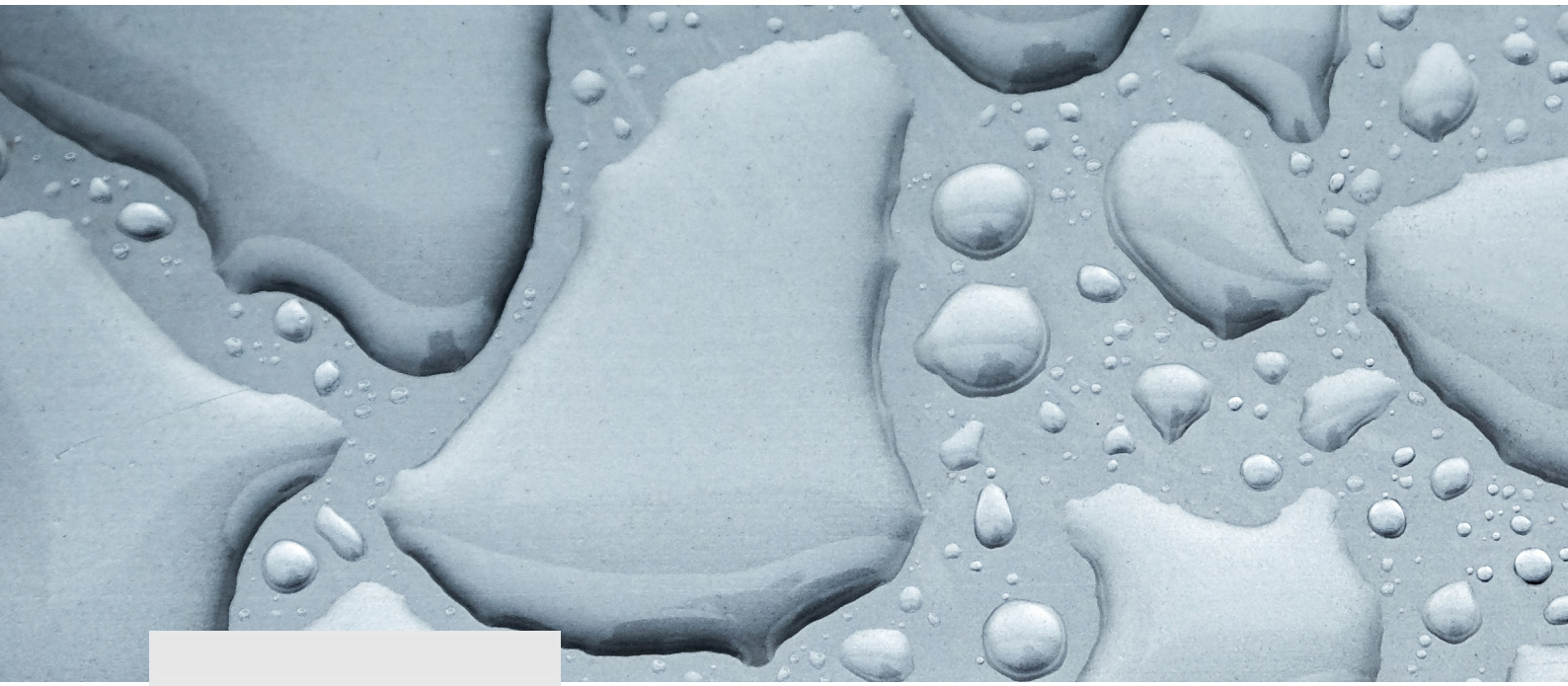

Challenge

Trace impurity control and quantification of matrix elements in matrix-rich etching solutions from a single measurement run.

Solution

HR ICP-OES with industry-leading high-resolution optical system and superior sensitivity and matrix tolerance to achieve trace element analysis in the heavy matrix of electrolytic etching solutions.

Composition Analysis of an Electrolytic Etching Solution by HR ICP-OES

Introduction

Surface modifications of prefabricated metal parts are a crucial step in the manufacturing and construction process of machinery in industries such as automotive, aerospace, and mechanical engineering. In this regard, etching solutions are used for surface cleaning of ferrous metals copper, aluminum, or alloys (e.g., brass) to remove metallic (burring) or surfactant residues and to alter surface properties such as roughness or the ability to be coated or bonded to other materials (e.g., plating).

Etching solutions mainly contain acids such as hydrochloric acid, sulfuric acid, hydrofluoric acid, nitric acid, and phosphoric acid in different mixtures. Often the etching process is assisted by the application of electrical current to either speed up the cleaning/etching process or to perform electroplating processes. Electroplating is used to apply functional materials to the base metals in order to achieve smoothing of the surface, color effects (e.g., gloss), or to enhance physical properties such as abrasion resistance.

The efficiency of these processes highly depends on the properties of the etching/plating solutions. In electrolytic processes, impurities of redox active metals hamper a successful plating process. Therefore, frequent quality control of the employed solutions is a key criterion in QC labs of the electroplating industry.

Analytical challenges for QC control of etching solutions comprise the complexity of the matrix consisting of varying ratios of concentrated acids as well as the presence of matrix elements in varying concentrations.

