Application Bulletin

Of interest to:	Plating and electroplating, PCB production, semiconductor, copper plating, CVS, suppressor, brightener	

ProcessLab plating bath analyzer

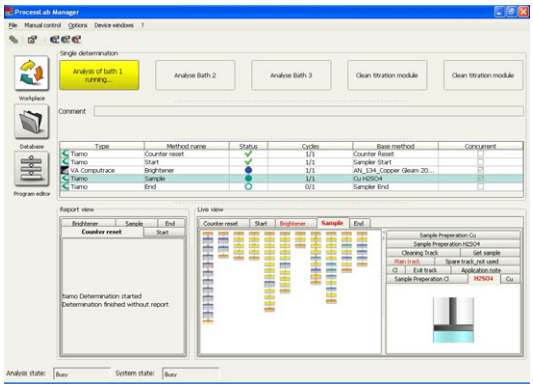
General introduction

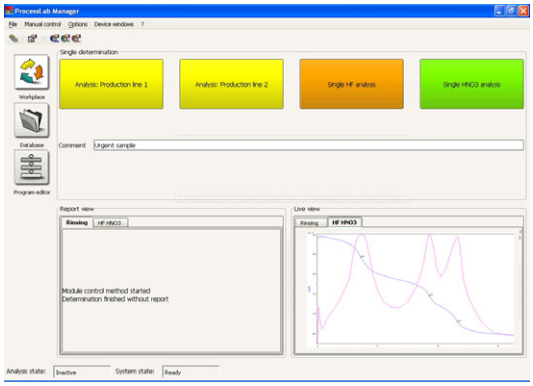
In today's electronics-dominated world a lot of different equipment is manufactured. The basis of every electronic device are the so-called PCBs (printed circuit boards) which are manufactured in a complex production process. This production step is usually carried out by contract manufacturers. The most delicate step is the galvanic copper plating process. Thin layers of copper are deposited onto a pre-treated surface, into small contact vias and drilled holes. This sensitive process needs very closely monitoring in order to achieve the product quality specified.

Key features

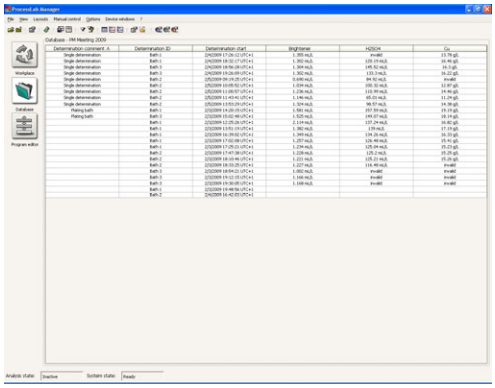
- Simple and safe in operation using Touch Screen interface
- Modular and extendable concept for all requirements
- Sealed and robust housing
- Graphical SPC (Statistical Process Control)
- Example parameters
  - Copper
  - Sulfuric acid
  - Traces of chloride
  - Suppressor
  - Brightener
  - …

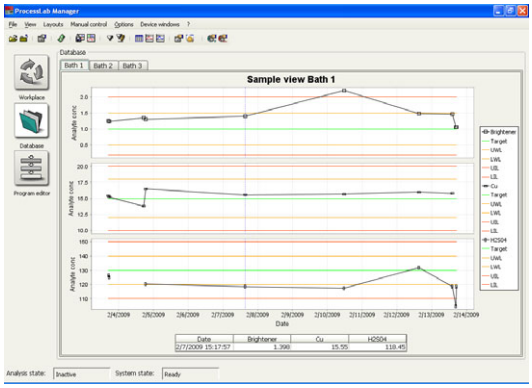
ProcessLab Manager





This system combines cyclic voltammetric stripping (CVS) and potentiometric measurements in one single setup. Both analytical techniques are carried out at the same time and completed in one single run. The ProcessLab Manager software combines the functionalities of our well-proven ***tiamo***™ and 797 *VA Computrace* software packages, which facilitates operation. At the same time, full comparability is maintained as the same methods may be used as in the central QC lab.





