temperature dependent,[4] it should be possible to have crystallization when the elution process is operated at a higher temperature. By running the elution in a packed bed column, the $KAu(CN)_2$ concentration of the effluent can reach the saturation limit under appropriate operating conditions.

The objective of this study is to demonstrate the feasibility of recovering directly the $Au(CN)_2^-$ ions from resins as potassium gold cyanide. Process implementation is also discussed.

Experimental

Large scale gold desorption columns (height 40 cm,

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* Trademark of Rohm and Haas Co.,Philadelphia, PA.

d=2.6 cm) were run with AMBERLITE IRA-400 and IRA-900 OH form resins. The gold-containing resins were prepared by mixing the resins (as received) with the appropriate amount of potassium gold cyanide solution to make 16 wt% gold in the dry resins. The eluent was 4.88 M KSCN in 50 vol% dimethylformamide. For each experiment the column was kept at 50°C with an external water jacket.

The AMBERLITE IRA-900 resin was filtered from the gold solution and placed immediately into the column. To pack the resin, the column was filled with distilled water, which was then pumped out. The resulting height of the resin bed was 40 cm. The column was pumped at 3.5 ml/min with fresh eluent entering the top of the column. Eluent samples were taken every minute with an automatic sampler. Approximately 400 ml of eluent passed through the column. The gold content of the eluted resin (107 grams dry) was determined gravimetrically to be <0.01%.

With AMBERLITE IRA-400 resin, two columns were run (~90 g dry resin) at two flow rates, 3 ml/min and 18 ml/min. The column was packed by pouring the resin in its original gold solution into the column, and this solution was displaced as fresh eluent was added. In both runs, potassium gold cyanide crystallized out rapidly.

The eluent samples were analyzed for gold using atomic

absorption spectroscopy and for SCN^- using the Volhard method. Samples containing potassium gold cyanide crystals were collected and cooled to 0^oC before filtering. Some samples were washed with 10 ml of 0^oC distilled water. The crystals were dried in a 50^oC vacuum oven and then analyzed for their Au and SCN^- content.

Results

Figure 2 depicts the gold concentration of the effluent versus the amount of eluent passed through the ion exchange column containing AMBERLITE IRA-900 resin. The breakthrough curve is sharp as expected because the exchange between $Au(CN)_2^-$ and SCN^- at 50^oC reaches equilibrium in about 10 minutes.[3] To determine the extent the gold was eluted, the gold content of the resin was analyzed. Because the dried resin contains less than 0.01% gold, the elution is complete. Another observation from this experiment was that potassium gold cyanide did crystallize out as white crystals. Without washing, one sample of the dried crystals contained 60.8% gold or 89% $KAu(CN)_2$. The difference is attributed to KSCN contamination. This is reasonable because the sample filtrate has a relatively high SCN^- concentration. Figure 3 shows the SCN^- concentration of the effluent.

Experiments with AMBERLITE IRA-400 resin showed similar

behavior--the potassium gold cyanide crystallized out quantitatively. Without washing, the crystals also had a 90% content of potassium gold cyanide. With washing, the crystals had a gold content of 68.3%, i.e., they were 100% pure $KAu(CN)_2$.

Discussion

Pure potassium gold cyanide is recovered quantitatively and better than 99.99% of the gold is eluted from AMBERLITE resins in the column operation. It takes less than 4 ml of eluent/gram of dried resin to accomplish such a separation. This ratio of eluent volume/gram of dried resin is much smaller than that of the work of Burstall et al.[1] With the laboratory set-up, the complete elution of gold takes less than two hours. When the process is optimized, a shorter time may be expected. Scale-up of this arrangement should not pose any difficulty.

These promising results suggest a new approach to recovering gold based on the gold plating facility. Major sources of gold to be reclaimed are the spent plating bath, dragout solution, and parts rinse solution. A set-up involving anion exchange resin columns can perform most of the recovery work. First consider recovering gold from solutions. The spent plating bath and dragout solution have a high concentration of gold. A typical bath (75 liters) in

a high speed strip plater has five pounds of gold in $Au(CN)_2^-$ form. Instead of reducing the $Au(CN)_2^-$ ions to metallic gold either by plating or by adding zinc, only about 7.6 pounds of dried resin are needed to absorb that amount of gold. A column containing Ø.5 cubic foot of AMBERLITE IRA-4ØØ wet resin would have 45% extra capacity.

Figure 4 depicts one process scheme. Two columns are used in the absorption step. The first column removes most of the gold and the second column provides the back-up. Column #2 becomes the first column when gold is eluted from Column #1. The effluent from the crystallizer may be recycled if the KOH is removed either by electrodialysis or Donnan dialysis.[5] Once any start-up problems are solved, it should take at most three days to recover the potassium gold cyanide from the plating bath: one day for absorption, one day for elution and crystallization, and one day for drying of the potassium gold cyanide. At other times, the columns can be used to absorb gold from the rinse solutions.

This proposed scheme of using resin columns to recover gold as potassium gold cyanide is more cost effective than other processes. It is also simple enough that each plating facility could have its own recovering system. The reduction of inventory cost and the savings from shipping the scrap to the refiner would be substantial.

ACKNOWLEDGMENT

Rohm and Haas Co., Philadelphia, PA, kindly supplied the resins used in this study.

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TABLE 1

CAPACITY OF AMBERLITE IRA-400 RESIN FOR SEVERAL METALLIC CYANIDE COMPLEXES[1,7]

METAL	COMPLEX	Capacity, Metal Adsorbed per g Dried Resin	
		GRAM	MILLIMOLE
Gold	$Au(CN)_2^-$	0.66	3.3
Silver	$Ag(CN)_2^-$	0.34	3.2
Nickel	$Ni(CN)_2^-$	0.11	1.8
Copper	$Cu(CN)_4^{-3}$	0.08	1.3
Cobalt	$Co(CN)_6^{-3}$	0.08	1.3
Zinc	$Zn(CN)_5^{-3}$	0.08	1.3
Iron	$Fe(CN)_6^{-4}$	0.05	0.9

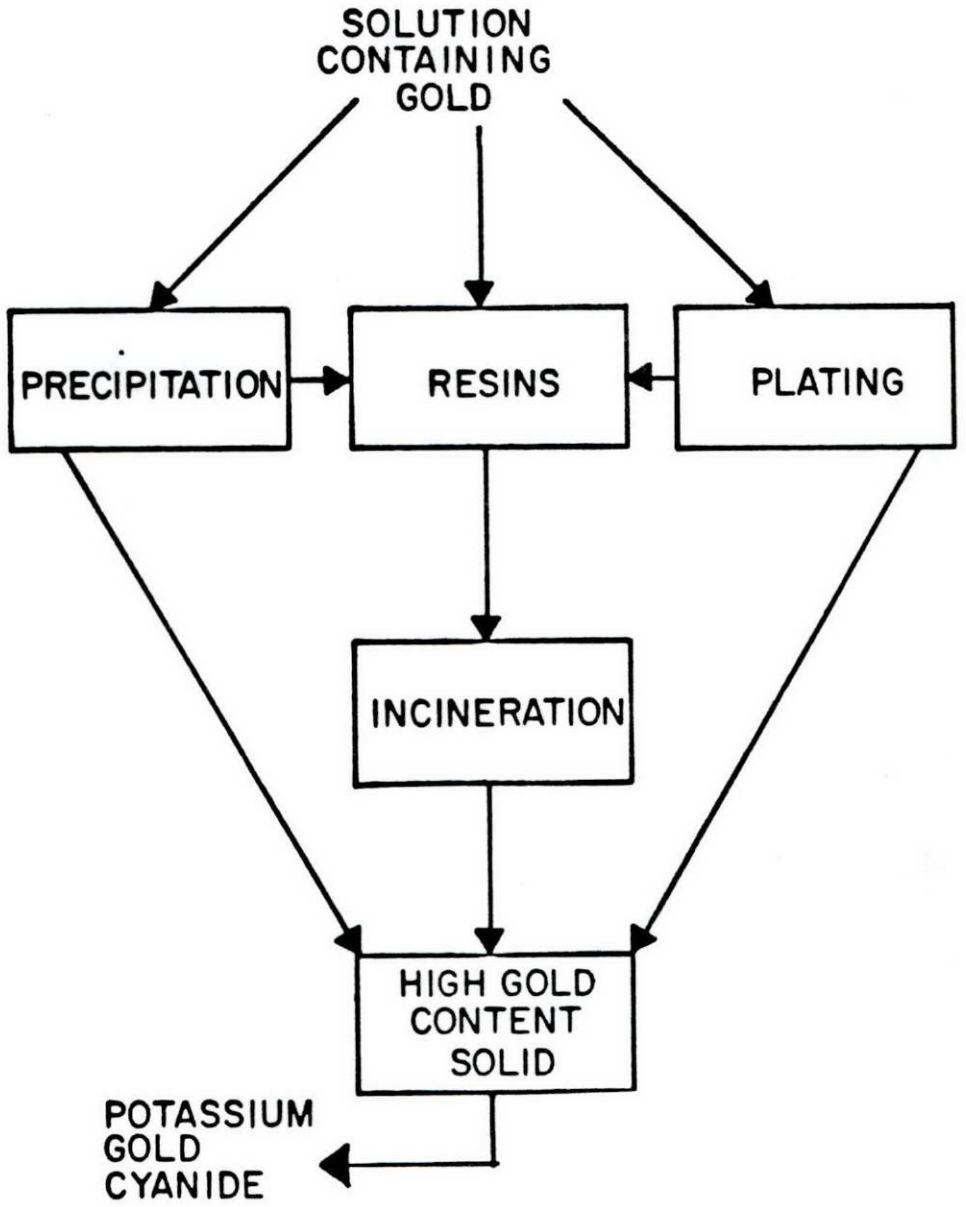


Figure 1 Present process scheme of recovering gold.

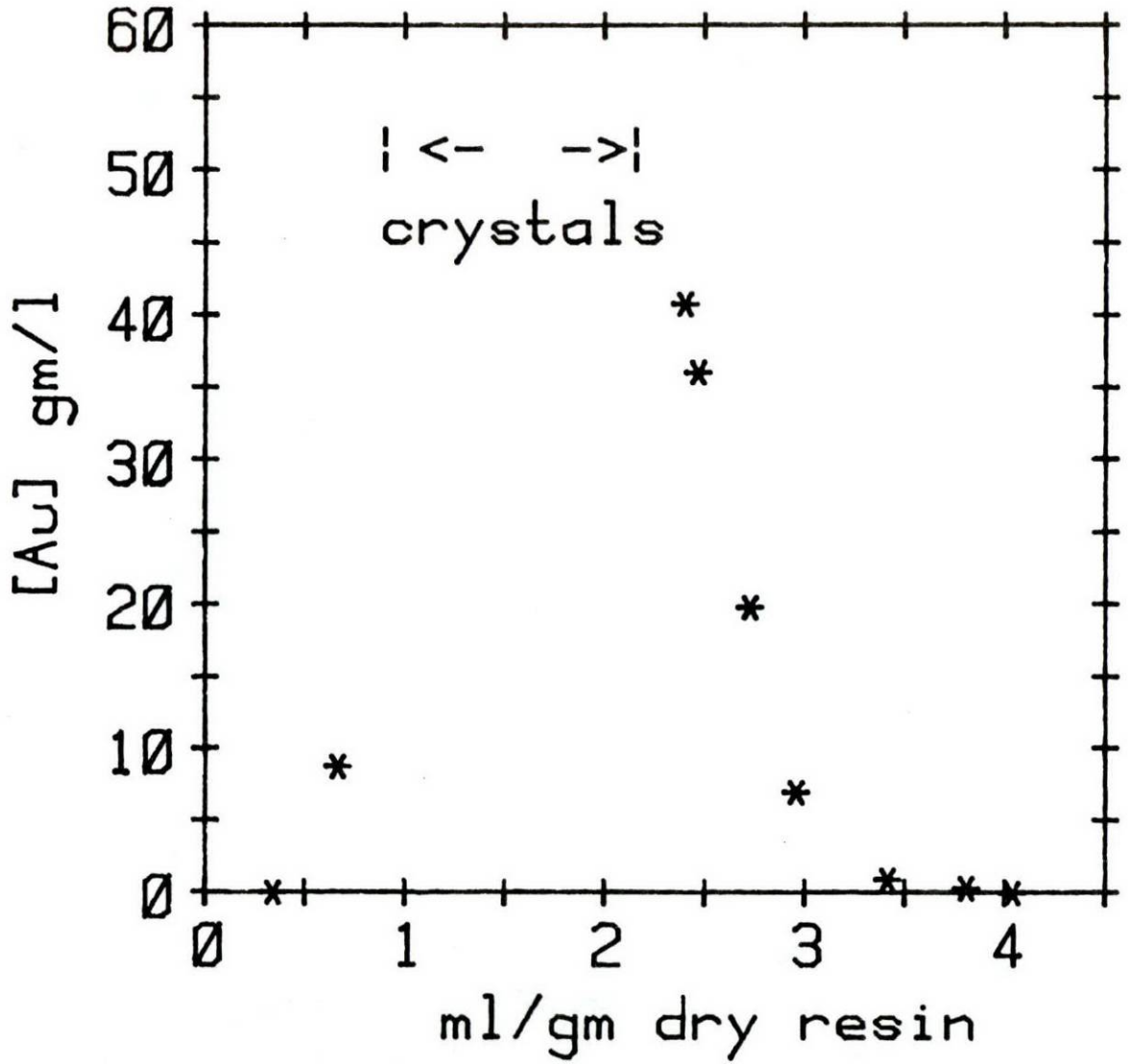


Figure 2 Gold concentration of the effluent versus eluent volume/gram dried resin, 50°C, 3.5 ml/min, 107 grams of dried resin (AMBERLITE IRA-900 OH).

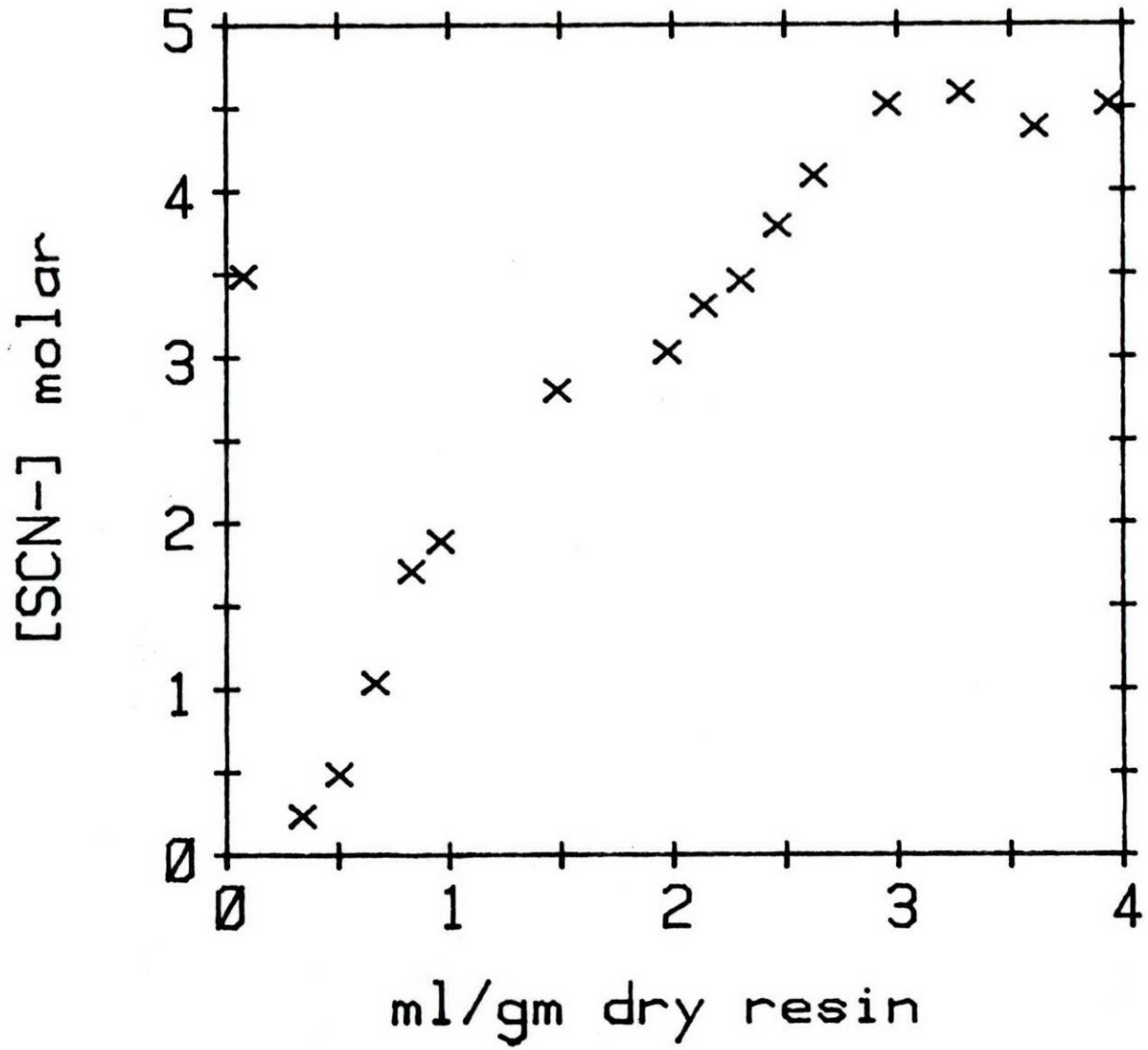


Figure 3 Thiocyanate concentration of the effluent versus eluent volume/gram dried resin, same column as Fig. 2.

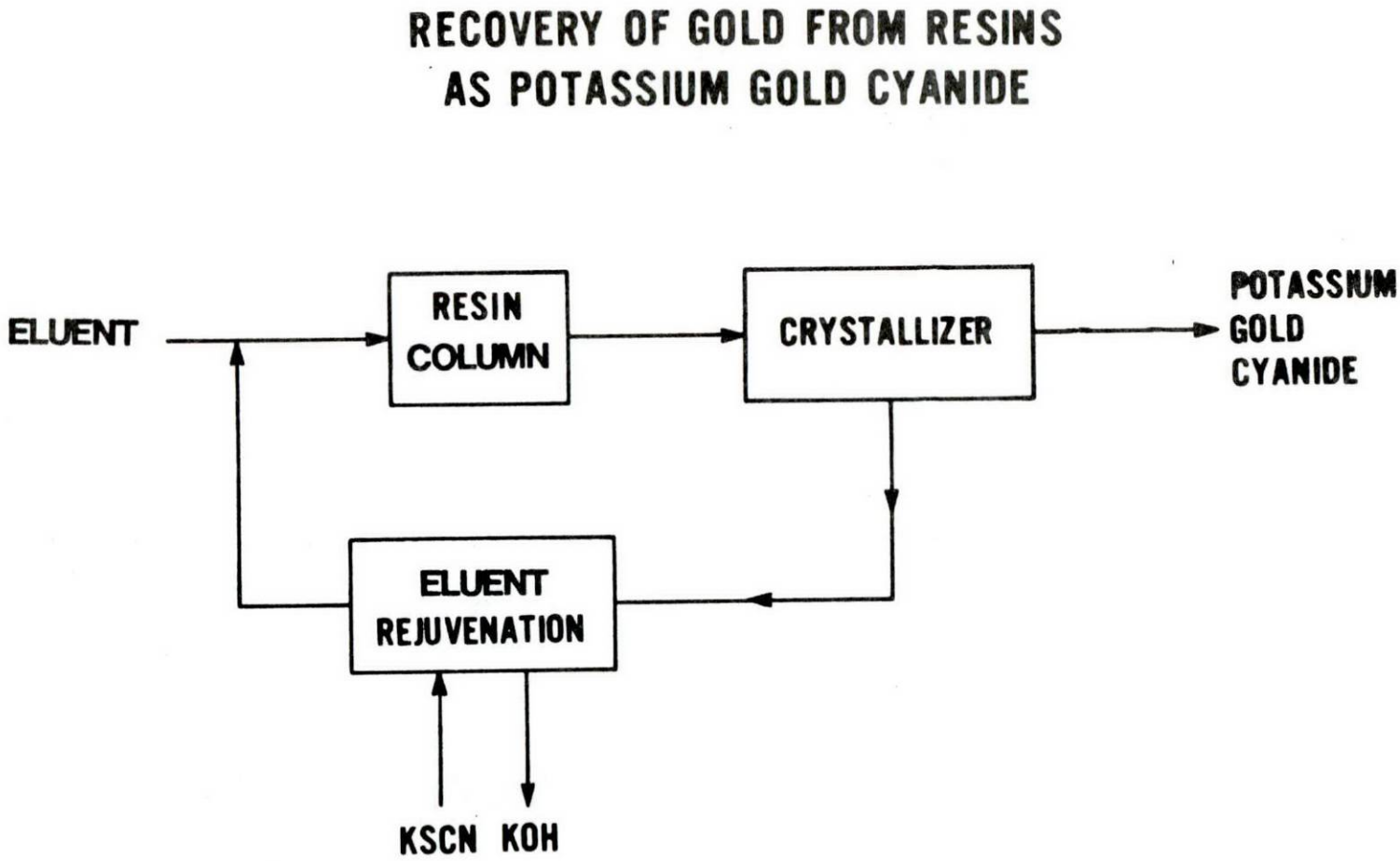


Figure 4 Proposed process scheme for recovering gold from solution as potassium gold cyanide.

