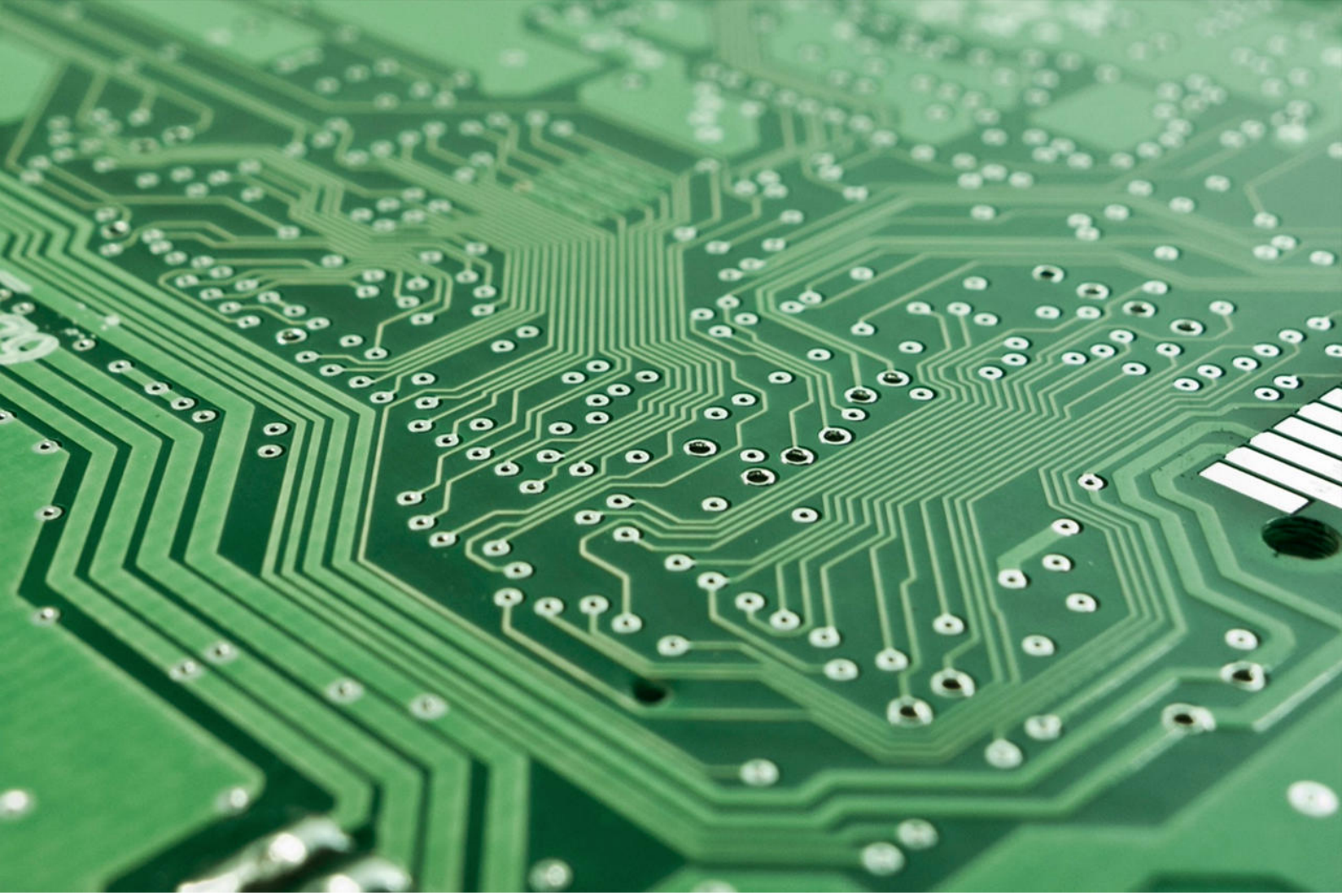


Application Note AN-T-100

# Chloride in acidic copper baths

## Fully automated determination

Acid copper baths are mainly used for the copper deposition on semiconductor wafers. Small amounts of chloride increase the speed of deposition and reduce anode polarization. However, higher concentrations are undesired, as this will decrease the quality of the copper deposition. Therefore, it is quite important to monitor the amount of chloride to have an effective, yet high-quality copper deposition process.

In this Application Note, a fully automated solution based on titration is presented. In comparison to ion chromatography, titration offers the benefit that no dilution of the sample is necessary, and the hardware is comparatively low-priced. Furthermore, the fully automated solution allows users to minimize handling errors, to reduce workloads, and to guarantee outstanding reproducibility.

### SAMPLE AND SAMPLE PREPARATION

The method is demonstrated for an acid copper bath.

No specific sample preparation is required.

## EXPERIMENTAL

This analysis is carried out on an automated system consisting of an 814 Sample Processor and a 905 Titrando equipped with an iAg-Titrode with $Ag_2S$ coating.

To a reasonable amount of sample, 5 mL of nitric acid is added to acidify the sample. Then, deionized water is added to cover the glass membrane and silver ring of the electrode, and the sample is titrated with standardized silver nitrate titrant until after the equivalence point.

**Figure 1.** 814 Sample Processor and 905 Titrando equipped with an iAg-Titrode with Ag2S coating controlled by tiamo software.

## RESULTS

The analysis demonstrates an acceptable result and well-defined titration curves. The sample analyzed contained 49.17 mg/L chloride with a relative standard deviation of 0.31% (n = 10). An example titration curve is displayed in Figure 2.