Database and graphical charts at a glance – different control charts allow a quick view of the latest results. A view by bath is as well available as a view by parameter. The included limit monitoring automatically reacts on specified warning or intervention limits and may even notify the staff by means of an optical or acoustical alarm.

Significance and use

The analysis of acidic copper plating baths is an important control measure that has to be carried out regularly in order to maintain bath quality at the required level. Usually analyses are carried out several times daily by shift workers and allow conclusions on the replenishment.

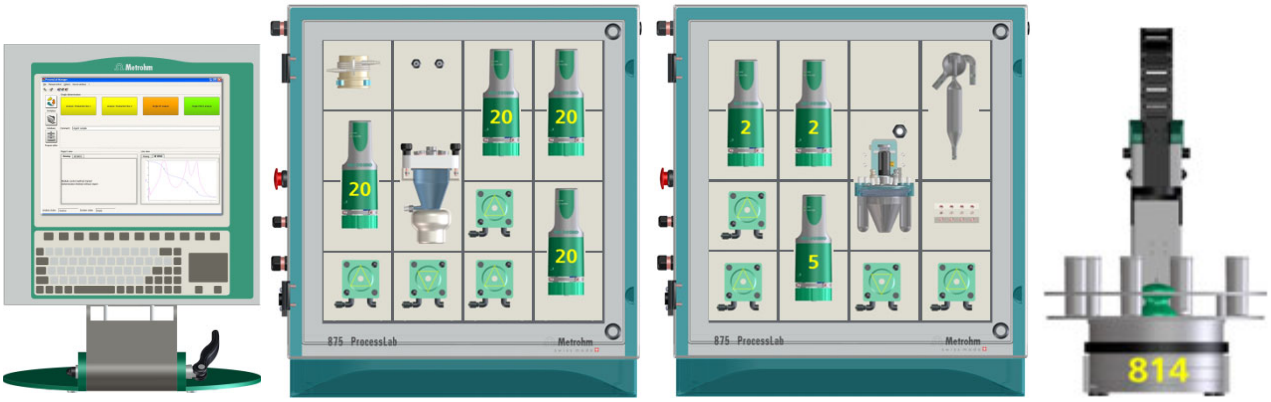
In most cases samples are sent to the QC lab for carrying out the analysis – the time and efforts needed for the result to come back is a dead time in which a process may infringe the limits. ProcessLab ideally fills this time gap by being situated in the process area – directly at the place where the result is needed. At the same time the ease-of-use concept allows to run the system also by semi-skilled users. It is started by a simply pressing of a button. Different analytical techniques (titration and CVS in the present case) may even run in parallel to save time. The result will be very quickly available to the user or any type of external equipment or database.

ProcessLab reduces production costs and allows to achieve a higher yield. It is a robust industrial analyzer that incorporates all needed equipment in a sealed case. It is delivered ready to use – including an industrial PC and operating unit as well as all needed analytical instrumentation. After the user has placed the sample and pressed the start button, the system autonomously carries out the selected analysis. The results are available for export via ethernet or output lines and are saved at the same time in a traceable and compliant database.

Analyzer features

- Monitored parameters
  - Copper content (potentiometry) g/L
  - Sulfuric acid (potentiometry) mL/L
  - Chloride (potentiometry) mg/L
  - Suppressor (CVS) mL/L
  - Brightener (CVS) mL/L
  - Additional or different parameters are possible
- Automatic calculation of chemicals or additives for replenishment
- Sealed and robust analyzer – ideal for harsh process environments
- Single- or multiple-line monitoring
- Simple and safe touchscreen operation
- Unique ProcessLab Manager software offering
  - Control charts at a glance
  - Limit monitoring
  - Simple embedding of existing methods
  - One single database for all results
- Automated and autonomous
- Comprehensive communication possibilities
  (ethernet, RS 232, digital/analog in- and outputs 4 – 20 mA)
- Flexible and modular concept

Wet part setup and system overview



Reagents

Potentiometric titrations

- Demineralized water
- EDTA, c(Na_2EDTA) = 0.1 mol/L
- Buffer pH 10: 54 g NH_4Cl, 350 mL w(NH_3) = 25% → 1000 mL
- Sodium hydroxide, 1 mol/L
- Silver nitrate, 0.01 mol/L

CVS Determinations

- Demineralized water
- Suppressor concentrate
- Brightener concentrate
- VMS (virgin make-up solution)

Details and analytical procedures

Potentiometric titrations

Potentiometric titration is an absolute method that uses a chemical reaction to determine an endpoint which corresponds to the same concentration of analyte and reactant. This endpoint is detected potentiometrically by means of appropriate electrodes.