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Session F

Analysis of Organic Components in Copper Plating Baths by Liquid Chromatography

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Analysis Of Organic Components In Copper Plating Baths By Liquid Chromatography

David A. Zatko and Walter O. Freitag
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INTRODUCTION

While the copper plating of printed circuit boards is a straight-forward chemical operation in many installations, present and future computer boards require finer lines, higher aspect ratio of thru-holes and ever larger number of layers. A single load of multilayer substrates may be worth several tens of thousands of dollars at the stage when the thru-holes are plated, and loads lost through plating defects cannot be tolerated.

Improving the quality of acid copper plating evolves into a task of monitoring the chemical state of the plating bath. This is trivial with respect to the basic ingredients: $CuSO_4$ and H_2SO_4. The particularly difficult part is monitoring the low concentration level of organics that are added as plating modifiers and the extra contaminants that arrive by leaching or accident. Generally, the problem is further compounded by the proprietary nature of the additives and the fact that the actual active organics may be 1) decomposition products of the orignial additives, 2) impurities accompanying the additives, and 3) combinations of normally inactive constituents. In the past, even the additive manufacturers have had only a rough quality control over their productions.

Typically the Hull cell test is used to judge the state of a bath and its future performance. However, bath analysis must be considered at all steps: during plating, during clean-up, during conditioning and during storage. This paper shows how high performance liquid chromatography (HPLC) can be used to obtain information about the organic constituents in a acid copper bath.

HPLC TECHNIQUE

In its simplest form the HPLC technique involves pushing a small liquid aliquot of the sample through a fine particle material chosen to selectively retard components relative to the sample liquid front. The retarded components can then be detected by various means and even collected separately if desired.

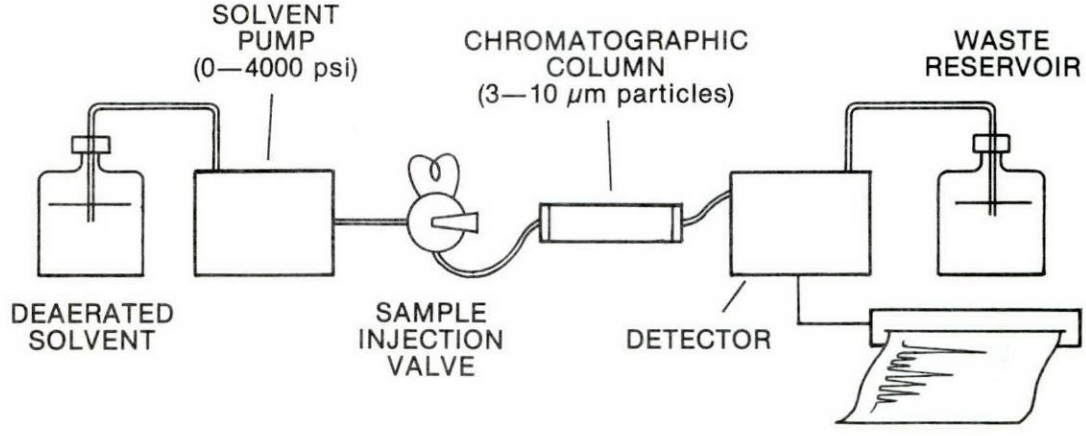


Figure 1. Components of a Typical High Performance Liquid Chromatograph

Development of an HPLC method for a particular analysis requires finding the best choice of solvent, column packing and detector based upon the starting material being analyzed. Since the starting additives are proprietary secrets and the decomposition products are undocumented, the preliminary HPLC investigation must be wide ranging in scope; several columns, solvents and detectors must be tried. HPLC cannot identify the molecular composition of a component without ancillary information from a standard or from other characterization techniques. This identification can be a very time-consuming and difficult task.

HPLC can provide an easy way of monitoring a component if conditions can be found to separate that component from the rest of the sample. Of all the components found in a bath, presumably only a few are critical to the quality of the deposit. Therefore once components have been detected by HPLC, they should be tested by an electrochemical technique to determine their effect on the plating. It would be best if only the important components could be monitored.

INSTRUMENTATION

The HPLC system used consisted of a high pressure pump*, an injector valve** with 200 μl filling loop, Z Module column holder***, a U.V. detector**** equiped with a 254 nm filter and a 10 mV strip chart recorder. The columns were #RPC18 bonded phase on 10 μm silica. Solvents were filtered and deaerated using a 0.2 μm filter. Samples of additives were filtered before injection into the HPLC system. Since the plating bath contains 10% H_2SO_4 which may be detrimental to the silica packing, the column was checked by frequently running a standard solution of an additive. The column was not seen to degrade significantly over the time of 100 injections.

PROCEDURES

Samples were run in the isocratic mode. Water was used to elute water-soluble components; then the system was flushed with acetonitrile to remove the more non-polar components. It was found that the acetonitrile had to be flushed out with at least 100 ml of H_2O in order to obtain reproducible retention times in subsequent sample runs.

Isocratic runs were made on pure additive formulations with 30% acetonitrile/ 70% H_2O to resolve components and obtain a total distribution of components. Addition of a paired-ion reagent was used to obtain better separation of peaks. Tetrabutylammonium tetrafluroborate was preferred; tetrabutylammonium phosphate could not be used because it forms insoluble copper phosphate species in the column.

RESULTS

This study was confined to using ultraviolet detection of components in the samples. The U.V. detector is selective for those compounds having significantly strong chromaphores at 254 nm. Peak height is dependent on both concentration and U.V. molar absorptivity and the latter is unknown for any of the single components in the samples used here. Consequently the chromatographic peaks should not be taken as a direct indication of sample concentration.

*Milton Roy Co., Riviera, FL
**Waters Associates, Milford, MA
***Rheodyne Inc., Cotati, CA
****ISCO, Lincoln, NE

Figure 2 shows the effect of the paired ion reagent on the resolution of PCM-T***** components using the C18 column and 30% acetonitrile. The intense U.V. peak at 2.2 minutes is moved to around 5.3 minutes by the reagent. Thus this component is probably an anionic system that interacts strongly with the $(Bu)_4N^+$ ion. The other components show only small shifts and therefore are probably not anionic.

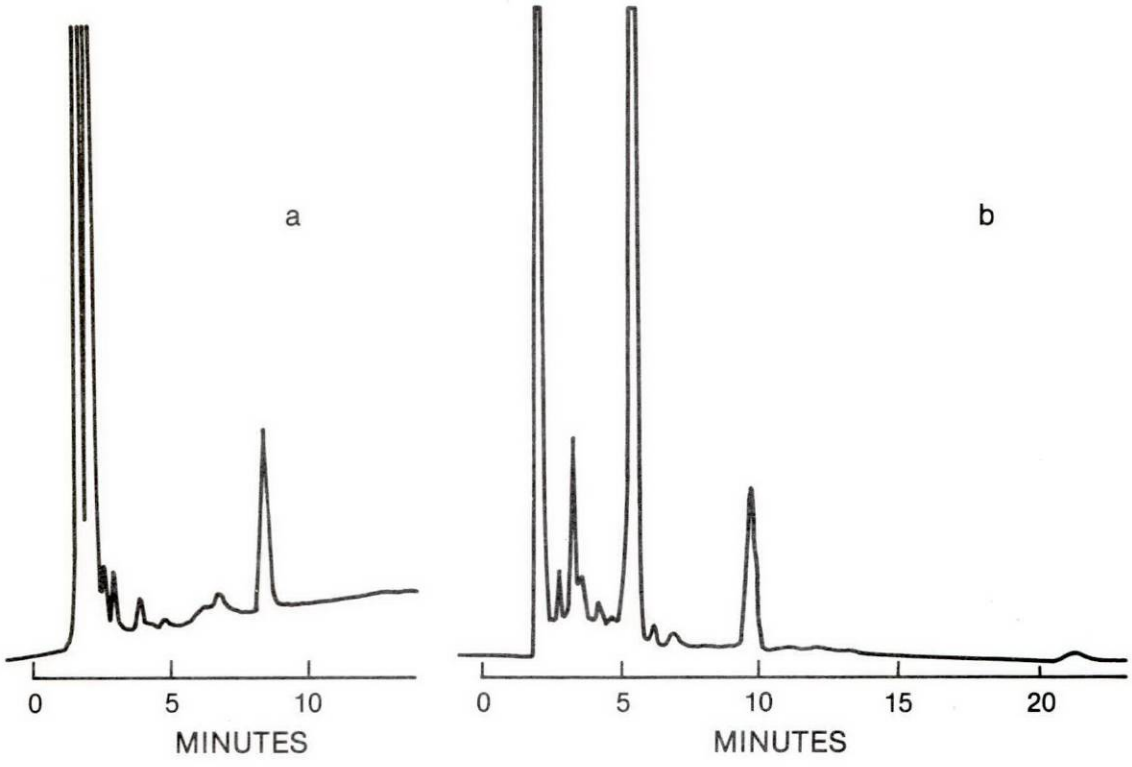


Figure 2. Chromatograms of Pure PCM-T, U.V. Detection:

a) 30% acetonitrite/70% H_2O, 0.2A full scale, 254 nm, C18 column

b) Same as A but with 0.1F paired ion reagent in eluent

Several components are particularly sensitive to detector wavelength. Figure 3 shows typical chromatograms taken at 254 and 280 nm. The components at 3.2 and 9.7 minutes are obviously strongly dependent upon the wavelength. Preliminary data from another U.V. detector system has indicated that additional peaks will appear if detection is done at 210—220 nm.

Several columns were tried in order to obtain as large a separation of components as possible. Figure 4 shows the results with an SCX column which has a bonded cation exchange functional group on silica. Water elution gives high resolution but the peaks are asymmetric indicating a particularly strong component interaction with the stationary phase. Increasing the acetonitrile content of the mobile phase decreases the retention time and resolution of all the components. The general conclusion was that the SCX column offered no distinct advantage over the C18 column.

*****LeaRonal, Freeport, NY

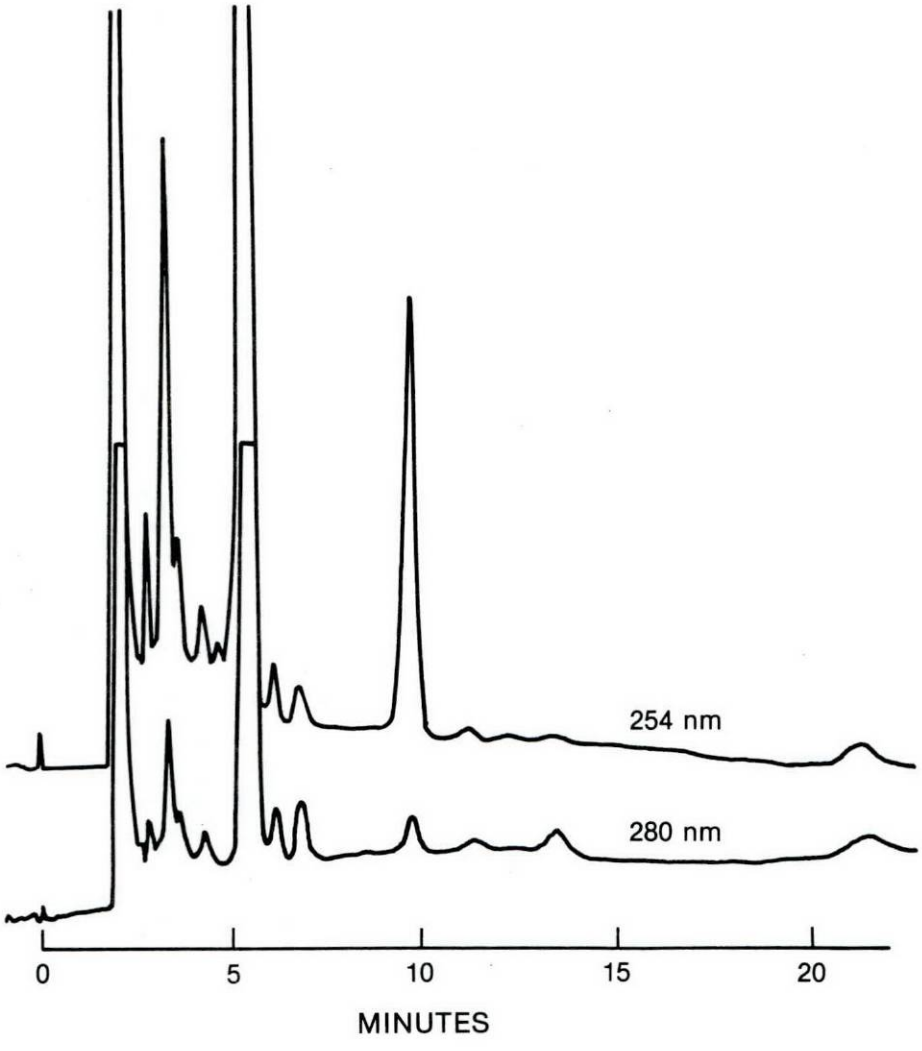


Figure 3. Chromatograms of Pure PCM-T at Two Wavelengths:
a) 254 nm
b) 280 nm

One of the operations in the management of production baths is carbon treatment to remove impurities and reestablish a "clean" bath. Figure 5 shows the effect of carbon treatment done on a laboratory scale on a diluted pure additive sample to determine which components are sensitive to absorption. Only 10 minutes was allowed for the treatment before the sample was filtered and injected into the HPLC system.

As can be seen the peaks above 5 minutes showed considerable changes, whereas the presumably polar components (below 5 minutes) showed little or no reduction in intensity on carbon treatment. It is not surprising that the less polar compounds would be more sensitive to carbon treatment. It indicates that carbon treatment may not remove all the components. Apparently additional chemical treatments often used prior to carbon treatment are needed to affect the more polar components. It is apparent from Figure 5 that the completeness of carbon treatment can easily be monitored by HPLC measurements.

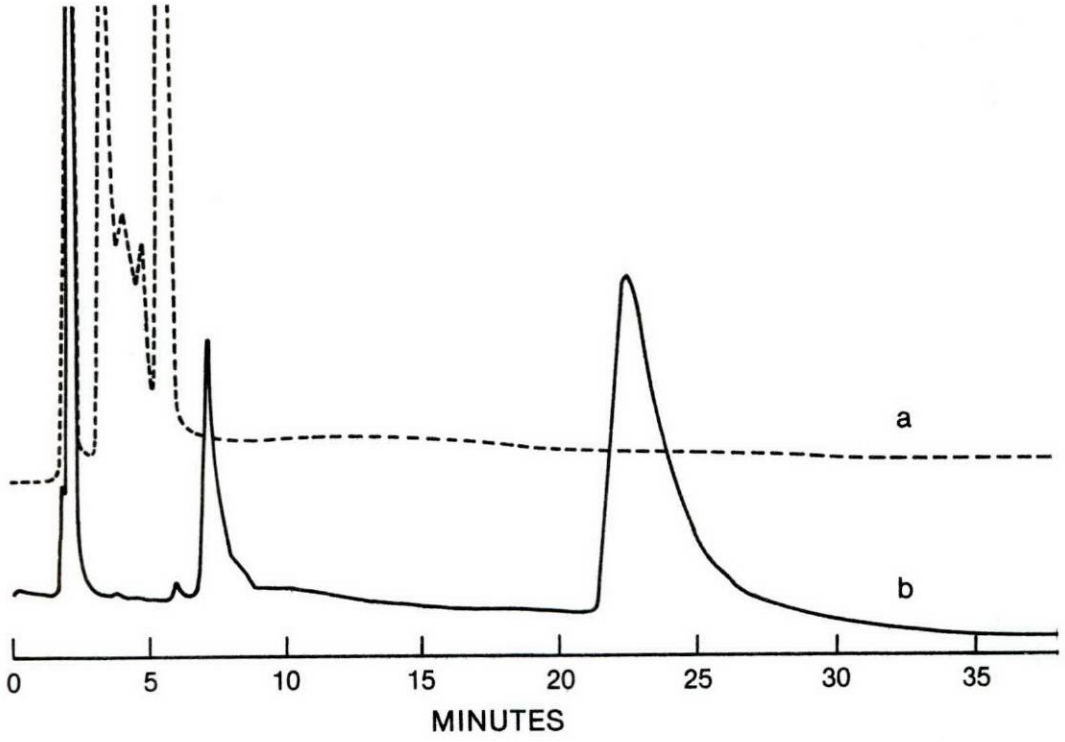


Figure 4. Chromatograms of pure PCM-T on a Cation Exchange Column:
a) 50% acetonitrile/50% H_2O, 254 nm, 0.2A full scale
b) 100% H_2O, 254 nm

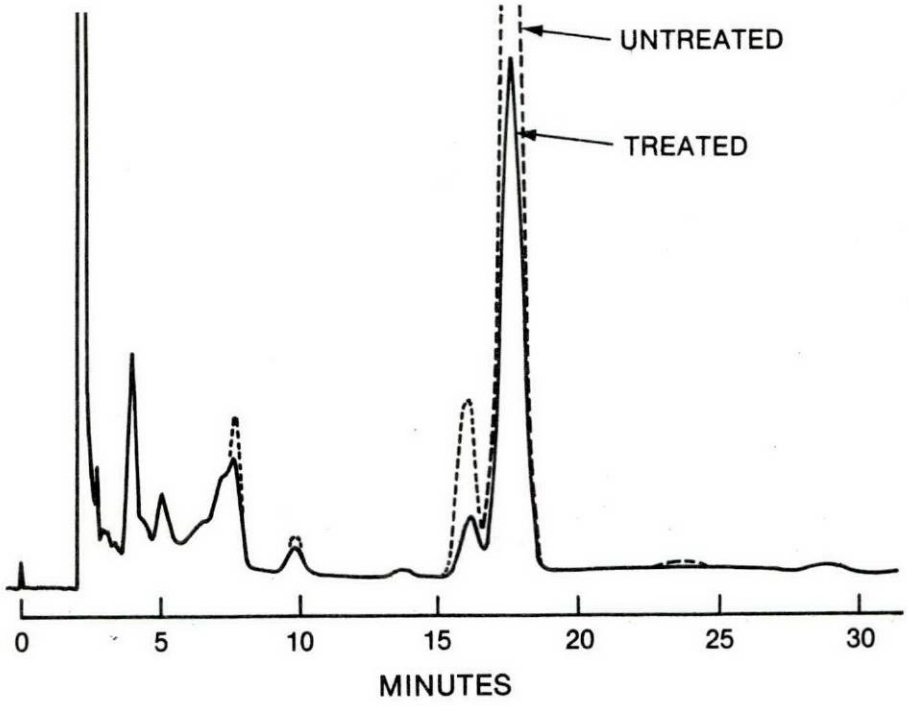


Figure 5. Chromatograms of Carbon Treated and Untreated 50% PCM-T, 254 nm, 0.05A full scale

Analysis of samples from actual production baths has centered upon the water elution fractions. Figure 6 shows several typical chromatograms. Samples contained $CuSO_4$ and H_2SO_4 in the usual concentrations and PCM-T nominally at a level of 4 ml per liter of bath solution, but actually much higher based on cyclic voltammetic methods [1]. The peak at 5 minutes in these solutions comes from the original PCM-T. This PCM-T peak changes in intensity with use and processing of the bath. Significantly the peaks between 2 and 5 minutes in the production bath are absent in pure PCM-T. These may be indicators of the amount of additive decomposition that has occurred in using the bath. Just before carbon treatment these peaks are very intense. They are reduced significantly by chemical and carbon treatments and then build up again upon adding brightener and using the bath.

Figure 7 shows samples from a bath which was not behaving correctly, following a carbon treatment. Surprisingly, no additive peaks showed up in this bath when brightener was added or after plating resumed. These HPLC results clearly show that the additives had not been brought up to the levels existing prior to the carbon treatment cycle.

Separation of the sample components into fractions make it possible to study the electrochemical behavior of each component or group of components. A preliminary study of the cyclic voltammetry of the HPLC water-eluted components has been done. When $CuSO_4$ and H_2SO_4 was added to the water-eluted fraction and subjected to cyclic voltammetry, no copper deposition suppression was found. This indicates that the HPLC water fraction components and the CV suppressors are different species in the plating baths.

CONCLUSIONS

The water eluted, U.V. detected, HPLC technique measures one of the components in the original PCM-T (the 5 minute peak, Figure 6) and a group of polar compounds (below 5 minutes) which are absent in PCM-T but present in production tanks. A third group, the copper-deposition suppressors, are monitored independently by CV.

(1) W. O. Freitag and M. Manning, "Analysis of Additives in Acid Copper Baths by Cyclic Voltammetry" in these preceedings.

