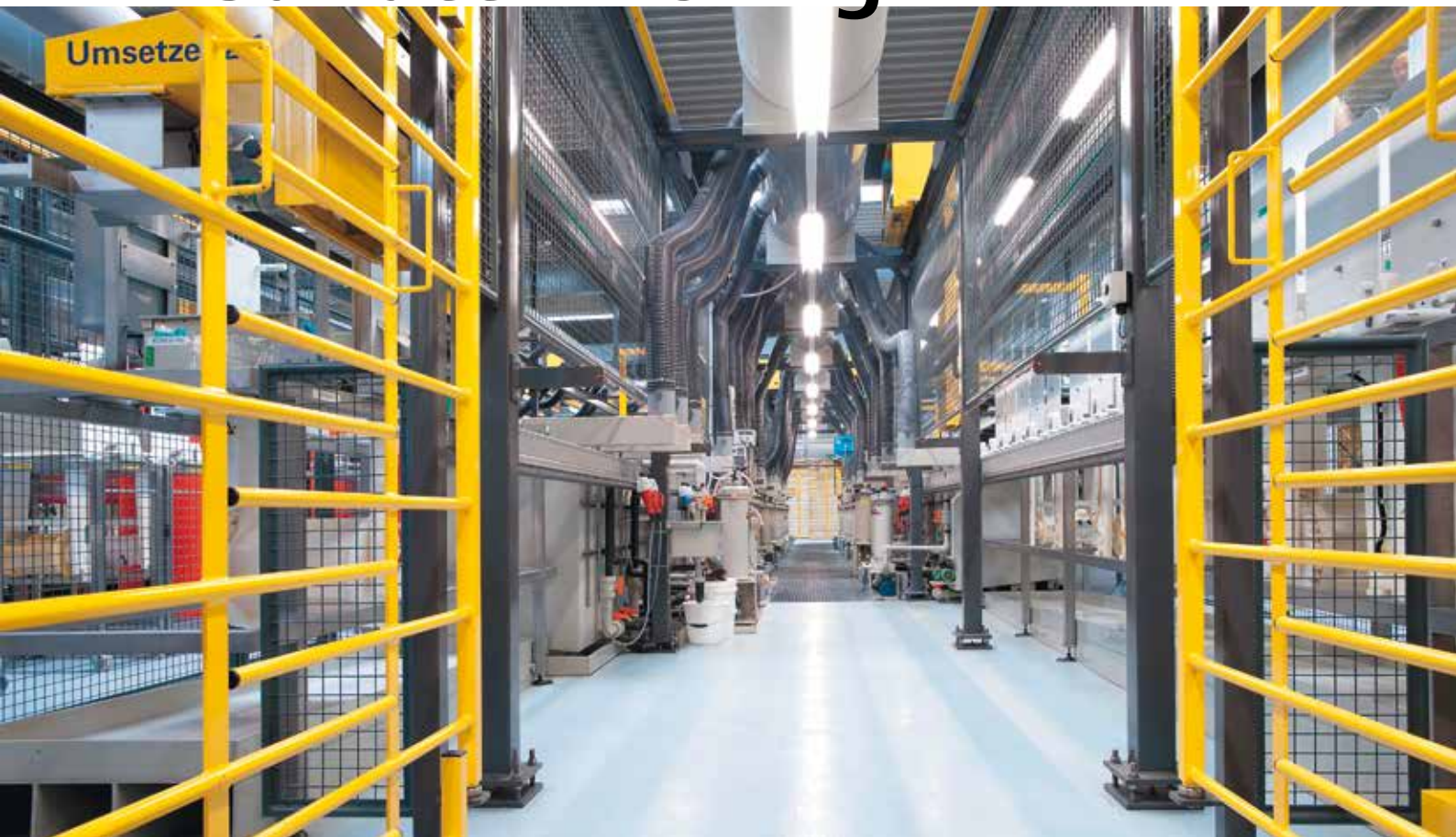


# Surface finishing



Process control in electroplating and  
PCB manufacturing



## Metrohm...

- is the global market leader in titration
- offers a complete portfolio for NIR and Raman analysis, in addition to all of the methods of ion analysis – titration, voltammetry, and ion chromatography
- is a Swiss company and manufactures almost exclusively in Switzerland
- grants a 3-year instrument warranty and a 10-year warranty on chemical suppressors for anion chromatography
- provides you with unparalleled application expertise
- offers you over 2000 applications free of charge
- supports you with dependable on-site service worldwide
- is not listed on the stock exchange, but is owned by a foundation
- takes a sustainable approach to corporate management, putting the interests of customers and employees ahead of maximizing profit

# Metrohm – customized analysis for surface finishing

## An industry with high standards

The coating and finishing of surfaces using electroplating techniques is a highly sophisticated process. Be it the finishing of metal parts or the coating of printed circuit boards, the quality required in the intermediate and end products is only achieved if the composition of the process baths is right. At the same time, rising costs of raw materials and energy make it absolutely essential to drive production as efficiently as possible.

As a leading manufacturer of instruments for chemical analysis we know about these challenges. That is why we offer you state-of-the-art instrumentation to control and optimize the quality of your coating processes with the

required precision – both in the laboratory and atline and online in the process environment.

## Count on our support

We offer you not only first-rate instrumentation, but rather complete solutions for the particular task at hand. Your Metrohm contacts are experienced specialists, who develop customized applications for you and support you in every aspect of the production process.

Discover on the following pages what solution Metrohm offers you to ensure the quality of your products. Challenge us!

<b>Part I: Solutions for laboratory analysis</b>	<b>pages 4–12</b>
<b>Part II: Processes and applications</b>	<b>pages 13–27</b>
<b>Part III: Solutions for atline, online, and inline analysis</b>	<b>pages 28–39</b>



## Part I: Solutions for laboratory analysis

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### Titration and pH/conductivity measurement

Titration is an established analytical technique in quality control of electroplating processes. Titration combines utmost precision with a very easy procedure. In most cases it is possible to use undiluted sample solution to determine the components of reaction solutions. This enables even semiskilled users to carry out the analysis quickly and accurately. Because of the wide range of opportunities for automation, the amount of work required for analysis is generally limited to providing an aliquot of sample and pressing a <Start> key.

#### Versatile and convenient

Another benefit of titration is its versatility. Different analyses can be performed with one and the same basic instrument: e.g., monitoring the content of electroplating baths, analyzing acid mixtures in etching baths or checking the purity of rinsing solutions.

#### Solutions for every budget and every requirement

The 912 Conductometer, 913 pH Meter, and 914 pH/Conductometer are "two-in-one" meters for laboratory and field use and therefore ideally suited for routine analyses in the lab and for applications in the field.

The rugged, compact instruments are characterized by their ability to measure anywhere and by an exceptional ease of use that is thanks to their well-organized user interface and offer various options for data management, like printout, storage to a PC or LIMS.



#### 848 Titrino plus

The 848 Titrino plus is the most economical solution for all routine potentiometric titrations, such as acid/base, redox, precipitation and surfactant titrations, and also complexometry. Its ease of use, the output of results on paper and the collection of results in the database software *tiBase* make documentation of results perfectly easy.



### Plate Titrando

The Plate Titrando offers a comprehensive package for the most common potentiometric analyses in the electroplating industry. It contains all the accessories for acid/base and redox titration and for the determination of chloride. Its complete intelligence monitors all the important system components, such as buret or sensor. The patented Dosino technology provides for contact-free handling of reagents and burets.



### Robotic Transfer Analyzer

Metrohm offers you comprehensive solutions for the complete automation of your titrimetric analyses. The benefit is evident: higher sample throughput, minimized risk for operating errors, more precise and consistent results and, of course, enormous savings on time and costs. All of this comes to your lab with the Robotic Transfer Analyzer. Just put your samples on the rack – everything else from sample preparation to analysis is taken care of by the automated system.

**OMNIS – The new, fully modular titration platform offers titration performance on a whole new level****Expand your system as you go**

Start with a single OMNIS titrator and add titration and dosing modules when needed for further applications or samples to be analyzed. By including additional measuring interfaces and burets, you can have up to five different applications ready for use – even in parallel.

If sample throughput is increasing, add an OMNIS Sample Robot for fully automated titration. Thanks to modular work stations, racks, and pumps, OMNIS is capable of analyzing four samples fully automatically in parallel.

**OMNIS combines all measurement results for a sample**

If multiple parameters were measured in a sample, OMNIS links them all directly to the sample and shows the results at a glance.

For a brass plating bath, the results for the determination of the copper content, zinc content, free cyanide, and carbonate are all linked.



OMNIS Sample Robot M with 4 Work Stations for simultaneous, fully automated analysis of 4 samples.



