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Acid Copper Sulfate Plating Bath: Control of Chloride and Copper

K. J. Borhani

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Final Report

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Allied-Signal Aerospace Company
Kansas City Division

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Plated-through holes in high-reliability printed wiring boards require a ductile copper plate of uniform consistency. The level of control of the chemical constituents in the electroplating solutions dictates the physical properties of the copper plate. To improve the control of the chemical bath constituents, in-situ methods for electrochemically determining copper and chloride in acid copper sulfate baths were developed. A solid-state ion-selective electrode was used for the chloride ion and proved to be more reproducible than conventional silver chloride turbidimetric methods. The use of a copper solid-state ion-selective electrode in-situ was also successful in this application.

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CONTENTS

4

ILLUSTRATIONS

TABLES

SUMMARY

This is the final report on the project, "Electrochemical Techniques for Control of Copper Plating Baths," which involved investigating the controlling of organic and inorganic chemical constituents that critically influence the copper electrodeposit in the through-holes of printed wiring boards. The organic brightener and ammonia studies related to the copper pyrophosphate electroplating bath were published in earlier reports. The investigation detailed in this report focuses on the control of chloride and copper in the acid copper sulfate electroplating bath.

The direct measurement of chloride in the parts-per-million range *in-situ* via ion-selective electrode proved to be more reliable (accuracy = ±0.91 ppm, precision = ±0.90 ppm) and more sensitive than chloride analysis by the following conventional silver chloride turbidimetric procedures: the mercuric nitrate titration method, the Jackson turbidimeter method, and the spectrophotometric method for measuring turbidity. The chloride electrode used in this investigation was a solid-state electrode consisting of silver halide/sulfide salts in an epoxy matrix. Of the 14 different bath formulations from 12 vendors only one was not amenable, primarily due to the presence of bromide, to chloride determination by ion-selective electrode.

The direct measurement of cupric ion *in-situ* via ion-selective electrode in the 60 to 120 gram/liter range proved to be more reliable (accuracy = ±3.0 g/L, precision = ±2.0 g/L) than the titration methods with visual end points suggested by the plating bath vendors, namely the ethylenediamine tetraacetic acid titration and the iodometric titration methods. A solid-state silver sulfide copper electrode was used in this investigation.

Conventional reference electrodes such as silver/silver chloride and saturated calomel could not be used because of the introduction of chloride ion from the electrode bridge into the sample. A double-junction reference electrode with a sulfuric acid outer fill solution to serve as the bridge was initially employed; however, it required considerable maintenance and the cap deteriorated with time due to attack by the 10 percent sulfuric acid environment. A pseudoreference electrode consisting of a platinum wire proved to be reliable on-line and to be able to withstand the harsh chemical nature of the production acid copper sulfate electroplating bath.

With a calibration check every two hours, chloride and copper solid-state electrodes, used with a platinum pseudoreference electrode, provided reliable on-line analysis of production acid copper sulfate electroplating baths for 13 of the 14 bath formulations studied.

DISCUSSION

SCOPE AND PURPOSE

This project was established to apply electrochemical techniques to the control of critical chemical parameters in copper plating baths for printed wiring boards in high-reliability applications. Only two chemical solutions, copper pyrophosphate and acid copper sulfate, are in wide use for military-grade printed wiring boards with plated-through holes. The concentrations of both organic and inorganic chemicals in the two baths directly influence the ductility and uniformity of the copper deposit. The reason for selecting electrochemical analytical techniques was twofold: the electroplating mechanism is inherently electrochemical in nature; and the sensors are selective and relatively inexpensive.

The initial work concentrated on the copper pyrophosphate electroplating bath because this was the chemical process being used in the production of printed wiring boards at Bendix Kansas City Division. During the course of the project,the production bath was changed to acid copper sulfate which offered the following advantages over copper pyrophosphate: a more ductile copper plate, no evidence of foldback, no breakdown of primary salt with use, operation at room temperature, no volatilization of critical bath constituents, and fewer chemical parameters to monitor. As a result, the emphasis of the project was shifted from the copper pyrophosphate bath to the acid copper sulfate bath. Initially, the project did not include on-line monitoring; however, because under selected conditions the ion-selective electrodes proved to function reliably in-situ, on-line chemical sensing for certain chemicals was included in the project.

PRIOR WORK

The initial study[1] of chemical solution constituents and their influence on copper plated-through holes of printed wiring boards dealt with the organic proprietary additive PY61H (M&T Chemicals) in the copper pyrophosphate electroplating bath. Because of the need to understand the interaction of organic and inorganic constituents in copper plating baths as well as the need to control them on-line, a more in-depth investigation was initiated. Under this project, two electroplating systems were studied: copper pyrophosphate and acid copper sulfate. The control of ammonia[2] via a gas-sensing electrode was the major objective accomplished for the copper pyrophosphate bath.

ACTIVITY

Background

Nature of Plating Baths

Plating baths are highly ionic solutions in which metal salts are present in large concentration. Addition agents, which are typically present in concentrations far less than that of the primary salt, can be either organic or inorganic and usually are present to brighten and/or level the deposit. In the alkaline copper pyrophosphate bath, two addition agents--the dipotassium salt of dimercaptothiadiazole or a similar compound[1,2] and ammonia--brightened and leveled the deposit. In the acid copper sulfate electroplating bath the additives are also organic and inorganic.[3-8] Chloride in the range of 20 to 100 ppm is present in nearly every modern acid copper sulfate bath formulation. Below 20 ppm chloride the bath increases its consumption of organic addition agents while producing a copper deposit that is rough, "burnt," dull, or discolored. Above 100 ppm chloride the consumption of brightener in the bath is affected and produces a deposit that is nonuniform, streaked, and "burnt." It should be noted that chloride excesses are expensive to correct because they usually involve treatment of the bath with silver nitrate (silver chloride precipitates and is removed). Besides chloride, some other inorganic additives that have been used in acid copper sulfate baths are sodium sulfite, sodium thiosulfate, cyanide salts, and potassium-sodium titrate (Rochelle salt). The organic addition agents are typically mixtures of one or more nitrogen- and/or sulfur-containing compounds from one of three categories.

