MICAP-OES 1000

Monitoring of plating baths with a compact N$_2$ ICP-OES system

Introduction

Plating is a long-utilized process where a thin layer of metal is deposited onto a surface, coating it for the purposes of decoration, corrosion resistance, reduction of friction, conductivity, hardening and many other end purposes. It is most commonly performed on conductive surfaces through a process called electroplating, where the object is immersed in a chemical solution bath and a charge is applied to draw the metal ions in the solution to the object. These ions plate onto the surface of the item, forming the desired metallic coating.

To control the quality of the metallic coating, it is important to monitor the concentrations of both the plating ions and any contaminating metallic ions present in the plating baths. Traditionally the analytical techniques of titration and Flame Atomic Absorption (FAA) have been used in many plating shops. Unfortunately, these measurement tools are very limited as they only provide single element analysis capability. The multi-elemental technique Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) has been more recently used, due to its ability to measure plating metals and any contaminating metals concurrently.

This note describes the use of the simultaneous MICAP N$_2$ ICP-OES system for routine analysis of various plating baths. Measurement examples of both major bath components as well potential contaminates are demonstrated, allowing the performance of these plating baths to be closely monitored.

Instrumentation

The MICAP-OES 1000 N_2 ICP was configured with an aqueous sample introduction system for the analysis of these plating bath solutions.

Microwave energy in the MICAP is coupled into the Cerawave™ ring in a highly efficient process that creates the magnetic fields required to inductively couple energy into the robust N_2 plasma emission source. The 4 MP sCMOS camera simultaneously collects the emission lines from the high-resolution spectrometer to detect the trace elemental signals. All detection is performed in the axial view mode on the MICAP, with an air knife deflecting the tail of this vertical N_2 plasma.

A random-access ASX-560 autosampler (Teledyne Cetac, Omaha, NE, USA) was utilized to introduce all the blanks, standards, QC samples, and the plating bath solutions to the MICAP. Analysis time for each sample was approximately 2 min 30 sec with this system configuration (Figure 1).

Experimantal Conditions

The analyses were performed on the simultaneous MICAP N_2 ICP-OES system utilizing the conditions listed in Table 1. Six different plating bath solutions were supplied for multielement analysis. Each of these solutions are quite different in makeup and concentration levels, including three bath samples in acidic conditions (Group A) and three in alkaline conditions with sodium and potassium cyanide salts (NaCN & KCN) present (Group B). Due to these different sample types and safety procedures required when handling CN-containing samples, the analysis of these two sample groups was split into separate analysis sessions.

The standard single-pass cyclonic spray chamber was equipped with a high-solids concentric nebulizer, as it is common for these process solutions to contain particulates. A standard one-piece torch was utilized to introduce the samples into the N_2 plasma. A complete list of the instrumental conditions is displayed in Table 1, followed by the analytical wavelengths chosen for the acidic and basic (CN-containing) sample groups (Table 2). All sample results were internal standard corrected during the simultaneous measurement using the Y 371.029 nm emission line.

Table 1. MICAP operational conditions

Parameter	Value
Torch	Quartz 1-piece, 1.5mm injector
Spray Chamber	Single-pass cyclonic
Nebulizer	GE Slurry concentric glass
Sample Tubing	Blk/Blk PVC (0.76 mm ID)
Drain Tubing	Blu/Yel PVC (1.52 mm ID)
Coolant Gas Flow	14 L/min
Auxiliary Gas Flow	0.4 L/min
Nebulizer Gas Flow	0.7 L/min
Peristaltic Pump	45 rpm
Plasma Viewing	Axial
Camera Exposure	10 sec (1000 ms @ 10 reps)
# of Repeats	3

Table 2. Analyte and internal standard wavelengths for Acidic and Basic plating bath sample groups

Acidic Group A Analyte Wavelength (nm)	Basic Group B Analyte Wavelength (nm)
Al 394.410	Ag 328.068
Cr 425.435	Al 396.152
Cu 324.754	Au 242.795
Fe 259.940	Cd 228.802
Si 251.611	Cr 425.435
Zn 213.857	Cu 327.396
	Fe 259.940
	Ni 346.165
	Zn 213.857

Figure 1. MICAP and ASX-560 autosampler

Table 3. Analytes and standard concentrations, in mg/Kg (ppm)