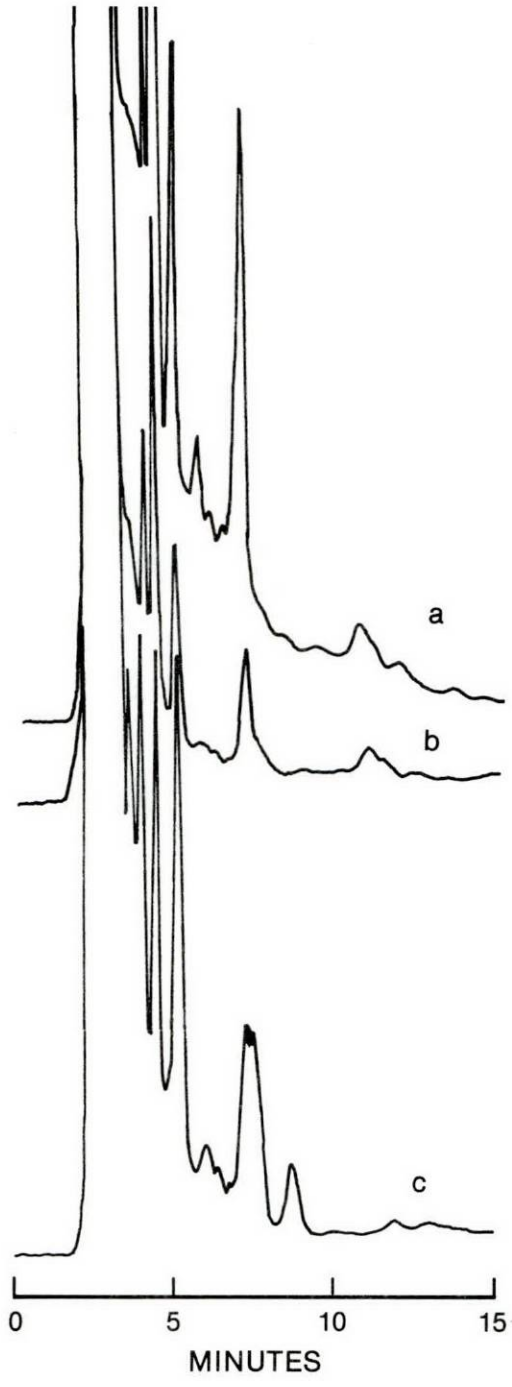


Figure 6. Chromatograms of H_2O Elution Fraction of Production Bath Samples:

a) Bath after long period of use

b) Bath after typical clean-up treatment

c) Bath after put back in use

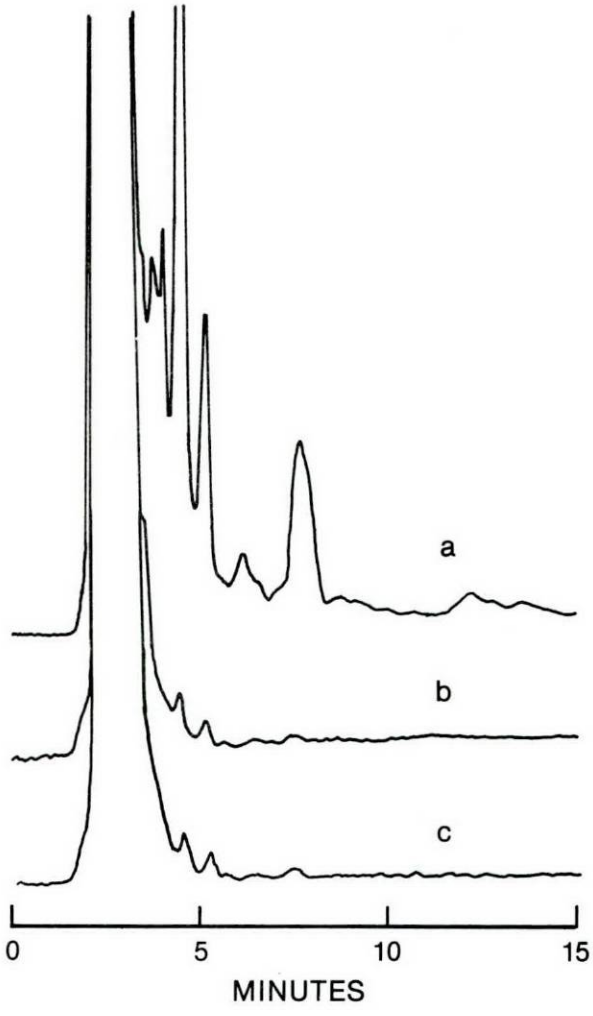


Figure 7. Chromatograms of H_2O Elution Fraction of Production Bath Sample:

a) Bath after long period of use

b) Bath after cleanup

c) Bath put back into use but malfunctioning

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Electronics II
Session F

Multi-Test Capability of Plating Parameters Using a Continuous Flow Analyzer

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MULTI-TEST CAPABILITY OF PLATING PARAMETERS USING A CONTINUOUS FLOW ANALYZER

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Introduction

Analytical chemistry is a science of measurement that affects every technical discipline, whether it be for process information, quality control or to satisfy government regulations. The analytical requirements will vary with respect to need from infrequent individual analyses to continuous on-line monitoring of critical parameters.

The plating industry is no exception. Analysis of key parameters and plating contaminants continue to be of moderate concern. Depending upon the particular need, the kinds of analyses and total number, will vary considerably in scope and whose workload cannot be predicted in advance. To obtain maximum efficiency in the laboratory flexibility of procedures is most important.

Laboratory management must weigh the quality of data needed against factors influencing the cost of obtaining them. Further, other criteria must be satisfied for an approach to qualify in handling a variable, unknown workload. Qualifications are:

- high analysis rates to process samples quickly
- excellent precision and accuracy
- highly-selective methods to meet individual requirements
- wide spread use to establish validity through round-robin sample analysis and controls.

In addition, the methodology that is used, emphasis must be placed on the:

- type of analyst required
- laboratory environment.

To meet the above stated criteria, instrumental methods are always preferred because of its inherent objectivity. More specifically, continuous flow analysis provides the additional wherewithal to automate wet-chemical procedures. Flexibility of the analyzer is accomplished by changing the metering of reagents specific for a particular assay by a low-cost pump tube harness.

Experimental

The multi-test continuous flow analyzer consists of the following basic modules: sampler, pump, colorimeter, recorder, and multi-test cartridge. The physical arrangement of these modules is schematically represented in Figure 1.

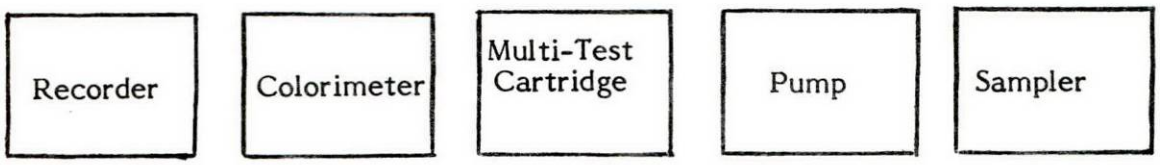


Figure 1. Schematic Representation of the Multi-Test Continuous Flow Analyzer

Samples and standards to be analyzed are placed on the turntable of the sampler which is then automatically sequenced into the analytical system. The pump via its pump tube harness continuously meters reagents into the multi-test cartridge where the wet-chemical reaction takes place. The absorbance of the chromogen that is produced is measured by the colorimeter and the results are displayed on the strip chart recorder. With appropriate calibration of the system by using standards, the results are read directly off the recorder and simultaneously provides a permanent record.

To convert the analyzer to accommodate another test only the pump tube harness located in the pump along with the optical filter in the colorimeter must be changed. Each harness is specific for each assay. The sequence of events that follow when an assay is completed is to first cleanse the system with water, remove the pump tube harness, replace it with the next harness of interest, and allow the reagents time to equilibrate in the analyzer. The system is now ready to test for the next parameter. The changeover time requires an elapsed time of approximately 25 minutes of which only 5 minutes are required to change the pump tube harness.

The pump tube harness and multi-test cartridge interface is schematically represented in Figure 2.

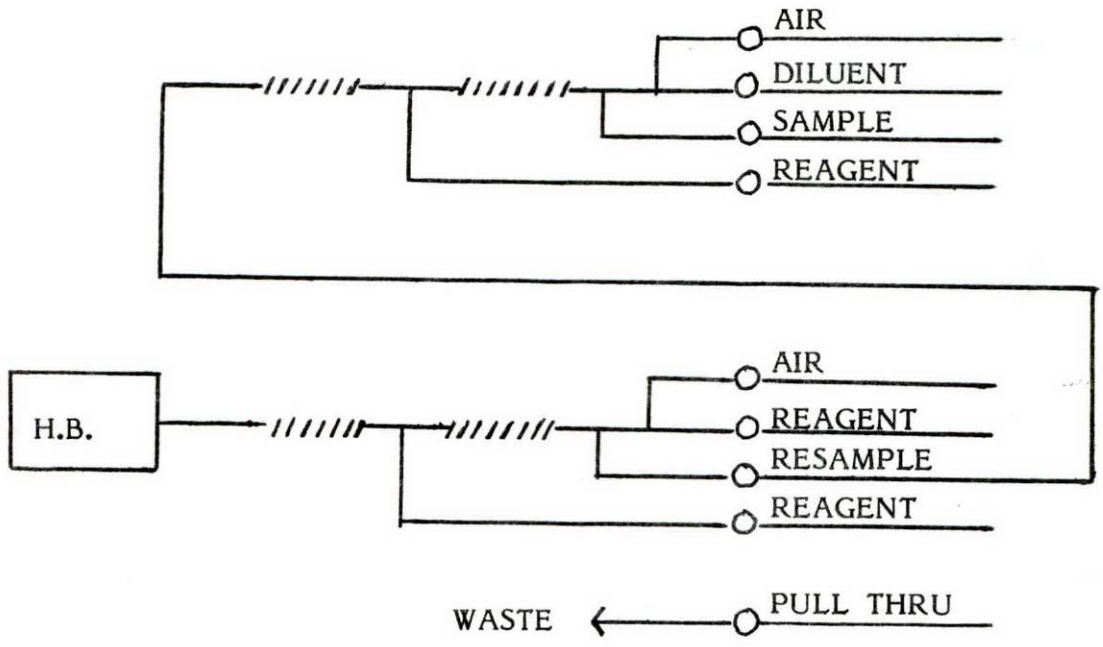


Figure 2. Interface of Pump Tube Harness and Multi-Test Cartridge

Discussion

Presently there are a total of 19 different parameters covering a wide concentration range. Table I lists these parameters in their respective baths. Several of the bath parameters require manual pretreatment. The pretreatment is necessary because of the following:

- dilution to meet the stoichiometric needs of the multi-test cartridge
- prevent precipitation
- maintain oxidation-reduction states.

Based on a workload of 50 samples and 10 standards, an analyst can perform a total of six (6) different assays in an eight (8) hour day. All the assays exhibit a coefficient of variation of $\pm$ 1% or less.

Conclusion

The multi-test continuous flow analyzer provides a highly flexible system to perform many different types of plating bath related analyses. The flexibility is accomplished by replacing pump tube harnesses that are specific for each analysis along with the optical filter. The pump tube harness is a low cost item that is treated as a disposeable item after 200 hours of use.

Change over time takes approximately 25 minutes and as many as six assays can be accomplished in one day based on a workload of 50 samples.

Table I. Parameters Applicable to the Multi-Test Continuous Flow System

PARAMETERS	RANGE	BATH	HEAT BATH / WAVE LENGTH		COMMENTS
1. Acid	.25-25% HCl	Regeneration	RT	520	
2. Acidity	.06-3.0%	Acid/Persulfate	RT	550	
3. Chloride	60-120mg/L	Copper-Dye	RT	480	10 fold dilution with reagents
4. Copper	1-10%	Cyanide Brass	RT	590	
5. Formaldehyde	.2-10 g/L	Electroless Copper	45°C	560	Dilution with reagents
6. HCl	3-10% v/v	Immersion Tin	RT	520	Manual 1:5 Dilution with water
7. Na Carbonate	1.-50 g/L	Carbonate Bath	RT	600	
8. Na Chlorite	1.6-80 g/L	OH/Chlorite	RT	480	No dilution
9. NaOH	.1-8.0 g/L	OH/Chlorite	RT	600	
10. Na Silicate	1.6-80 g/L	Silicate Bath	RT	550	
11. Palladium	1.2-2.6 g/L	Proprietary	RT	550	Manual dilution 1:20 with reagents
12. Palladium	0.02-0.2 g/L	Regeneration	RT	470	
13. Persulfate	100-140 g/L	Acid/Persulfate	37°C	450	
14. Tin II	80-150 g/L	Proprietary	RT	660	Manual dilution 1:20 with reagents
15. Tin II	0.5-55 g/L	Regeneration	RT	450	
16. Total Tin	42-80 g/L	Proprietary	37°C	520	Manual dilution 1:20 with reagents
17. Total Tin	.0-14 g/L	Immersion Tin	37°C	520	Manual dilution 1:20 with reagents
18. Total Tin	20-40 g/L	Regeneration	37°C	520	Manual 1:10 dilution with reagents
19. Zinc	.2-2.0%	Cyanide Brass	RT	620	Manual dilution 1:15 with reagents

F-4

Electronics II
Session F

Analysis of Additives in Acid Copper Baths by Cyclic Voltammetry

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Analysis of Additives in Acid Copper Baths by Cyclic Voltammetry

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Sperry Univac, Blue Bell, Pa.

INTRODUCTION

The control of additivies and contaminant concentrations in acid copper baths for multilayer printed circuit boards has been an elusive goal. The traditional means, such as Hull cell plates or "J" cell tests, are insufficiently precise and frequently yield misleading results. A major difficulty is that the additive systems consist of mixtures of proprietary materials, the individual components of which are not necessarily pure components and may themselves vary in strength or activity from lot to lot. The mechanisms by which the additives achieve their beneficial results are usually not known by the plater, and frequently not even by the vendor. The components are consumed or converted at different rates as a bath is used so that continued addition of the complete mixture may result in a gradual build-up of one of them until it is far out of proportion with respect to the others. Furthermore, some additive species are converted by oxidation or reduction at the electrodes to other species which also affect brightness, leveling, or mechanical properties of the deposits. And added to these are whatever other compounds are introduced accidentally into the plating bath such as photo-resist leachates.

The work reported here was done as part of a major effort involving research and production personnel to provide analytical methods using cyclic voltammetry (CV), HPLC, and other techniques.

A very attractive approach to this complex situation has been proposed recently by Tench and co-workers who applied CV at a rotating disk electrode (RDE) to the measurement of brightener concentration in pyrophosphate [1,2] and acid copper baths [3,4]. The assumption is made that those species responsible for brightening or leveling action are also active in a CV scan. Briefly, their method consisted of cycling a platinum RDE between a cathodic voltage just below where copper begins to deposit, to an anodic limit determined by the nature of the additive system. An anodic current peak is obtained which represents the dissolution of the copper deposited during the cathodic part of the cycle. This peak is integrated and its area, A_r, obtained while the RDE is rotating, is compared with the area obtained when the RDE is stationary, A_s, in the same sample of solution. The ratio A_r/A_s was found to correlate well with additive concentrations in freshly made-up (virgin) solutions.

Applied to production solutions, the method is more successful with pyrophospate than with acid copper solutions. With pyrophospate baths, additional information about the chloride ion concentration and the level of organic contaminants can be obtained by recording anodic currents in other parts of the voltage scan. A dedicated microprocessor-controlled instrument has been developed to carry out this analysis and is available commercially.*

This method has also been recommended for acid copper solutions using both polyether-sulfide-based additives [3] and sulfonium alkanesulfonate (SAS) additives [4]. But when applied to production solutions using these additive systems, it became apparent that contaminants and/or conversion products dominated the CV results. Correlations could not be made between data on production samples and calibration curves made on virgin baths. Modifications to this approach were necessary before information useful to plating line management could be obtained.

EXPERIMENTAL

Most of the measurements described here were made using the Qualiderm* instrument and the RDE assembly supplied with it. Additional experiments were made using an IBM** rotating disk electrode. The RDEs were fitted with platinum disks 4 mm in diameter which were pretreated by repeated cycling in additive-free copper bath (with chlorides). The "dilution-titration" experiments were done using the cell assembly shown in Figure 1. The microburette shown was often replaced by a micropipette for making additions to the Test Solution.

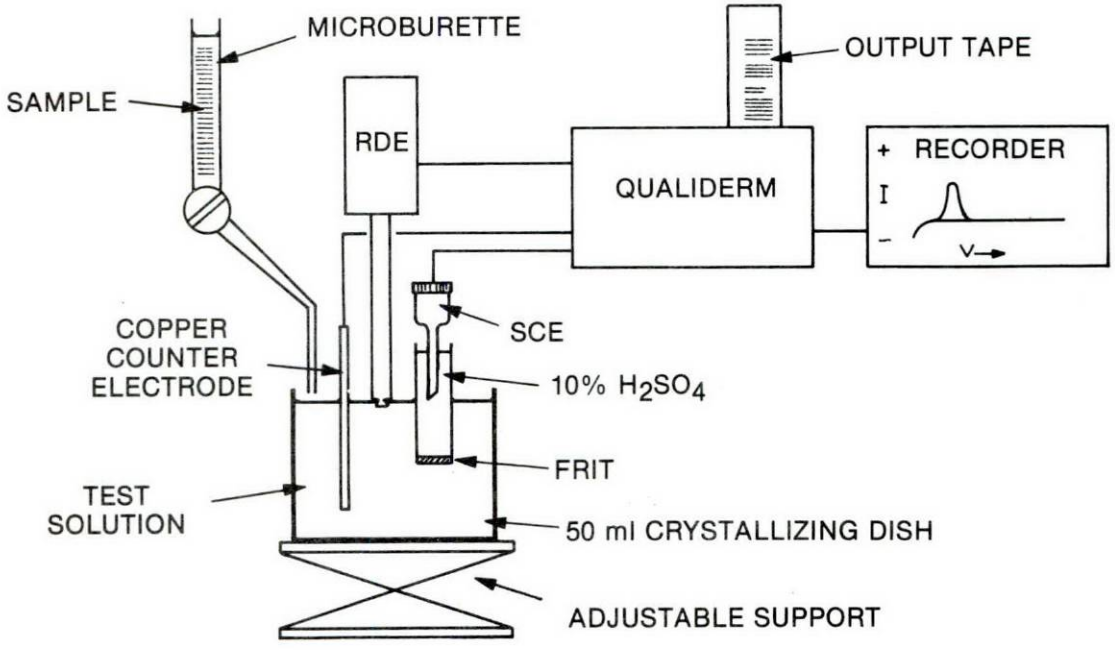


Figure 1. Test Cell for Dilution-Titration Procedure

The additive systems studied were Copper Gleam PCM*** which is an SAS-type system, and Cubath M-HY,**** a sulfide-polyether type.

The dilution-titration is carried out as follows: 25.00 ml of Test Solution is added to the test cell and the electrodes are immersed. The Test Solution was usually additive-free acid copper bath such as Cubath M make up or equivalent. The copper sulfate and sulfuric acid concentration closely matched those used in production. The chloride level was 60 ppm. The Qualiderm is set in the mode in which it continuously cycles between its voltage limits while printing out the value of A_r for each cycle. RDE speed is 2500 RPM. The anodic voltage limits are set at +1.9V SCE for M-HY and +1.6V SCE for PCM. The scan rate is 200 mV/sec. The negative voltage limit is set so that the starting Test Solutions displays an A_r value of 10 milli-Coulombs (± 10%); usually this is around −0.2V SCE. In this way, an A_r value is printed out about every 20 sec.

This initial A_r reading, before adding any Sample, is designated A_{ro}. The A_{ro} values become stable in less than 5 CV sweeps. Then increments of Sample are

* (Qualiderm™) UPA Technology, Syossett, NY
** IBM Instruments, Inc., Danbury, CT
*** LeaRonal, Freeport, NY
**** Sel-Rex, Nutley, NJ

added and a new A_r is read. Conveniently, 5 A_r values are printed for each increment (with some notation being made on the output tape at each increment) and the fifth value is taken as the data point. Additions are continued until A_r falls below 1 or 2 mC. A_r values are then normalized to A_{ro} and A_r/A_{ro} is plotted against volume of Sample added. (Linear or semi log paper can be used.) The end-point is taken as the volume where $A_r/A_{ro} = 0.50$. The entire procedure takes 15 to 20 minutes.

CALIBRATION CURVES WITH VIRGIN SOLUTIONS

The amount of copper which is deposited in the cathodic part of the cycle is sensitive to the amount of additive mixture added to the test solutions. At least one of the components of the mixture suppresses the deposition of copper, so that less copper is available for dissolution during the anodic part. This has been shown by Ogden and Tench for the polyether-sulfide system [3]. In their calibration curve, A_r/A_s decreases (after a slight initial rise) as the suppressing species is added. In this region of concentration for the M-HY system, A_s changes little because when the electrode is stationary, the amount of suppressor at the electrode surface is diffusion limited and is practically nil, so $A_s \cong A_{ro}$. Thus, curves for A_r/A_{ro} vs. volume of additive are essentially identical to plots of A_r/A_s.

In the PCM system, the suppressor is either far more active or far more concentrated in the solution supplied by the vendor. Small amounts immediately supress Cu deposition to very low values. Further additions result in a very slight increase in A_r. [4] When the initial PCM additions are on the order of microliters per liter, rather than ml/l, the suppressive effect can be shown clearly. The two additive systems produce very nearly the same shape of curve as shown in Figure 2.

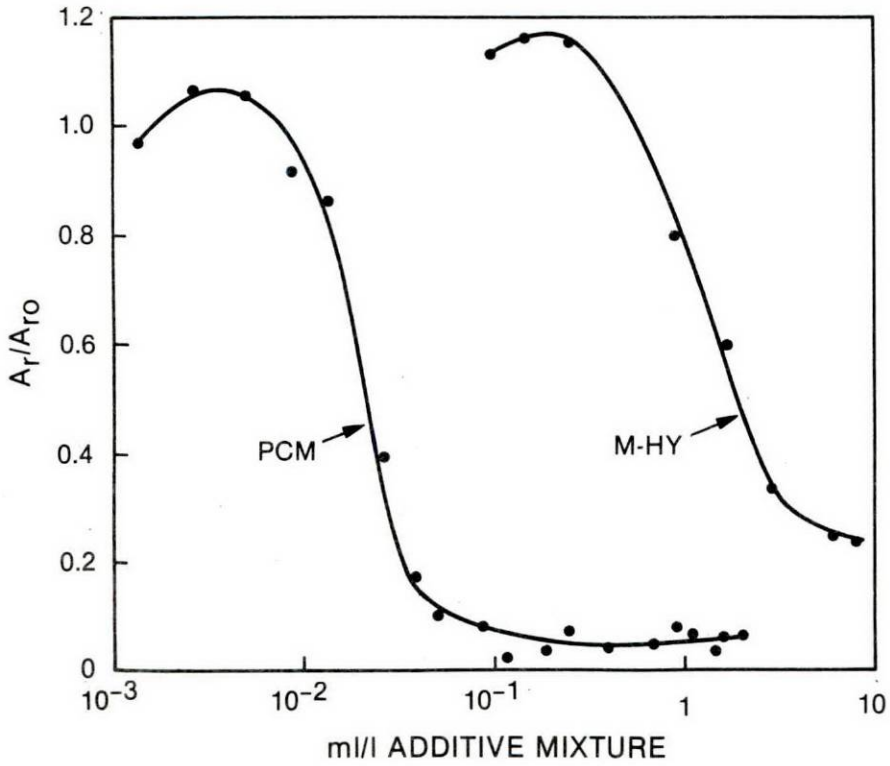


Figure 2. Calibration Curves for PCM and M-HY Additives.