Copper

Copper is the most important ingredient in an acidic copper plating bath as it is the metal being deposited on the substrate passing through the bath. The copper content is determined using EDTA as complexing agent. This reaction has to be carried out at pH 10 – for this reason an ammonia buffer is added immediately before the determination. This is a standard and routine analysis method which is characterized by its high precision and excellent repeatability.

$$Cu^{2+} + Na_2EDTA \rightarrow CuEDTA + 2\ Na^{+}$$

H_2SO_4

A strongly acidic pH is needed for the deposition process. The sulfuric acid is determined using sodium hydroxide (NaOH) as reagent. This determination is very quick and characterized by an excellent repeatability.

$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$$

Chloride

The bath contains traces of chloride, which catalyzes the suppressor effect. Too much chloride may result in a too large effect of the suppressor and too little can prevent it from acting at all. The content is therefore determined using silver nitrate ($AgNO_3$) as titrant in a strongly acidic medium (usually 2 mol/L HNO_3 is added). Also this determination is very quick and accurate.

$$Cl^- + AgNO_3 \rightarrow AgCl\downarrow + NO_3^-$$

CVS Determinations

Cyclic Voltammetric Stripping (CVS) and Cyclic Pulse Voltammetric Stripping (CPVS) are techniques widely used in plating industry for the determination of organic additives in plating solutions. The method is an indispensable part of production control of many technical coating processes, especially in the production of printed circuit boards. The quantitative determination of the additives is done indirectly using their influence on the deposition of the main component of the plating solution. A simple and robust rotating disk electrode made of platinum is used for the analysis.

Suppressor

This method involves a calibration followed by a determination of the sample.

Calibration curve
The curve is achieved by adding small portions of a standard solution to a VMS (virgin make-up solution). The obtained curve is valid for a certain time and is checked regularly.

Sample measurement
The same parameter set used for the calibration curve is used for every measurement. In a dilution titration (DT) the deposition properties of the sample are measured. The result is used for the subsequent calculation of the suppressor content.

Brightener

The LAT (Linear approximation technique) and MLAT (Modified LAT) allow a quick and easy measurement of brightener.

Sample measurement
A certain amount of sample is analysed and the influence of brightener upon the deposition process of copper is investigated. The quantification of the brightener then allows conclusions upon the deposition process at the process line.

Accessories used

1 x 2.875.0220; ProcessLab Base Unit CVS Touch

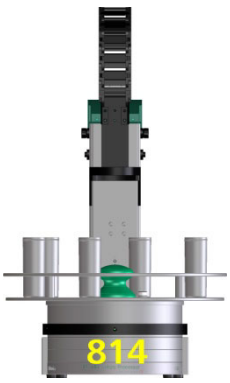
- 2 x 2.800.0010; Dosino 800
- 1 x 6.3032.120; Dosing Unit 2 mL
- 1 x 6.3032.150; Dosing Unit 5 mL
- 1 x 6.7206.210; ProcessLab solenoid valve module, includes 1 valve
- 1 x 6.7206.110; Overflow pipette 10 mL compl., for 875
- 1 x 6.7206.050; Overflow pipette holder
- 1 x 6.7205.020; ProcessLab peristaltic pump 120 mL/min