**Make your laboratory safer with 3S adapter technology**

We have made chemical handling easier and safer. The result is our patented Liquid Adapter with 3S Technology. 3S stands for:

**Safe** chemical handling: Just connect the OMNIS Liquid Adapter to the bottle cap and avoid contact with the bottle contents.

**Secure** information transfer: The RFID chip in the bottle cap provides all relevant information on the content of the bottle.

**Smart** connection: The reagent data is automatically transmitted to the titration system.



# Ion chromatography

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## Multicomponent determination with a single analysis

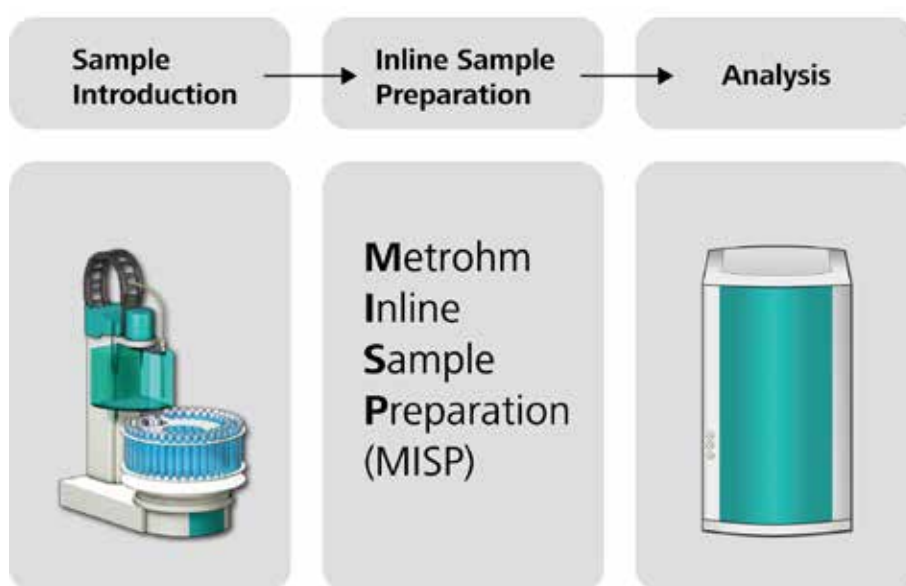
Ion chromatography (IC) enables the determination of numerous main and secondary components of electroplating baths as well as traces of impurities in the form of organic and inorganic ions or polar substances with utmost reliability and precision. A major benefit of ion chromatography is that chemically similar substances can be determined in parallel in a single analysis. The analyte concentrations may extend from the ng/L to % ranges.

## Save time and costs with automated sample preparation

Ion chromatographic analyses can be automated easily and efficiently; interfering matrix effects can be avoided by choosing the appropriate detection method or combining the sample delivery with one of our numerous Inline Sample Preparation Techniques. These inline techniques, some of them patented by Metrohm, make it possible to integrate the sample preparation into the analysis and to automate it completely. This increases reliability, saves manual work and guarantees traceability of the entire analysis.

## Metrohm Inline Sample Preparation Techniques in surface coating:

- Inline Ultrafiltration to remove particles from various samples
- Inline Dialysis for ion analysis in emulsions and soap-containing rinsing solutions
- Inline Dilution to monitor acid baths and component analysis of electroplating bath solutions
- Inline Matrix Elimination to analyze rinsing solutions such as isopropanol
- Inline Preconcentration for trace analysis in ultrapure water
- Inline Neutralization and Inline Cation Removal for analyzing impurities in electroplating baths
- Intelligent Partial-Loop Injection Technique guarantees variability and simplicity in your analysis





### **940 Professional IC Vario – solution for demanding tasks**

The 940 Professional IC Vario system can be used both to analyze acid baths and for trace analysis of impurities in ultrapure water, rinsing solutions, and adsorption solutions. Because of the system's self-monitoring functions operating errors are virtually eliminated. Owing to the complete automation, including Metrohm Inline Sample Preparation (MISP), the system can be recommended both for routine analysis and for complex applications in research and development.



### **930 Compact IC Flex – predestined for routine analysis**

The 930 Compact IC Flex is the ideal solution for routine analysis, if the focus is on only one application. Like the 940 Professional IC Vario, the 930 Compact IC Flex is also equipped with intelligent hardware components. Together with the MagIC Net ion chromatography software the system enables intuitive operation. Just like the 940 Professional IC Vario, the 930 Compact IC Flex can be automated in various ways and complemented by Metrohm Inline Sample Preparation Techniques.

# Voltammetry

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Voltammetry is an electrochemical analytical method that provides information on – among other substances – the type and amount of metals contained in a dissolved sample on the basis of a current-voltage relationship. The importance of voltammetry is based on its high degree of accuracy and sensitivity, the possibility of speciation analysis and the good price-to-performance ratio.

## Precise measurements even in the presence of high salt concentrations

The particular challenge for analysis in the electroplating sector are the large quantities of salts typically contained in electroplating samples. For such samples, many measuring techniques can at best provide unsatisfactory results; others cannot provide any results at all. Here, electrochemical analysis is able to demonstrate its strengths; the disadvantage for other methods is transformed into a big advantage: large amounts of salt equal good conductivity, which is a prerequisite for electrochemical analysis.

Furthermore, the infrastructure required for a voltammetric measurement system requires hardly any expenditure. All it needs is electricity and a supply of nitrogen. Ventilation, flammable gases and associated safety requirements are no issues.

## 884 Professional VA

The 884 Professional VA is a flexible measuring instrument for accurate and sensitive voltammetric and polarographic analyses. The analyses can be easily automated by adding Dosinos and a sample changer. The accompanying viva software enables individual optimization of methods.

## Convenient data management

All the relevant measurement data and results obtained with the 884 Professional VA and viva can be transferred very easily to your LIMS – as text data or in xml format.



884 Professional VA

# CVS (Cyclic Voltammetric Stripping)

## Standard method in PCB manufacturing

Cyclic Voltammetric Stripping (CVS) and Cyclic Pulse Voltammetric Stripping (CPVS) are widely used methods in the electroplating industry for the determination of organic additives. The CVS method is an essential component of production control in many industrial coating processes, especially in the manufacture of printed circuit boards or semiconductors.

With CVS or CPVS it is possible to determine the concentration of additives exactly. The effective concentration of the particular additive in the bath sample is shown directly in mL additive per L bath. Precise subsequent dosing to meet the target concentration then becomes possible. This ensures continuous, trouble-free operation of the plant.

## The main CVS applications in the electroplating and semiconductor industries

	Suppressor	Brighteners	Leveler
Process	DT – Dilution Titration	<ul style="list-style-type: none"> <li>LAT – Linear Titration Approximation Technique</li> </ul>	RC – Response Curve
		<ul style="list-style-type: none"> <li>MLAT – Modified Linear Approximation Technique</li> </ul>	

## Complete voltammetry systems – the right system for each application

Metrohm offers systems packages that are ready-to-use and suit the needs of the electroplating and semiconductor industries. There are systems available for manual

operation, systems with automatic addition of solutions and fully automated systems for high sample throughput.



### 884 Professional VA semiautomated for CVS

The 884 Professional VA semiautomated is the standard system for routine determination of organic additives in individual samples. Automatic addition of auxiliary solutions such as VMS, intercept or standard solutions is carried out with Dosinos. For brightener determination the sample only has to be added manually. In the case of suppressor determination, this is also done automatically.



### MVA-23 – fully automatic determination of organic additives in sample series

The MVA-23 is the high-end system for the determination of additives in electroplating baths with the samples being added automatically by an 858 Professional Sample Processor. The suppressor content of up to 56 samples can be determined. When determining brighteners, up to 28 samples can be analyzed. Various methods can also be combined in a single measuring procedure.

## Potentiostats/Galvanostats by Metrohm Autolab

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### Systems for electrochemical analysis in research and development

The electrochemical interface has been of particular interest in fundamental and applied research for many decades. The understanding of the nature of the processes involved at the electrochemical interface, from mass transport to electron transfer kinetics, provides invaluable information which can be used to optimize existing surface preparations processes and develop new methods.

For example, *Electrochemical Atomic Layer Deposition* (EALD) and *Surface-Limited Redox Replacement* (SLRR) are two particular examples of novel electrochemical methods which are now used in technologically relevant applications. Other novel electrochemical surface preparation techniques involve the use of the macromolecular assemblies using dendrimers or nanoscale templating.

### Autolab PGSTAT-potentiostats for all electrochemical methods

At the fundamental level, the **Autolab PGSTAT** provides the scientist with all the electrochemical methods of interest for surface science. Potentiostatic and galvanostatic control allow the researchers to accurately control the reactions taking place at the electrochemical interface as well as the rate of these reaction and the quantity of material involved. Using these methods, the composition, roughness, structure, and growth mode of deposited materials can be controlled.