Thus the copper deposition suppressors in both the PCM and M-HY additive systems apparently behave in basically the same way, but in different concentration ranges. It is not possible, of course, to distinguish a very active suppressor at low concentrations from a mild supressor at high concentration by this CV technique alone. As suppressors reach the RDE in increasing amounts, the amount of copper deposited, and hence A_r, decreases until the electrode is saturated. After this the electrode is relatively insensitive to further supressor activity until other, presently undefined, mechanisms come into play.

Therefore, the only analytically useful information is contained in that part of the curve where supression is going on, but is not yet saturated. Experience has shown that A_r/A_{ro} values are not readily reproducible in the high range (0.9 to 1.1) nor in the low range (0 to 0.2). Therefore, the end point is selected as that value for which the electrode is half-saturated, i.e., when $A_r/A_{ro} = 0.5$. The effective suppressor concentration in the samples is then proportional to the reciprocal of the amount of Sample added to the Test Solution, that is:

$$\text{Effective Concentration} = \left| \frac{V + X_{1/2}}{X_{1/2}} \right.$$

$$EC = \left. \frac{25}{X_{1/2}} \right| \text{ for Small X}$$

where V is the Volume of Test Solution at start and $X_{1/2}$ is the Volume of Sample added when $A_r/A_{ro} = 1/2$ as read from the plot.

Figure 3 shows EC values obtained when virgin solutions containing the indicated amounts of PCM or M-HY are used as Samples for a dilution-titration performed according to the method outlined in the Experimental Section. Straight lines are obtained which pass through the origin. The reproducibility of the EC values obtained in this way is ± 10% or better. The effective concentration value can be considered as a number proportional to the product of the concentration of a suppressor and its "activity" or efficiency as a suppressor.

EFFECT OF MASS TRANSPORT

The amount of suppressive activity seen at the RDE is a function not only of the amount of suppressor present in the bulk of the Test Solution and its efficiency, but also of the rate of mass transport of that species to the electrode surface. The mass transport rate was varied in one experiment by varying the speed of rotation of the RDE. For this purpose, an IBM electrode was substituted for the UPA assembly on the instrument and its speed was varied from 0 to 5000 RPM (524 rad/sec). Additive-free Test Solution was titrated with PCM and the family of curves shown in Figure 4 was obtained.

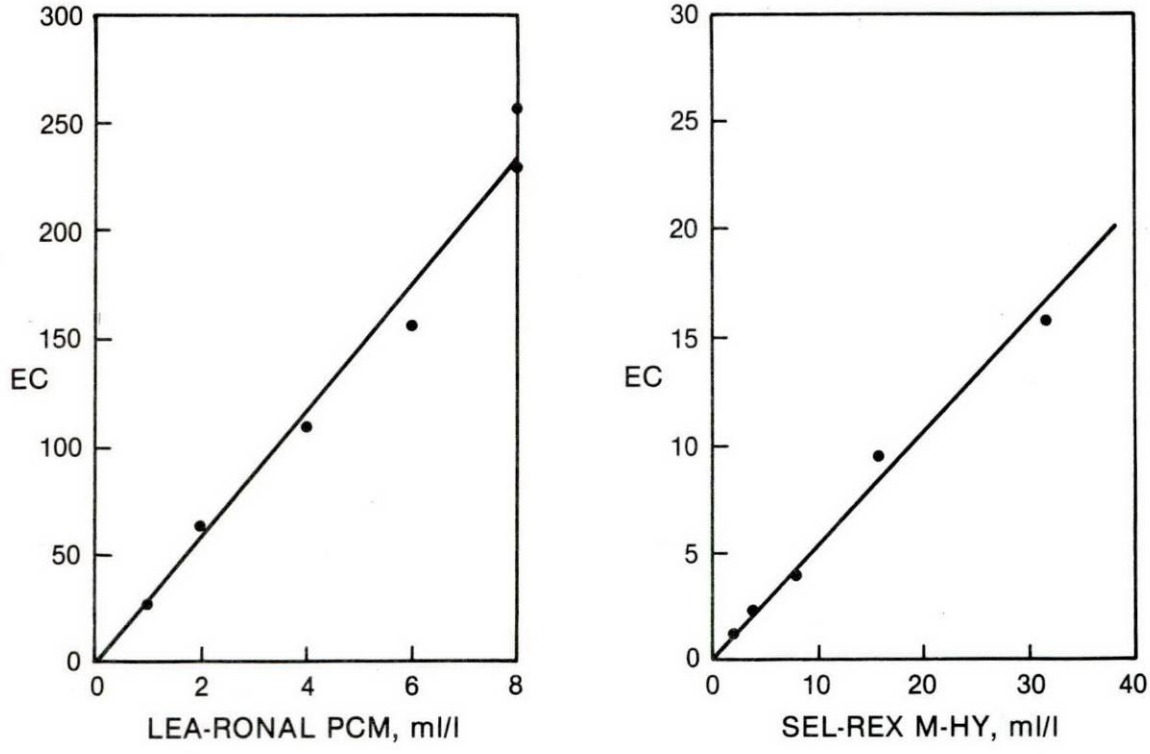


Figure 3. Effective Concentrations (EC) as Determined by Dilution-Titrations for Virgin Solutions at Various Additive Levels.

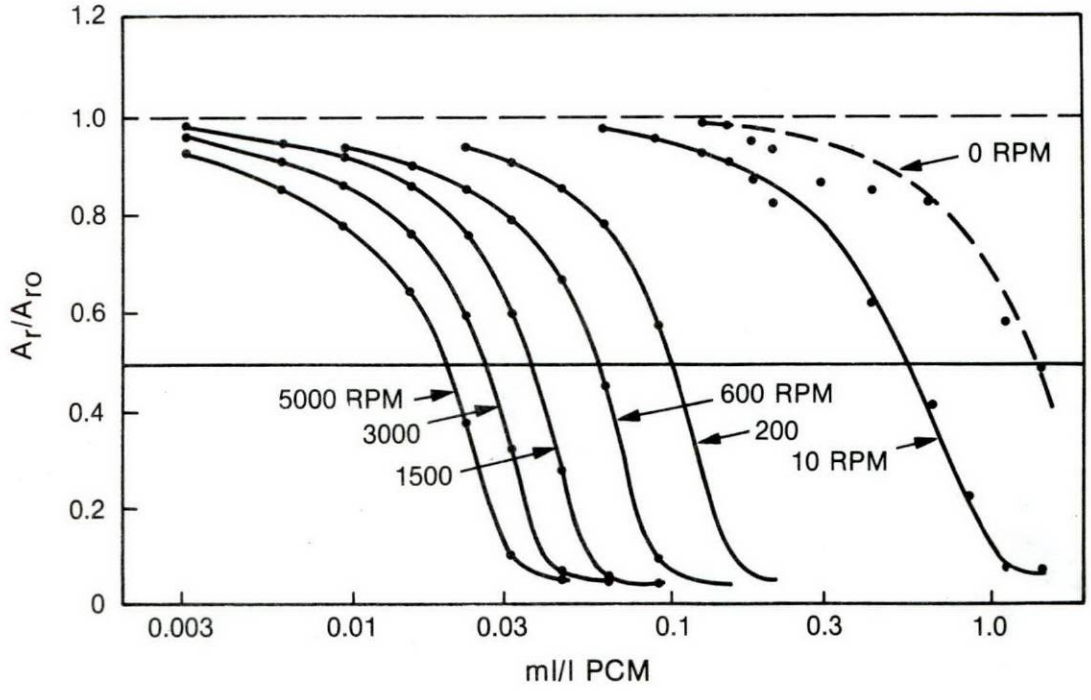


Figure 4. Effect of Electrode Speed on Calibration Curves for PCM Additive Mixture

According to the Levich equation, the rate of mass transport of a species to a RDE surface is proportional to the product $c_o \omega^{1/2}$ where c_o is the concentration of the species in the bulk of the solution and ω is the angular velocity. Therefore, for equal mass transport rates, $c_o \omega^{1/2}$, or $c_o(RPM)^{1/2}$, is a constant. For each curve in Figure 4, the value of c_o was read at $A_r/A_{ro} = 1/2$:

RPM	c_o for $A_r/A_{ro} = 1/2$ from Figure 4 - ml/l	Relative Mass Transport Rate - c_o (RPM) 1/2
0	1.4	—
10	0.56	1.77
200	0.103	1.46
600	0.060	1.47
1500	0.037	1.43
3000	0.026	1.42
5000	0.0196	1.39

Their product is seen to be reasonably constant across the RPM range. This shows that the concentration at which $A_r/A_{ro} = 1/2$ is a good measure of the concentration of the major suppressive species present, when measurements are made at constant RPM. At 10 and 0 RPM, there is a transition from rotating disk diffusion kinetics to planar diffusion: here mass transport no longer drops off as predicted by the Levich equation, and the $c\omega^{1/2}$ product rises. Planar diffusion is strongly affected by residual currents around the electrode. Their effects predominate at these low speeds and are also reflected in the increased scatter of the data points in Figure 4.

APPLICATION TO PRODUCTION SOLUTIONS

Samples were taken from active production line tanks at three plant locations over a period of several months and the EC values were determined by the above procedure. In two cases the monitoring period straddled a carbon treatment cycle. The two tanks represented in Figure 5 were operating with the PCM system, but at 2 different nominal PCM levels. (Note the difference in vertical scales). Actual levels of EC are 4 to 5 times higher in aged production baths than in a virgin solution at the same nominal PCM level. The removal of CV active species by carbon treatment is clearly evident. The first data point following the carbon treatment is the EC after bringing up the brightener level and fully dummying the tank, ready for production loads. Even in this initial "fresh solution", EC level is twice the nominal make-up level.

The situation is similar for a tank using Cubath M-HY as shown in Figure 6, the EC level rises with bath usage. EC values in this additive system are typically much lower than those for PCM. This bath had been carbon treated two weeks before the start of the monitoring period. It also experienced a period of partial shut-down late in July. Presumably the dip in EC values during that time indicates that CV-active species somehow are lost during idle periods; this is consistent with platers' experience that many tanks need an extra shot of brightener after an idle week-end.

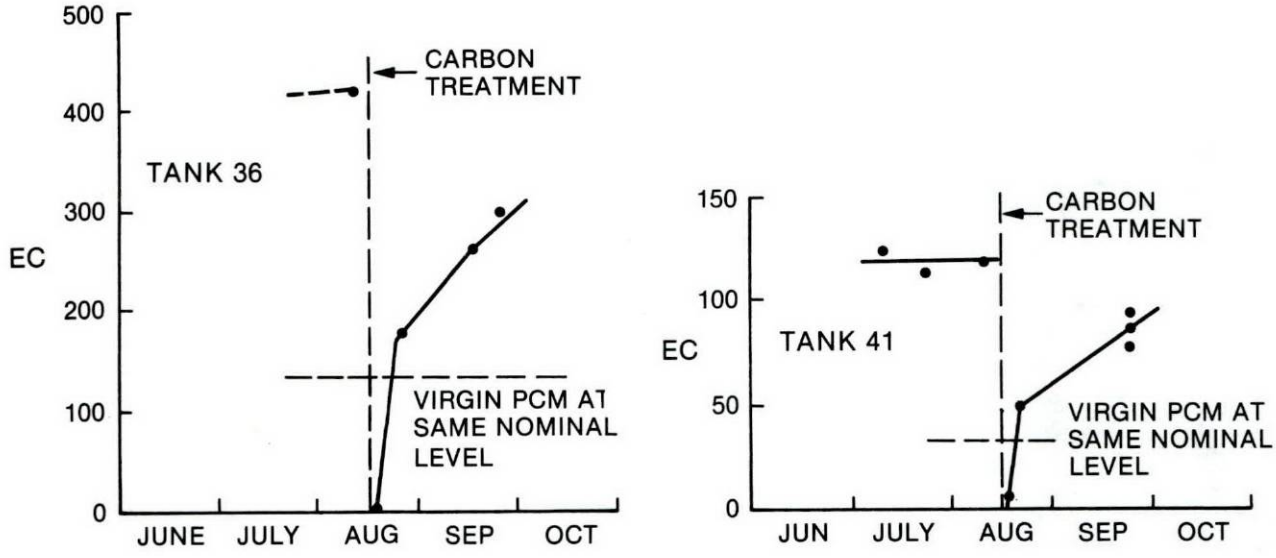


Figure 5. EC of Solutions from Production Tanks using PCM System Determined by Dilution-Titration.

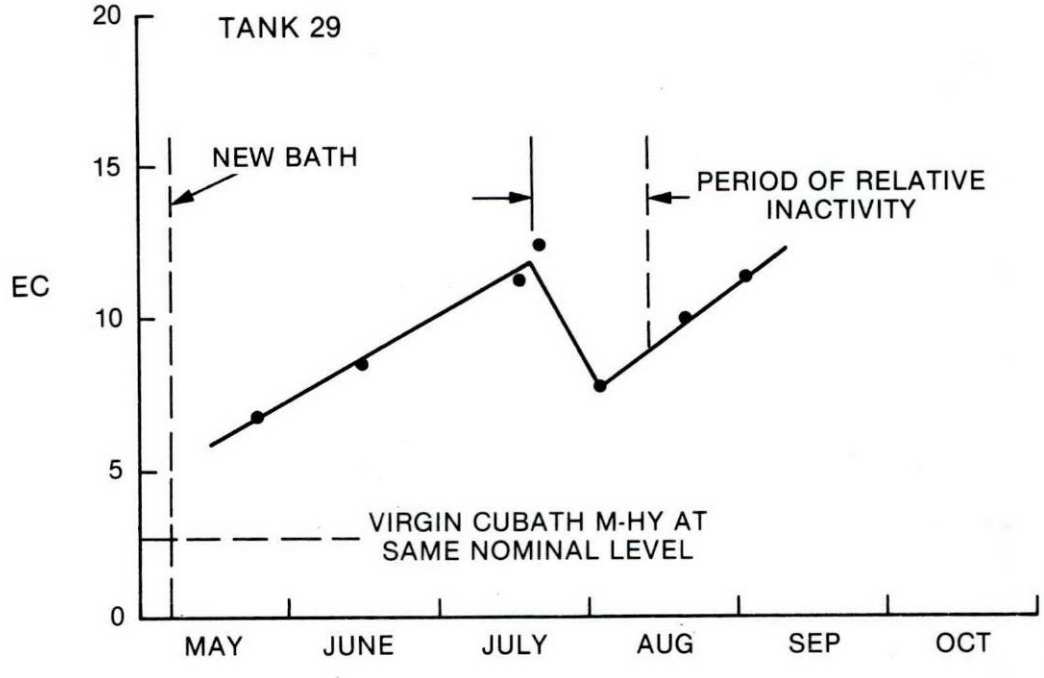


Figure 6. EC of Solutions from Production Tanks using a Cubath M-HY System Determined by Dilution-Titration.

The species which accumulate and contribute to suppressor activity in production tanks are apparently longer-lived than the original species added with the brightener mixture. The depletion of CV-active components was followed in the laboratory by prolonged plating without brightener replentishment. The CV activity of a virgin PCM solution was monitored by performing a dilution-titration every half hour while the solution was being electrolysed at 2 A in a 250 ml. Hull cell. The drop in EC with time is evident in Figure 7. When the experiment was repeated using samples from the production line, suppressive action did not diminish measurably during the three-hour test. However, the appearance of the Hull cell cathodes showed that brightening action was diminishing during this time. Thus some species responsible for the brightening of the deposits were being consumed even though the major copper deposition suppressors were not.

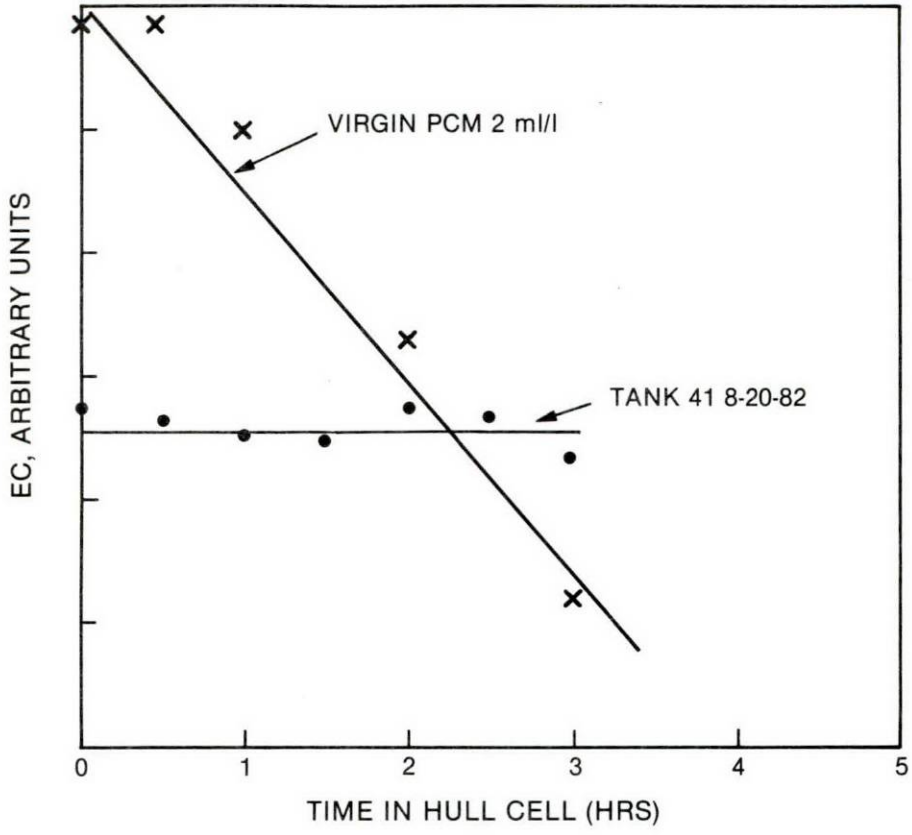


Figure 7. Depletion of Suppressors in Hull Cell Tests at 2A.

CONCLUSIONS

Cyclic voltammetry using essentially the test conditions described by Ogden and Tench can provide useful information about acid copper production baths if measurements are made at copper suppressor levels where changes in A_r are rapid with changes in concentration; i.e., on the descending part of the curve. This can be accomplished rapidly and conveniently by titrating an additive-free reference Test Solution with the unknown Sample and determining the point at which copper deposition is cut in half. The reciprocal of the volume added at this point is proportional to the effective concentration of copper deposition suppressors in the unknown.

The EC value so determined is useful in monitoring the build-up of copper suppressors which has been found to occur during use of a production bath. This should prove useful in correlating suppressor levels with board quality, in predicting the need for carbon treatment and in determining whether or not the carbon treatment is complete. The latter use is especially advantageous when more efficient carbon treatment procedures are being sought.

Production baths differ from freshly made-up baths in that they apparently contain "conversion products" from reaction of some of the original additive components at the electrodes. Some of these products are themselves copper suppressors, contribute to the EC, and are more slowly consumed than the original components.

An alternate explanation of the observed behavior is that a copper-suppressing species is not depleted with use at all, or depleted only slowly with respect to the other additive components, and simply accumulates as the bath is used and continuing brightener adds are made. This is less likely, in view of the results in Figure 7, but it is not ruled out.

The preliminary work on depletion in the Hull cell indicates that at least some component responsible for brightening is depleted under conditions where the EC remains unchanged. This places some limit on the usefulness of the EC value alone as a bath monitor and other complementary analyses are clearly needed. The assumption that activity in the CV test is a measure of brightening and leveling action in the tank is not entirely valid. However, the CV approach is providing vital new information in an otherwise chaotic area.

ACKNOWLEDGEMENTS

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F-5

Electronics II
Session F

Differential Pulse Polarography of Organic Additives in Acid Tin and Bright Tin-Lead Plating Baths

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Winston-Salem, NC

DIFFERENTIAL PULSE POLAROGRAPHY OF ORGANIC ADDITIVES IN ACID TIN AND BRIGHT TIN-LEAD PLATING BATHS

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AMP Incorporated
Winston-Salem, N.C.

Abstract

Due to the increased use of high-speed plating, frequent and rapid plating bath analyses are needed in order to control the quality of the electrodeposited metal. Organic addition agents play important roles in plating and must be replenished more frequently in high-speed plating. Procedures have been developed using differential pulse polarography for the analysis of the grain refiner in a commercial acid tin plating bath and the brighteners in a commercially available bright tin-lead bath. This method has advantages over conventional methods by offering a simple, rapid analysis for more precise control of organic additives in the acid tin and the bright tin-lead plating baths studied and should be adaptable to other similar systems commonly used today.