1 x 2.875.0110; ProcessLab Extension module L

- 2 x 6.7205.030; ProcessLab peristaltic pump 320 mL/min.
- 1 x 6.7205.010; ProcessLab peristaltic pump 40 mL/min.
- 1 x 6.7205.020; ProcessLab peristaltic pumpt 120 mL/min.
- 4 x 2.800.0010; Dosino 800
- 4 x 6.3032.220; Dosing Unit 20 mL
- 1 x 6.7206.040; Sample loop 10 mL var. compl., for 875
- 1 x 6.7204.000; Vessel mounting with stirrer
- 1 x 6.7204.110; Measuring vessel 20 – 90 mL for 875
- 1 x 6.7203.200; ProcessLab sensor connection
- 1 x 6.7201.210; ProcessLab MDM Controller with 2 measuring amplifiers
- 1 x 6.7201.200; ProcessLab MDM Controller with 1 measuring amplifier

Sensors

- 1 x 6.0259.100; LL Unitrode
- 1 x 6.0430.100; Ag Titrode
- 1 x 6.0502.140; Cu ISE
- 1 x 6.0750.100; ISE Reference



Automation, optional

- 1 x 2.814.0010; 814 USB Sample Processor
- 1 x 6.2041.310; Sample rack 12 x 250 mL

Results

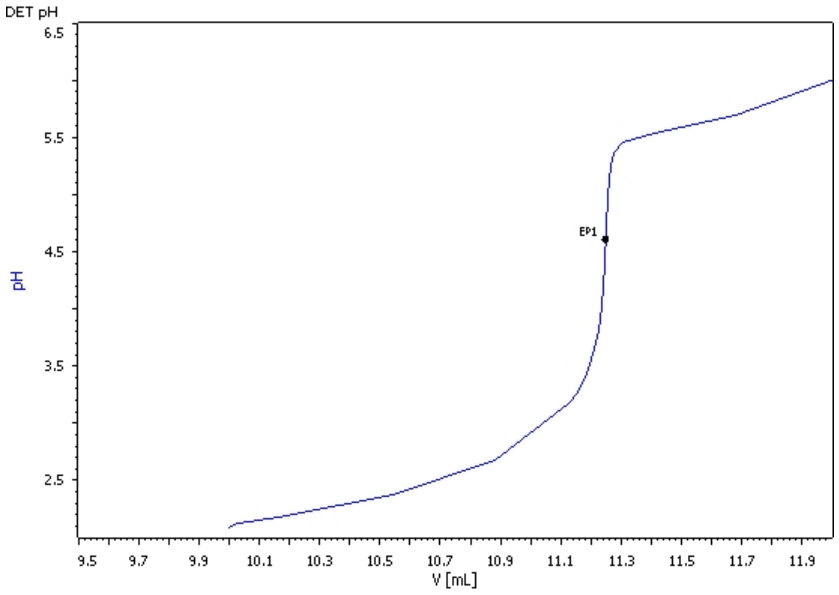
Sample No.	H_2SO_4 content	Cu content	Chloride content	Brightener content	Suppressor content
1	125.21 mL/L	15.26 g/L	66.4 mg/L	1.304 mL/L	12.75 mL/L
2	125.20 mL/L	15.25 g/L	67.4 mg/L	1.300 mL/L	12.83 mL/L
3	125.04 mL/L	15.23 g/L	65.9 mg/L	1.301 mL/L	12.72 mL/L
Mean	**125.15 mL/L**	**15.25 g/L**	**66.5 mg/L**	**1.302 mL/L**	**12.77 mL/L**
s (abs.)	*0.095 mL/L*	*0.015 g/L*	*0.76 mg/L*	*0.002 mL/L*	*0.056 mL/L*
s (rel.)	*0.08 %*	*0.10 %*	*1.14 %*	*0.16 %*	*0.44 %*

Discussion of results

- The results show a high precision and repeatability for all measured parameters
- The standard deviation for the chloride is slightly higher due to the sampling system used (50 mL sample are added using a peristaltic pump)

