

Challenge

Accurate determination of trace contaminants and major constituents in Ni- and Cr-based electroplating baths and wastewater despite severe spectral interferences and high matrix loads.

Solution

High-resolution ICP-OES with Dual View PLUS enables reliable trace and major element analysis across a wide concentration range in a single method.

Intended audience

Electroplating laboratories, surface-finishing companies, contract labs, and wastewater monitoring facilities.

High-resolution ICP-OES for the analysis of nickel and chromium electroplating baths and wastewater

Introduction

Electroplating laboratories must maintain tight control over the composition of process baths to ensure consistent coating quality and stable production conditions. In nickel- and chromium-based plating solutions, this involves both monitoring major bath constituents and detecting trace contaminants introduced through raw materials, process chemicals, equipment, drag-in, or bath aging. Even low concentrations of foreign metals can adversely affect deposit properties, while the high concentrations of Ni or Cr create an analytically demanding, line-rich matrix. Reliable elemental analysis therefore requires sufficient sensitivity for trace contaminants, effective resolution of spectral interferences, and the ability to quantify major constituents over a wide concentration range. In addition, electroplating laboratories often need to determine relevant metals in wastewater, extending the analytical requirements from concentrated process solutions down to low concentrations relevant for discharge monitoring.

In this application, nickel plating baths, a chromium plating bath, and electroplating wastewater were analyzed using the PlasmaQuant 9200 Elite high-resolution ICP-OES. The system was equipped with a medium-TDS sample introduction configuration, with an added 2 mm ID alumina injector, as well as a Teledyne CETAC ASX-560 autosampler. Matrix-specific dilution was applied to the concentrated plating solutions, whereas the wastewater sample was analyzed without dilution after acidification. The method combines high-resolution spectral evaluation with axial, radial, and attenuated radial plasma observation to cover both major bath constituents and trace elements within one ICP-OES method.

The PlasmaQuant 9200 Elite is particularly suited to this analytical task by combining high spectral resolution with a wide working range and robust handling of challenging matrices. High resolution supports reliable separation of

analyte signals from the dense emission spectra of Ni- and Cr-rich samples, while Dual View PLUS extends the accessible concentration range through different plasma observation modes. This enables trace contaminants and high-concentration bath constituents to be analyzed using the same method while also covering low-level measurements in wastewater. The resulting workflow reduces the need for extensive dilution, separate analytical methods, and repeat measurements, providing electroplating laboratories with a versatile solution for routine bath control, contamination monitoring, and wastewater analysis.

Materials and methods

Samples and reagents

- Nickel plating bath (Ni bath)
- Galvanic nickel solution (Galv. Ni)
- Nickel electrolyte (Ni electrolyte)
- Chromium bath (Cr bath)
- Wastewater
- HNO_3 65% p.A. (Carl Roth)
- Single-element standard solutions of Si, Sn, Cr for ICP (1,000 mg/L; Sigma-Aldrich)
- Single-element standard solutions of Ni for ICP (10,000 mg/L; Sigma-Aldrich)
- Multi-element standard solution IV for ICP (23 elements, 1,000 mg/L; Merck)
- Deionized (DI) water from a PURELAB system (18.2 MΩ·cm, ELGA LabWater, High Wycombe, England)

Sample preparation

All chemicals were of analytical-reagent grade. The Ni bath, Galv. Ni, and Ni electrolyte samples were diluted tenfold, whereas the chromium bath sample was diluted 100-fold using 2% (v/v) HNO_3. For spike-recovery experiments, the stock solution was added prior to dilution to obtain a final spike concentration of 0.5 mg/L.

The wastewater sample was acidified with 2% (v/v) HNO_3 and analyzed without further dilution. For the spike experiment, no volume correction was applied, since the added volume of stock solution was less than 0.5% of the total volume.

No internal standard was added to the samples. However, the Ar 420 nm emission line was used as internal standard. The spike-recovery results confirmed the suitability of this approach.

Instrument settings

Table 1: Instrument configuration and settings

Parameter	Specification
Plasma power	1,350 W
Plasma gas flow	9 L/min
Auxiliary gas flow	0.8 L/min
Nebulizer gas flow	0.5 L/min
Nebulizer	Concentric nebulizer for high TDS, borosilicate, 2 mL/min*
Spray chamber	Cyclonic with dip tube, 50 mL, borosilicate*
Outer tube / inner tube	Quartz / quartz*
Injector	Alumina, 2 mm ID#
Pump tubing	PVC (black/black for sample; red/red for waste)
Pump rate	1.0 mL/min
Fast pump rate	4.0 mL/min
Torch position	± 0 mm
Accessories	Teledyne CETAC ASX-560 autosampler

* Part of Sample Introduction Kit for medium TDS
# Alumina injector used for easier cleaning

