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Analysis of plating baths using the Thermo Scientific iCAP 7400 ICP-OES

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Keywords

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Goal

This application note describes the performance of the Thermo Scientific iCAP 7400 ICP-OES Duo analyzing different elements in different types of plating baths. The duo viewing offers optimal method conditions using axial view for traces and radial view for major elements.

Introduction

The plating of metal is an ancient technique, used for hundreds of years. It can be defined as the act of covering the surface of objects by depositing a metal on a conductive surface. This is typically carried out by immersing the object in a solution in which the metal ions are moved by an electric field. The applications are rather vast, ranging from the merely decorative, to the enhancement of the physical properties of the material being covered (i.e. to prevent corrosion, reduce friction, alter conductivity, or to improve characteristics such as hardness or durability). It is widely used in the production of jewelry pieces to achieve a silver or gold finish.

Manufacturers frequently establish optimum specifications in order to guarantee maximum solution efficiency and uniformity of the plating solution. Plating solutions should be analyzed regularly in order to maintain the recommended formulations and to prevent problems related to improper levels of bath constituents and contaminants. A current problem faced by the plating industry is gradual and continuous changes in pH, metal or cyanide content of plating baths, leading to a significant decrease in efficiency. Some of the most common plating solutions and their main applications are presented in Table 1.

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There are several different methods that can be employed for the quantitative analysis of plating solutions; these are classified as volumetric, gravimetric or instrumental. Both volumetric and gravimetric methods are simple, accurate, and rapid and can be performed with common laboratory equipment. Nevertheless they only rely on chemical reactions instead of measuring the physical properties associated with the composition of the substance.

Additionally, instrumental methods are far quicker and allow for the automatization of the analysis, leading to less mathematical errors and higher reproducibility. A common instrumental technique is spectroscopic analysis, in particular inductively coupled plasma-optical emission spectroscopy (ICP-OES), which is used in the analysis of major components and trace contaminants in plating solutions. When using this technique there are some aspects that need to be taken into consideration, such as physical interferences (e.g. viscosity or surface tension) and chemical interferences. They can be overcome easily by sample dilution and accurate matrix matching. The analysis of sulphuric acid (H_2SO_4) levels in plating baths is commonly performed by electroanalytical methods, specifically potentiometry. This is a simple and relatively low cost method but the sensitivity is limited at low concentrations, not allowing for accurate measurements in highly dilute solutions and it can also encounter a number of interferences. Manufacturers that use plating in their processes are increasingly using ICP-OES instrumentation to quantify H_2SO_4 levels. This method allows for a rapid, sensitive and interference free measurement of sulphur, directly proportional to H_2SO_4, resulting in high accuracy even at low levels.

Table 1. Plating solutions commonly used and their main applications.

Plating baths	Main applications
Alloy	Hardness improvement
Cadmium	Corrosion resistance
Chrome	Decorative and industrial
Composite	Physical properties improvement
Gold	Jewelry manufacturing and electronics
Nickel	Decorative and corrosion resistance
Rhodium	Jewelry manufacturing
Silver	Jewelry manufacturing and electronics
Tin	Food processing and electronics
Zinc	Corrosion resistance

Instrumentation

The Thermo Scientific™ iCAP™ 7400 ICP-OES Duo was used for the analysis of a range of plating baths. This is a compact duo view ICP-OES instrument based on the innovative technologies of the Thermo Scientific iCAP 7000 Plus Series ICP-OES. The instrument achieves powerful analyte detection and provides a highly cost effective solution for routine analysis of liquids in laboratories with standard sample throughput requirements.

Sample and standard preparation

Elements analyzed in each plating bath are presented in Table 2. For the chromium and aluminium baths the quantification of sulphur was performed in order to quantify the amount of H_2SO_4 in the samples.

Table 2. Elements analyzed in each plating bath.

Type of plating bath	Elements analyzed
Chromium and ammonium fluoride (Cr & NH_4F)	Al, Cr, Zr
Nickel (Ni)	B, Ni
Chromium (Cr)	Fe, S
Chromium (Cr)	S
Chromium and aluminium (Cr & Al)	S

Quantification of the samples was done by Method of Standard Addition (MSA) to avoid any possible matrix effect. Standard addition calibration was prepared by spiking samples with traceable 1000 $mg \cdot L^{-1}$ aqueous, single element standards, to the concentrations listed in Table 3. All solutions were made to 50 mL with ultra-pure deionized water.