Low Molecular Weight Organic Sulfur-Containing Compounds

- dithiooxamide
- phenosulfonic acid
- saccharin
- thioacetamide
- thioglycollic acid
- thiosemicarbazide
- thiourea

Heterocyclic Organic Nitrogen-Containing Compounds

- phthalocyanine (dye)
- safranine (azophenylene based dyes)

Organic Mixes Derived From Biological Sources

- hydrolyzed starch (dextrin)
- hydrolyzed collagen (gelatin)
- hydrolyzed keratin (cystine)

The first category contains those organic additives more generally used in high-volume military-grade production baths.

The additives in this category are frequently supplied from the vendor in 5 to 10 percent polyethylene glycol or polyprophylene glycol solutions. The second category of additives is usually referred to as the dye brighteners which, along with those in category three, tend to break down chemically more readily and, as a result, require more bath maintenance in order to maintain adequate additive level.

Knowledge of the chemical natures of bath additives is critical to the successful implementation of on-line chemical monitors because the chemicals in the additives may influence the signals received by the monitor.

Solid-State Silver Salt Electrodes

General Characteristics of Silver Sulfide Electrodes. Silver salts, particularly silver sulfide, are ionic conductors of low resistance in which the silver ions are the mobile species.

The solubility product constants (K_{sp} at 25°C) are listed for three salts:

- $CuS = 8.7 \times 10^{-36}$
- $Ag_2Cl = 1.2 \times 10^{-10}$
- $Ag_2S = 1.0 \times 10^{-51}$.

The exceedingly low solubility product ($K_{sp} = 10^{-51}$) of Ag_2S, its resistance to oxidizing and reducing agents, and the ease with which it can be fabricated into dense polycrystalline membranes by conventional pellet pressing techniques, make it a desirable material for electrode use.[9] Calibration curves obtained with silver sulfide membrane electrodes are Nernstian; that is, their behavior can be described by the Nernst Equation.

Reaction:

$$Ox + ne^- \rightleftarrows Red$$

where

Ox = oxidized chemical species;
Red = reduced chemical species; and
n = number of electrons.

Nernst Equation:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox}}$$

where

E = electrode potential;
E° = standard electrode potential;
R = molar gas constant ($8.314\ J \cdot mol^{-1} \cdot K^{-1}$);
T = absolute temperature;
n = number of electrons;
F = Faraday's constant ($96,484.57$ Coulombs$\cdot mol^{-1}$);
a_{Red} = activity of reduced species; and
a_{Ox} = activity of oxidized species.

When the chloride-ion-selective electrode is in contact with the chloride-containing solution, silver ions dissolve from the membrane surface and the electrode develops a potential due to the silver ion concentration. The measured potential corresponds to the level of the chloride ion (Cl^-) in solution as described by the Nernst equation. Since the silver chloride is much more soluble (see K_{sp}) than silver sulfide, the sulfide can be considered as a chemically inert material through which silver ions are free to move.

When the cupric-ion-selective electrode is in contact with the cupric-containing solution, cupric ions (Cu^{2+}) dissolve from the membrane surface and the electrode develops a potential because of the silver ion concentration:

$$Cu^{2+} + Ag_2S \rightleftarrows CuS + 2Ag^+ \ .$$

The measured potential corresponds to the level of cupric ion in solution as described by the Nernst equation. Note that this is a two-electron transfer. (There is a 29.5 mV change for every tenfold change in concentrations.) It should also be noted that because of the divalent ion in cupric measurements the uncertainty in potential measurement will be greater.

By substituting concentrations for activities, common logarithms for natural logarithms, numerical values for constants, and by assuming the temperature to be 25°C, the Nernst equation can be rewritten in the simpler form:

$$E' = \frac{0.059}{n} \log \frac{\text{Red}}{\text{Ox}} \text{ where } E' = E - E^\circ \ .$$

Typically, if a one-electron charge transfer were being monitored, the sensor should show a 59 mV change for every tenfold change in concentration. This would be ideal Nernstian behavior.

The dynamic range of the silver sulfide electrode extends from saturated solutions down to the 0.1 ppm level. The lower limit (0.1 ppm) is too high to be caused by the solubility of the membrane ($K_{sp} = 10^{-51}$); it reflects instead the difficulty of preparing extremely dilute solutions of ions without extensive ion adsorption on and desorption from the surfaces of the containing vessels and the electrodes.

Mixed Salt-Silver Sulfide Electrodes for Ion Selectivity. In the project being described in this report, two types of mixed-salt silver sulfide electrodes were used (Table 1). For chloride-ion selectivity the silver-sulfide sensing membrane contains silver chloride. For cupric-ion selectivity the silver-sulfide sensing membrane contains cupric sulfide.

An electrode in an average laboratory will show a noncumulative drift of about 2 mV per day. Under process control conditions (for example, in-situ) even larger fluctuations occur. The presence of drift requires periodic restandardization at a frequency which depends on the accuracy required and the rate of temperature variation.

Reference Electrodes

Unlike combination pH electrodes or the ammonia gas-sensing electrode described in an earlier report,[2] the silver sulfide electrodes, being solid ("solid-state"), do not have internal reference electrodes.[10] As a result, an external reference electrode must be inserted, along with the silver sulfide electrode, into the solution in order to have a complete circuit. The primary requirements for a reference electrode are reversibility of the half-cell reaction, reproducibility, and stability. The half cell of the reference electrode provides a constant potential regardless of solution composition. The conventional reference electrodes used with ion-selective electrodes are the silver/silver chloride electrode and, to a

Table 1. Uncertainty in Chloride-Ion and Cupric-Ion Selectivity

Precision in E (mV)	Uncertainty (Percent) Monovalent Ion*	 Divalent Ion**
0.1 mV	0.4	0.8
2.0 mV	7.5	15.0

*such as Cl^-
**such as Cu^{2+}

lesser extent, the saturated calomel (Hg/Hg_2Cl_2) electrode. Both of these reference electrodes rely on an internal chloride (usually saturated potassium chloride) filling solution as the electrolyte which forms a low-junction-potential liquid junction with the sample solution. Because the filling solution could contaminate the acid copper sulfate bath with chloride ion, a double junction silver/silver chloride reference electrode would be the reference electrode of choice from those commercially available (see Figure 1).

