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

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**Key Words**
Method of standard addition, plating baths, sulphuric acid levels

## Goal

This application note describes the performance of the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo analysing 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, and the pre-loaded template allows for rapid and simple method development.

## 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 jewellery pieces to achieve a silver or gold finish. Due to the ability to cover objects as small as an atom this technique has a high potential to be used in the nanotechnology area.

Manufactures frequently establish optimum specifications in order to guarantee maximum solution efficiency and uniformity of the plating solution. Plating solutions should be analysed 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 are gradual and continuous changes in pH and metal or cyanide content, leading to a significant decrease in efficiency. Some of the most common plating solutions and their main applications are presented in table 1.

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 |
| Golden | Jewellery manufacturing and electronics |
| Nickel | Decorative and corrosion resistance |
| Rhodium | Jewellery manufacturing |
| Silver | Jewellery manufacturing and electronics |
| Tin | Food processing and electronics |
| Zinc | Corrosion resistance |

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 (such as 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. Maufacturers 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.

## 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 iCAP 7000 Series ICP-OES spectrometers. 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. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) incorporates several pre-loaded templates (see Figure 1) for common methods, simplifying normal method development and providing an option of immediate analysis.

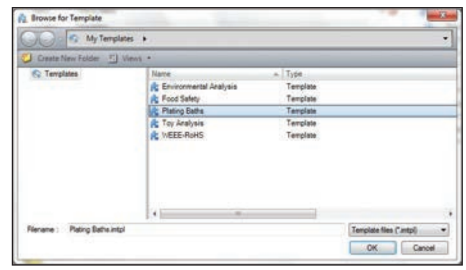


Figure 1. Plating Baths template selection

## Sample and standard preparation

Elements analysed in each plating bath are presented in table 2. For the Chromium and Chromium & Aluminium baths the quantification of sulphur was performed in order to quantify the amount of $H_2SO_4$ in the samples.

Table 2. Elements analysed in each plating bath

| Type of plating bath | Elements analysed |
|---|---|
| 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 made by Method of Standard Addition (MSA) to avoid any possible matrix effect. Standard addition calibration was prepared by spiking samples with traceable 1000mg/L aqueous, single element standards, to the concentrations listed in table 3. All solutions were made to 50 mL with ultra pure de-ionized water.

Table 3. Standard addition concentrations (mg/L)

| 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

A LabBook was created in Qtegra ISDS 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 | Sample Tygon® 1.016 mm<br>Drain Tygon® 1.524 mm |
| Pump speed | 50 rpm |
| Nebulizer | Glass concentric |
| Nebulizer gas flow | 0.5 L/min |
| Spray chamber | Glass cyclonic |
| Center tube | 2 mm |
| RF Power | 1150 W |
| Coolant gas flow | 12 L/min |
| Auxiliary gas flow | 0.5 L/min |
| Exposure times | Low 10 sec<br>High 5 sec |

## 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 is multiplied by 3.06 [$M(H_2SO_4)\backslash M(S)=3.06$], in order to calculate the concentration of $H_2SO_4$. Results obtained for all the elements were within the expected range.

Table 5. Results of the analysis of the different plating baths. All concentrations are in mg/L.

| 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 | 456.0 | 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.

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 overtime.

## 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 in conjunction with the Qtegra ISDS. 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.

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