Method parameters

Table 2: Method and evaluation parameters

Element	Line [nm]	Plasma view	Integration	Measure-ment time [s]	Evaluation			
					Eval. pixel	Baseline	Polynom. degree	Correction
Ar (IS)	420.0680	axial	Peak	1	3	ABC	auto	
Al	309.2713	axial	Peak	3	3	ABC	auto	IS, CSI
Bi	306.7720	axial	Peak	10	3	ABC	auto	IS, CSI
Cd	228.8018	axial	Peak	3	3	ABC	auto	IS
Co	237.8625	axial	Peak	3	3	ABC	auto	IS
Cr	267.7160	axial	Peak	3	3	ABC	auto	IS
Cu	327.3960	axial	Peak	3	3	ABC	auto	-
Fe	259.9396	axial	Peak	3	3	ABC	auto	IS
Mn	259.3724	axial	Peak	3	3	ABC	auto	IS
Ni	231.6036	axial	Peak	3	3	ABC	auto	IS
Ni	294.3912	rad. atten.	Peak	3	3	ABC	auto	IS
Pb	220.3534	axial	Peak	3	10	ABC	auto	IS, CSI
Sn	189.9270	axial	Peak	3	3	ABC	auto	IS
Si	251.6112	axial	Peak	3	3	ABC	auto	-
Zn	206.2000	axial	Peak	3	3	ABC	auto	IS

Ar (IS): Internal standard (Argon); ABC: Automatic Baseline Correction; CSI: Correction of Spectral Interferences; rad. atten.: radial attenuated plasma view used to extend linear working range

Calibration

Multi-element stock solutions were prepared from commercially available single- and multi-element standards (Merck, Sigma-Aldrich). Calibration standards were prepared by appropriate mixing of the stock solutions and dilution with 2% (v/v) HNO_3 in polypropylene tubes.

The final calibration concentrations are summarized in Table 3. To accommodate the different concentration levels encountered in the analyzed samples, nickel was calibrated using two independent concentration ranges: a low-level calibration (Standards 1-3) for wastewater analysis and a higher concentration range for electroplating bath samples.

The corresponding calibration functions and regression parameters are presented in Figure 1.

Table 3: Calibration standards (external calibration)

Standard	Concentration Al, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn [mg/L]	Concentration Sn, Si [mg/L]	Concentration Ni [mg/L]
Cal. 0	0	0	0
Std. 1	0.1		
Std. 2	1		
Std. 3	10		
Std. 4		0.1	
Std. 5		1	
Std. 6		10	
Std. 7			1,000