Introduction

Addition agents have been used for many years in the plating industry to produce specific effects such as leveling or brightening of a deposit. The concentrations of these addition agents in the plating baths are usually quite small and exact concentrations are often quite difficult to determine. Two emerging techniques which show promise for rapid and simple analysis of organics in plating baths are High-Performance Liquid Chromatography (HPLC) and Polarography.

Since these addition agents are consumed during plating, maintenance of and sometimes balance between addition agents are required for better quality control. Due to the increased use of high-speed plating, frequent and rapid plating bath analyses are needed in order to control the quality of the electrodeposited metal.

In the past, no simple quantitative methods have existed for analysis of organic additives in plating baths. Conventional methods such as the Hull Cell or the bent cathode test, which are informative to experienced platers, do not provide simple and rapid quantitative analyses. Also, methods used for analysis of wetting agents or grain refiners by surface tension measurements are somewhat difficult and are not often used.

The addition agents in most acid tin plating baths and bright tin-lead plating baths are typically organic additives. Due to the electroactivity of most organics, polarography has been applied to the analysis of organics in plating baths. This paper deals with the determination of the concentration of the grain refiner in an acid tin plating bath and the brightener system in a tin-lead plating bath.

The grain refiner is added to provide a useful deposit. Without the grain refiner, the deposit contains loosely adherent large crystals. Too much grain refiner causes problems when a plastic is laminated to the deposit. Therefore, the concentration of the grain refiner must be maintained within a certain range to provide a quality product. With the use of polarography, this can be done quite readily.

The brightener system in this tin-lead plating bath consists of three organic additives. The first component (#1) is the main brightening agent and has been analyzed in an acetate solution using differential pulse polarography. The third component (#3) is a grain refiner and has been analyzed in the bath itself with differential pulse voltammetry with a glassy carbon electrode. The second component (#2) is a wetting agent used to emulsify the third component. Presently, the second component can not be analyzed using voltammetry. However, this component has been analyzed using UV-VIS spectroscopy, although interferences pose problems.

Background

Polarography is an analytical technique which was developed in the 1920s. Early instruments were difficult to use and thus were not utilized extensively. With the invention of improved electronics in the 1960s, better instrumentation has been made available and has gained popularity as an analytical technique, especially for environmental analysis.

Polarography is a branch of voltammetry in which the working electrode is a dropping mercury electrode (DME). Voltammetry is an electrochemical technique in which the faradaic current through the electrolytic solution is measured as a systematic varied potential is applied between a reference electrode and a working electrode. The reference electrode is almost always a saturated calomel electrode (SCE) or a silver/silver chloride (Ag/AgCl) electrode. Typical working electrodes are the dropping mercury electrode, the glassy carbon electrode (GCE), and the wax-impregnated graphite electrode. The amount of faradaic current is proportional to the concentration of the species being either reduced (gaining electrons) or oxidized (losing electrons). Therefore, the species can be quantitated.

The electrolyte solution is employed in voltammetry to provide a conductive media for electron flow during oxidation or reduction. The electrolyte is an important consideration for analysis of plating solutions, since certain species are rendered electroinactive in certain electrolytes. Organic additives are used in low concentrations in plating baths, so they often require little or no dilution with an electrolyte, since plating baths are good electrolytic solutions.

Voltammetry appears to be a good choice for analyses of plating baths, since it is an electrochemical technique. Probably the most used voltammetric technique for analysis of plating baths is the differential pulse mode. This technique offers excellent sensitivity (parts per billion in many cases) with modern equipment, and provides rapid and simple quantitative analysis for control of plating solutions.

Experimental

Acid Tin Plating Bath

This work was carried out using the PARC Model 384 Polarographic Analyzer in the DC differential pulse polarography mode (DPP) using a dropping mercury electrode (DME) with a Ag/AgCl reference electrode and a Pt wire was a counter electrode. A blank (acid tin plating bath without any grain refiner) and three standards of 0.5% (1 ml of grain refiner diluted to 200 mls with acid tin plating bath), 1.0% (1 ml of grain refiner diluted to 100 mls with acid tin plating bath), and 5.0% (5 ml of grain refiner diluted to 100 mls with acid tin plating bath) were purged with nitrogen for 4-6 minutes and then scanned from 0.200 to -0.200V. The peak of 0.020V was labelled peak 1 and used for a calibration curve. (See Appendix I).

Bright Tin Lead Bath

This work was also carried out using the PARC Model 384 Polarographic Analyzer in the DC differential pulse mode with a Ag/AgCl reference electrode and a Pt wire as a counter electrode. A dropping mercury electrode was used to analyze the additive #1. A blank solution was prepared by adding 1.5% of additives #2 and #3 to a tin-lead plating bath solution without any additives. The blank solution was then used to make three standards of 0.5% (125µl of additive #1 diluted to 25 mls with the blank solution), 1.5% (375µl of #1 diluted to 25 mls with the blank solution), and 5.0% (1.25 ml of #1 to 25 mls with the blank solution). In each case a sample of 100µl was diluted to 10 mls with an acetate buffer (0.1M, pH 4.5), purged with nitrogen for four (4) minutes, and then scanned from -0.200V to -1.20V. The peak at -0.90V was labelled peak 1 and used for calibration.

Additive #3 was analyzed with a glassy carbon electrode. A blank solution was prepared by adding 1.5% of additive #2 to a tin-lead plating bath solution without any additives. The blank solution was then used to make three standards of 0.5% (125µl of #3 diluted to 25 mls with the blank solution), 1.5% (375µl of #3 diluted to 25 mls with the blank solution), and 3.0% (750µl of #3 diluted to 25 ml with the blank solution). A sample (10 ml of each) was then purged with nitrogen for four (4) minutes and then scanned from 0.000V to 1.000V. The peak at 0.70V was labelled peak 3 and used for calibration.

Results and Discussion

Voltammetry has been successfully used in analyzing organic additives in an acid tin and a bright tin-lead plating bath. The differential pulse technique gave acceptable results for analysis of plating baths. In the case of the acid tin bath, a 3.0% standard was prepared and analyzed after the instrument had been calibrated. The results as shown in Appendix I gave an accuracy of 5-6%. Also, analysis of acid tin plating baths which had been in operation in production gave comparable results (within experimental error) as those analyzed by a HPLC method. In the case of the bright tin-lead bath, a 3.0% standard of additive #1 was analyzed and gave an accuracy of 2%. (See Appendix II). A 1.5% standard of additive #3 was analyzed and

gave an accuracy of 3%. (See Appendix II). These results are well within the requirements of accuracy needed for plating bath analyses.

The methods developed are simple to use, such that less technically oriented people can be trained to operate the polarograph. Also, these methods are fairly rapid, so that an analysis can be performed in less than ten minutes. Unlike the HPLC which requires expensive solvents for operation, the polarograph should be more cost effective to operate.

On-line control should be possible with these methods. General Dynamics has successfully designed an Automatic Monitoring and Control System (AMCS)[1] for improving printed wire board (PWB) yield and reliability. This system utilizes a Model 384 Polarographic Analyzer for doing the analyses. Such analyses are needed to maintain good quality control. For example, the concentration of organic additives has been shown to affect alloy, brightness, carbon content, and solderability of the tin-lead deposit.[2]

In conclusion, the polarographic methods developed for analysis of organic additives in acid tin and bright tin-lead baths are simple, rapid, and adaptable for on-line control for providing better quality control than conventional methods.

Acknowledgement

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MODEL 384 POLAROGRAPHIC ANALYZER

21-SEP-81
DPP
INITIAL E 0.200 V
FINAL E -0.200 V
PURGE 240 SECONDS
DROP TIME 1.0 SECONDS
SCAN INCREMENT 2 MV
PULSE HEIGHT 0.050 V
REPLICATIONS 1

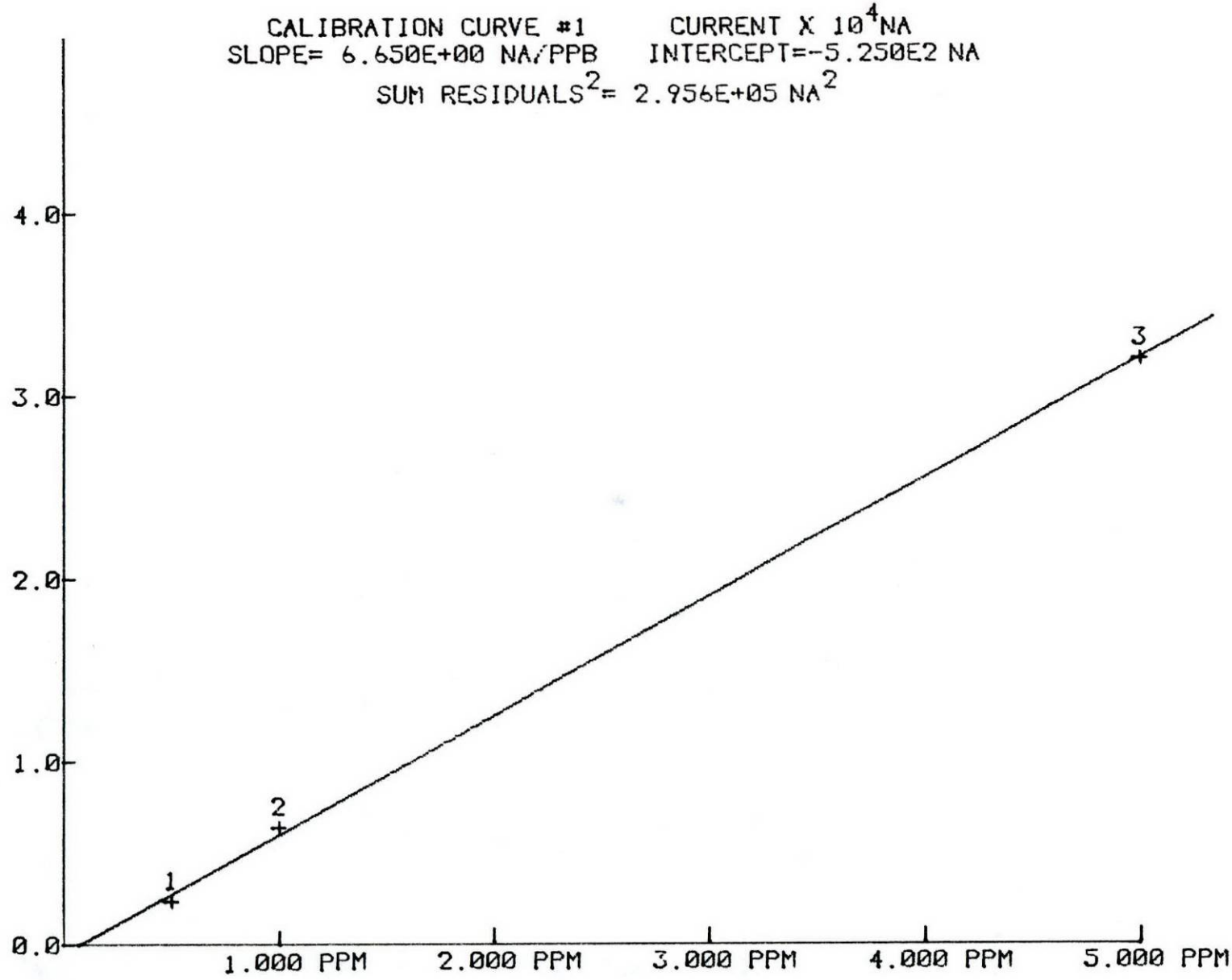
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DERIVATIVE: NO
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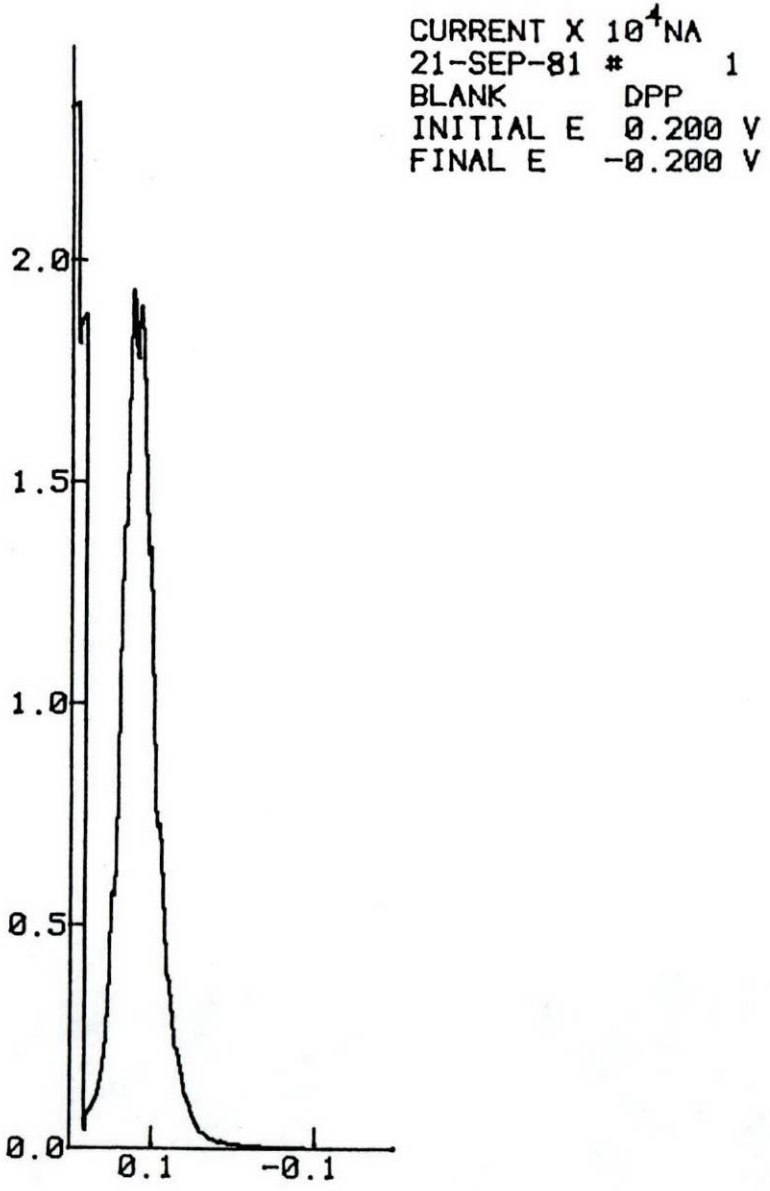
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OVERRIDE	Y	N	Y	Y	N	N	Y	N	N	Y	N

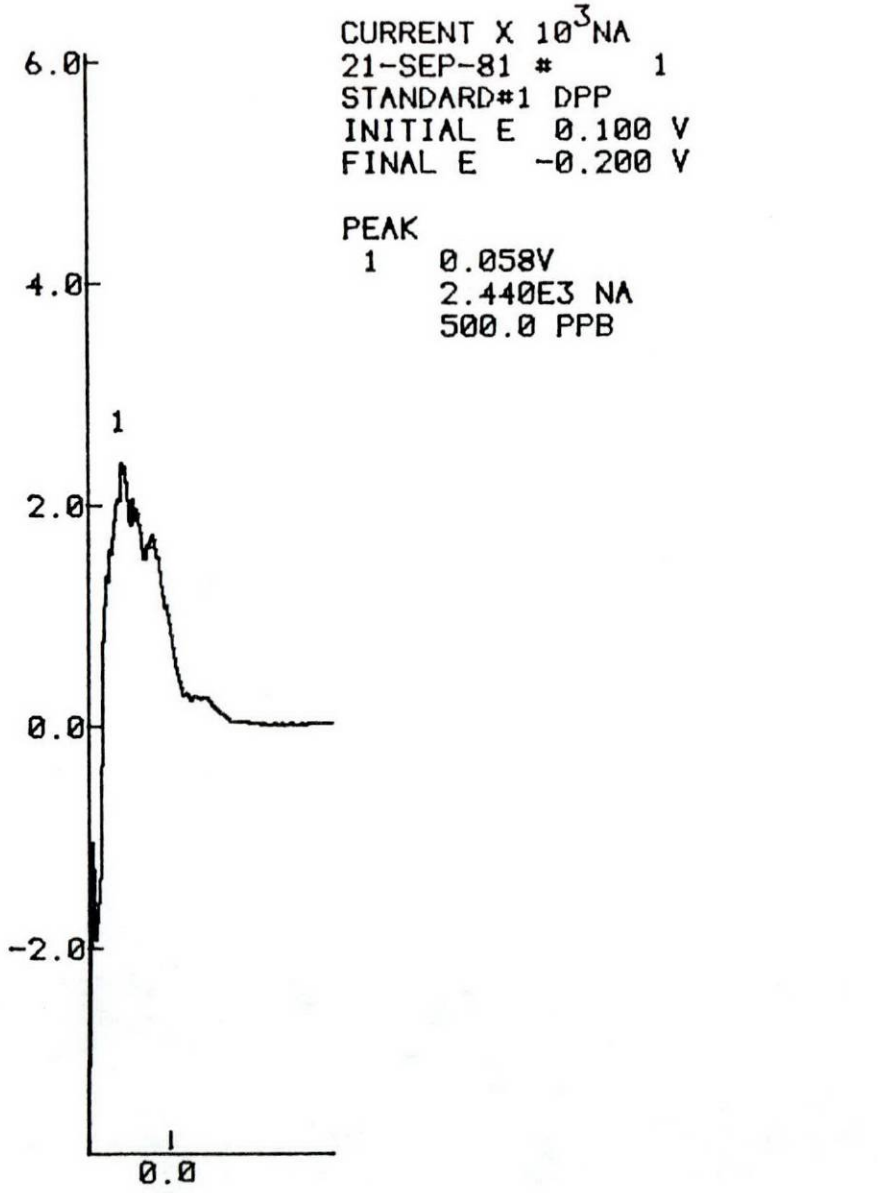
PEAK	POT	STD 1	STD 2	STD 3
1	0.020 V	500.0 PPB	1.000 PPM	5.000 PPM

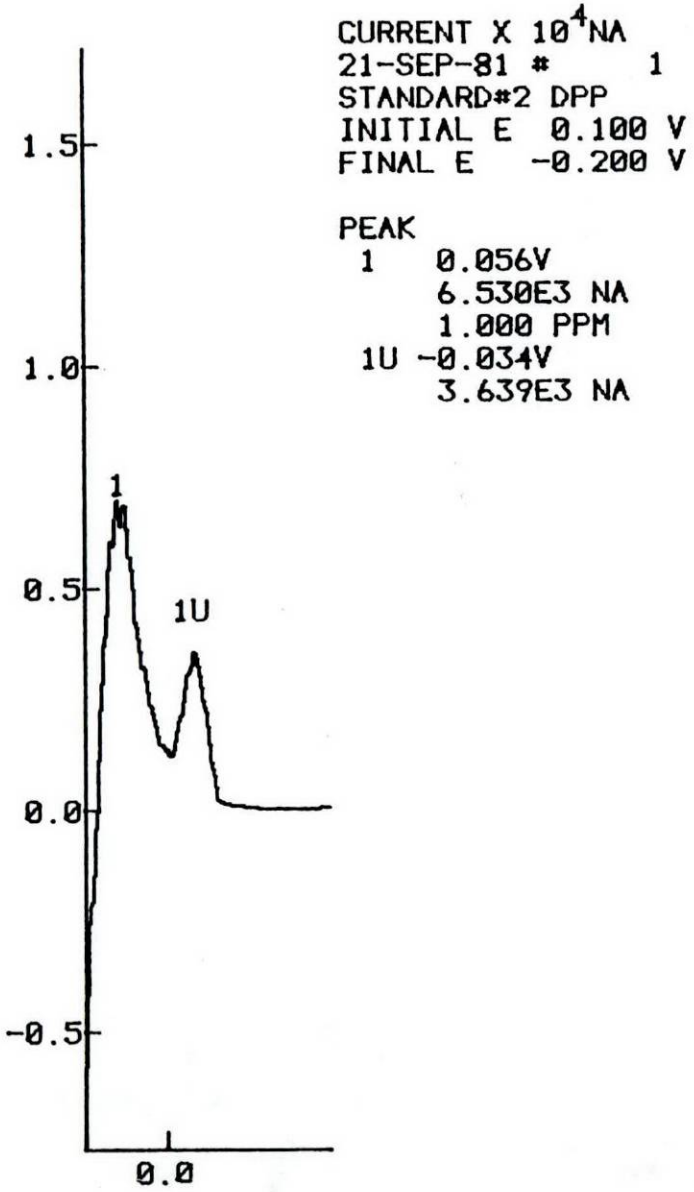
SAMPLE Acid Tin Plating Bath
ANALYTE Grain Refiner
SUPP. ELEC. Bath itself
SAMPLE PREP. No dilution of bath
Standards are recorded in %