## Part II: Processes and application solutions

### Quality control of basic chemicals and raw materials

Quality assurance in production begins when the used basic chemicals are checked. Analytical instruments from Metrohm make it possible to establish the concentrations of acids or bases reliably, quickly and easily, determine the metal content of various raw materials or detect any impurities in trace quantities.

#### Titrimetric applications

Sulfuric acid, hydrochloric acid, sodium hydroxide, ammonia, and hydrogen peroxide are some of the most frequently used basic chemicals in the electroplating industry. Normally their content is checked by means of potentiometric titration when incoming goods are examined, to ensure the particular mixture is in the right proportions for subsequent use or dilution.

Sample	Titrant	Metrohm Electrode
H <sub>2</sub> SO <sub>4</sub>	c(NaOH) = 0.1 mol/L	6.0255.100 Profitrode
HCl	c(NaOH) = 0.1 mol/L	6.0255.100 Profitrode
NaOH	c(HCl) = 0.1 mol/L	6.0255.100 Profitrode
NH <sub>4</sub> OH	c(HCl) = 0.1 mol/L	6.0255.100 Profitrode
H <sub>2</sub> O <sub>2</sub>	c(KMnO <sub>4</sub> ) = 0.1 mol/L	6.0431.100 Pt Titrode

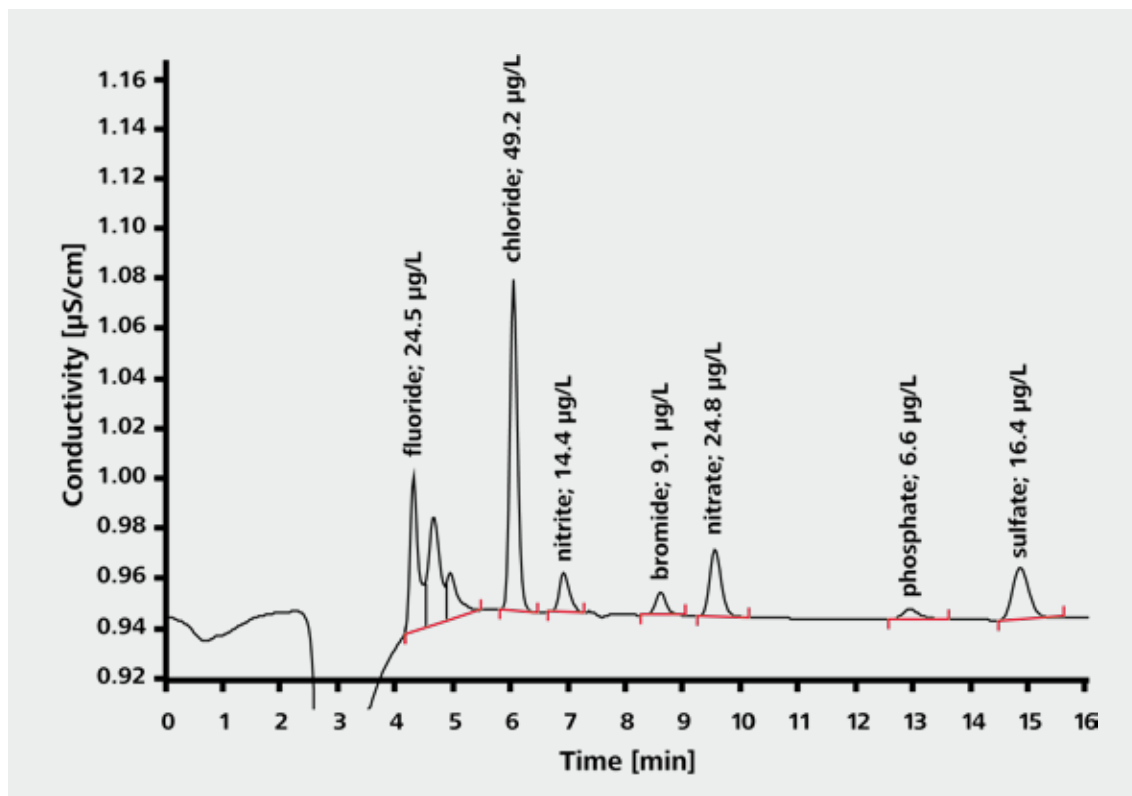
### Ion chromatographic applications

#### Impurities in hydrogen peroxide, isopropanol, etc.

Ion chromatographic applications are used to monitor etching, extracting and rinsing solutions. Analyses of impurities, e.g., in hydrogen peroxide or isopropanol, play a big role here. For this, an IC system is equipped with Inline Matrix Elimination. This rules out any matrix effect and makes reliable analysis possible.

#### Determination of ultratraces

When ultratraces need to be determined, Inline Preconcentration is added to Inline Matrix Elimination. The requirements here are not only work that is free of blank readings and of any carryover, but also exact measurement of the preconcentration volume. All this is made possible by the patented 800 Dosino. This state-of-the-art liquid handling system provides complete flexibility in the choice of injection volume and can be adapted at any time to the required degree of sensitivity. At the same time the method can be calibrated with just one standard solution.



Determination of 30% hydrogen peroxide spiked respectively with 10 µg/L F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>; column: Metrosep A Supp 5 - 150/4.0; preconcentration column Metrosep A PCC 2 HC/4.0; eluent: 3.2 mmol/L Na<sub>2</sub>CO<sub>3</sub> + 1.0 mmol/L NaHCO<sub>3</sub>, 0.8 mL/min; column temperature: 25 °C; sample volume: 20 µL



### Voltammetric applications

#### Traces of heavy metals in basic chemicals

Heavy metal ions present in the basic chemicals can cause interference during the production process. For this reason, a purity check is carried out when goods are received.

On the other hand, in the electroplating industry large quantities of basic chemicals are used and as a result sizeable quantities of heavy metals are introduced into the production process. This contamination needs to be prevented as far as possible right at the start of the production chain, to avoid the need to remove it at great cost later. Such checks are a classic application of voltammetry.

#### Nickel in sodium hydroxide by means of adsorptive stripping voltammetry (AdSV)

To analyze the concentration of nickel in a solution of sodium hydroxide, the solution is first acidified to bring the nickel into its ionic form. The pH is then adjusted to 9.6 with an ammonium chloride buffer. Dimethylglyoxime (DMG) is added to produce a Ni-DMG complex, which can be preconcentrated on the mercury dropping electrode. Quantification is by means of standard addition.

Analytes	Raw material
Zinc, cadmium, lead, nickel, cobalt	Sodium hydroxide
Zinc, cadmium, lead, nickel, cobalt	Hydrochloric acid
Iron	Phosphoric acid
Iron, nickel, cobalt	Sulfuric acid



## Metal production by means of electrodeposition

In metal production by means of electrodeposition, the high purity of the metals used is crucial for the quality of the resulting surfaces. Metrohm offers you reliable methods to detect any impurities with highest precision.

### Zinc electrolysis

In the production of zinc the metal is deposited electrolytically on a cathode. The zinc electrolyte used contains impurities due to heavy metals. Using voltammetry it is possible to determine traces of heavy metals in the electrolyte reliably and, as a result, to monitor metal deposition in the electroplating process with the required precision.

Analyte	Sample
Cadmium	Zinc electrolyte
Lead	Zinc electrolyte
Copper	Zinc electrolyte
Thallium	Zinc electrolyte
Nickel	Zinc electrolyte
Cobalt	Zinc electrolyte
Iron	Zinc electrolyte
Antimony(III)	Zinc electrolyte
Germanium	Zinc electrolyte
Selenium	Zinc electrolyte

# Metals as main components of electroplating baths

The concentration of metals in electroplating baths can vary considerably depending on intended purpose. The required thickness of the coating, the nature of the material and market prices for the expensive noble metals are the key parameters. The appropriate analytical technique is selected according to the concentration of the metal to be determined. Metrohm offers suitable systems for carrying it out.

## Titrimetric applications

### Copper and nickel in acidic metal baths

Multilayer systems are widespread in corrosion protection. For example, corrosion-inhibiting nickel is applied on top of an intermediate layer of copper. In the deposition processes the concentration of the metal being deposited is an important parameter for the electric current to be applied. If the concentrations are too low, a stronger current has to be applied, which can drive up the production costs significantly.

The copper content in acidic copper baths is determined by redox titration with  $c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1 \text{ mol/L}$ , following prior reduction of Cu(II) to Cu(I) by means of potassium iodide. The nickel content is determined by way of complexometric titration with  $c(\text{Na}_2\text{EDTA}) = 0.1 \text{ mol/L}$ .