The outer fill solution is typically 10 percent potassium nitrate, but for the purpose of performing measurements in acid copper sulfate plating baths the outer chamber was filled with 10 percent sulfuric acid.

Chloride Analysis

Because chloride in the acid copper sulfate bath is typically in the range of 20 to 100 ppm, it was felt that the diversity in chemical nature of the organic additives commercially available may not allow certain chloride analytical methods, particularly analysis by ion-selective electrode. In this project, 14 bath formulations from 12 vendors were investigated.

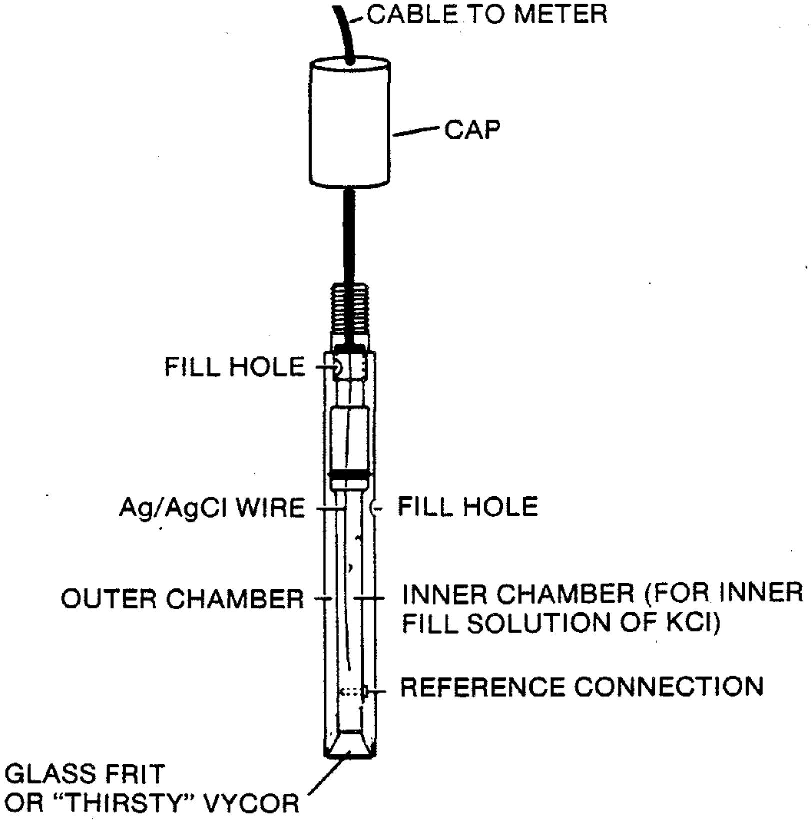


Figure 1. Double Junction Reference Electrode

Of the 12 acid copper sulfate plating bath vendors, only nine supplied analytical methods for the plating bath constituents. For chloride analysis only three methods were recommended, all of which rely on silver chloride formation by the addition of silver nitrate to the bath sample:

$$\underset{\text{from bath}}{Cl^-} + \underset{\text{from silver nitrate}}{Ag^+} \longrightarrow \underset{\text{Insoluble.}}{AgCl \downarrow}$$

Since silver chloride is insoluble in the bath sample, the solution becomes turbid and it is the "cloudiness" of the sample that is measured, either manually or instrumentally. Of the nine vendors suggesting analytical methods, two suggested the mercuric nitrate titration method, three suggested the Jackson turbidimeter approach, and four suggested the spectrophotometric measurement of turbidity.

AgCl Turbidimetric Method: $Hg(NO_3)_2$ Titration

The mercurimetric method has been in use for over 30 years for the titration of chloride in the 0 to 100 ppm range in natural waters.[11] Silver nitrate is introduced to the bath sample, and the subsequently formed silver chloride creates a cloudy solution. The sample is then titrated with a standard solution of mercuric nitrate until the cloudiness is observed to disappear,

$$2Cl^- + Hg^{2+} \rightleftarrows HgCl_2 \; .$$

AgCl Turbidimetric Method: Jackson Turbidimeter

The Jackson turbidimeter relies on silver nitrate additions to the bath solution until the turbidity of the solution no longer allows direct viewing of the light source. The turbidimeter used in this project (Figure 2) was in accordance with American Public Health Association (APHA) requirements.[12]

With a visual end point the accuracy and precision became considerably operator-dependent; however, using the light source, the end point was more easily determined than the unaided visual end point in the mercurimetric method. Figure 3 gives the typical calibration curve showing the inverse relationship between turbidimeter readings and chloride ion concentration. It should be noted that for chloride concentrations below 45 ppm the Jackson turbidimeter would be of little use for 4 of the 12 bath formulations because the vendor recommended 40 ppm or lower as the low end of the chloride concentration range.