Element / Wavelength	Element	Std 1	Std 2	Std 3	Std 4	Std 5	CCV
A	Al	0.25	0.5	2.5	10	20	2.5
A	Cr	0.25	0.5	2.5	10	20	2.5
A	Cu	0.25	0.5	2.5	10	-	2.5
A	Fe	0.25	0.5	2.5	10	20	2.5
A	Si	0.25	0.5	2.5	-	-	2.5
A	Zn	0.25	0.5	2.5	10	-	2.5
B	Ag	0.25	0.5	2.5	10	20	2.5
B	Al	0.25	0.5	2.5	10	20	2.5
B	Au*	0.25	-	2.5	-	20	2.5
B	Cd	0.25	0.5	2.5	10	20	2.5
B	Cr	0.25	0.5	2.5	10	20	2.5
B	Cu	0.25	0.5	2.5	10	20	2.5
B	Fe	0.25	0.5	2.5	10	20	2.5
B	Ni	0.25	0.5	2.5	10	20	2.5
B	Zn	0.25	0.5	2.5	10	20	2.5

Au standards prepared separately to ensure stability

Standard and Sample Preparation

The calibration standards, blanks, and QC samples were all prepared in 5% (v/v) HNO_3 (PlasmaPure grade, AnalytiChem, Bale-D'Urfe, QC, Canada). Multielement standards were prepared from aqueous standards (Inorganic Ventures, Christiansburg, VA, USA) and diluted with 18 MΩ deionized water (DI) and the 5% HNO_3. See Table 3 above for the specific concentrations for each plating bath analysis group. Additionally, 5 ppm Yttrium (Y) was added to all samples, standards and blanks to provide internal standard monitoring throughout the sample analysis sessions.

The types of plating bath samples analyzed are listed in Table 4. The Group A samples were simply diluted into the calibration range with 5% HNO_3 prior to analysis.

Due to the presence of cyanide in the Group B samples, care and planning is required to remove the CN^- by acidifying the samples in a laboratory hood with carefully monitored air flow. This acidification step generates hydrogen cyanide gas (HCN) that is highly toxic and flammable. In this process, 2 mL of the concentrated bath samples were individually placed into a flask (inside the lab hood) along with 20 mL of DI water. They were then slowly acidified with 10 mL of conc. HNO_3, heated to near boiling and allowed to react for 30 minutes. Once these samples were cooled to room temperature, they were brought up to 100 mL. The gold plating bath sample additionally had 10 mL of conc. HCl added during the process to aid the gold dissolution.

These three neutralized plating samples (Group B) were then diluted into the calibration range with 5% HNO_3 prior to analysis.

Table 4. Plating Baths Analyzed

Group A Acidic Baths	Group B Basic w CN- Baths
Boric Sulfuric Anodize	Silver Strike
Chromate Seal	Cadmium
Hexavalent Chromate	Gold

Results

The two plating bath sample groups were successfully analyzed with MICAP and the results compiled. The system was calibrated for each sample group and all calibration curves were linear with correlation coefficients of r^2 greater than 0.9999. Examples of the emission peaks obtained are shown in Figure 2, displaying the Cu 324.754 nm line measured in the Boric Sulfuric Anodize bath and the Ni 346.165 nm measured in the Gold plating bath. The orange regions indicate the peak integration area selected for each of these analyte signals. The accuracy of results obtained for each wavelength utilized was confirmed with secondary emission lines for each element.

The results from the acidic Group A samples are shown (on the next page) in Table 5 followed by the Group B samples in Table 6. Calibration checks were performed at the beginning and end of each analysis and all recoveries fell within ± 4%. Limits of quantitation (LOQ) were set at 5x the limits of detection (LOD). LOD values were calculated from 3x standard deviation of 10 blank measurements.