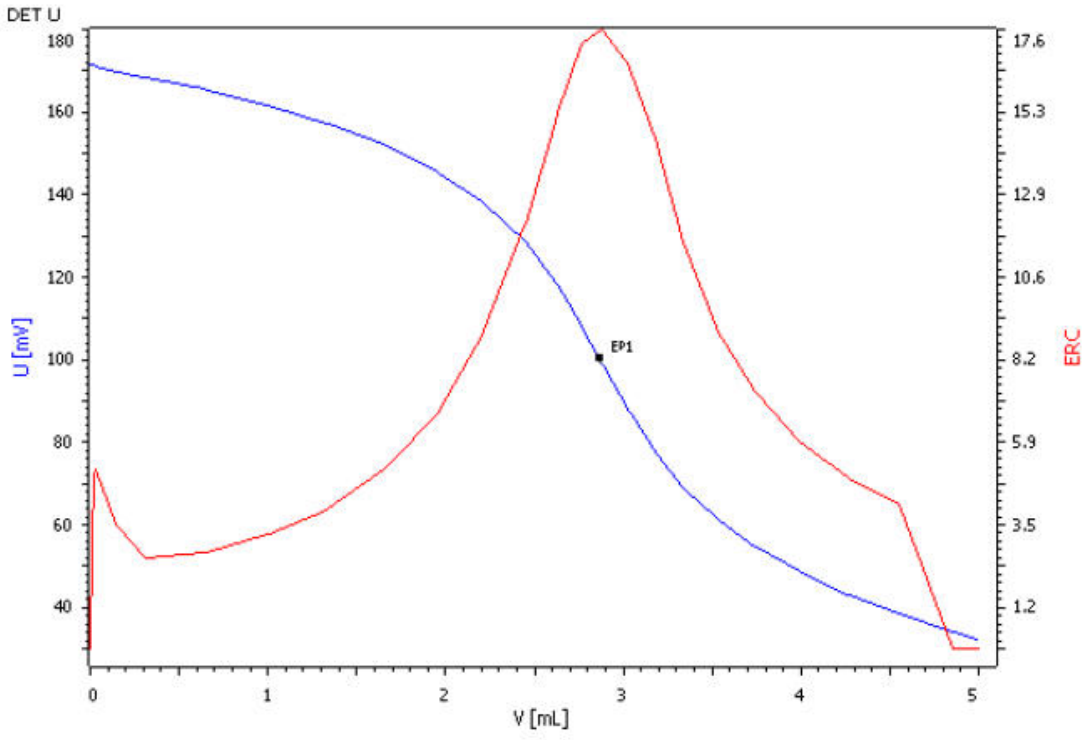



**Figure 2.** Example titration curve of the chloride determination in an acid copper bath.

## CONCLUSION

Titration is a precise and reliable method to determine the chloride content in acid copper baths.
Using the 814 Sample Processor allows a fully automated determination, freeing up valuable time of the operator and thus increasing the productivity in the lab. Furthermore, by fully automating the analysis, the reproducibility can be increased and sample analysis failures due to improper handling can be reduced.

Internal reference: AW TI CH1-1130-022013

## CONTACT

Metrohm Middle East FZC
E2-05 SAIF Zone
120747 Sharjah, UAE
info@metrohm.ae

## CONFIGURATION

905 Titrando

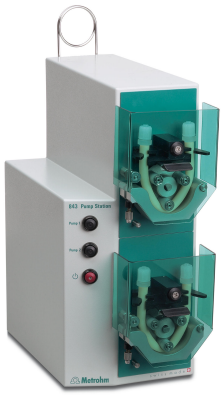
High-end titrator for potentiometric titration with one measuring interface for use with Dosino dosing systems.

- up to four dosing systems of the 800 Dosino type
- dynamic (DET), monotonic (MET), and endpoint titration (SET)
- Measurement with ion-selective electrodes (MEAS CONC)
- Dosing functions with monitoring, Liquid Handling
- four MSB connectors for additional stirrers or dosing systems
- "iTrode" intelligent electrodes
- USB connector
- For use with OMNIS Software, *tiamo* software, or Touch Control unit
- Compliance with GMP/GLP and FDA regulations such as 21 CFR Part 11, if required

### 814 USB Sample Processor (1T/0P)

USB Sample Processor with one workstation for the automatic processing of routine samples in series with small to medium quantities. Up to two pumps (membrane or peristaltic) and three dosing devices for Liquid Handling tasks can be connected.

Because of the multitude of application variants, rack, stirrer, titration head, Swing Head and sample vessels must be tailored to the application and ordered separately.
The control is "stand alone" using Touch Control. The following software products can be selected for the PC control: tiamoTM titration software, MagIC Net chromatography software, viva voltammetry software, or OMNIS.



### 843 Pump Station (peristaltic) - rinse/aspirate for Sample Processors

The 843 Pump Station (peristaltic) has two built-in peristaltic pumps. These can be controlled directly from the Sample Processors via pump commands. The rinse/aspirate version is provided with all the accessories needed for automatically emptying the titration beaker and rinsing the titration equipment. The accessories are intended for use with the 814 and 815 Sample Processors.

### iAg Titrode with Ag2S coating

Intelligent, combined silver ring electrode with a pH glass membrane as reference electrode and integrated memory chip for storing sensor data.
The silver ring is coated with sulfide ($Ag_2S$) for higher sensitivity and a better limit of detection.
This maintenance-free electrode is suitable for precipitation titrations when the pH value remains constant (titrant silver nitrate), for example of:

- Chloride, Bromide, Iodide
- Sulfides
- Hydrogen sulfide
- Mercaptans
- Cyanides

This electrode is stored in distilled water.
iTrodes can be used on Titrando, Ti-Touch oder 913/914 meters.