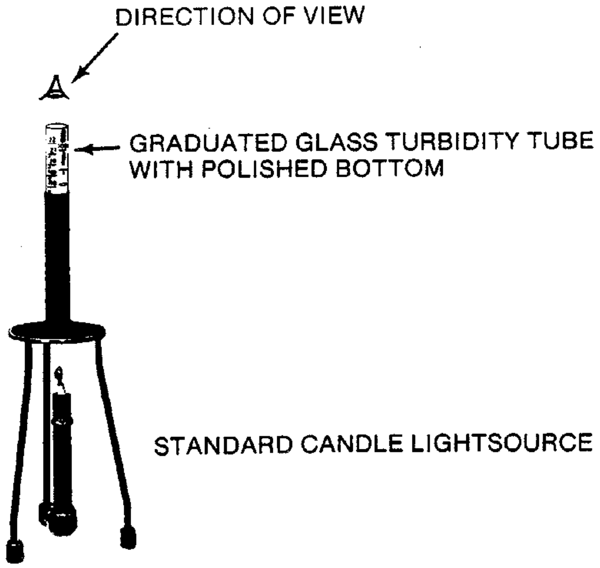


Figure 2. Jackson Turbidimeter

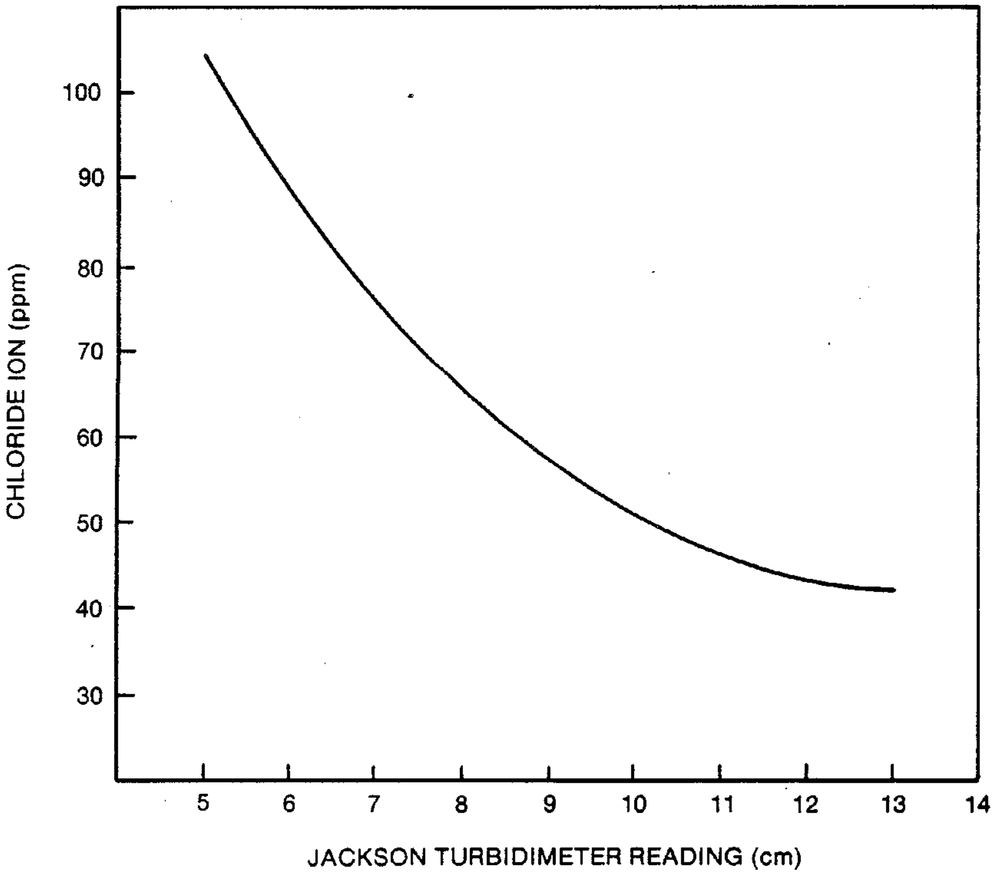


Figure 3. Typical Calibration Curve for Chloride Measurements Using the Jackson Turbidimeter

AgCl Turbidimetric Method: Spectrophotometry

Of the turbidimetric techniques, the spectrophotometric measurement of the cloudiness of acid copper sulfate bath samples treated with silver nitrate proved to be the most reliable. Using a Bausch and Lomb Spectronic 20 with the wavelength set at 440 nm, bath samples with more chloride present gave a higher light absorbance reading since less light was transmitted through the suspension. A linear calibration curve was observed for concentration versus absorbance (see Figure 4). It should be mentioned that success of the spectrophotometric method depends on protection of the silver chloride suspension from normal room light (AgCl darkens on exposure to light). Low-actinic glassware and ruby-red illumination were used in the preparation of the standards and bath solutions prior to absorbance measurements.

Influence of Organic Addition Agents

During analysis of the 14 bath samples containing different organic addition agents, the mercuric nitrate titration and the Jackson turbidimeter methods were not influenced by any of the agents, primarily because the bath samples were carbon-treated (i.e., the organics were removed) prior to analysis. For the spectrophotometric method in which the baths were not carbon-treated, the varied responses from one organic addition agent to another can be attributed to the shifting of the wavelength of maximum absorbance experienced with certain dye additives. By preparing the standards with the organic addition agents present and by selecting the proper wavelength for the absorbance measurement, the spectrophotometric method is optimized for the organic addition agent of interest.