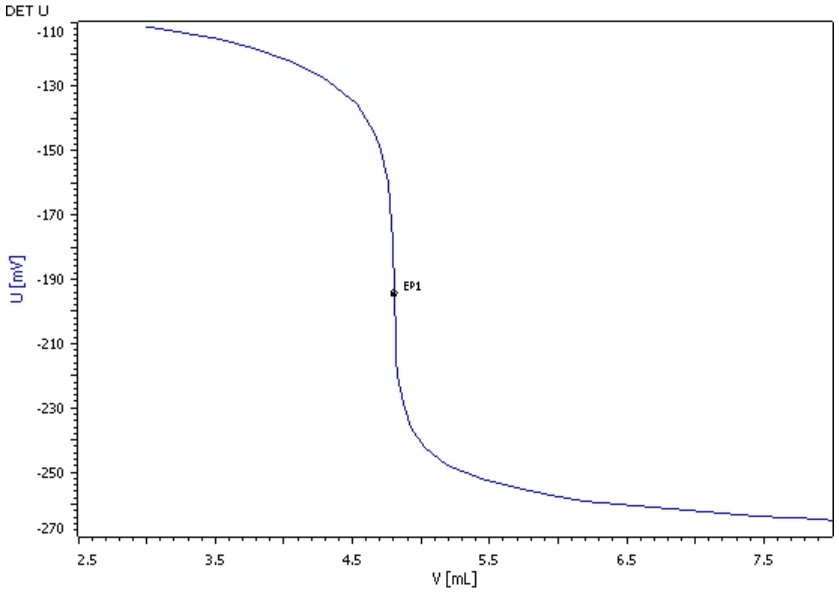
Practical examples

Determination of sulfuric acid using sodium hydroxide 1 mol/L



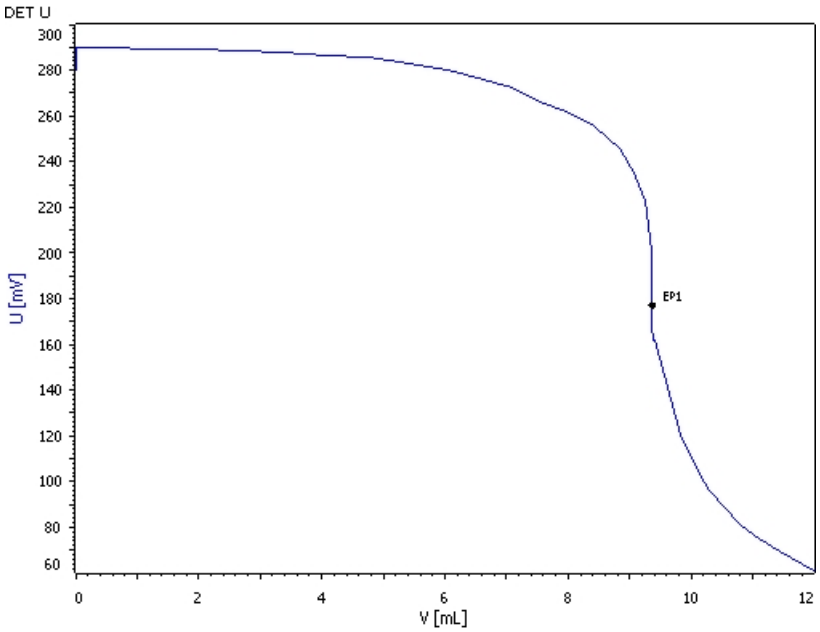
- V_{start} = 10 mL
- V_{stop} = 12 mL

Determination of copper using EDTA 0.1 mol/L



- V_{start} = 3 mL
- V_{stop} = 8 mL

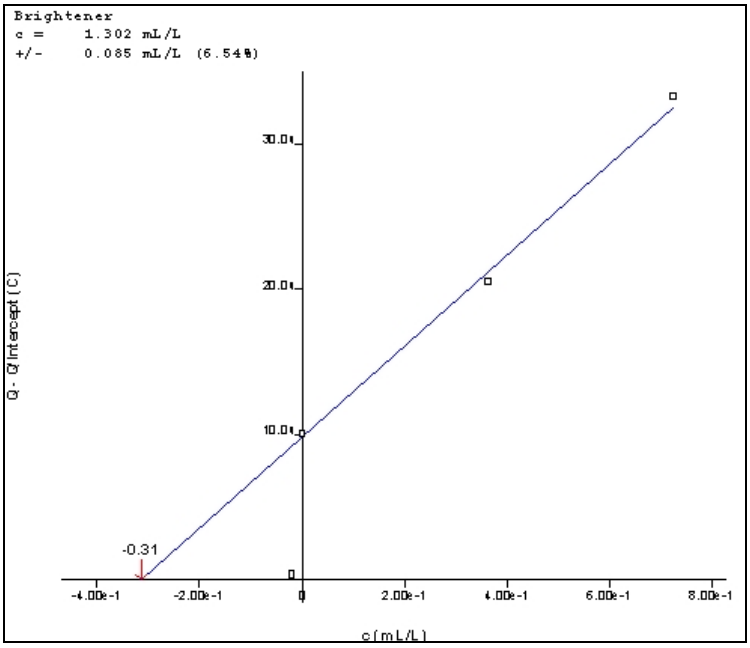
Determination of chloride using silver nitrate 0.01 mol/L