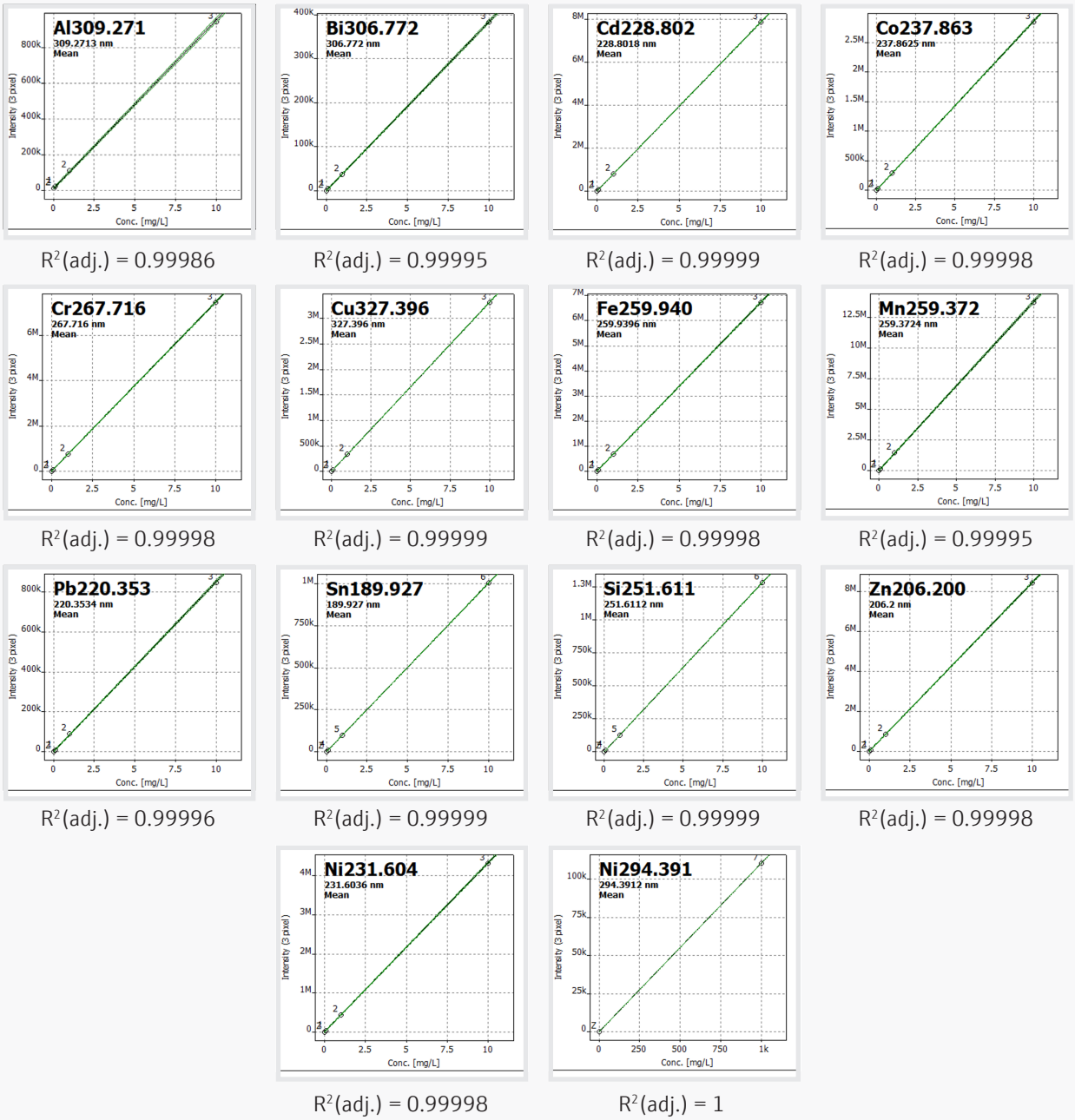


Figure 1: Calibration functions (external calibration)

Results and discussion

The determination of trace contaminants such as Al, Bi, Cd, Co, Cu, Fe, Mn, Pb, Si, Sn, and Zn in nickel- and chromium-rich electroplating matrices is often challenged by spectral interferences and elevated background emission. The high optical resolution of the PlasmaQuant 9200 Elite (2 pm at 200 nm) effectively resolves many of these overlaps, enabling reliable quantification of both major bath constituents and trace-level impurities in electroplating baths and wastewater samples.

The high sensitivity of the PlasmaQuant 9200 Elite is demonstrated by the method detection limits (MDLs) listed in Table 4. MDLs were determined using the blank-value method, calculated as three times the standard deviation of eleven replicate measurements of the respective reagent blank. Matrix-specific blanks were used to account for the different sample types:

2% (v/v) HNO_3 for wastewater samples, 1 g/L Ni for nickel-based electroplating solutions, and 1 g/L Cr for chromium baths. The reported MDLs include all applied dilution factors (Ni-based samples: 1:10; Cr bath: 1:100; wastewater: undiluted). For the electroplating matrices investigated here, analytical wavelengths were selected to provide the highest robustness and accuracy in the presence of intense spectral background and matrix-specific emission lines. Consequently, the most sensitive emission line was not always chosen. Instead, preference was given to wavelengths showing the lowest susceptibility to spectral interference from the matrix. If even lower detection limits are required, particularly for wastewater analysis, more sensitive analytical wavelengths can be selected for certain elements, such as Al and Bi.

Table 4: Method detection limits (MDLs) for different matrices

Element	Line [nm]	MDL wastewater (in 2% (v/v) HNO_3, no DF)	MDL Ni bath and electrolyte (in 1 g/L Ni in HNO_3, DF 10)	MDL Cr bath (in 1 g/L Cr in HNO_3, DF 100)
Al	309.2713	1.2 µg/L	24 µg/L	1.63 mg/L
Bi	306.7720	16 µg/L	370 µg/L	0.59 mg/L
Cd	228.8018	0.2 µg/L	2.3 µg/L	0.014 mg/L
Co	237.8625	0.4 µg/L	3.6 µg/L	0.19 mg/L
Cr	267.7160	0.3 µg/L	1.7 µg/L	Not determined
Cu	327.3960	0.7 µg/L	6.6 µg/L	0.059 mg/L
Fe	259.9396	0.3 µg/L	1.8 µg/L	0.258 mg/L
Mn	259.3724	0.09 µg/L	0.5 µg/L	0.013 mg/L
Ni	231.6036	0.3 µg/L	Not determined	0.021 mg/L
Pb	220.3534	0.7 µg/L	13 µg/L	0.059 mg/L
Sn	189.9270	0.8 µg/L	9.5 µg/L	0.084 mg/L
Si	251.6112	0.7 µg/L	7.3 µg/L	0.461 mg/L
Zn	206.2000	0.09 µg/L	3.7 µg/L	0.065 mg/L

Method detection limits take matrix and dilution into account; DF: dilution factor

The analytical results for all samples are summarized in the following Tables 5 and 6. Reported concentrations were corrected for the respective sample dilution factors. In addition, spike recoveries of 0.5 mg/L are shown to assess analytical accuracy. For all investigated samples, recoveries generally ranged from 90-110%, confirming the reliability of the method. The average RSD of all measurements above the method quantification limit (MQL) was approximately 0.9%, demonstrating excellent precision even in highly concentrated electroplating matrices.