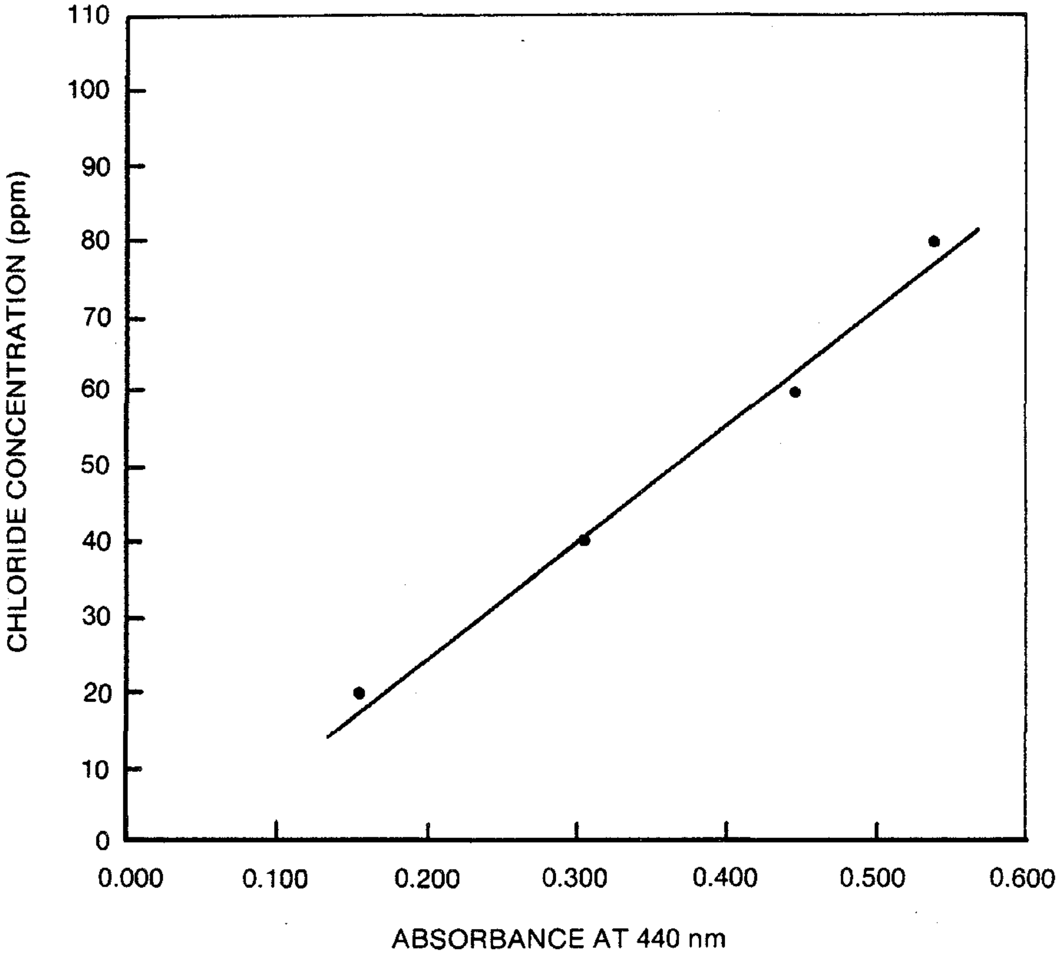


Figure 4. Calibration Curve for the Spectrophotometric Measurement of Turbidity (Bausch and Lomb Spec 20)

Chloride-Ion-Selective Electrode Method

The chloride electrode has been considered by others[13] as applicable for the analysis of chloride in acid copper sulfate plating baths. Until now, no one has considered the in-situ monitoring of chloride with electrodes or the influence of organic addition agents on the chloride measurement (10 to 100 ppm). Standards varying in chloride concentration were prepared from analytical-grade reagents; sodium chloride was added to a stock bath comprised of cupric sulfate pentahydrate, sulfuric acid, and 18.3 MΩ·cm water. Using a double-junction reference electrode with a 10 percent sulfuric acid outer-fill solution, the chloride-ion-selective electrode produced a calibration curve with a slope of 55 (ideal Nernstian slope = 59) when the electrode was left in contact in the solution only during chloride measurement (see Figure 5). A lower slope was observed when the electrode was maintained continually in the acid copper sulfate bath. To ascertain whether organic addition agents would have a cumulative effect on the electrode performance, the chloride-ion-selective electrode was immersed in an acid copper sulfate bath with a non-dye organic addition agent for six weeks with slope measurements taken periodically. For an additional six weeks the electrode was kept continually immersed in an acid copper sulfate bath with a dye organic addition agent. In each case, the slope was consistently 48 ±3. Since the double-junction reference electrode required weekly disassembly/reassembly and since the cap was showing evidence of chemical attack, an alternative reference electrode was sought. A clean platinum wire was used as a reference--actually as a pseudoreference--electrode since a reversible half-cell reaction is not defined.[14] A slightly lower slope was observed; however, it proved to give reproducible measurements and was not adversely affected by the 10 percent sulfuric acid environment (see Table 2).

High concentrations of ions which form insoluble salts of silver and complex silver, and/or salts which are capable of reducing silver ion, interfere with chloride-ion monitoring. Known interferences for the chloride-ion-selective electrode are OH^-, Br^-, I^-, S^{2-}, CN^-, NH_3, and $S_2O_3^{2-}$. Also, if chloride complexing agents are present (such as Bi^{3+}, Cd^{2+}, Mn^{2+}, Pb^{2+}, Sn^{2+} and Tl^{2+}), the measured concentration of chloride ion will be lower because the electrode responds only to free ions.

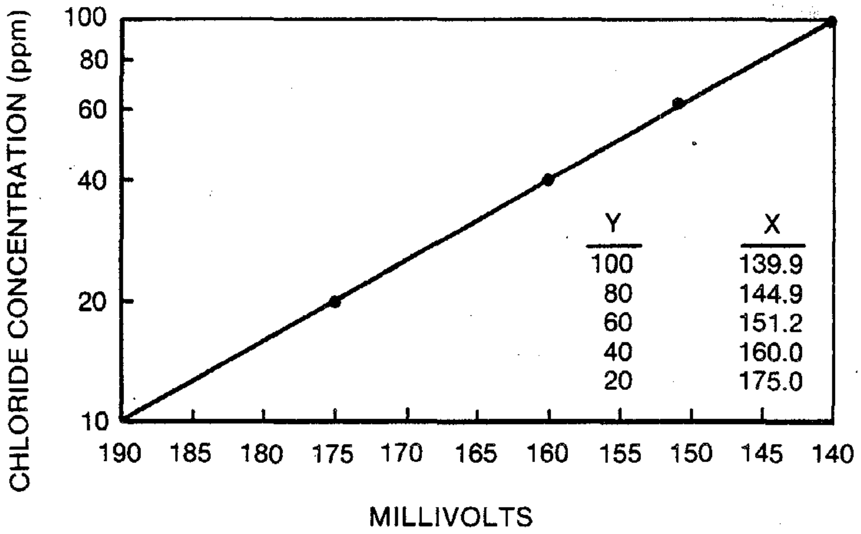


Figure 5. Typical Calibration Curve for Chloride Electrode Versus Double Junction Reference Electrode With 10 Percent H_2SO_4 Bridge

Of the 14 acid copper sulfate organic bath additives, only one was not amenable to chloride measurement via the electrode. From energy-dispersive X-ray fluorescence analysis the atypical brightener was observed to contain bromine. After treating the bromine-containing bath with sodium bromate in an attempt to oxidize the bromide, an electrode less sensitive to bromide interference was employed for chloride analysis. However, even after these measures, the bromine-containing organic additive did not lend itself to chloride analysis via ion-selective electrode.