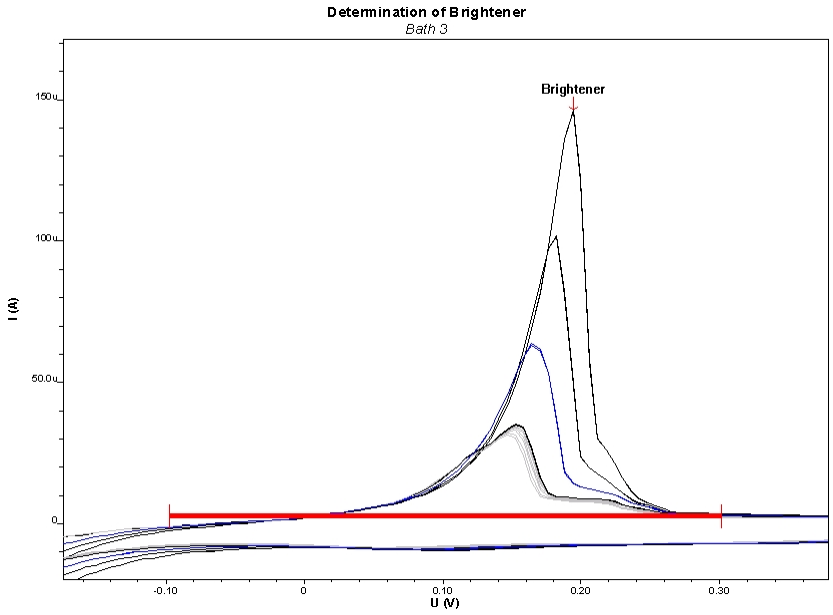
- V_{start} = 0 mL
- V_{stop} = 12 mL

Determination of brightener in copper plating bath

Brightener calibration curve

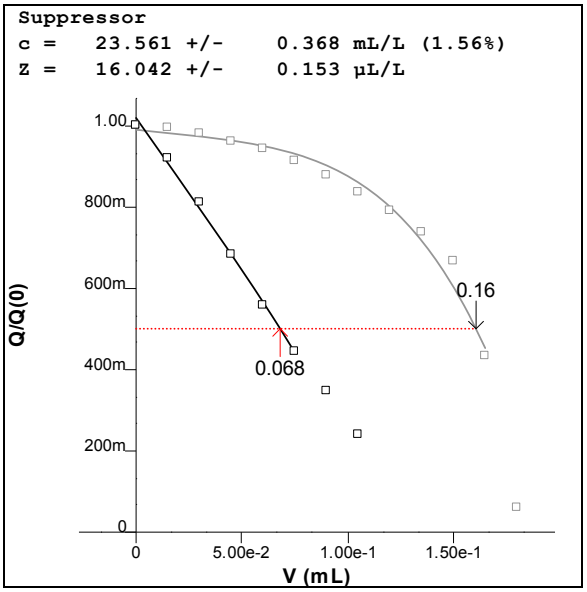


Brightener additions resulting in more copper beeing deposited



Example of determination of suppressor in copper plating bath

Suppressor dilution titration curve



References

Metrohm Application Bulletin no. 101; Complexometric titrations with the Cu ISE

Metrohm Application Bulletin no. 130; Chloride titration with potentiometric endpoint indication