Table 5: Measurement results sample Ni bath and Galv. Ni (dilution factor 10)

Element	Concentration Ni bath [mg/L] (RSD)	Spike recovery [%]	Concentration Galv. Ni [mg/L] (RSD)	Spike recovery [%]
Al309.271	< MDL	90.3	< MDL	94.9
Bi306.772	< MDL	94.0	< MDL	100.4
Cd228.802	< MDL	98.6	< MDL	95.9
Co237.863	< MDL	94.2	2.717 (1.04%)	93.9
Cr267.716	0.0346 (1.61%)	98.7	0.0586 (1.16%)	97.9
Cu327.396	0.1845 (1.94%)	97.2	0.5338 (1.33%)	98.0
Fe259.940	0.2006 (0.65%)	97.1	0.0483 (0.85%)	96.1

Continuation of Table 5

Element	Concentration Ni bath [mg/L] (RSD)	Spike recovery [%]	Concentration Galv. Ni [mg/L] (RSD)	Spike recovery [%]
Mn259.372	1.427 (0.76%)	97.1	2.582 (0.40%)	96.3
Ni294.391	74,450 (0.14%)	-	78,660 (0.42%)	-
Pb220.353	0.1699 (3.17%)	89.6	0.1975 (1.36%)	90.4
Sn189.927	< MQL	92.8	0.1237 (1.47%)	91.3
Si251.611	26.01 (0.39%)	98.1	4.248 (0.42%)	91.5
Zn206.200	0.1959 (0.66%)	94.6	0.0131 (0.54%)	90.5

RSD: Relative standard deviation of spike sample, obtained from 3 measurement cycles; Spike of 0.5 mg/L of the analytes; MDL: method detection limit

Table 6: Measurement results sample Ni-electrolyte (dilution factor 10) and Cr bath (dilution factor 100)

Element	Concentration Ni electrolyte [mg/L] (RSD)	Spike recovery [%]	Concentration Cr bath [mg/L] (RSD)	Spike recovery [%]
Al309.271	0.1681 (4.73%)	90.4	880.1 (0.33%)	*
Bi306.772	< MDL	99.9	< MQL	92.2
Cd228.802	< MDL	98.9	0.5355 (1.43%)	93.0
Co237.863	0.0192 (3.90%)	96.0	16.70 (0.72%)	92.8
Cr267.716	0.3171 (0.82%)	98.1	-	-
Cu327.396	< MQL	97.6	2,383 (0.38%)	*
Fe259.940	56.3 (0.10%)	96.8	8,836 (0.20%)	*
Mn259.372	0.2342 (0.43%)	96.4	48.25 (0.67%)	92.1
Ni294.391	5397 (0.73%)	-	462.7 (1.04%)	*
Pb220.353	0.0634 (3.38%)	93.0	5.192 (1.18%)	91.6
Sn189.927	< MDL	100.2	0.7975 (4.34%)	96.4
Si251.611	1.564 (0.71%)	96.1	74.95 (0.58%)	101.8
Zn206.200	0.1731 (0.73%)	99.6	327.0 (0.53%)	99.8

* Spike of 0.5 mg/L of the analytes. Spike recovery could not be reliably quantified because the spike concentration was negligible relative to the sample concentration; MDL: method detection limit; MQL: method quantification limit

The benefits of high spectral resolution in line-rich electroplating matrices are illustrated by two representative examples. Figure 2 shows the spectral region around Cd 228.802 nm in a nickel-rich matrix. A pronounced interference originating from the nickel matrix is visible and can also be observed in a spectrum of an aqueous single element solution of nickel (10 g/L Ni). Nevertheless, the high resolution of the PlasmaQuant 9200 Elite enables clear baseline separation between the analyte signal and the interfering emission line. In combination with the automatic baseline correction (ABC), reliable background correction and quantification are achieved even under these challenging conditions.