Comparison of Turbidimetric and Cl^- Electrode Methods

The direct measurement of chloride ion via ion-selective electrode proved to be the easiest, most reliable, and most sensitive of all the methods investigated for 13 of the 14 acid copper sulfate bath formulations (see Table 3).

Table 2. Slopes for the Chloride-Ion-Selective Electrode

	Reference Electrode	
Conditions	Double Junction*	Platinum Pseudoreference
Laboratory	55 ±2	54 ±3
Production	48 ±3	47 ±3

*90-02, 10 percent H_2SO_4 bridge

With certain bath vendors recommending a 20 ppm range (40 to 60 ppm Cl^- control range), only the spectrophotometric and electrode methods would suffice unless more expensive analytical methods were employed, and even these may not necessarily result in improved reliability. (For example, in high-pressure ion chromatographic analysis, accuracy for chloride in acid copper sulfate baths is ±1 ppm with a reproducibility of 2.2 percent.)[15]

Copper Analysis

Copper in the acid copper sulfate bath is added as copper sulfate pentahydrate. Copper is also introduced, to a far lesser degree, from the corroding (oxidizing) anodes. The concentration range for copper in the bath is approximately 60 to 120 g/L with 70 to 90 g/L being the most desirable range. Control of the copper concentration is important since plating below the copper range will give a "burnt" deposit, while plating above the copper range will produce a nonuniform deposit. This is due to the increased resistivity of the solution which in turn adversely affects the throwing power.

Table 3. Comparison of Chloride Measurement Methods

	Chloride Measurement Method			
		AgCl Turbidimetric Techniques		
	Chloride Ion-Selective Electrode	Mecuric Nitrate Titration	Jackson Turbidimeter	Spectro-photometer
Detection Limit	5	20	45	20
Accuracy	±0.91	±12.0	±9.3	±2.0
Precision	±0.90	±11.8	±8.4	±1.3

Measurements in ppm

Of the nine acid copper sulfate plating bath vendors supplying chemical analysis methods on bath constituents, six recommended an iodometric titration while the remaining three suggested the ethylenediamine tetraacetic acid (EDTA) complexometric titration.

Titratium Method: Iodometry[16]

For many years copper has been determined by the iodine-thiosulfate couple. Iodine ion (I^-), in a quantity known to be more than sufficient, is added to the sample and it reacts immediately with the copper, setting iodine free; the amount of iodine formed is directly proportional to the quantity of copper present. This liberated iodine is then titrated against a standard thiosulfate solution, using starch as the indicator.

Ammonium hydroxide is first added to the acid copper sulfate bath sample resulting in the following reaction:

$Cu(H_2O)^{+2} + 4NH_3 \rightleftarrows Cu(NH_3)_4^{+2} + 4H_2O$.

When potassium iodide is added to a solution containing copper (II) ion, the following reactions takes place:

$2Cu^{+2} + 4I^- \rightleftarrows 2CuI \downarrow + I_2 \uparrow$
$2Cu^{+2} + 5I^- \rightleftarrows 2CuI \downarrow + I_3^-$.

The iodine is titrated with thiosulfate as follows:

$2\ S_2O_3^{-2} + I_2 \rightleftarrows S_4O_6^{-2} + 2I^-$
$2\ S_2O_3^{-2} + I_3^- \rightleftarrows S_4O_6^{-2} + 3I^-$.

The equivalents of thiosulfate used will be equal to the equivalents of copper present. Since starch imparts an intense blue color to solutions containing iodine, at the equivalence point a suddenly colorless solution appears.

Low results can occur because the liberated iodine can and does tend to be absorbed onto the surface of the precipitated cuprous iodide. Because it is only slowly released, premature end points can be observed. Thus, rigorous mixing throughout the titration is essential.

Titration Method: EDTA Complexation[17]

Because of the low results which can be obtained with the iodometric titration method, the complexometric (or chelometric) titration of copper (II) with EDTA is preferred by some for cupric analysis in acid copper sulfate baths. For the titration of cupric with a titrant that is a complexing ligand such as EDTA, the formation constant must be large so that the titration reation will be stochiometric and quantitative. This condition is satisfied with the Cu^{+2} - EDTA complex which has a $\log K_f =$ 18.8:

$$Cu^{+2} + Y^{-4} = CuY^{-2}$$

$$K_f = \frac{CuY^{-2}}{(Cu^{+2})(Y^{-4})}$$

where Y represents ethylenediamine tetraacetic acid, which is represented in Figure 6.

The preferred indicator for the titration is PAN [(1-(2-Pyridylazo-2-naphthol)]. Buffering of the acid copper sulfate bath sample prior to the titration is necessary in order to favor the quantitative formation of CuY^{-2}.

Copper (Cu^{2+}) Ion-Selective Electrode Method

As was the case with the chloride-ion-selective electrode, others have considered the use of the copper-ion-selective electrode for analyzing copper in the acid copper sulfate bath,[13] but as with the chloride electrode, the in-situ application and organic additive influence have until now not been reported. Standards varying in copper concentration were prepared from analytical-grade reagents dissolved in 18.3 MΩ-cm water. Sodium chloride, as well as a non-dye brightener, was added to the standard stock solution (60 ppm Cl^-). Figure 7 is the calibration curve obtained for the copper-ion-selective electrode; as predicted by the Nernst equation for a two-electron transfer, the slope is 29.