Table 3. Standard addition concentrations in $mg \cdot L^{-1}$.

Type of plating bath	Element	Blank	Standard 1	Standard 2	Standard 3
Cr & NH_4F	Al	0	1	2	-
	Cr	0	20	40	-
	Zr	0	50	100	-
Ni	B	0	5	10	-
	Ni	0	50	100	-
Cr	Fe	0	50	100	-
	S	0	50	100	-
Cr	S	0	50	100	150
Cr & Al	S	0	25	50	75

Method development and analysis

A LabBook was created in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software which contained the method parameters and standard concentrations as listed in this note. A standard sample introduction kit was used for the analysis. The instrument was calibrated and the samples analyzed in a single run. The method parameters are shown below in Table 4.

Table 4. Method parameters.

Parameter	Setting
Pump Tubing (Standard Pump)	Sample Tygon® orange/white Drain Tygon® white/white
Spray Chamber	Glass cyclonic
Nebulizer	Glass concentric
Center Tube	2.0 mm
Pump Speed	50 rpm
Nebulizer Gas Flow	0.5 L·min^{-1}
Auxiliary Gas Flow	0.5 L·min^{-1}
Coolant Gas Flow	12 L·min^{-1}
RF Power	1150 W
Exposure Time	UV 10 s, Vis 5 s

Results

The results obtained in the analysis of the different bath samples are shown in Table 5. It is assumed that all of the sulphur present in the sample is in the form of H_2SO_4, therefore the results obtained for sulphur are multiplied by 3.06 [M(H_2SO_4)\M(S)=3.06], in order to calculate the concentration of H_2SO_4. Results obtained for all the elements were within the expected range. Concentration ranges were established by the manufacturers taking into account the concentrations usually found in these types of plating baths to obtain maximum efficiency. This gives the plating operators the status of the bath simplifying the assessment of how the bath composition evolves over time.

Table 5. Results of the analysis of the different plating baths. All concentrations are in mg·L^{-1}.

Type of plating bath	Elements and wavelengths (nm)	Concentration found	Established concentration/range	Dilution factor*
Cr & NH_4F	Al 167.079	2.2	<10	100
	Cr 205.560	456	500	
	Cr 206.550	454.9		
	Cr 267.716	446.7		
	Zr 274.256	1504	1700	
	Zr 327.305	1486		
	Zr 339.198	1567		
	Zr 343.823	1689		
Ni	B 208.959	6380	<7000	1000
	B 249.678	6270		
	B 249.773	6150		
	Ni 221.647	95470	80000	
	Ni 231.604	94770		
Cr	Fe 259.837	2892	<5000	100
	Fe 259.940	2907		
	Fe 371.994	2823		
	S 180.731 (H_2SO_4)	1021.6 (3126)	2500 – 3000 (H_2SO_4)	
	S 182.034 (H_2SO_4)	1035.0 (3167)		
	S 182.624 (H_2SO_4)	983.7 (3010)		
Cr	S 180.731 (H_2SO_4)	85.6 (2020.3)	2250 – 2500 (H_2SO_4)	10
	S 182.034 (H_2SO_4)	79.4 (2429.6)		
	S 182.624 (H_2SO_4)	74.2 (2271.7)		
Cr & Al	S 180.731 (H_2SO_4)	5.7 (35.1)	<150 (H_2SO_4)	2
	S 182.034 (H_2SO_4)	7.5 (45.9)		
	S 182.624 (H_2SO_4)	7.5 (45.9)		

* All dilutions were prepared using ultra-pure water.

Conclusion

The analysis of plating baths, specifically those that require the analysis of sulphuric acid, is rapid and highly sensitive when using the Thermo Scientific iCAP 7400 ICP-OES Duo in conjunction with the Thermo Scientific Qtegra ISDS Software. This enables the accurate quantification of metals and sulphuric acid content, while the powerful, easy to use iCAP 7400 ICP-OES allows both experienced and inexperienced users alike to vastly reduce the method development time required for these sample types, resulting in cost effective analyses.

Find out more at **thermofisher.com/ICP-OES**

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