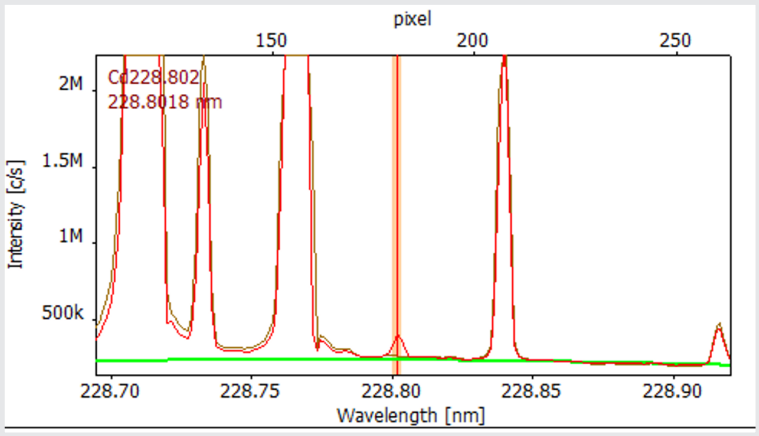


Figure 2: Analyte spectra of Cd 228.802 nm in a nickel-rich matrix,
--- Ni bath+spike, --- Ni 10 g/L, --- Eval. pixel, --- Baseline (ABC)

A similarly demanding situation is observed for Mn at 259.372 nm in the chromium bath matrix. As shown in Figure 3, multiple emission lines from the Cr matrix contribute to a complex interference pattern across the entire spectral region. Despite the small spectral distance of only 6.4 pm between the analyte and the nearest interference peak, the Mn signal remains clearly distinguishable and baseline-resolved, allowing accurate quantification.

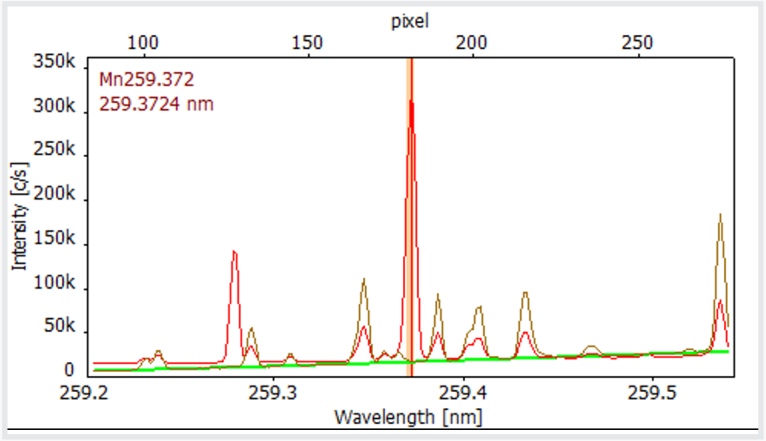


Figure 3: Analyte spectra of Mn 259.372 nm in Cr-rich matrix,
--- Cr bath, --- Cr 1 g/L, --- Eval. pixel, --- Baseline (ABC)

For particularly challenging spectral situations, the software-based Correction of Spectral Interferences (CSI) can be applied. CSI uses reference spectra of known matrix components to mathematically correct interfering signals, enabling reliable quantification even when analyte and interference partially or fully overlap. Representative examples are shown for Al at 309.271 nm (Figure 4) and Pb at 220.353 nm (Figure 5), where the spectrum of a 10 g/L Ni reference solution was used as the correction spectrum. By combining high spectral resolution with CSI correction, even strongly affected analytical lines can be utilized, allowing the determination of elements such as Pb on their most sensitive emission line while maintaining excellent accuracy and robustness in nickel-rich electroplating matrices.

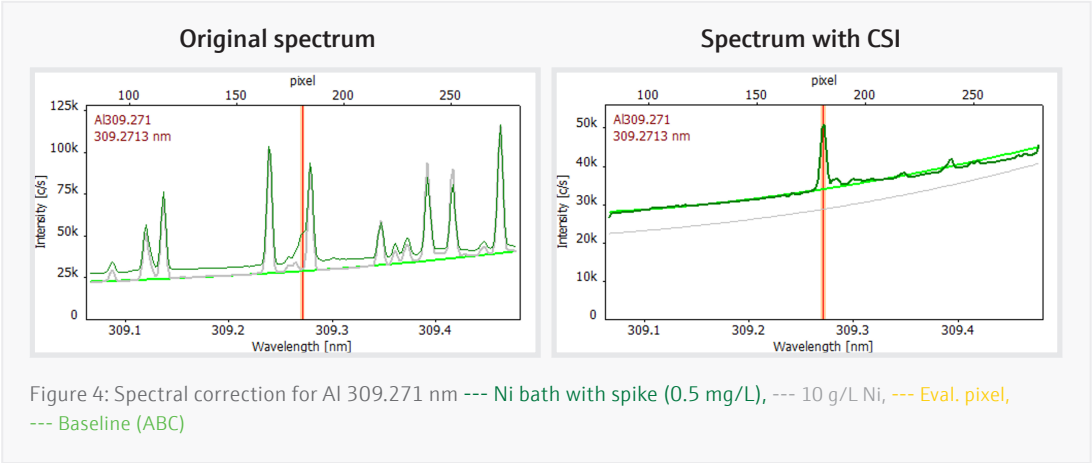


Figure 4: Spectral correction for Al 309.271 nm --- Ni bath with spike (0.5 mg/L), --- 10 g/L Ni, --- Eval. pixel, --- Baseline (ABC)