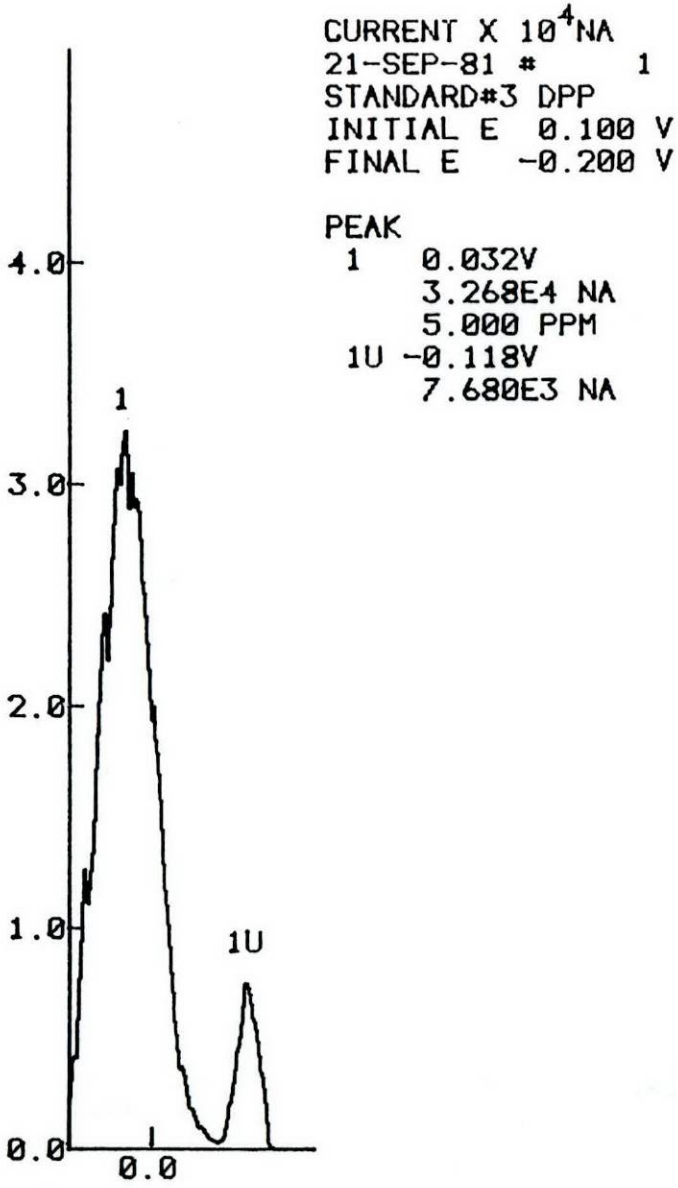
APPENDIX I

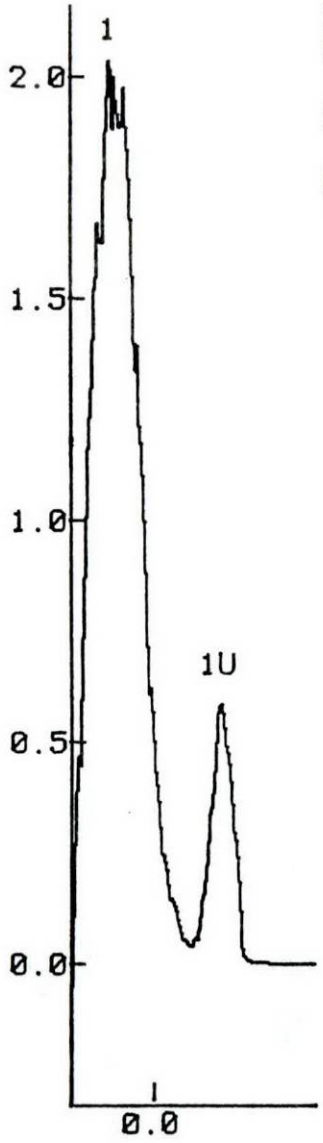

CALIBRATION CURVE #1 CURRENT X 10^4NA
SLOPE= 6.650E+00 NA/PPB INTERCEPT=-5.250E2 NA
SUM RESIDUALS^2= 2.956E+05 NA^2
4.0
3.0
2.0
1.0
0.0
1
2
3
1.000 PPM
2.000 PPM
3.000 PPM
4.000 PPM
5.000 PPM


CURRENT X 10⁴NA
21-SEP-81 # 1
BLANK DPP
INITIAL E 0.200 V
FINAL E -0.200 V
2.0
1.5
1.0
0.5
0.0
0.1
-0.1


CURRENT X 10^3NA
21-SEP-81 # 1
STANDARD#1 DPP
INITIAL E 0.100 V
FINAL E -0.200 V
PEAK
1 0.058V
2.440E3 NA
500.0 PPB
6.0
4.0
2.0
0.0
-2.0
1
0.0


CURRENT X 10^4NA
21-SEP-81 # 1
STANDARD#2 DPP
INITIAL E 0.100 V
FINAL E -0.200 V
PEAK
1 0.056V
6.530E3 NA
1.000 PPM
1U -0.034V
3.639E3 NA
1.5
1.0
0.5
0.0
-0.5
0.0
1
1U

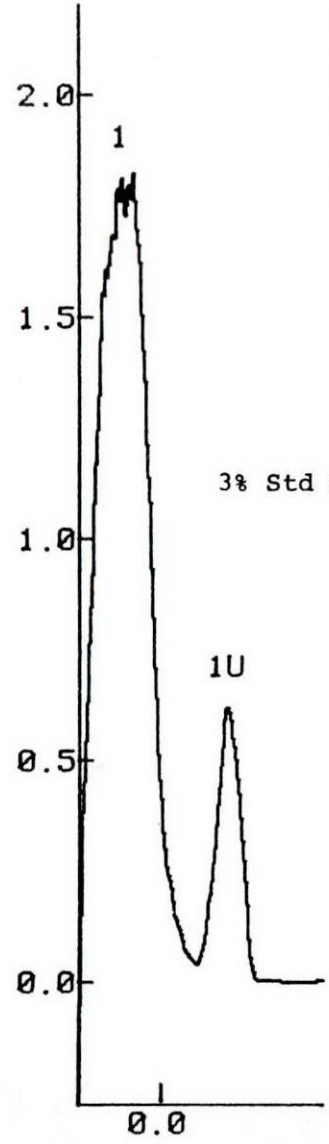

CURRENT X 10^4 NA
21-SEP-81 # 1
STANDARD#3 DPP
INITIAL E 0.100 V
FINAL E -0.200 V
PEAK
1 0.032V
3.268E4 NA
5.000 PPM
1U -0.118V
7.680E3 NA
4.0
3.0
2.0
1.0
0.0
0.0
1
1U



CURRENT X 10^4NA
21-SEP-81 # 6
SAMPLE DPP
INITIAL E 0.100 V
FINAL E -0.200 V

PEAK
1 0.050V
2.056E4 NA
3.171 PPM
1U -0.084V
5.920E3 NA

3% Standard



CURRENT X 10^4NA
21-SEP-81 # 3
SAMPLE DPP
INITIAL E 0.100 V
FINAL E -0.200 V

PEAK
1 0.046V
1.850E4 NA
2.861 PPM
1U -0.084V
6.300E3 NA

3% Std x 3 Replications

MODEL 384 POLAROGRAPHIC ANALYZER

23-DEC-82
DPP
INITIAL E -0.200 V
FINAL E -1.200 V
PURGE 240 SECONDS
DROP TIME 1.0 SECONDS
SCAN INCREMENT 2 MV
PULSE HEIGHT 0.050 V
REPLICATIONS 1

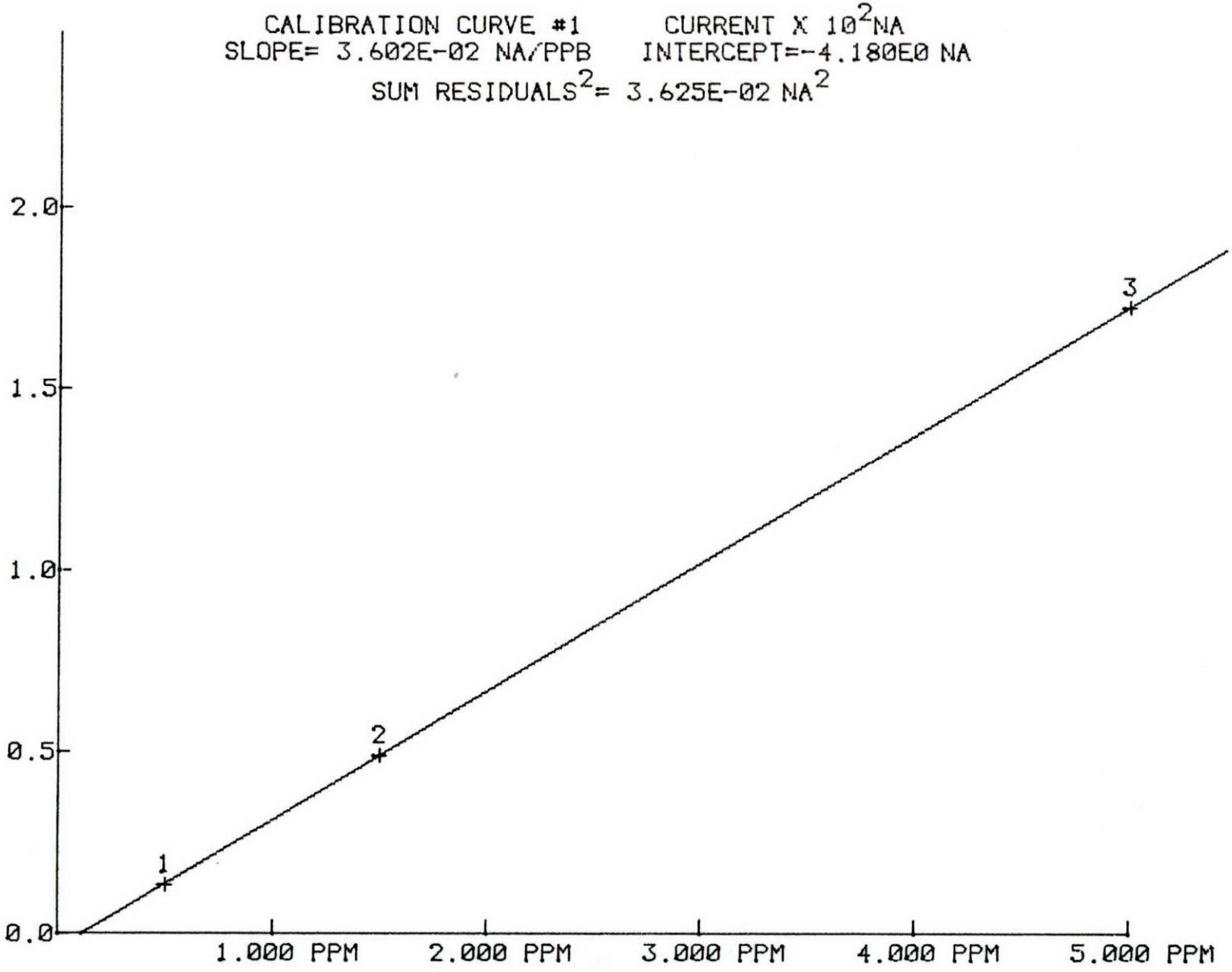
STANDARD CURVE
BLANK SUBTRACTION: YES
TANGENT FIT: YES
PEAK LOCATION: YES
DERIVATIVE: NO
FORCE LINEAR FIT: YES

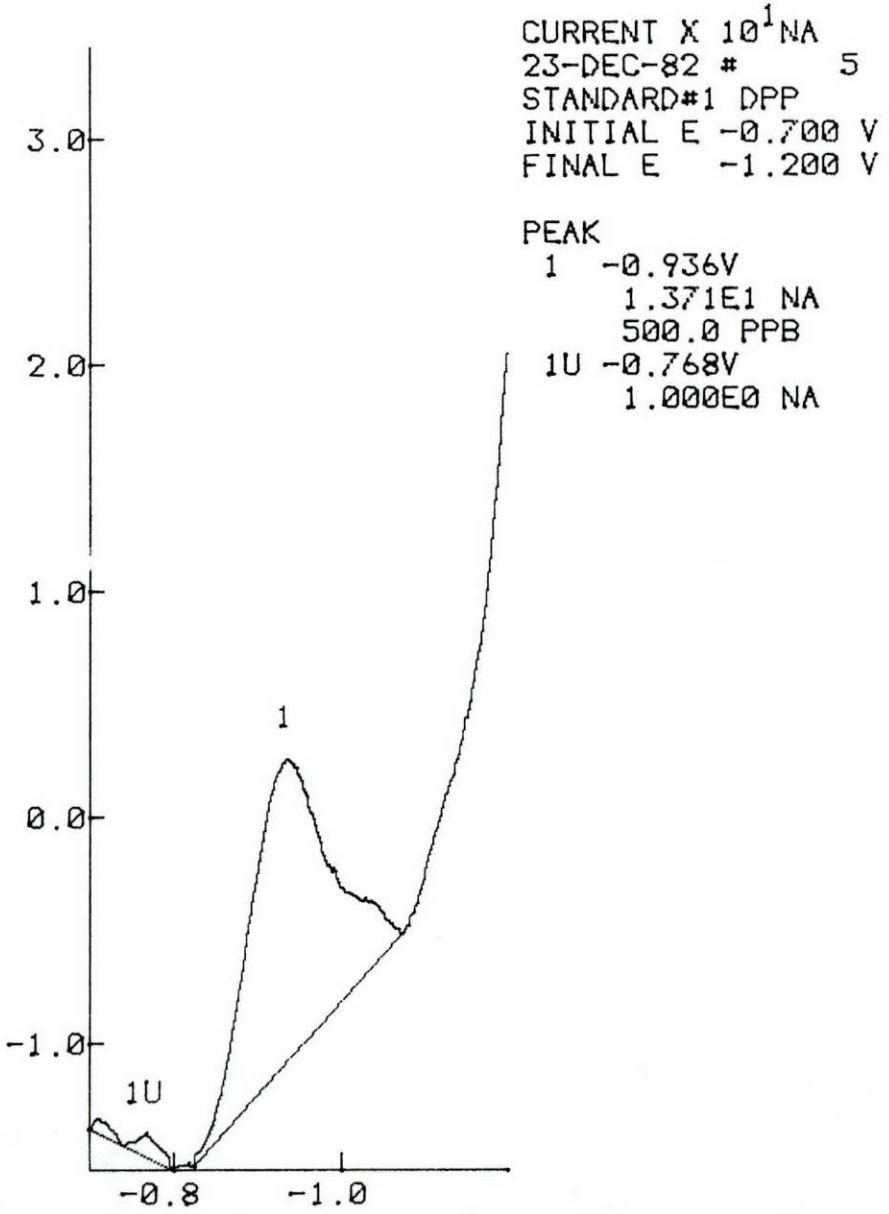
	10	11	12	13	14	15	16	17	18	19	20
OVERRIDE	Y	N	Y	Y	N	N	Y	N	N	Y	N

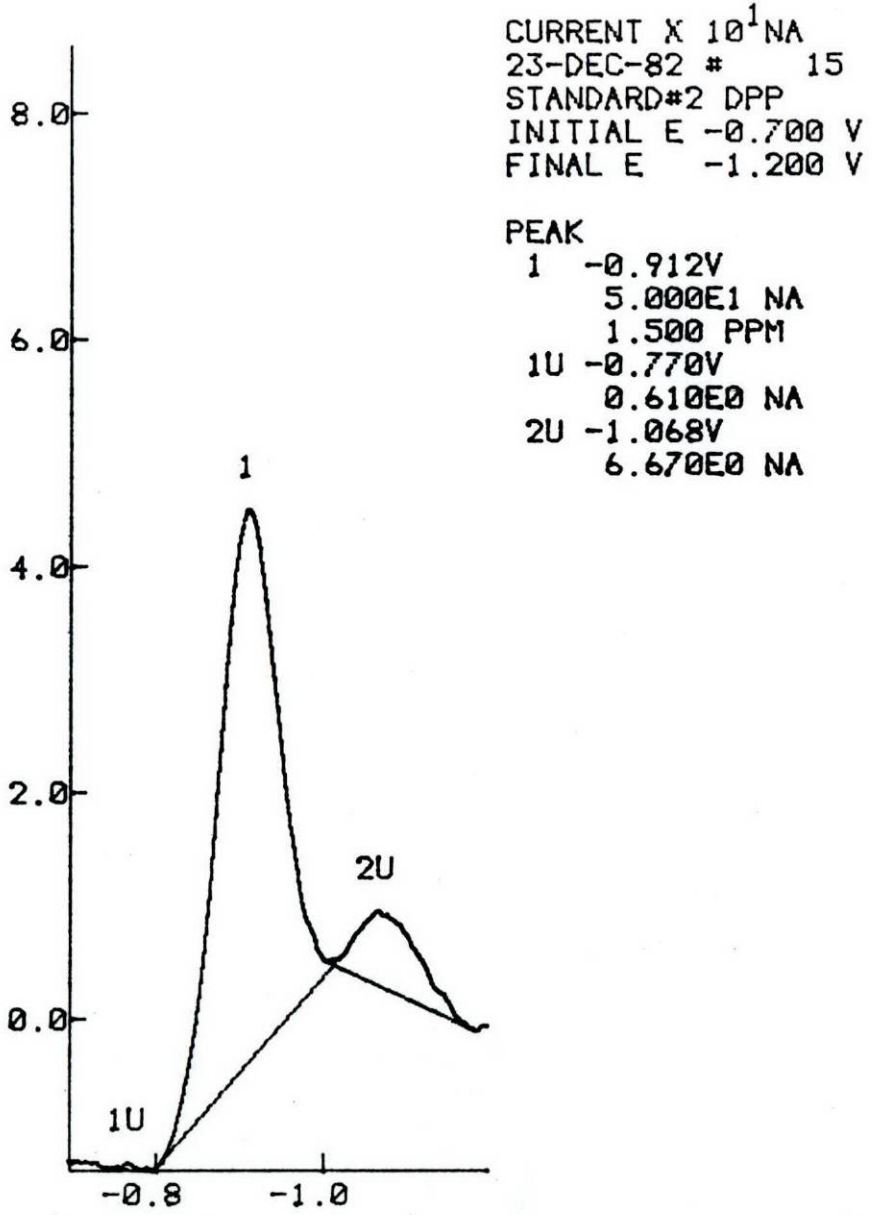
PEAK	POT	STD 1	STD 2	STD 3
1	-0.900 V	500.0 PPB	1.500 PPM	5.000 PPM

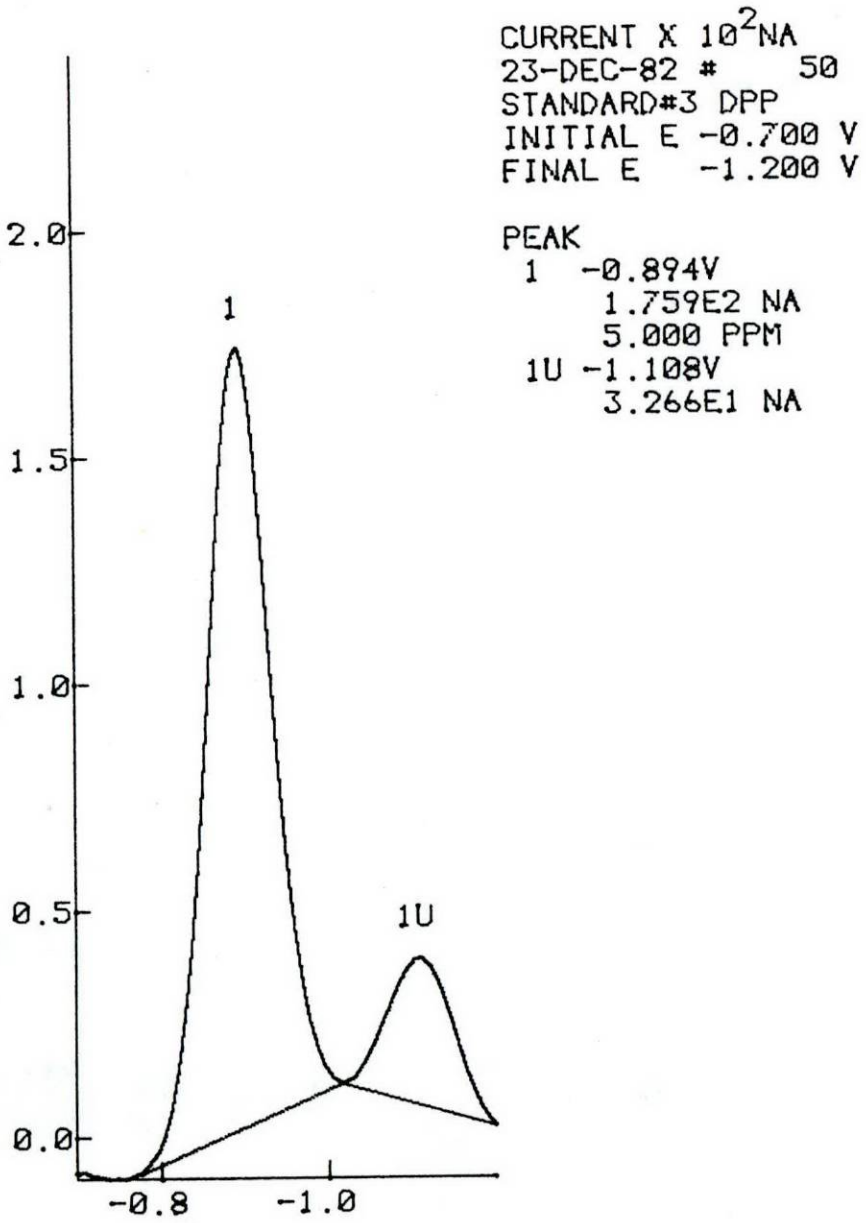
SAMPLE Bright Tin-Lead Plating Bath
ANALYTE Organic Additive #1
SUPP. ELEC. Acetate Buffer (0.1M, pH 4.5)
SAMPLE PREP. 100µℓ of sample diluted to 10 milliliters with Buffer.
Standards are recorded in %.