## Ion chromatography applications

### Silver and ammonium in etching baths containing hydrofluoric acid

Ion chromatography is often used to determine medium to low concentrations of metals in etching solutions and electroplating baths. Because such solutions and baths often contain high ionic matrices, Metrohm Inline Dilution is used here. An example of a typical ion chromatography application is the determination of silver in the mg/L range along with ammonium in the g/L range in etching baths containing hydrofluoric acid.





### Voltammetric applications

#### Metal determination and speciation analyses in electroplating baths

Of course, the concentration of the metal used as the main bath component can also be determined by means of voltammetry. In addition, it is possible to differentiate between various oxidation states of metal ions or between free and bound metal ions. Typical applications are:

Analyte	Type of bath
Gold (I)	Cyanidic gold bath
Palladium	Activator
Chromium(III), chromium(VI)	Chromium bath
Nickel	Nickel bath
Cobalt	Cobalt bath

## Inorganic and organic secondary components of electroplating baths

Organic and/or inorganic additives are included in electroplating baths to control the physical properties (ductility, hardness, tear strength, brazeability, etc.) of the deposited metal layer. In the case of decorative electroplating, the visual appearance of the surface is optimized with additives. Complexing agents are also added to baths to keep large quantities of metal in solution.

Essentially, acids, bases and ions in low concentrations can be used to influence the nature of the surfaces of printed circuit boards, contacts, metal components etc. These bath additives must be analyzed at regular intervals, so the production process is most efficient and a consistent end product quality ensured.





### Titrimetric analyses

#### **Boric acid and tetrafluoroboric acid in nickel baths**

Apart from chloride and sulfate, nickel plating baths also contain boric acid, which is used as a buffer to maintain a certain pH value. Using potentiometric titration it is possible to determine both the free boric acid and the free tetrafluoroboric acid. After addition of mannitol, the formed mannitol complexes are titrated with sodium hydroxide solution. The determination is carried out directly in the plating bath sample; nickel and other metal ions do not interfere.

#### **Surfactant determination in electroplating baths**

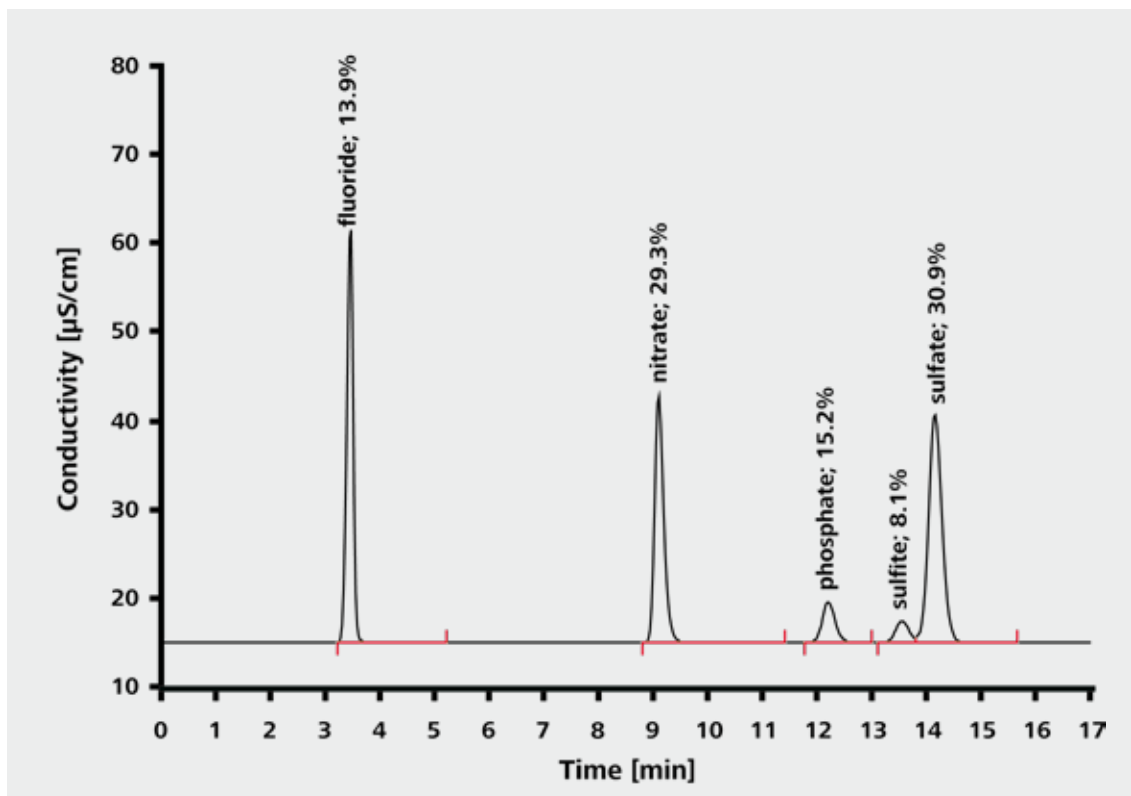
To improve surface properties, surfactants are added to electroplating baths, because they improve surface wetting and emulsify brighteners. Standard anionic surfactants (like, for example, in nickel baths) are determined by means of potentiometric titration with TEGO®trant A100 and an «Ionic Surfactant» electrode.

### Ion-chromatographic analyses

#### Concentrated acids in etching solutions

One of the uses of ion chromatography is to check the content of an electroplating bath. For this, the anion concentrations of the acids and acid mixtures used are determined. The unique combination of Metrohm Inline Dilution Technique and a minimum injection volume

(0.25  $\mu\text{L}$ ) makes possible, for example, fully automatic analysis of concentrated acid mixtures such as an etching solution containing 10% HF, 30%  $\text{HNO}_3$ , 30%  $\text{H}_2\text{SO}_4$  and 13%  $\text{H}_3\text{PO}_4$ .



Etching solution diluted inline 1:100, column: Metrosep A Supp 5 - 150/4.0; eluent: 3.2 mmol/L  $\text{Na}_2\text{CO}_3$ , 1.0 mmol/L  $\text{NaHCO}_3$ , 0.7 mL/min; sample volume: 0.25  $\mu\text{L}$  (internal loop)

### Nitrate in nickel baths

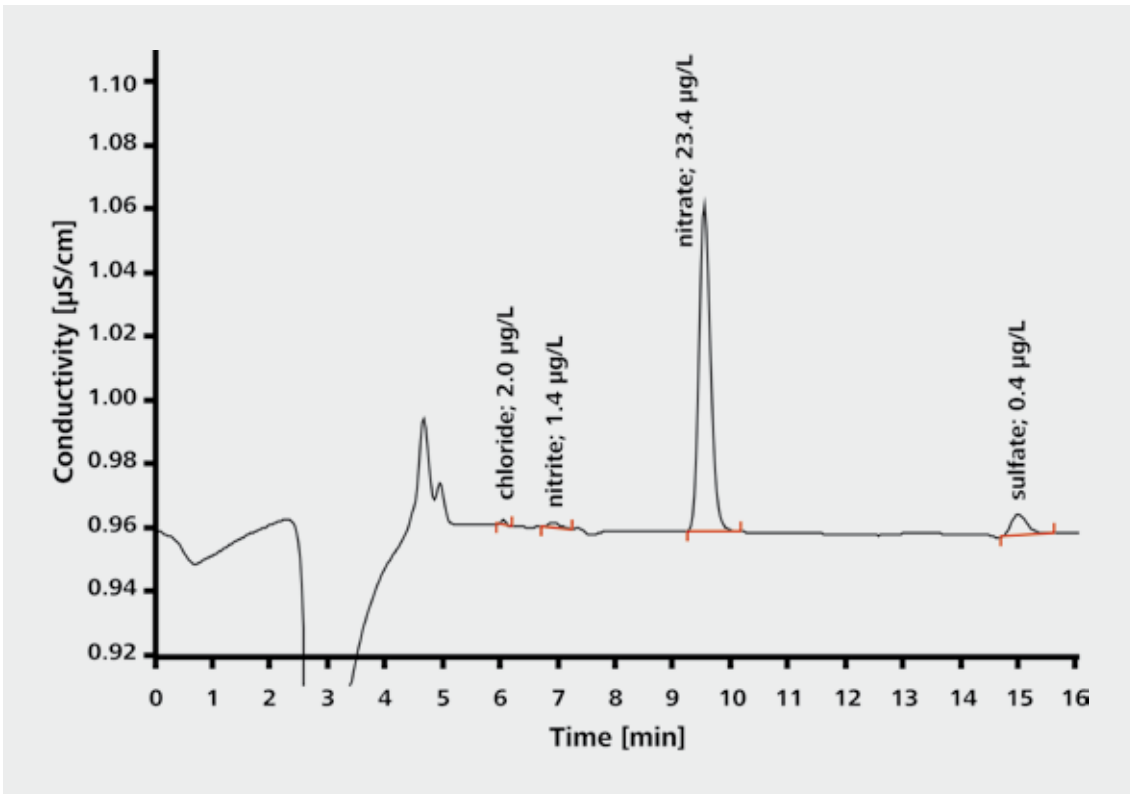
Starter substances, catalysts or contamination from previous steps in the  $\mu\text{g/L}$  to  $\text{mg/L}$  range can be determined by way of ion chromatography for the purpose of process control.