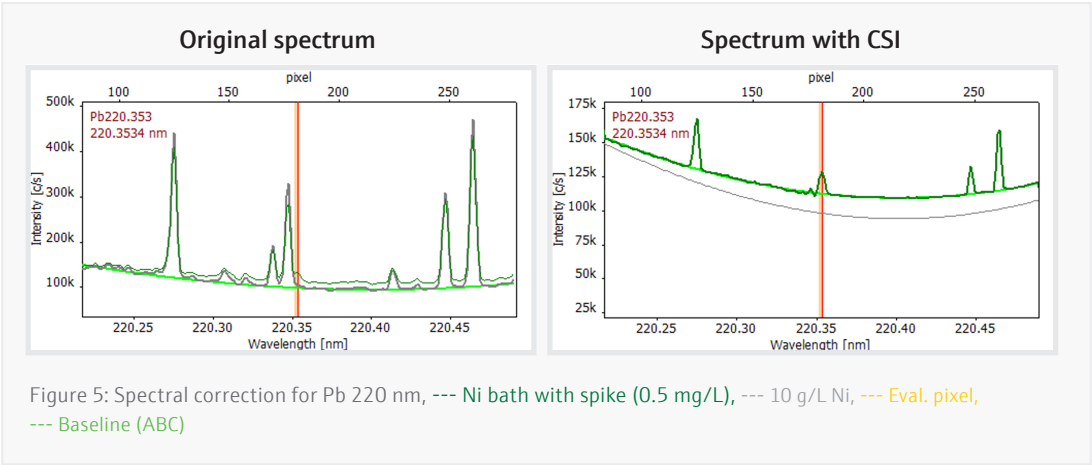


Figure 5: Spectral correction for Pb 220 nm, --- Ni bath with spike (0.5 mg/L), --- 10 g/L Ni, --- Eval. pixel, --- Baseline (ABC)

In addition to highly concentrated electroplating baths, many laboratories rely on ICP-OES instruments for routine wastewater monitoring, often within the same analytical sequence. Since nickel and chromium are among the key parameters in wastewater control, accurate results require an instrument capable of handling drastic concentration changes without memory effects or carry-over.

To evaluate the robustness of the analytical workflow, a representative wastewater sample was analyzed both before and after a measurement sequence consisting of fifteen electroplating samples, including ten nickel-based baths and five chromium-based baths. The resulting concentrations are summarized in Table 7 and compared in Figure 6. Excellent agreement was observed between the initial and final measurements, with no significant differences detected for any of the investigated elements. For analytes with concentrations below the method detection limit (MDL), the corresponding spiked wastewater samples are shown instead, while Si is displayed at one tenth of its concentration to facilitate comparison.

These results demonstrate the ability of the PlasmaQuant 9200 Elite to handle samples spanning several orders of magnitude in concentration within a single analytical sequence, without measurable carry-over effects, even after the analysis of highly concentrated Ni and Cr plating baths. The excellent agreement between the wastewater measurements performed before and after the electroplating bath analyses confirms both the effectiveness of the sample introduction system and the suitability of the PlasmaQuant 9200 Elite for routine electroplating laboratories, where bath control and wastewater monitoring are frequently combined within the same measurement sequence.

Table 7: Measurement results sample wastewater before (pre) and after (post) 15 electroplating samples

Element	Concentration $wastewater_{pre}$ [mg/L] (RSD)	Spike recovery [%]	Concentration $wastewater_{post}$ [mg/L] (RSD)	Spike recovery [%]
Al309.271	0.0884 (1.34%)	90.6	0.0999 (0.17%)	91.0
Bi306.772	< MDL	96.0	< MDL	103.7
Cd228.802	< MDL	96.7	< MDL	98.6
Co237.863	0.1393 (0.61%)	88.7	0.1417 (0.59%)	97.5
Cr267.716	0.0856 (0.47%)	100.8	0.1161 (1.07%)	91.3
Cu327.396	< MDL	89.6	< MDL	94.2
Fe259.940	0.0963 (0.37%)	90.1	0.1060 (0.51%)	102.0
Mn259.372	0.2740 (0.05%)	91.8	0.2818 (0.52%)	101.7
Ni231.604	0.1697 (0.33%)	94.2	0.1689 (0.36%)	97.2
Pb220.353	< MDL	89.0	< MDL	92.4
Sn189.927	< MDL	92.7	< MDL	98.4
Si251.611	4.669 (0.18%)	101.9	4.740 (0.66%)	103.2
Zn206.200	0.8587 (0.36%)	101.2	0.8854 (0.39%)	96.9