Studies of long-term exposure of the copper electrode to the harsh acid copper sulfate bath environment (six weeks in bath with non-dye organic additive then six weeks in bath with dye organic additive) revealed no adverse effects to the electrode's function. Also, when any of the 14 organic addition agents were present, they did not interfere with the copper measurements. When measured versus a platinum pseudoreference electrode, the

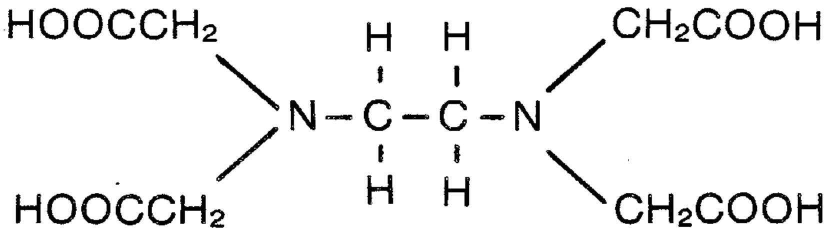


Figure 6. Ethylenediamine Tetraacetic Acid

slope for the calibration curve (as with chloride curves) was somewhat lower, at 27.

The chemical species known to damage or "poison" the electrode surface--mercury and silver--are not present in production acid copper sulfate baths. Ferric ion could be an interferent, but must be present in greater than one-tenth the cupric ion level in order to interfere; normal production baths would typically not contain such a large ferric ion concentration.

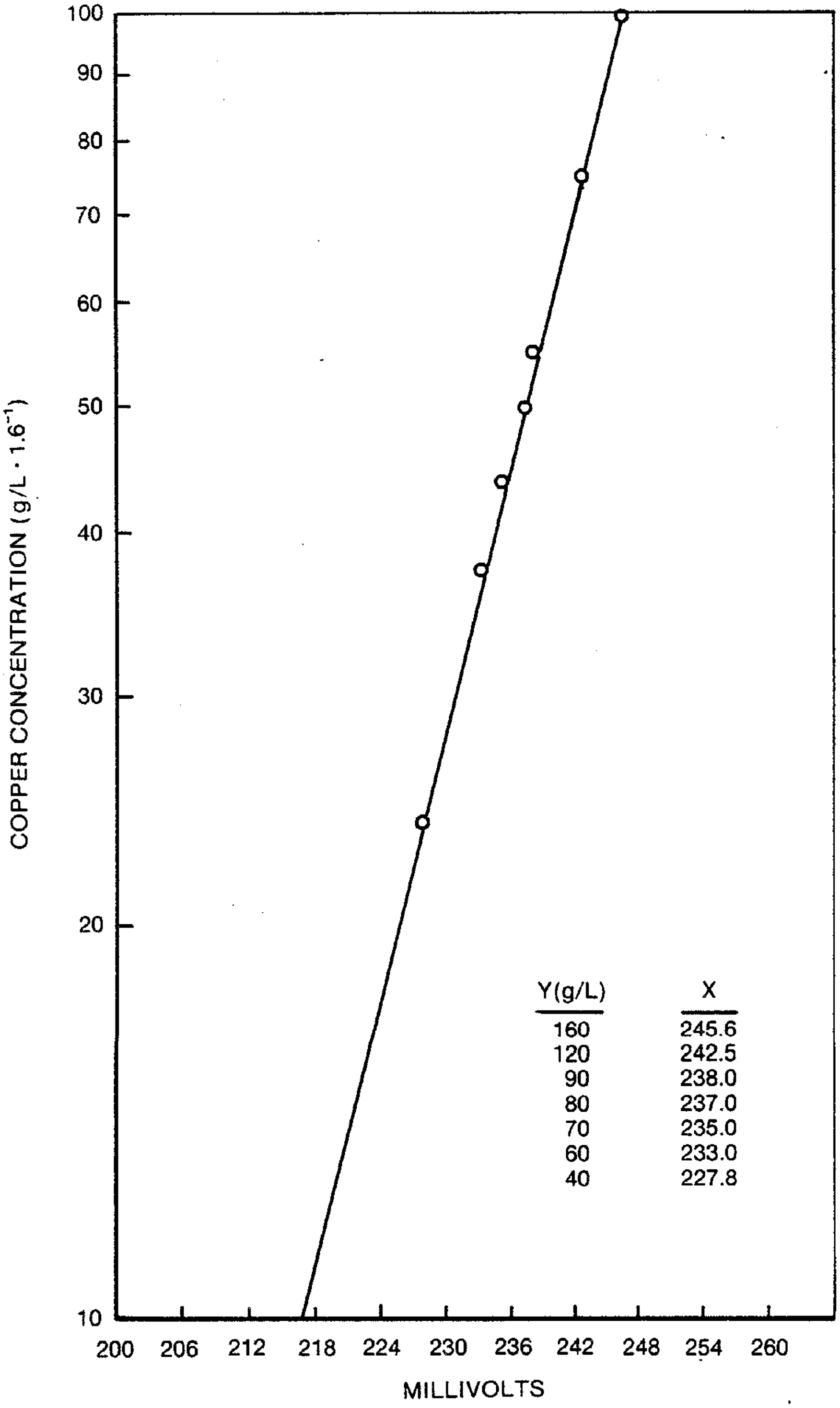
Comparison of Titration and Cu^{2+} Electrode Methods

The direct measurement of copper ion via selective electrode proved to be more reliable than the two titration methods suggested by the plating bath vendors (see Table 4).

It should be noted that the vendor-suggested methods were titrations with visual end-point detection. The titrations would have been more reliable if the end point had been detected potentiometrically.

Proposed Cl^-, Cu^{2+} On-Line Acid Copper Sulfate Bath Controller

Four chemical parameters must be in control for the acid copper sulfate production bath to plate through-holes of high-reliability printed wiring boards. They are copper, chloride, sulfuric acid, and organic additive(s). For organic additive(s) no direct method currently exists, though



Y(g/L)	X
160	245.6
120	242.5
90	238.0
80	237.0
70	235.0
60	233.0
40	227.8

Figure 7. Typical Calibration Curve for Cupric Electrode Versus Double Junction Reference Electrode With 10 Percent H_2SO_4 Bridge

Table 4. Comparison of Copper Measurement Methods

	Iodometric Titration	EDTA Titration	Copper-Ion-Selective Electrode
Accuracy	±5.0	±5.0	±3.0
Precision	±5.0	±2.5	±2.0

Measurements in g/L

considerable work has been reported on indirect, off-line measurement techniques.[18] For sulfuric acid (∿10 percent measurement) no direct, in-situ method exists, though automatic titration off-line could be used. It is reported that if the copper concentration and the density of the acid copper sulfate plating bath solution are known, sulfuric acid concentration can be derived.[19] The in-situ analysis of the two remaining parameters, copper and chloride, in acid copper sulfate production baths has been proved feasible in this project.