One example here is the determination of nitrate in nickel baths to check the rinsing procedure and to identify unwanted contamination in a newly prepared nickel electroplating bath. By using the intelligent Partial Loop Injection Technique it is possible to cover a concentration range of 1:10'000 with a single calibration. The sample volume varies within the range 2 – 200  $\mu\text{L}$ .

### Organic acids in electroplating baths

Organic ionic and polar substances can also be determined using ion chromatography. Typical applications are determinations of organic acids in electroplating baths. For example, citric acid, formic acid and lactic acid in the  $\text{g/L}$  range are monitored by means of ion-exclusion chromatography.

By contrast, ion-exchange chromatography is used to determine organic acids together with inorganic components in electroplating baths or starter substances (e.g., tartaric acid and citric acid together with hypophosphite and tungstate).



Rinsing solution after bath cleaning; column: Metrosep A Supp 5 - 150/4.0; eluent: 3.2  $\text{mmol/L}$   $\text{Na}_2\text{CO}_3$ , 1.0  $\text{mmol/L}$   $\text{NaHCO}_3$ , 0.8  $\text{mL/min}$ ; column temperature: 25  $^\circ\text{C}$ ; sample volume: 200  $\mu\text{L}$



### Voltammetric applications

#### Lead in nickel baths

Lead is added to nickel baths chemically as a stabilizer. In addition, it has a large effect on nickel deposition itself. The quantity of lead must be maintained in the low mg/L range, in order to be able to guarantee uniform deposition of nickel. Using voltammetry, it is possible to monitor limits reliably, quickly and easily.

#### Antimony/bismuth in nickel baths

Increasingly, nickel baths are being treated with antimony and/or bismuth as an alternative to lead. Here too, the use of voltammetry can be recommended.

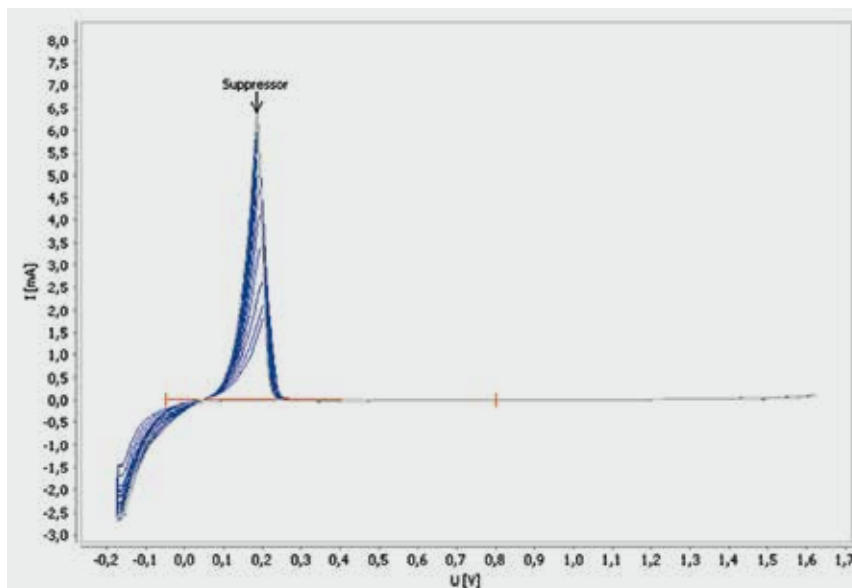
Analyte	Type of bath
Lead, antimony, bismuth	Nickel bath
Cobalt, sulfite	Gold bath
Cobalt, cadmium, thallium	Cyanide bath
Chromium(III) / chromium(VI)	Chromium bath
Saccharin	Acidic copper bath
Thiourea	Acidic copper bath



#### CVS and CPVS to determine organic additives

Cyclic Voltammetric Stripping (CVS) and Cyclic Pulse Voltammetric Stripping (CPVS) are widely used methods in the electroplating industry for the determination of organic additives. The CVS method is an essential component of production control in many industrial coating processes, especially in the manufacture of printed circuit boards and semiconductors.

Analyte	Type of bath
Suppressor	Acidic copper bath, tin bath, tin-lead bath
Brightener	Acidic copper bath
Leveler	Acidic copper bath



Measuring curve for a suppressor determination – dilution titration

## Monitoring of wastewater and process water

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In electroplating installations wastewater is produced at various points in the manufacturing process. Depending on the step in the process (degreasing, electroplating, passivating, pickling, etc.), this wastewater might be highly toxic and therefore require elaborate treatment, in order to eliminate any risks to humans and the environment. Strict limits apply to the substances concerned and these need to be monitored throughout. Metrohm offers you numerous solutions for analyzing process water and wastewater; with them you can optimize the productivity of your processes and ensure optimized compliance with environmental legislation.

### **pH and conductivity measurement in wastewater**

Whether directly in the process or in the laboratory, the pH and conductivity value can always be determined quickly, reliably and GLP conform with the 912/913/914 meters. The 912 Conductometer is ideal for determining conductivity as a single parameter. The pH value can be determined with the 913 pH meter. With the 914 pH/Conductometer it is possible to determine both parameters even in the same measuring vessel.

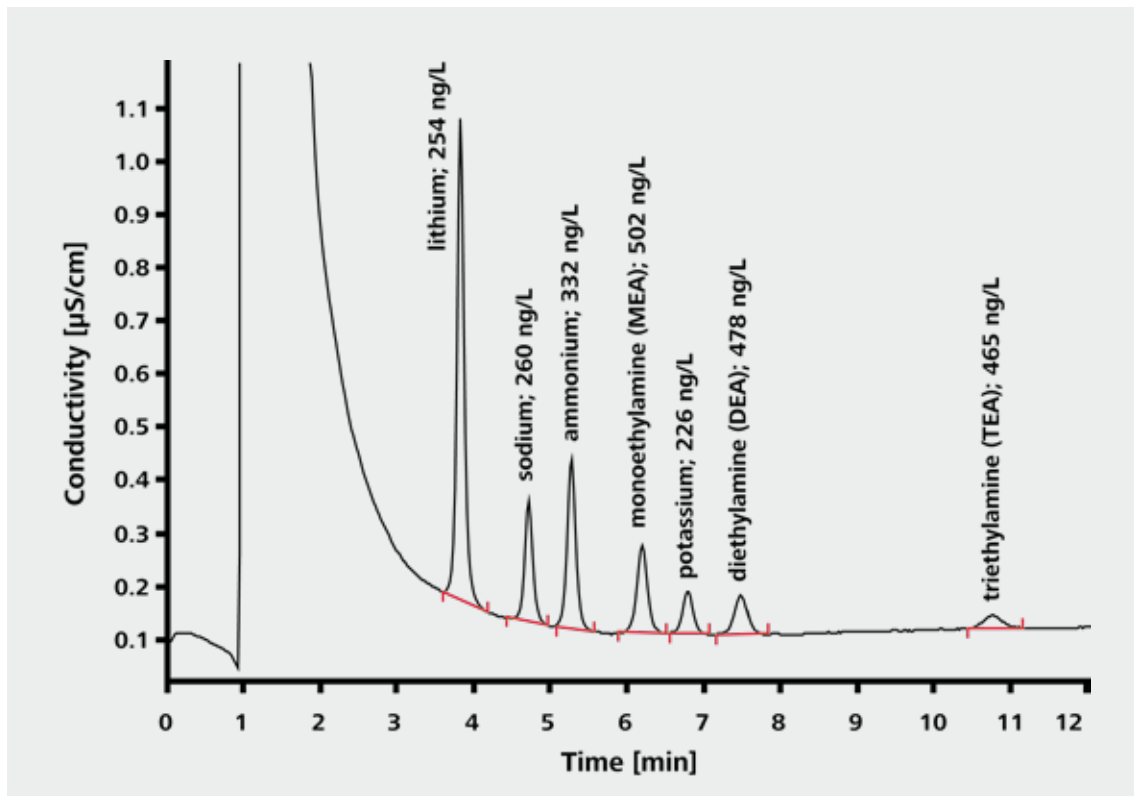


### Ion chromatographic applications

#### Trace analysis to monitor wastewater and rinsing water

The advantages of ion chromatography are most apparent in the monitoring of wastewater, rinsing water and process water. Because of its versatility a wide range of questions concerning compliance with environmental regulations, effectiveness of cleaning steps or quality requirements can be answered during production. Furthermore, ion chromatography makes it possible to detect impurities, carryover or discharges right down to the ng/L range.