RSD: Relative standard deviation of spike sample, obtained from 3 measurement cycles; MDL, method detection limits

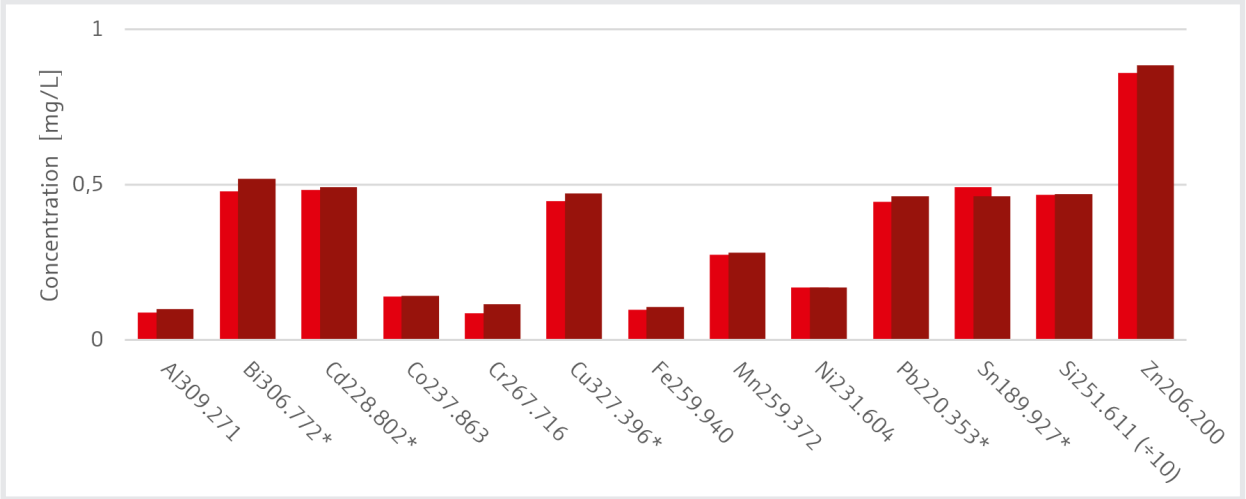


Figure 6: Comparison of relevant wastewater analyte concentrations before (light red) and after (dark red) 15 electroplating solution measurements. *indicates measurement of spike instead of original wastewater sample due to low concentration

Collectively, the recovery data, interference studies, and wastewater carry-over experiment demonstrate that accurate determination of trace contaminants can be achieved in nickel- and chromium-rich electroplating matrices without matrix-matched calibration or extensive sample preparation.

Summary

The results presented in this application note demonstrate that the PlasmaQuant 9200 Elite is ideally suited for the analysis of electroplating baths and related wastewater samples. Accurate determination of both major bath constituents and trace contaminants was achieved in challenging nickel- and chromium-rich matrices, despite the presence of severe spectral overlaps and elevated background emission. The combination of high optical resolution, robust plasma performance, and advanced spectral evaluation tools enabled reliable quantification of Al, Bi, Cd, Co, Cu, Fe, Mn, Pb, Si, Sn, and Zn across a wide concentration range.

To minimize sample preparation while maintaining extraordinary analytical performance, the argon emission line at 420 nm was used for matrix-effect correction. As this signal directly reflects plasma-related matrix effects, it provides a simple and effective correction strategy without the need for adding another internal standard element to each measurement solution. Excellent precision was obtained throughout the study, with average relative standard deviations below 1%, demonstrating the robustness of both the plasma and the optical system even in highly concentrated electroplating matrices.

The Dual View PLUS technology further expanded the analytical working range of the method. While trace contaminants were measured in axial view to maximize sensitivity, the major constituent Ni was determined at 294.391 nm using attenuated radial observation. Consequently, concentrations ranging from sub-mg/L levels to percent-level bath compositions could be determined within a single method and measurement sequence, eliminating the need for manual optimization or multiple analytical runs.

Routine analysis of electroplating baths places considerable demands on sample introduction components due to high salt loads and elevated metal concentrations. The V-Shuttle torch design of the PlasmaQuant 9200 Elite simplifies routine maintenance by allowing rapid disassembly and cleaning of individual torch components. Users can therefore efficiently remove accumulated deposits while replacing only those parts subject to significant wear, helping to minimize maintenance effort and operating costs.