On-line controllers designed specifically for copper plating-baths are not commercially available except for electroless bath analyzers. One-parameter analyzers are available from manufacturers supplying ion-selective electrodes, colorimeters, and automatic titrators. In the latter two categories of analyzers, the sample is usually diluted and treated in such a way that its return to the bath is not acceptable; it is instead considered chemical waste.

Figure 8 gives one way of utilizing the chloride- and copper-ion-selective electrodes with a production bath where the electrodes are thermally isolated to maximize reliability. A 1°C change in temperature of the sample compared to the standard results in a 4 percent error. The processor will need to be

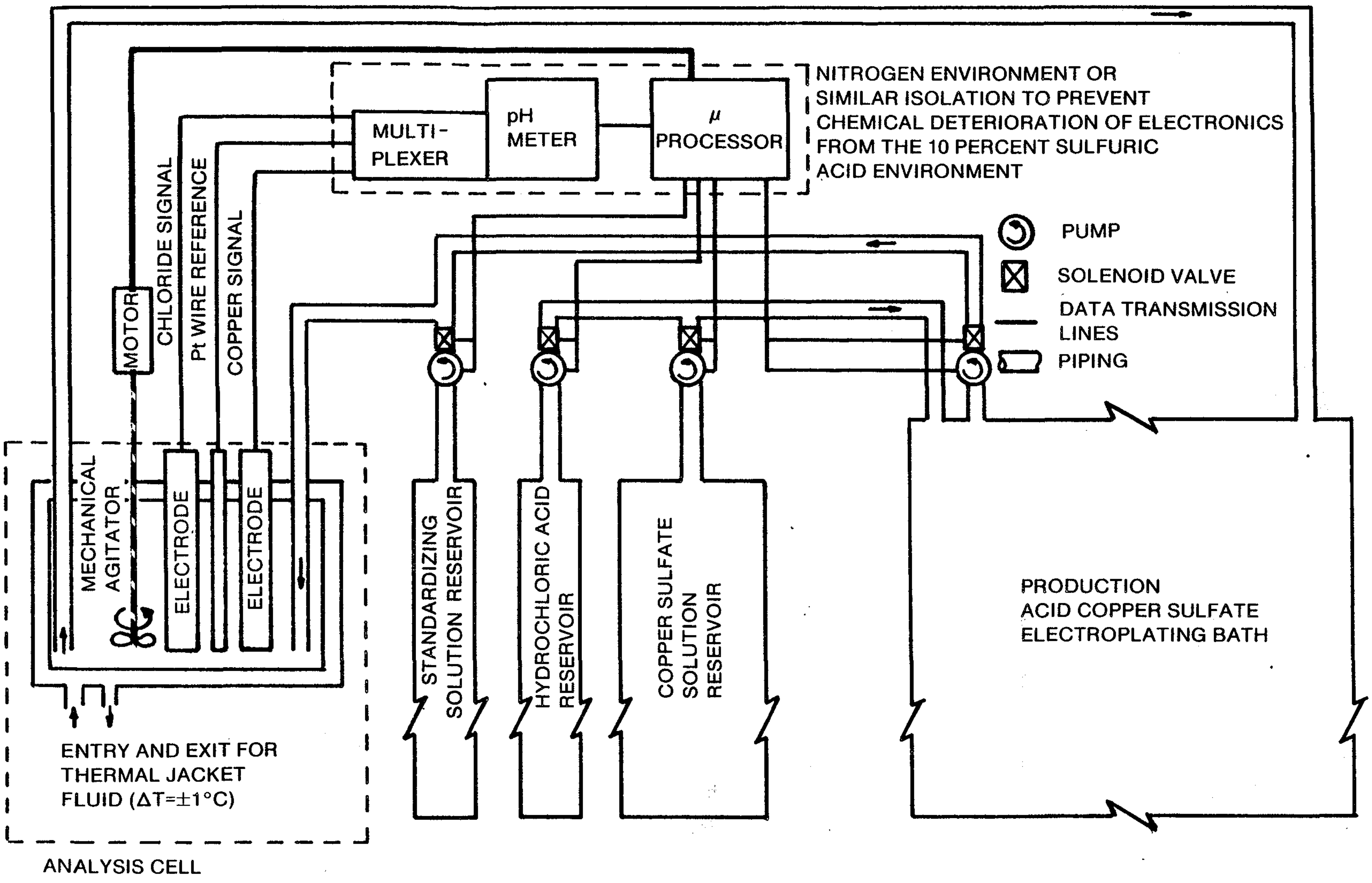


Figure 8. Proposed Two-Parameter On-Line Acid Copper Sulfate Bath Controller

programmed to recalibrate the analysis cell every two hours in order to achieve the accuracy and precision reported here.

ACCOMPLISHMENTS

A method for analyzing cupric and chloride ions in-situ for production acid copper sulfate baths containing organic addition agents has been demonstrated. The system relies upon electrochemical detection (via ion-selective electrode versus platinum pseudoreference electrode) and provides better accuracy and precision than the analytical bench-top methods suggested by the plating-bath vendors. The design of an on-line acid copper sulfate bath analyzer/replenishment system has been described.

FUTURE WORK

This project dealt primarily with the identification of electrochemical sensors to improve the control of copper electroplating baths. The project has been completed with the added success of proving the on-line capabilities of the copper and chloride sensors for the acid copper sulfate electroplating bath. In future projects, the following work, which is beyond the scope of this project, could be undertaken.

- Additional sensors could be developed, primarily for sulfuric acid and the organic additives, though non-electrochemical methods may be required.

- A prototype could be fabricated and proved-in for the two-parameter (or more) analyzer/replenisher.

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