An example of this is ultratrace analysis of anions and cations in ultrapure water. Reliable results, unaffected by interferences, are possible if Metrohm Inline Preconcentration is used in combination with Inline Calibration.



Fully automatic and precise analysis of cation traces of ion exchange eluates: column: Metrosep C 3 - 150/4.0; preconcentration column: Metrosep C PCC 1 HC/4.0; eluent: 2.5 mmol/L  $\text{HNO}_3$ , 1.0 mL/min; column temperature: 45 °C; sample volume: 10.0 mL



### Voltammetric applications

#### Heavy metal analysis in wastewater and process water

The strict regulations for environmentally compatible and efficient use of metals have always had a great impact on the operation of electroplating installations. With the 884 Professional VA you are fully able to satisfy the requirements for heavy metal analysis in wastewater.

Not only wastewater, but also the process waters used need to meet strict criteria, depending on the particular use. Whether you are determining the concentration of iron in boiler feed water or monitoring traces of metal in (rinsing) waters due to carryover – with voltammetric system solutions from Metrohm you are on the safe side.

Analyte	Sample
Tin	Wastewater, process water
Iron	Wastewater, process water
Zinc, cadmium, lead, copper	Wastewater, process water
Nickel, cobalt	Wastewater, process water
Chromium <sub>(total)</sub>	Wastewater, process water
Mercury	Wastewater
Arsenic	Wastewater
Thallium	Process water
Selenium	Process water

## Part III: Solutions for atline, online, and inline analysis

### Deviations from target values must be controlled

Many processes are controlled within tightly defined limits for many basic parameters such as temperature or pH. Other more unique parameters include acid concentration in etching solutions and organic additives in copper plating processes.

Often control of these parameters is critical to maintain product and process specifications to achieve optimal product quality and consistency. Deviation of these parameters from target values can negatively impact product quality and lead to excessive operating costs via:

- Excess chemical consumption
- Reduced throughput/fluctuations in plating rate
- Higher energy usage
- Out of specification product / rejects / reworks
- Lower yields

Processes that rely on any analytical measurement to maintain the process near to an operating target and within an operating window will be accurate dependent on:

- The analytical instrument employed
- Error of sampling from the process and sample preparation
- Frequency of analysis
- Process variation error

### Limitations of offline analysis

Offline laboratory analysis can have a negative impact on process accuracy by **introducing sampling error** and limiting analysis frequency due to manual limitations and differences between analysts.



2035 Process Analyzer configured for potentiometric titrations



#### **Improve accuracy, reduce sampling error**

Introducing inline, atline, or online process analyzers reduces the sampling error and increases the sampling frequency as well as improving the prediction error for the analysis.

Improving all these steps leads to **significant improvements in process accuracy** narrowing the normal operating window to ensure the process is operating at its most efficient.

#### **Increase your competitive advantage**

Moving from manual laboratory sampling to a process analyzer allows you to run production much closer to your operating target, resulting in increased yield, improved final product quality and consistency. All this leads to increased profit margins and less out of specification product.

Also, the reduction in process variation can mean product specifications may be further tightened, increasing the efficiency competitiveness of the manufacturing process.

# Atline process analysis with ProcessLab

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## Process monitoring in electroplating

In the electroplating process, material is continuously being deposited on the workpieces. To ensure that the quality of the treated surfaces is consistent, the concentration of the relevant bath ingredients and the reaction products must not exceed nor drop below the defined tolerance limits. This demands close process monitoring, which is normally carried out using wet chemical analyses.

It is a great advantage if samples do not first have to be taken to a laboratory, but can be analyzed directly on the production floor by shift personnel. This allows the yield of the raw materials used to be optimized and the plant to be operated at maximum efficiency while saving time and money over cumbersome laboratory techniques.

## ProcessLab – robust, flexible, and easy to use

ProcessLab is a robust and easy-to-use analysis system that is operated directly at the process line. With an IP54 protection classification the system is able to withstand even the harshest process conditions. The analysis system consists of a touchscreen TFT control unit, a customized analysis module and a sample delivery station. All modules are based on proven components from the Metrohm portfolio and are combined specifically for each customer according to applications.

Samples are taken from the process manually by the operating personnel and held ready. Analysis on the ProcessLab is started by a single press on the touchscreen and then proceeds fully automatically. Process integration comes with the usual process signals.

After analysis, the measurement data are passed on directly to the plant's process control system. The measurement data are shown on the ProcessLab with the appropriate action and warning limits.





### **Combination of analytical methods**

ProcessLab combines various analytical methods on a minimal footprint: titration, direct potentiometry, and photometry. The same principle applies throughout: fully automatic processing of samples with robust and proven modules and thus process control with minimized errors.

Consequently, entire process chains can be monitored with a single system – from pretreatment to finishing baths and on to wastewater monitoring. The performance of the individual subprocesses can be increased by the individual frequency of samples. Thus, the baths can be operated within the optimum parameters and, as a result, the required product quality can be guaranteed.

## Atline application examples

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### Monitoring electroless nickel baths: nickel sulfate, hypophosphite and pH value

Electroless nickel baths are used for many applications. The advantages of chemical nickel deposition are an even distribution of the coating as well as the possibility to use it with rack and barrel facilities.

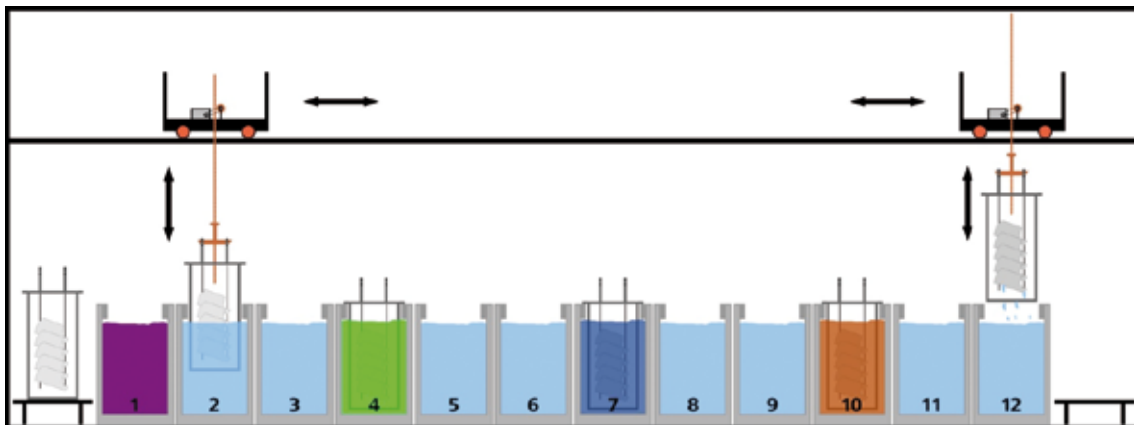
Control of this process is critical for consistent plating rates and bath stability. Nickel consumption is not replenished by a dissolving anode as in electroplating processes. Therefore, frequent analysis and chemical addition are required to control the bath within tolerated limits. Also increasing salt concentrations of the unincorporated ions in the solution can impair the coating properties or the rate of deposition. These increases must be monitored to prolong the bath life through regenerative measures. ProcessLab ensures economic and environmentally aware production throughout the process chain.

### Monitoring alkaline zinc baths: zinc, sodium hydroxide and carbonate

To shield iron and steel components from corrosion, zinc continues to be the main material used as a protective coating. The plating baths deposit zinc on the components electrolytically, thereby ensuring that the materials have a long life. The finishing baths are alkaline; over time the concentration of carbonates in solution increases, impairing the deposition properties and reducing cost efficiency of the process. The deposited zinc must be replaced so the parts being galvanized are coated evenly. The entire process chain, from cleaning of the components in degreasing baths and galvanizing to passivation of the zinc coating on the finished item can be monitored with ProcessLab.

### Process Application Note

- Online analysis of Ni and hypophosphite content.  
[AN-PAN-1012](#)



Schematic diagram of the various process stages in electrogalvanization. The various baths are:

- 1: Acid degreasing bath
- 2 + 3: Rinsing baths
- 4: Acid pickling bath
- 5 + 6: Rinsing baths
- 7: Alkaline zinc bath
- 8 + 9: Rinsing baths
- 10: Passivating bath
- 11 + 12: Rinsing and cleaning baths



### **Monitoring a phosphatizing process**

In cleaning, degreasing, and rinsing baths, and also in the phosphatizing bath itself, the various parameters involved must be adhered to exactly. Those determined in the degreasing and rinsing baths are pH value, conductivity, free alkalinity, and total alkalinity, while the phosphatizing bath is analyzed for free and total acids, accelerator, zinc, and fluoride.