The total applied dilution factors are provided along with the results. The internal standard Yttrium (Y) values all remained within the 95-105% recovery window throughout both analysis sessions.
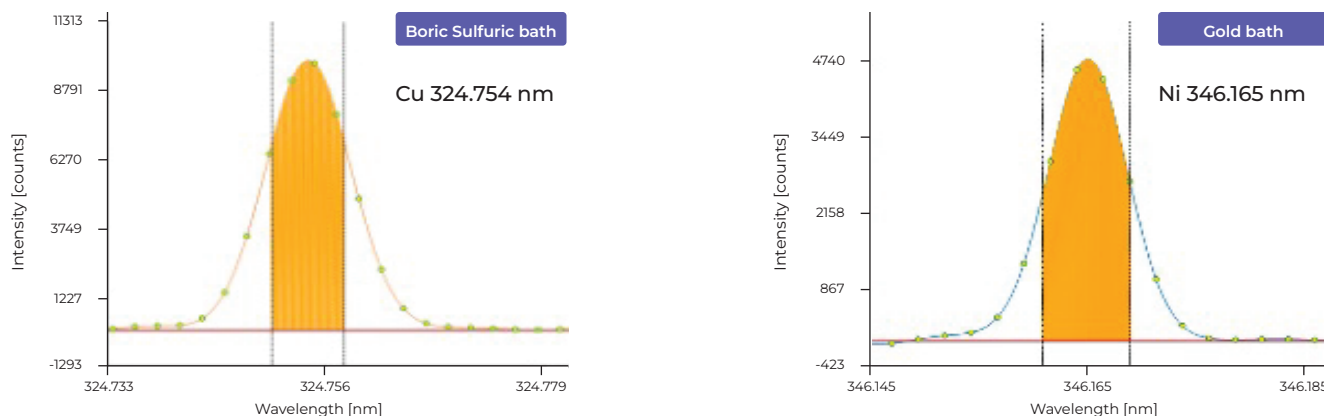
Figure 2. Example emission peaks obtained with MICAP in plating bath samples

Table 5. Acidic Group A plating bath results

Analyte Wavelength (nm)	LOQ (ppm)	Boric Sulfuric		Chromate Seal		Hexavalent Chromate	
		Result (ppm)	Spike (% Rec)	Result (ppm)	Spike (% Rec)	Result (ppm)	Spike (% Rec)
Al 394.401	0.045	1060	95	0.90	98.6	< LOQ	96
Cr 425.435	0.18	30.6	101	57.8	91.9	1,980	106
Cu 324.754	0.012	49.6	101	0.02	101.2	5.92	101
Fe 259.940	0.081	87.9	95	< LOQ	94.8	39.8	95
Si 251.611	0.060	8.9	98	0.11	98.1	13.8	99
Zn 213.857	0.14	< LOQ	100	< LOQ	100.2	505.3	95
Dilution Factor		100x		2x		100x	

Table 6. Cyanide-containing Group B plating bath results

Analyte Wavelength (nm)	LOQ (ppm)	Silver Strike		Cadmium		Gold	
		Result (ppm)	Spike (% Rec)	Result (ppm)	Spike (% Rec)	Result (ppm)	Spike (% Rec)
Ag 328.068	0.019	4430*	101	<LOQ	99	< LOQ	99
Al 396.152	0.027	10.4	101	<LOQ	108	49.7	106
Au 242.795	0.044	<LOQ	-	<LOQ	104	3820*	107
Cd 228.802	0.035	<LOQ	100	9630*	99	<LOQ	102
Cr 425.435	0.180	<LOQ	101	<LOD	109	<LOQ	106
Cu 327.396	0.019	41.5	97	24.3	102	14.8	101
Fe 259.940	0.080	27.6	93	97.6	98	163	99
Ni 346.165	0.120	36.6	96	<LOQ	100	1030	102
Zn 213.857	0.140	<LOQ	100	<LOQ	106	<LOQ	103
Dilution Factor (*1000x DF)		250x		250x		250x	

Conclusions

The performance of the MICAP-OES 1000 N_2 ICP-OES on these various plating baths demonstrates its ability to perform sensitive and accurate analysis of these high matrix samples. The capability of measuring both acidic and basic cyanide-containing plating baths displays its worth for the quick and flexible measurement of both major components and contaminating metals in these plating bath solutions. The excellent spike recoveries obtained in all the samples further proves this ability.

The multielement, simultaneous measurement design of the MICAP greatly simplifies the analysis of these metallic bath components. The N_2 microwave-powered ICP-OES system provides the capability for routine, cost-effective, and frequent monitoring to greatly improve the quality of the metal plating process.

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