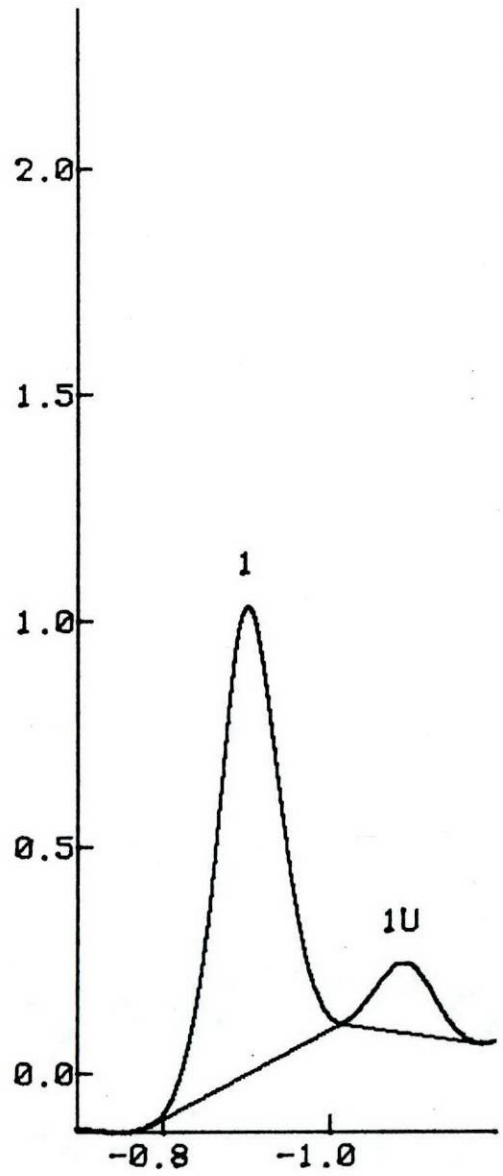
APPENDIX II


CALIBRATION CURVE #1 CURRENT X 10^2 NA
SLOPE= 3.602E-02 NA/PPB INTERCEPT=-4.180E0 NA
SUM RESIDUALS^2= 3.625E-02 NA^2
2.0
1.5
1.0
0.5
0.0
1
2
3
1.000 PPM
2.000 PPM
3.000 PPM
4.000 PPM
5.000 PPM


CURRENT X 10[1]NA
23-DEC-82 # 5
STANDARD#1 DPP
INITIAL E -0.700 V
FINAL E -1.200 V
PEAK
1 -0.936V
1.371E1 NA
500.0 PPB
1U -0.768V
1.000E0 NA
3.0
2.0
1.0
0.0
-1.0
1
1U
-0.8
-1.0


CURRENT X 10[1]NA
23-DEC-82 # 15
STANDARD#2 DPP
INITIAL E -0.700 V
FINAL E -1.200 V
PEAK
1 -0.912V
5.000E1 NA
1.500 PPM
1U -0.770V
0.610E0 NA
2U -1.068V
6.670E0 NA
8.0
6.0
4.0
2.0
0.0
1
2U
1U
-0.8
-1.0


CURRENT X 10^2NA
23-DEC-82 # 50
STANDARD#3 DPP
INITIAL E -0.700 V
FINAL E -1.200 V
PEAK
1 -0.894V
1.759E2 NA
5.000 PPM
1U -1.108V
3.266E1 NA
2.0
1.5
1.0
0.5
0.0
-0.8
-1.0
1
1U



CURRENT X 10^2NA
23-DEC-82 # 30
SAMPLE DPP
INITIAL E -0.700 V
FINAL E -1.200 V

PEAK
1 -0.904V
1.054E2 NA
3.041 PPM
1U -1.090V
1.566E1 NA

3% Standard

MODEL 384 POLAROGRAPHIC ANALYZER

10-JAN-83
DPP
INITIAL E 0.000 V
FINAL E 1.000 V
PURGE 240 SECONDS
DROP TIME 0.5 SECONDS
SCAN INCREMENT 2 MV
PULSE HEIGHT 0.050 V
REPLICATIONS 1

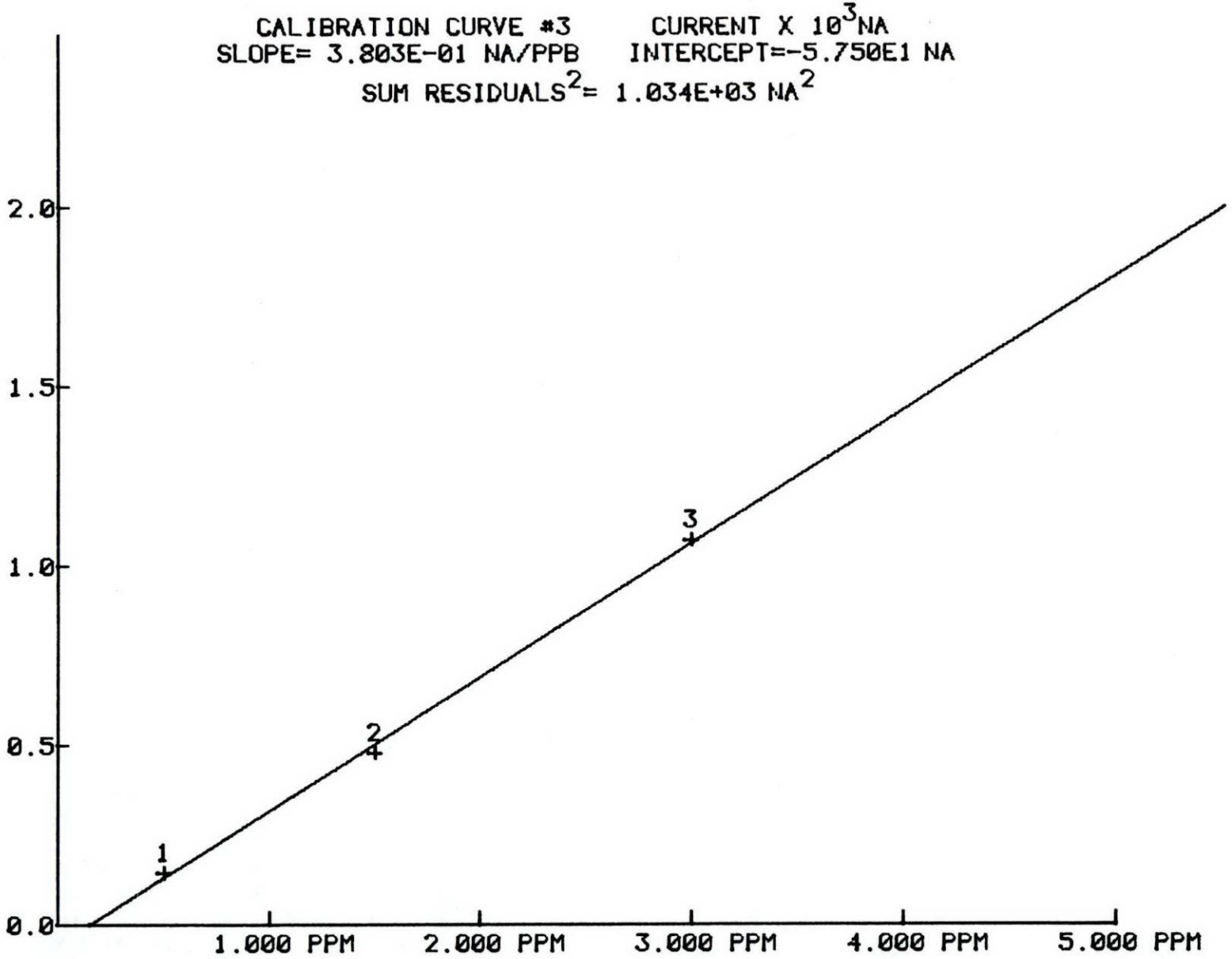
SAMPLE Bright Tin-Lead Plating Bath
ANALYTE Organic Additive #3
SUPP. ELEC. Bath itself
SAMPLE PREP. No dilution of bath
Standards are recorded in %.

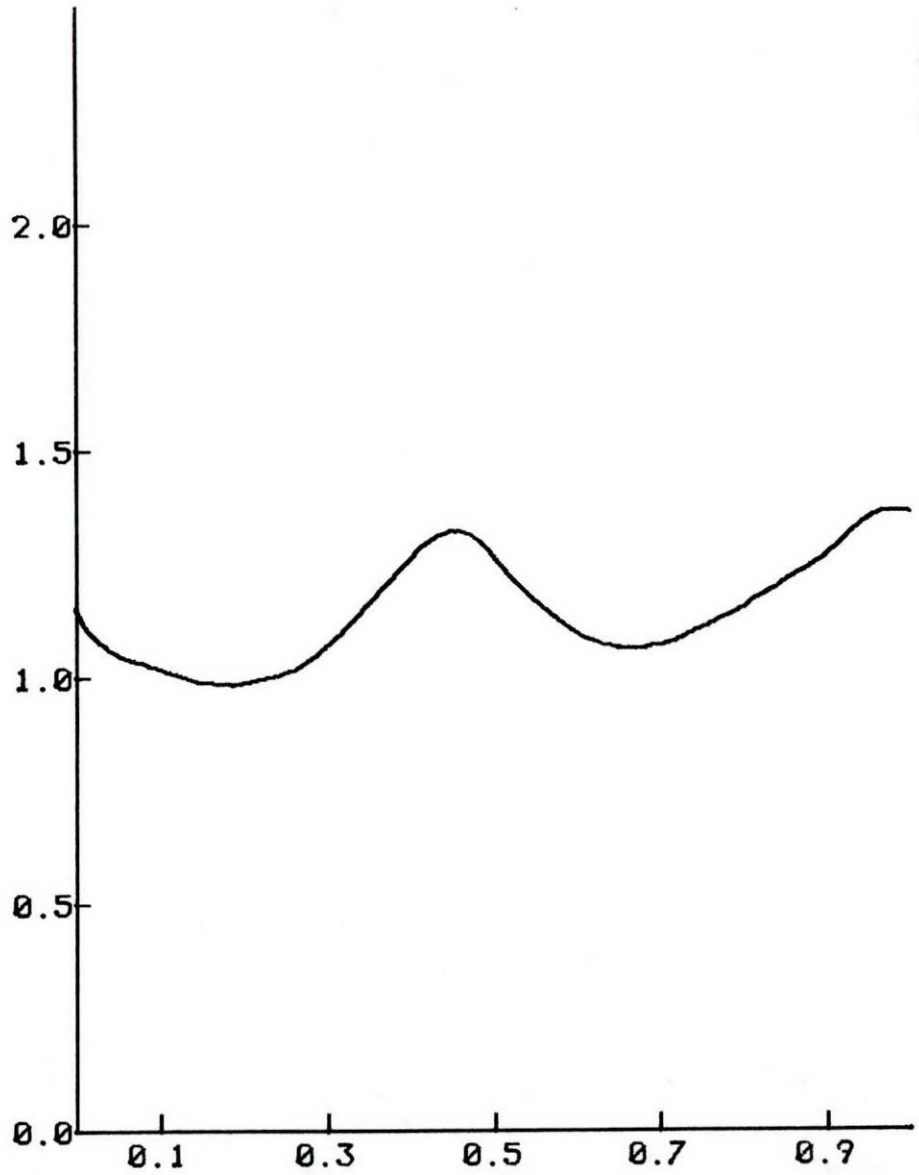
STANDARD CURVE
BLANK SUBTRACTION: YES
TANGENT FIT: YES
PEAK LOCATION: YES
DERIVATIVE: NO
FORCE LINEAR FIT: YES

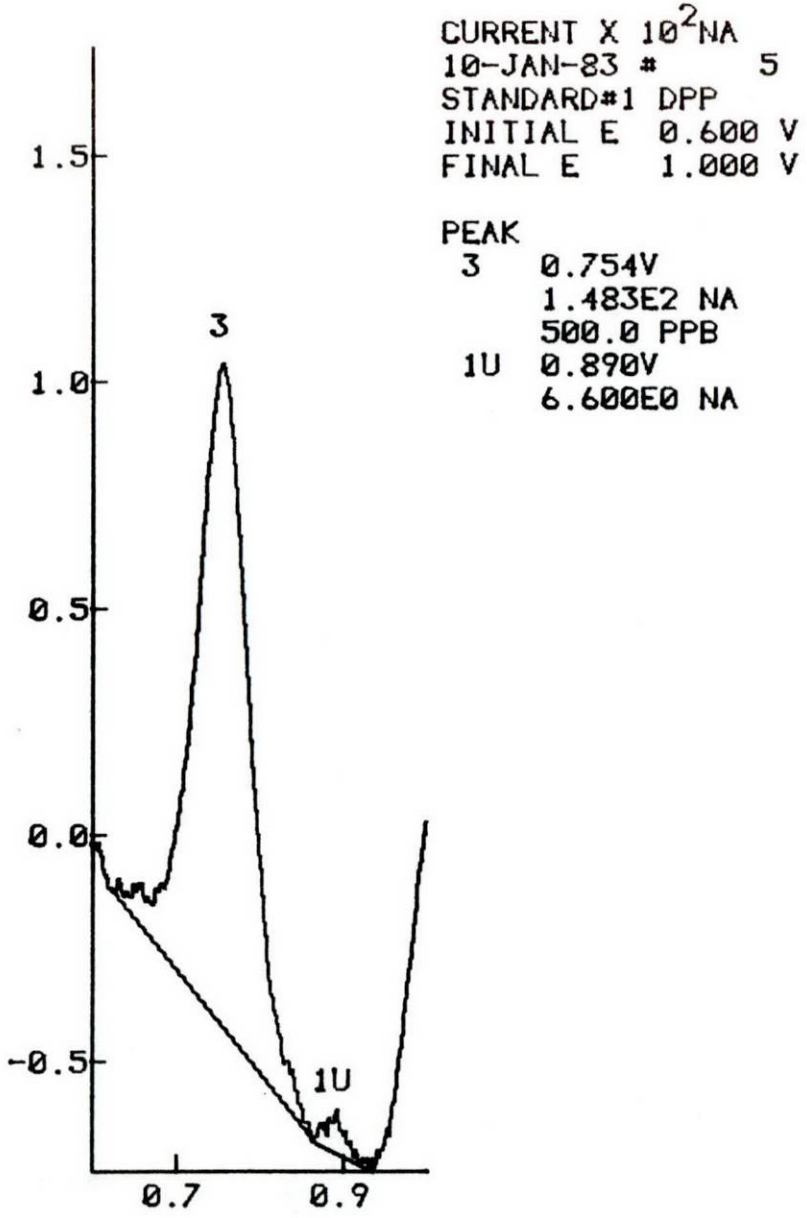
	10	11	12	13	14	15	16	17	18	19	20
OVERRIDE	Y	N	Y	Y	N	N	Y	N	N	Y	N

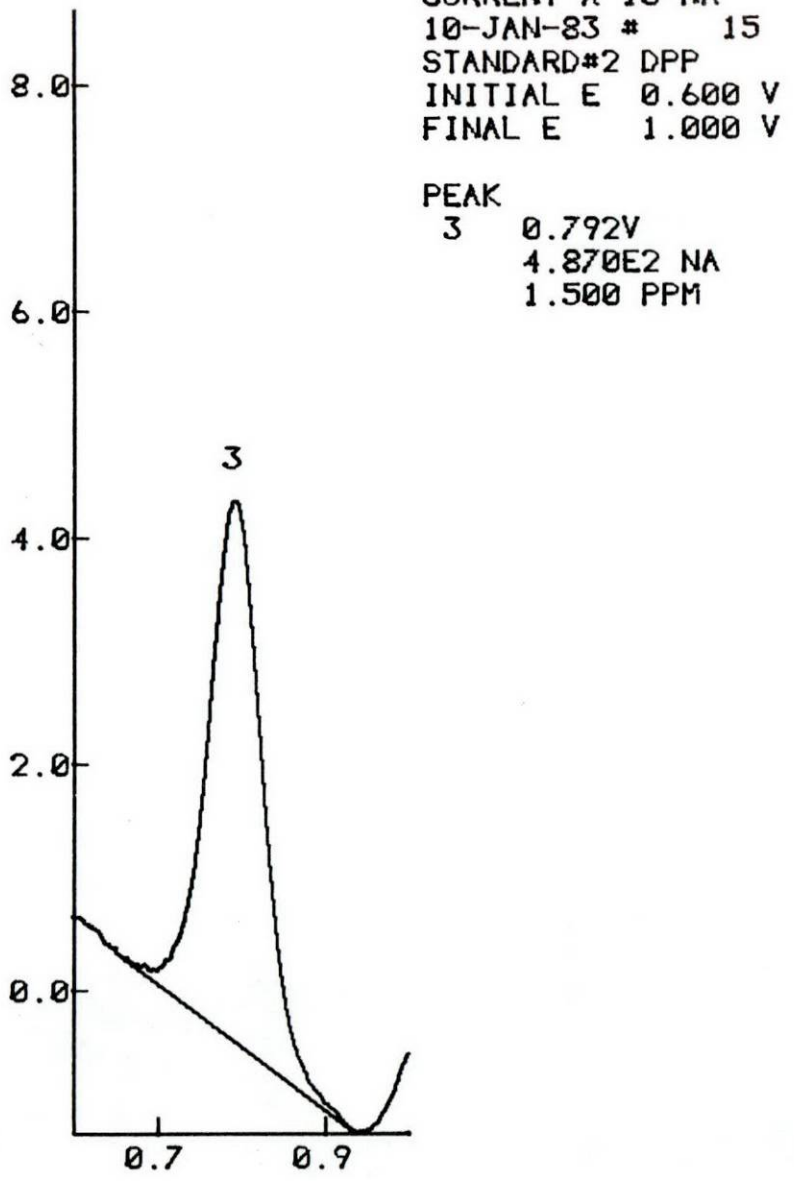
PEAK	POT	STD 1	STD 2	STD 3
3	0.775 V	500.0 PPB	1.500 PPM	3.000 PPM

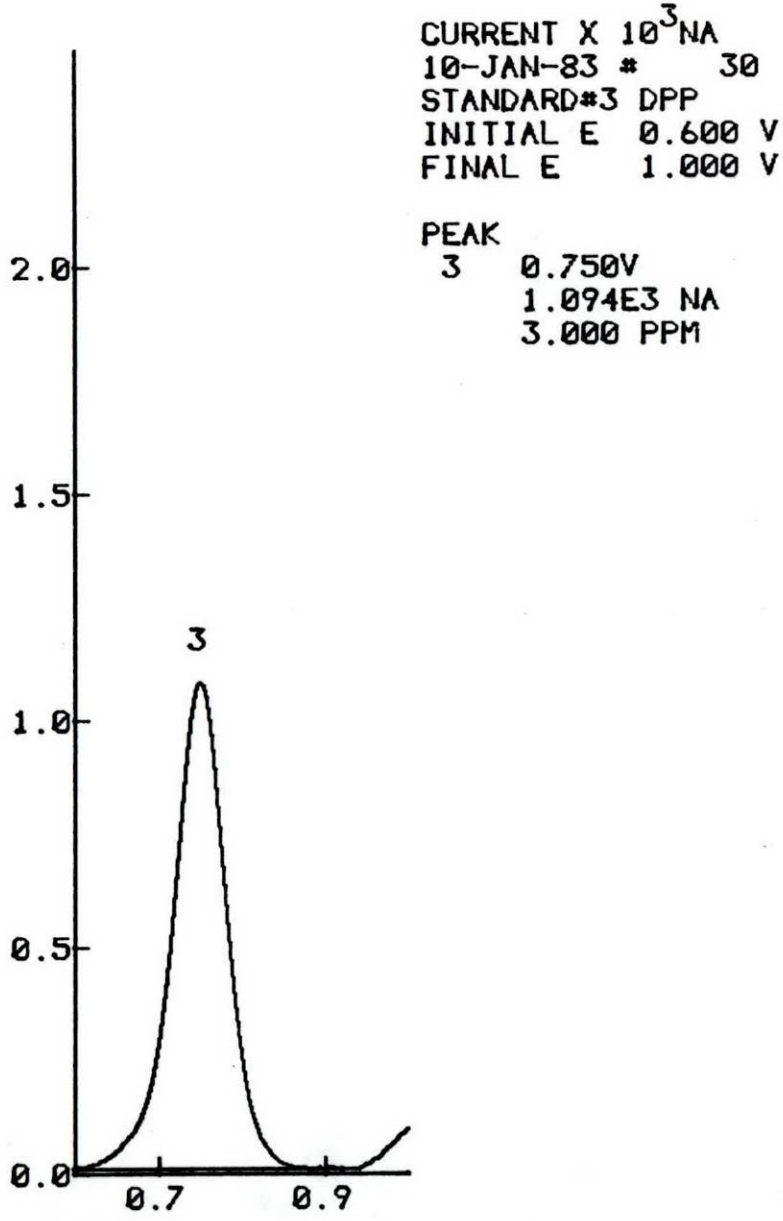
APPENDIX III

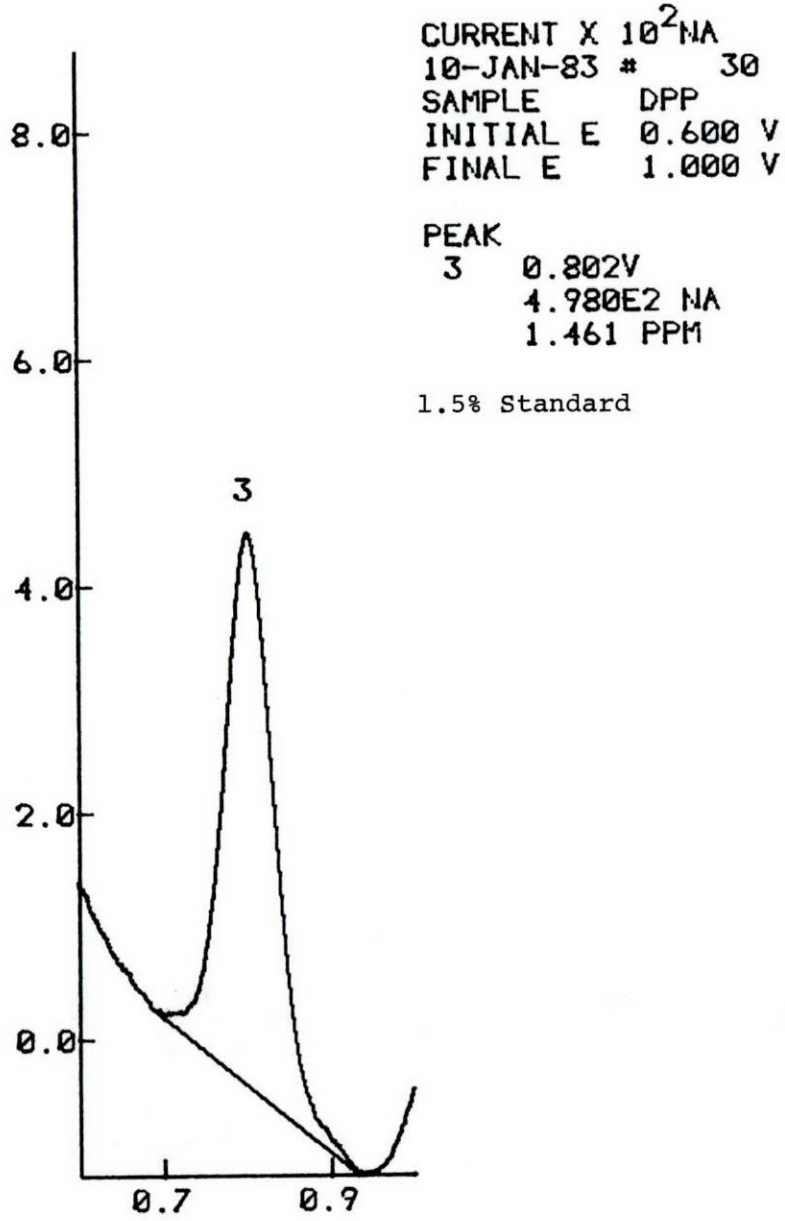

CALIBRATION CURVE #3 CURRENT X 10^3 NA
SLOPE= 3.803E-01 NA/PPB INTERCEPT=-5.750E1 NA
SUM RESIDUALS^2= 1.034E+03 NA^2
2.0
1.5
1.0
0.5
0.0
1
2
3
4
1.000 PPM
2.000 PPM
3.000 PPM
4.000 PPM
5.000 PPM