ProcessLab monitors, records and documents all the important analytical parameters of the phosphatizing process. The combination of the analytical methods within one system as well as the intuitive handling via the well-arranged user interface ensure easy and reliable monitoring of the entire process.

## Online process analysis

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### Customized process control

Online analyzers from Metrohm Process Analytics are designed for continuous operation and enable fully automatic monitoring of process baths in electroplating and PCB manufacturing – around the clock, seven days a week. There are no limits: whether your requirement is for one or several sample streams, for a single component or multiple parameters, we will configure the right system for you. Of course, your wastewater treatments can also be controlled or monitored with online analyzers from Metrohm Process Analytics.

### Proven wet chemistry methods

Metrohm Process Analytics online analyzers are based on proven wet chemistry methods such as titration, ion chromatography, photometry, and measurements with ion-selective electrodes. For these methods, sampling and sample preparation are at least as important as the analysis itself. Metrohm Process Analytics has great expertise in this field and configures the sampling system to exactly fit your application including, e.g., filtration, sample taking from pressurized containers, or degassing.

All Metrohm Process Analytics online analyzers come with digital and analog data outputs. Thus, results can be transmitted using the usual process signals and alarms triggered by digital outputs. Or digital inputs can be employed for remote start/stop commands.

### Robust design

Our process analyzers are designed for the rigorous demands of the production environment. The housings meet the specifications of NEMA 4 and protection class IP66.



ADI 2045TI with reagent cabinet

# Safety benefits of online process analysis

## Eliminate exposure to hazardous chemicals

Many hazardous substances are utilized to process different raw materials in the sector of metal surface finishing. When carrying out any risk assessment, the last resort is the use of personal protective equipment (PPE), and any potential exposure risks should ideally be engineered out of any process.

The use of an online analyzer completely eliminates risk of exposure to the hazards associated with the chemicals used in a process. There is no requirement for manual sampling from an acidic bath, for instance, as the analyzer can automatically carry this out making the process safer. There is also potential for automated dosing, further reducing handling of hazardous chemicals.

## Corrosive and lethal substances

Hydrofluoric acid (HF) is one of the most corrosive chemicals used in this industry, and it has serious acute and chronic health effects, if one has been exposed. Even exposures to dilute solutions of HF have led to amputation and even death, especially in cases where response time was slow. Potentially lethal cyanide (CN) is common in many plating baths. Handling of such solutions incorrectly could lead to generation of the highly toxic hydrogen cyanide gas.

## High temperatures

Hot alkaline solutions for etching and degreasing processes are universal, and dangerous incidents can occur in the vicinity of such substances. Process analysis removes the operator from direct involvement during sampling and measurement, limiting any unsafe contact.

## Sensitivity to metals

Sensitivity to some metals is also another common industrially-induced illness. This can be triggered by exposure to many metal compounds such as platinum group metals, nickel, and more. Once an operator is sensitized, he or she can no longer work in the vicinity of such substances due to serious allergic responses.

## Carcinogens

Carcinogenic nickel, chromium, and other toxic metals although not instant threats, can over a period of exposure lead to adverse health effects such as cancer, leading to death. Removal of the operator from process areas which utilize these metals reduces the probability of serious health issues by limiting exposure. Therefore atline or online process analysis is recommended in these situations.





## Online application examples

The majority of laboratory methods can be adapted to the requirements in an online system as they are. Some typical applications in the electroplating industry and PCB manufacturing are described on the following pages.

### **Heavy metals in wastewater**

Wastewater from the electroplating and electronics industries is normally polluted with metals, including heavy metals, e.g., copper, nickel, and cobalt.

The ADI 2045 Voltammetric Analyzer (2045VA) from Metrohm Process Analytics is an online system that ensures continuous monitoring of the concentration of these and other metals. In addition, non-metal components, such as hydrazine, can also be monitored.

### **Monitoring acidic copper baths in semiconductor production**

The most important processing bath in the production of printed circuit boards (PCBs) is the acidic copper bath. The components which are contained therein and need constant monitoring are copper, sulfuric acid, chloride, and also organic bath additives such as suppressors and brighteners. While the concentrations of copper, sulfuric acid, and chloride are determined titrimetrically, Cyclic Voltammetric Stripping (CVS) and Cyclic Pulse Voltammetric Stripping (CPVS) are used to analyze the organic bath additives.

The 2045VA records, all components centrally, thereby allowing the entire production facility to be monitored quickly and efficiently.

**Acidic components of etching baths**

Online analyzers from Metrohm Process Analytics can also be used to monitor the composition of acidic etching baths. By integrating different measuring methods within a single analytical system and developing analytical methods for each individual process bath it is usually possible to monitor the entire facility with just one ADI 2045 system.

**Composition of electroplating baths**

The ADI 2045 Process Analyzer can be recommended for fully automatic monitoring of nickel electroplating baths. Apart from quantifying the nickel content, it also allows measurement of hypophosphite.



## Inline analysis with near infrared spectroscopy (NIRS)

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### Real-time analysis inline

For the analysis of acids, baths, and finishing processes, inline NIR spectroscopic analysis is also an option. NIR analysis operates via taking a light source to the sample with fiber optics and analyzing the returning light to identify any changes in absorbance in the NIR region. The analyzer then can interpret the signal and convert this into concentrations of bath components.

The light is interfaced with the process using low-dispersion fiber optic cables. In this way, real-time data is collected quickly and without the need for chemical analysis.

Metrohm Process Analytics offers two spectroscopic instruments for process analysis: the NIRS Analyzer PRO and the NIRS XDS Process Analyzer. Dual lamp systems guarantee high uptimes, as there is always a pre-calibrated light source ready for action.



NIRS Analyzer PRO: with built-in diagnostics and factory standardization



NIRS XDS Process Analyzer

### Multicomponent analysis in a single scan

One of the major benefits of NIR process analyzers is that they are capable of analyzing multiple components at once. Many parameters can therefore be quantified in one simple scan. Scan times are generally < 1 minute and the methodology is as close to real time as you can get with continuous high resolution data obtained.

### Save on chemical costs – go reagent-free!

Because the methodology is based on the near-infrared light spectrum, there are no reagent requirements **reducing costs and complications** related to reagent handling.

### Expansion capabilities: 1 to 9 channels

The NIRS XDS process analyzer can expand from one to nine sampling points with an integrated multiplexer. This capability opens up expansion possibilities for measurements, such as monitoring a production line of process baths.



## Inline application examples

Reagent-free near infrared spectroscopic process analyzers enable comparison of real-time spectral data from the process to a primary method (such as titration) to create a simple, yet indispensable model for your process needs. NIRS is economical and fast, enabling qualitative and quantitative analyses that are noninvasive and nondestructive. Gain more control over your production and increase the safety of your operations by integrating inline spectroscopic techniques into the process.

### **Analysis of mixed acid baths**

Titanium is normally pickled in hydrofluoric acid and nitric acid, so-called «mixed acid». As the titanium ion concentration increases, HF is consumed by formation of titanium-fluoride complexes. The formation of these complexes has therefore a direct impact on the pickling rate and strongly affects the economics of the process. It is important to be able to monitor how the pickling process proceeds to be able to control the addition of fresh acid. This is also important during the very common batch processing to know when each bath is at the end of life and should be discarded. Maintaining the correct bath composition during pickling is critical for optimum etch conditions and quality processing.

NIRS process analysis utilizing flow cells means accurate inline monitoring of HF and HNO<sub>3</sub> can be accomplished safely and reliably at all times.



## Metrohm Quality Service – Service you can rely on

### Reliable results for the lifetime of your analytical instruments

Whether your field is electroplating or PCB manufacturing – you must always be able to rely on your process control. Systems that are installed and commissioned by professionals and maintained on a regular basis ensure a maximum degree of reliability and uptime.

Relying on the Metrohm Quality Service gives you peace of mind from the very start. From the professional installation of your instruments to regular maintenance care and – should a failure ever occur – instant quality repairs, we do everything to make sure that you can rely 100 percent on results produced during the entire lifetime of your Metrohm instruments.

### Metrohm Compliance Service

Benefit from the Metrohm Compliance Service when it comes to the professional initial qualification of your analytical instruments. Installation Qualification/Operational Qualification carried out by our experts saves you time and money, as your analytical system is configured according to your needs and put into operation fast and reliably.

Initial instructions and user training ensure error-free operation of your new instruments by your staff. The Metrohm Compliance Service includes comprehensive documentation and guarantees compliance with the standards of quality management systems such as GLP/GMP and ISO.



### Metrohm Quality Service

Metrohm Quality Service is available worldwide. Preventive maintenance carried out on a regular basis extends your instrument's lifetime while providing for trouble-free operation. All maintenance work done under the label Metrohm Quality Service is carried out by our own certified service engineers. You can choose the service contract that suits you best.