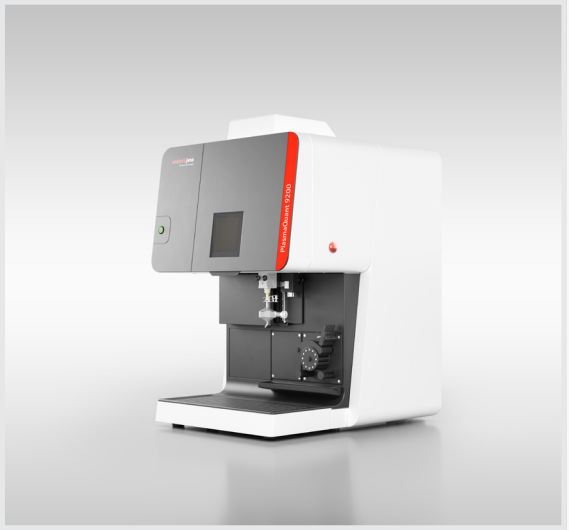


Figure 7: PlasmaQuant 9200 Elite

Despite the demanding matrices investigated, all measurements were performed at only 1,350 W plasma power and 9 L/min plasma gas flow, providing a robust yet argon-efficient plasma. A spiked Ni bath sample measured repeatedly over eight hours yielded recoveries between 97% and 106%, demonstrating excellent long-term stability and negligible signal drift. These results confirm reliable operation throughout a full working day without intermediate cleaning or the addition of conventional internal standards. This is shown in Figure 8.

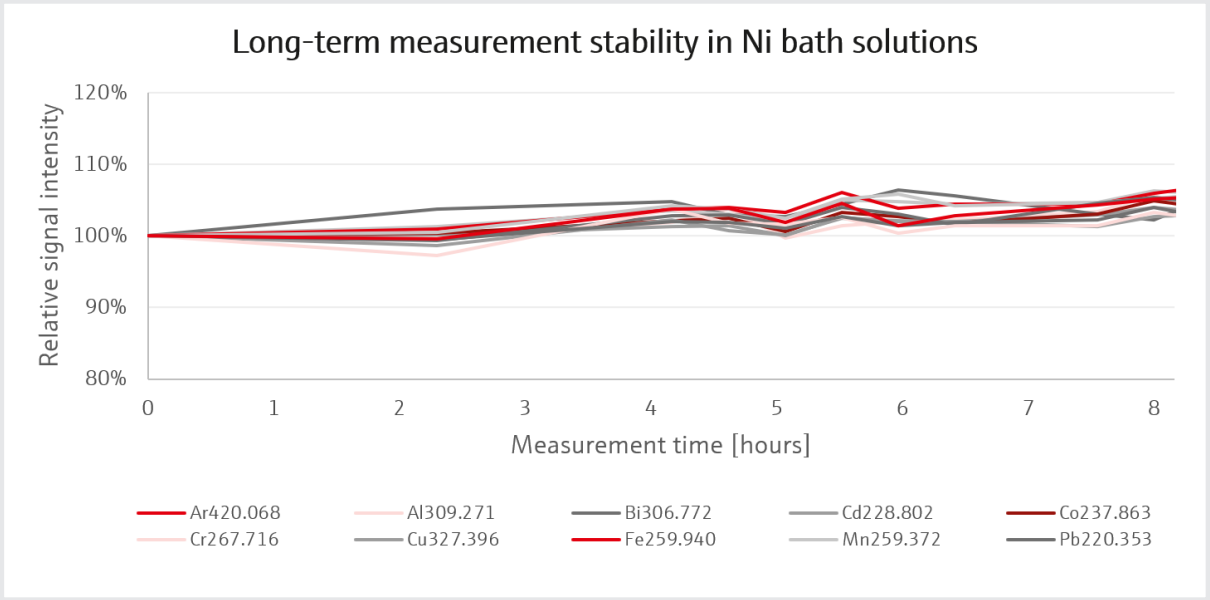


Figure 8: Long-term stability measurement of a spiked Ni bath solution over 8 hours.

Overall, the combination of exceptional spectral resolution, broad dynamic range, excellent sensitivity, low argon consumption, and robust long-term performance makes the PlasmaQuant 9200 Elite a powerful solution for routine electroplating laboratories requiring reliable bath control and wastewater monitoring within a single analytical platform.

Recommended device configuration

Table 8: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9200 Elite	818-09201-2	High-resolution ICP-OES instrument
Teledyne CETAC ASX-560 Autosampler	810-88015-0	Autosampler with integrated rinse function
Sample Introduction Kit for medium TDS	810-88009-0	Sample introduction kit, including spray chamber with dip tube and nebulizer for high TDS throughput
Alumina Injector, 2 mm ID	418-13-410-412	Alumina injector for V-shuttle torch for improved lifetime

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