CURRENT X 10^3 NA
10-JAN-83 # 1
BLANK DPP
INITIAL E 0.000 V
FINAL E 1.000 V
2.0
1.5
1.0
0.5
0.0
0.1
0.3
0.5
0.7
0.9


CURRENT X 10^2NA
10-JAN-83 # 5
STANDARD#1 DPP
INITIAL E 0.600 V
FINAL E 1.000 V
PEAK
3 0.754V
1.483E2 NA
500.0 PPB
1U 0.890V
6.600E0 NA
1.5
1.0
0.5
0.0
-0.5
0.7
0.9
3
1U


CURRENT X 10^2NA
10-JAN-83 # 15
STANDARD#2 DPP
INITIAL E 0.600 V
FINAL E 1.000 V
PEAK
3 0.792V
4.870E2 NA
1.500 PPM
8.0
6.0
4.0
2.0
0.0
3
0.7
0.9


CURRENT X 10^3 NA
10-JAN-83 # 30
STANDARD#3 DPP
INITIAL E 0.600 V
FINAL E 1.000 V
PEAK
3 0.750V
1.094E3 NA
3.000 PPM
2.0
1.5
1.0
0.5
0.0
3
0.7
0.9


CURRENT X 10^2NA
10-JAN-83 # 30
SAMPLE DPP
INITIAL E 0.600 V
FINAL E 1.000 V
PEAK
3 0.802V
4.980E2 NA
1.461 PPM
1.5% Standard
8.0
6.0
4.0
2.0
0.0
3
0.7
0.9

F-6

Electronics II
Session F

The Use of Cyclic Voltammetric Stripping for Determination of Additive Concentration in Copper Plating Baths

Gerry Bush
UPA Technology, Inc.
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The Use of Cyclic Voltammetric Stripping for Determination of Additive Concentration in Copper Plating Baths.

Gerry Bush

Director, Sales & Marketing

UPA TECHNOLOGY, INC.
SYOSSET, NY

Cracks, voids, discontinuities, thin copper plate ..... these are some of the major nemeses of the printed circuit board industry ..... until now.

A recently developed technique, Cyclic Voltammetric Stripping (CVS), has been applied to the analysis of copper plating baths, both pyrophosphate and acid copper sulfate.

The CVS method allows the manufacturer to determine the optimum conditions for circuit board plating by providing data on the additive and contaminant levels in the bath.

Research has shown that the major problems normally encountered in plating circuit board through-holes can be attributed to the brightener concentration or contaminant levels in the bath. When the brightener concentration is too low, deposits are burnt or folded-back and may not have acceptable tensile properties. Contrarily, excessive brightener in the deposit can induce brittleness or reduce solderability. Contaminants have a similar effect on the tensile and solderability properties of deposits. Only with close control via CVS can the effects of bath composition on deposit quality be accurately and precisely determined.

THE THEORY

The Cyclic Voltammetric Stripping method determines the concentration of brightening or levelling additives from the effect these additives exert on the electrodeposition rate. In this method the potential of an inert rotating electrode immersed in a sample of the bath is cycled at a constant rate so that a small amount of copper is alternately deposited on the electrode and stripped off by anodic dissolution. The charge required to strip the copper is related to the deposition rate and, therefore, to the additive concentration in the plating bath. Changes in the electrode surface, bath composition and other variables are compensated for by using the internal standard provided by a static electrode. The ratio (A_r/A_s) of the stripping peak (A_r) relative to that for the static

electrode in the same bath solution (A_s) is a measure of the effective additive concentration. (See Fig. 1 for typical CVS Voltammogram).

THE METHOD

A sample of the plating bath is placed in a beaker, and three electrodes (rotating, reference and auxiliary) are placed in the solution. The potential of a rotating electrode is cycled relative to a reference electrode, the current passing between the auxiliary and rotating platinum (working) electrodes. Consequently, when the working rotating electrode is sufficiently negative, copper is deposited and when the electrode becomes positive, the copper is stripped off. (Fig. 2).

Copper is being deposited all the time that the graph shows a current below the zero current line, first, when the potential is going more negative, but also when the potential is returning towards the zero potential. While copper deposition is occurring, generally some of the additive at the electrode interface is being used up, either being reduced, included in the deposit, or whatever. This parallels the experience in the regular plating bath. In fact, this beaker with its electrodes may be regarded as a miniature plating bath in its own right. When the copper is being stripped from the deposit back into the bath, the exact fate of the included additive is unknown. During the cycle, there is a net loss of additive in the region of the electrode.

Now, different additives work in different ways. Frequently they work by suppressing deposition at points of high current density. Thus allowing other regions to "catch up" and produce a smoother deposit. In this case (example, Cu-pyrophosphate with the additive in the 1 to 3 ppm region) during deposition with a rotating electrode, the additive is consumed, and on stripping, the copper is dissipated from the electrode. But the rotation brings fresh solution into contact with the rotating electrode all the time, so that the additive is always replenished and present. Thus copper deposition is influenced by the presence of the additive. On the other hand, when the electrode is stationary, no such replenishment of the additive occurs, even during copper stripping, because in fact the additive is changed (altered, destroyed) during the deposition. Consequently, during the CVS run, especially on the second and subsequent cycles, deposition occurs as if there were little or no additive present, and this is reflected in the numbers for A_r, A_s and ratio. In practise, a calibration curve is constructed using CVS and additive is replenished according to the calibration curve. One manufacturer using pyrophosphate merely adds additive to reach a ratio of 0.9 or 1.0.

In acid copper sulfate baths, a similar procedure is used. A calibration curve is prepared of "Ratio" vs. "ml of additive per liter" using fresh bath and additive. A sample of the bath in use is run and additive may be added until the correct ratio is attained.

Interestingly, when the voltammetric stripping rate parameter (A_r/A_s) is plotted as a function of the additive concentration in a fresh bath versus a contaminated production bath, the contaminants shift the curve to the right. This clearly indicates that more brightener is required in contaminated baths to produce the same effect on the electrodeposition rate. Additionally, the chloride ion level in acid copper sulfate baths can be measured with CVS. These measurements are considered to be the principal strengths of the voltammetric method.

THE INSTRUMENT

A sophisticated microprocessor based instrument has been developed to present the valuable data obtained by the CVS method. UPA TECHNOLOGY's QUALIDERM Q-100 (Fig. 3) computes and displays the A_r/A_s ratio for a given plating bath under analysis. It can also be connected to an X-Y plotter to provide a voltammogram ("fingerprint") of the bath. (Fig. 4).

CONCLUSION

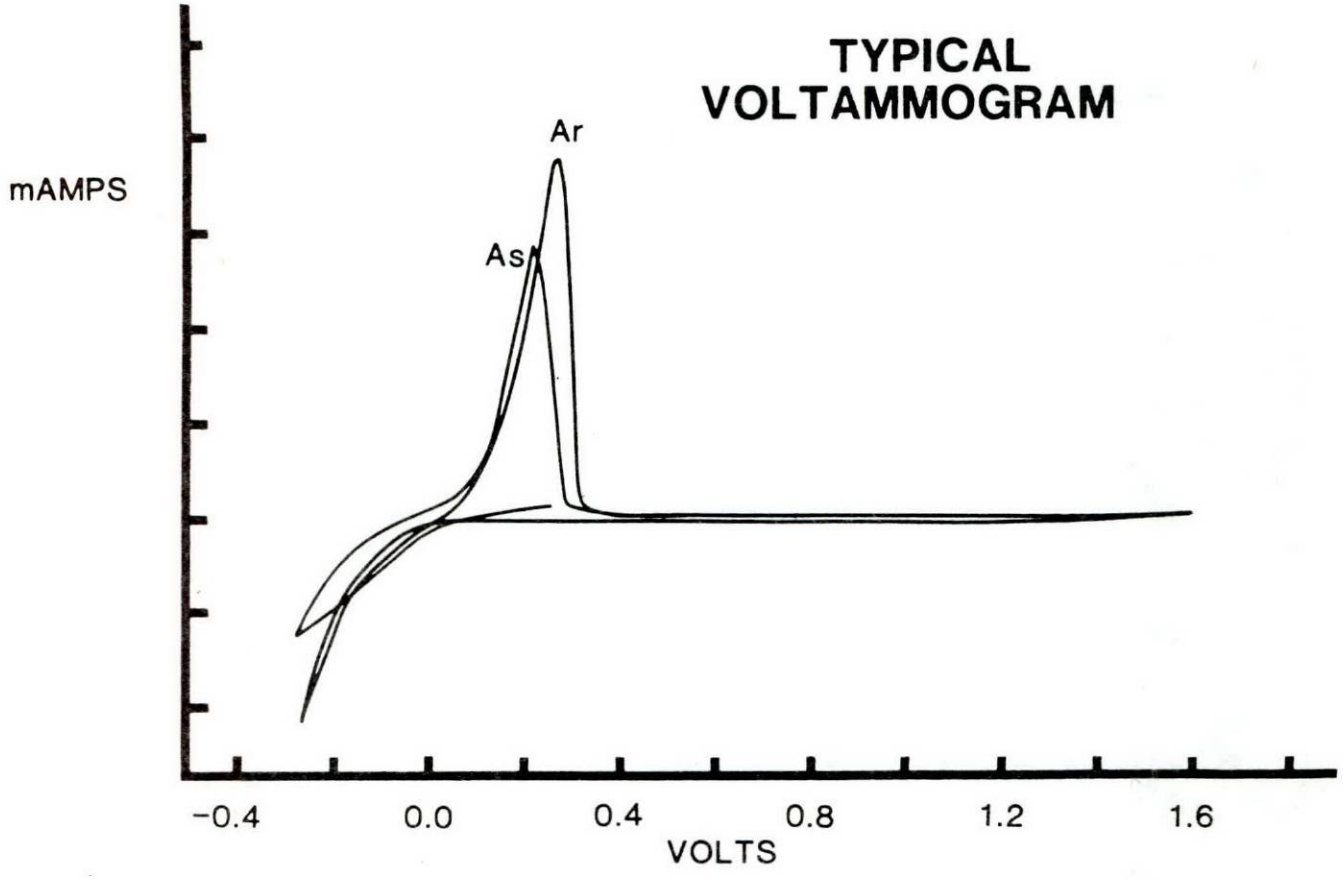
For the first time, producers of printed circuit boards can have quantitive control of their plating baths. Together, CVS and QUALIDERM yield data that allows for improved plating bath additive control and reduction of reject rates, additive waste, unnecessary carbon treatment.

References

1. C. Ogden and D. Tench, Plating & Surface Finishing, (Sept.79)

2. Haak, Ogden, Tench, Plating & Surface Finishing (April 1981)

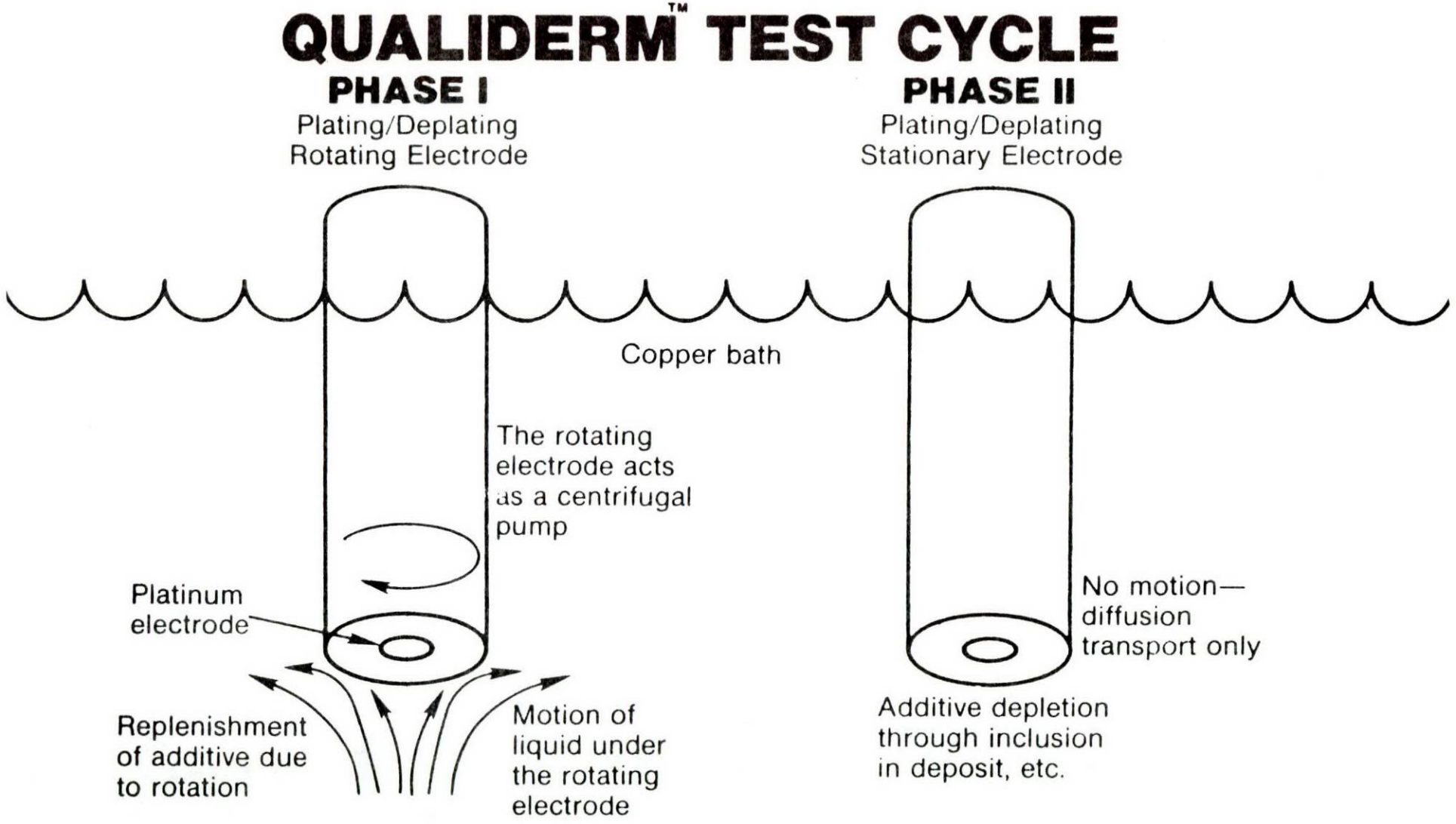
FIGURE 1



DIAG-1

Above is an example of a voltammogram, or "fingerprint" of a copper-plating bath produced by an X-Y recorder used with the QUALIDERM. The area under the peak, labeled Ar, represents the charge (coulombs) required to strip the plating from the platinum electrode while rotating. The area under the As peak represents the charge required to strip the plating from the platinum electrode while stationary. The ratio of Ar to As is an indicator of the effectivity of the plating bath and of the additive concentration.

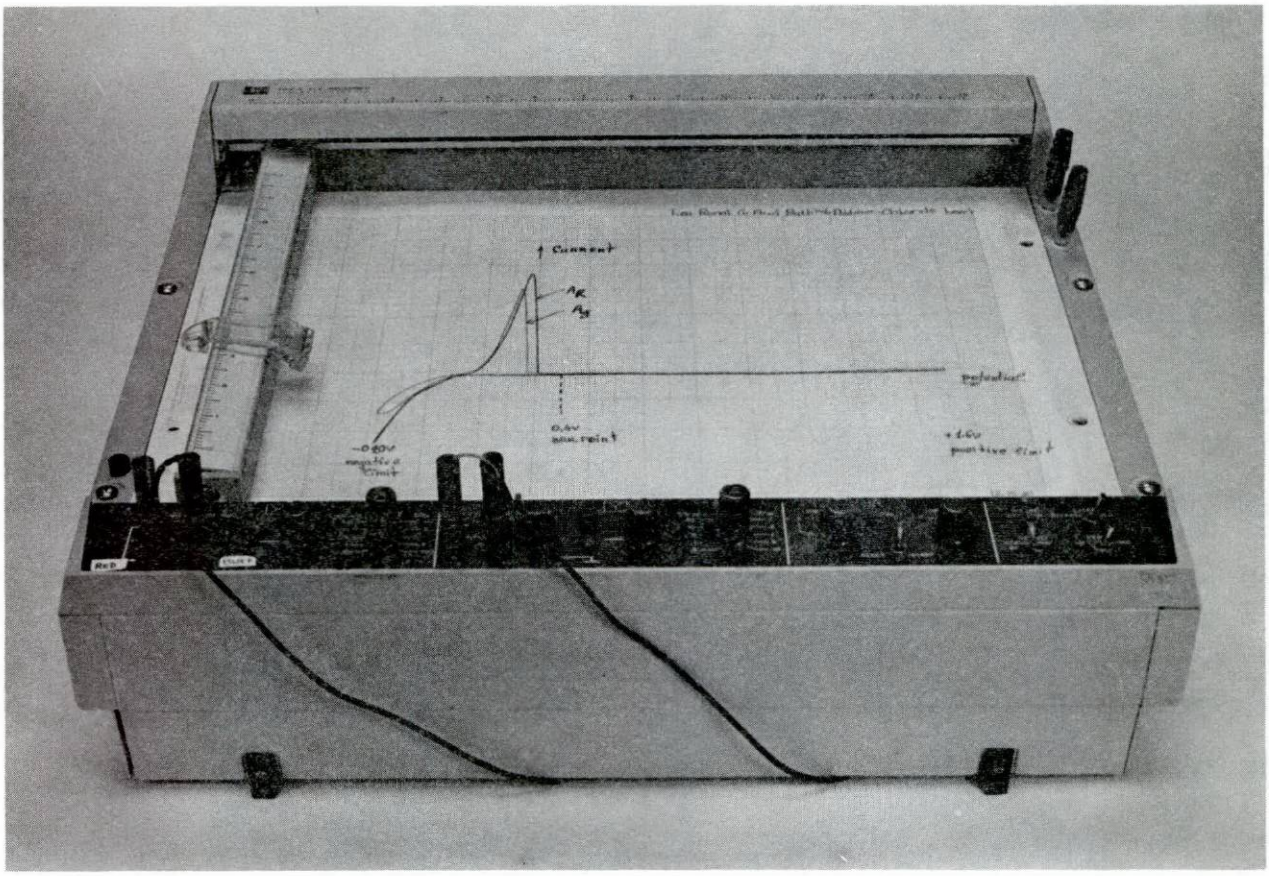
FIGURE 2


QUALIDERM™ TEST CYCLE
PHASE I
Plating/Deplating
Rotating Electrode
PHASE II
Plating/Deplating
Stationary Electrode
Copper bath
The rotating electrode acts as a centrifugal pump
Platinum electrode
Replenishment of additive due to rotation
Motion of liquid under the rotating electrode
No motion— diffusion transport only
Additive depletion through inclusion in deposit, etc.


READOUT
24.15
SWEEP
NEG
BREAK PT
STBY
RUN
MAN
POS
CONTAM
ERROR
QUALIDERM

FIGURE 3

FIGURE 4




AMERICAN ELECTROPLATERS' SOCIETY