With a full service contract, for example, you can rely on the optimum performance of your Metrohm instruments, incur no additional costs and benefit from complete and compliant verification documents. Thanks to our service you are perfectly prepared for audits.

Metrohm Quality Service	Customer benefits
Metrohm Care Contracts	<ul style="list-style-type: none"> <li>• Minimizes downtime through preventive maintenance</li> <li>• Cost control and savings through free or discounted replacement materials and consumables</li> <li>• Guaranteed reaction times and rapid on-site repair</li> <li>• Documented instrument certification as an ideal preparation for audits</li> </ul>
Metrohm Software Care	<ul style="list-style-type: none"> <li>• High data security and maximum system performance through regular, professional software maintenance</li> </ul>
Metrohm Compliance Service	<ul style="list-style-type: none"> <li>• Customized services and documentation for analytical instrument qualification (AIQ)</li> <li>• Professional start-up (IQ/OQ or Certified Installation) and requalification or recertification by specifically trained employees</li> </ul>
Metrohm Remote Support	<ul style="list-style-type: none"> <li>• Quick resolution of software and application issues directly at the workplace</li> </ul>
Metrohm Buret Calibration	<ul style="list-style-type: none"> <li>• Calibration of burets (e.g., dosing and exchange units) with certification</li> <li>• Accurate measurement results</li> <li>• Verification documentation for compliance with regulations and efficient audits</li> </ul>
Metrohm Repair Service	<ul style="list-style-type: none"> <li>• Rapid availability of repaired instruments thanks to decentralized repair workshops around the world and a central workshop at the manufacturer site</li> <li>• Highly qualified service technicians ensure sustainable repair success</li> <li>• Rapid resolution of problems and minimized downtimes through on-site emergency services and express repairs</li> </ul>
Metrohm Spare Parts	<ul style="list-style-type: none"> <li>• Original spare parts, made in Switzerland and available worldwide</li> <li>• Short delivery times through warehousing from local distributors</li> <li>• Investment security through ten-year spare parts guarantee after discontinuation</li> </ul>
Metrohm Application Support	<ul style="list-style-type: none"> <li>• Free access to the Metrohm Application Finder (<a href="http://www.metrohm.com/en/applications/">www.metrohm.com/en/applications/</a>) with more than 2000 applications (Application Bulletins, Application Notes, monographs, technical posters, and technical articles)</li> <li>• Rapid and professional resolution of any application issues through personal consultations with our specialists by e-mail, telephone, or remote support</li> <li>• Support for the solution of complex analytical problems, as well as method optimization on-site or at our application laboratory</li> </ul>
Metrohm Training Programs	<ul style="list-style-type: none"> <li>• Basic and advanced training with local representatives, at the Metrohm Academy or directly on-site</li> <li>• Efficient and proper use of all analytical methods, as well as results reliability through competently trained users</li> <li>• Training documentation and certificates for trouble-free audits</li> </ul>

## Ordering information

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### Instruments for titration

2.912.0210	Conductometer Lab with stand plate
2.913.0210	pH Meter Lab with stand plate
2.914.0220	pH/Conductometer Lab with stand plate
2.912.0110	Conductometer with conductivity sensor in case with various accessories
2.913.0110	pH Meter with Primatrode in case with various accessories
2.914.0120	pH/Conductometer with Primatrode, conductivity sensor in case with various accessories
OMNIS Titrator	Please contact your local Metrohm distributor to customize the titration system to your current or future titration needs
2.905.2020	Plate Titrando The Plate Titrando offers you a complete package for the most common analyses of plating baths. Apart from the titration software <b>tiamo</b> light and determination methods described in detail, you will also receive comprehensive accessories for your titrations.
2.856.0010	Conductivity Module – conductivity measuring module for upgrading Titrando systems or use as stand-alone unit in combination with a 900 Touch Control.

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### Electrodes and buffer solutions

6.0255.100	Profitrode – comb. pH electrode with DJ reference system for titration
6.0258.010	Unitrode with Pt1000 temperature sensor (fixed cable) for measuring pH
6.0430.100	Ag Titrode for precipitation titrations with AgNO <sub>3</sub>
6.0431.100	Pt Titrode for redox titrations
6.0507.120	«Ionic Surfactant» electrode for titration of anionic and cationic surfactants
6.0750.100	LL ISE Reference
6.0915.130	Five-ring conductivity measuring cell, $c = 1.0 \text{ cm}^{-1}$
6.0917.080	Sturdy conductivity measuring cell, $c = 0.5 \text{ cm}^{-1}$ with Pt1000 for 912/914 meter
6.0918.040	Conductivity measuring cell of stainless steel, $c = 0.1 \text{ cm}^{-1}$ , with Pt1000 temperature sensor for the 912/914 meters
6.0919.140	Conductivity measuring cell $c = 1.6 \text{ cm}^{-1}$ with Pt1000 for the 912 and 914 Conductometers
6.2104.020	Electrode cable 1 m
6.2106.020	Electrode cable for LL ISE Reference
6.2307.230	Buffer solutions pH 4/7/9 (3 x 10 x 30 mL)

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### Intelligent Exchange Units for the 848 Titrino plus

6.3026.110	Exchange Unit 1 mL
6.3026.150	Exchange Unit 5 mL
6.3026.210	Exchange Unit 10 mL
6.3026.220	Exchange Unit 20 mL
6.3026.250	Exchange Unit 50 mL

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### Intelligent Dosing Units for the Titrando

6.3032.120	Dosing Unit 2 mL
6.3032.150	Dosing Unit 5 mL
6.3032.210	Dosing Unit 10 mL
6.3032.220	Dosing Unit 20 mL
6.3032.250	Dosing Unit 50 mL

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**Instruments for ion chromatography**

2.940.2500	940 Professional Vario TWO/SeS/PP
2.930.2560	930 Compact IC Flex Oven/SeS/PP/Deg
2.850.9010	IC Conductivity Detector
2.858.0020	858 Professional Sample Processor with peristaltic pump and valve
2.919.0020	919 IC Autosampler plus
ProfIC Vario 4	Fully automatic Professional IC Vario System for inline dilution
ProfIC Vario 5	Fully automatic Professional IC Vario System for inline preconcentration
ProfIC Vario 9	Fully automatic Professional IC System Vario for inline preconcentration and inline matrix elimination
6.1006.520	Metrosep A Supp 5 - 150/4.0
6.1010.420	Metrosep C 3 - 150/4.0
6.1006.340	Metrosep A PCC 2 HC/4.0
6.1010.310	Metrosep C PCC 1 HC/4.0
6.2832.000	MSM Rotor A
6.2842.000	MSM-HC Rotor A
6.2844.000	MSM-LC Rotor A
6.2842.200	MSM-HC Rotor C

**Instruments for voltammetry**

2.884.1110	884 Professional VA semiautomated with 2 Dosinos for automatic addition of solutions
2.884.1210	884 Professional VA semiautomated for CVS with 2 Dosinos for automatic addition of solutions. Optional additional Dosinos for further solutions can be connected.
MVA-22	Automated analysis system for trace determinations with voltammetry and polarography. Comprising 884 Professional VA for MME, 919 IC Autosampler plus for VA, two 800 Dosinos, 843 Pump Station. For sample series of up to 28 samples.
MVA-23	Automated analysis system for the determination of organic additives in electroplating baths using CVS ("Cyclic Voltammetric Stripping"), CPVS ("Cyclic Pulse Voltammetric Stripping"). Comprising 884 Professional VA for CVS, 858 Professional Sample Processor, four 800 Dosinos, 843 Pump Station. For sample series of up to 56 samples.

**Instruments for process analysis**

We offer online, inline, and atline process analyzers that meet any requirement for industrial processes: from single-parameter to the most advanced multiparameter analyzers. Every analyzer can be custom-tailored to the specific task at hand.

2045PL	ProcessLab system for atline determination of various parameters using titration, colorimetry, and ISE
2045 Series	Multifunctional process analyzers, available for titration, ISE, photometry, and voltammetry
2035 Series	Modular process analyzers designed for either photometry, potentiometric titration, or thermometric titration
202X Series	Single method process analyzers, available for titration, pH, ISE or photometry
ICON Analyzer	Entry-level process analyzer for single parameter photometric analysis
NIRS XDS	Inline analyzers based on nondestructive near-infrared (NIR) analysis, with a scan range of 800–2200 nm and capable to expand from 1 to 9 measuring channels
NIRS PRO	Inline analyzers based on high-resolution diode array technology, the entire wavelength range (1100–1650 nm) is measured instantaneously for real-time analysis
Process Ion Chromatograph	Based on Metrohm ion chromatography, this process analyzer can monitor several ionic compounds in aqueous media from ng/L to %

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