Furthermore, leached components of the base metals and their additives (chromium, nickel, cobalt, vanadium, molybdenum, etc.) result in complex spectra due to their wealth of emission lines and therefore give rise to the occurrence of spectral interferences. Thus, analyzing electrolytic etching solutions with high precision regarding trace impurities of Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Li, Mg, Mo, Pb, Sn, Sr, Ti, V and matrix components Fe, K, Mn, Na, Ni, P, Si, and Zn requires a highly robust plasma to handle matrix-rich samples, high spectral resolution to resolve severe spectral interferences, high sensitivity to achieve low specification limits for impurities, and a wide working range to quantify trace impurities and matrix components from the same measurement run.

Within this study, a commercially available etching solution used by the aerospace industry was investigated by using a high-resolution ARRAY ICP-OES, the PlasmaQuant 9100 Elite, equipped with HF sample introduction kit. The PlasmaQuant 9100 Elite addresses the analytical challenges of the analysis of etching solutions by its plasma robustness (HF Generator), exceptional spectral resolution, and industry-leading sensitivity (HR Optics) and wide working range (DualView Plus) features. Furthermore, ease of use is achieved by its intelligent sampling design, including the V-Shuttle Torch and powerful data evaluation algorithms such as the automatic baseline correction ABC.

The methodology applied here results in limits of quantification of less 1 µg/L with respect to the electrolytic etching solution for thirteen out of seventeen trace elements, as the most sensitive emission lines are interference-free on the PlasmaQuant 9100 Elite. In addition, a spike recovery test for 50 µg/L of an EPA method 200.7 calibration standard was conducted for further proof of method robustness.

Materials and Methods

Samples and Reagents

The analysis of a commercially available etching solution used in the aerospace industry including spike recovery with an EPA 200.7 standard was conducted on a PlasmaQuant 9100 Elite.

Sample Preparation

The sample was analyzed in 1:200 and 1:50 dilution by both; an aqueous standard calibration without matrix-matching (A) and standard-addition calibration routine (B) using 1000 mg/L multiple and single element standards from SIGMA-ALDRICH for preparation of calibration standards. In addition, a spike recovery test for 50 µg/L of an EPA method 200.7 calibration standard from HIGH-PURITY STANDARDS was conducted for further proof of method robustness.

Calibration

Table 1: Concentration of the standards for aqueous calibration as well as for standard-addition calibration

Element	Unit	Cal.0	Cal.1	Cal.2	Cal.3	Cal.4	Cal.5	Cal.6
Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Li, K, Mg, Mn, Pb, Sn, Sr, Ti, V[1]	µg/L	0	10	20	330	50	100	200
Mo, Na, Ni, Zn[2]	mg/L	0	0.2	2.5	5	10		
Ag, P, Si[2]	mg/L	0	1.0	12.5	25	50		
Y[3]	mg/L	1.0	1.0	1.0	1.0	1.0	1.0	1.0

1 … from a multiple element standard
2 … from single element standards
3 … internal standard

Instrument Settings/Method parameters

For the analysis, a PlasmaQuant 9100 Elite equipped with HF kit and ASPQ 3300 autosampler was used. The detailed system configuration is given in Table 2.

Table 2: Configuration of the PlasmaQuant 9100 Elite equipped with HF kit

Parameter	Settings
Power	1200 W
Plasma Gas Flow	12 L/min
Auxiliary Gas Flow	1.0 L/min
Nebulizer Gas Flow	0.6 L/min
Nebulizer	PFA parallel path nebulizer, 1.0 mL min^{-1}
Spray Chamber	PTFE cyclonic spray chamber, 50 mL
Injector	Alumina, inner diameter 2 mm
Outer Tube / Inner Tube	Syalon /Alumina
Pump tubing	PVC
Sample pump flow	1.0 L/min
Rinse /Read delay	45 s
Auto Sampler	ASPQ 3300

Evaluation Parameters

Table 3: Overview of method-specific evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of Pixel	Baseline fit	Polynomial degree	Correction
Ag	328.068	axial	spectrum	3	3	ABC[1]	auto	Y[2]
Al	396.152	axial	spectrum	3	3	ABC	auto	Y
B	249.773	axial	spectrum	10	3	ABC	auto	Y
Ba	455.403	axial	spectrum	3	3	ABC	auto	Y
Ca	396.847	axial	spectrum	3	3	ABC	auto	Y
Cd	214.441	axial	spectrum	3	3	ABC	auto	Y
Co	228.615	axial	spectrum	3	3	ABC	auto	Y
Cr	267.716	axial	spectrum	3	3	ABC	auto	Y
Cu	324.754	axial	spectrum	3	3	ABC	auto	Y
Fe	259.940	axial	spectrum	3	3	ABC	auto	Y
K	766.491	axial	spectrum	3	3	ABC	auto	Y
Li	670.791	axial	spectrum	3	3	ABC	auto	Y
Mg	279.553	axial	spectrum	3	3	ABC	auto	Y
Mn	257.610	axial	spectrum	3	3	ABC	auto	Y

1 ... Automatic Baseline Correction
2 ... Yttrium used as internal standard

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of Pixel	Baseline fit	Polynomial degree	Correction
Mo	202.030	axial	spectrum	3	3	ABC	auto	Y
Na	588.995	radial	spectrum	3	3	ABC	auto	Y
Na	589.592	radial	spectrum	3	3	ABC	auto	Y
Ni	341.476	axial	spectrum	3	3	ABC	auto	Y
P	213.618	axial	spectrum	3	3	ABC	auto	Y
Pb	220.353	axial	spectrum	3	3	ABC	auto	Y
Si	251.611	axial	spectrum	3	3	ABC	auto	Y
Sn	189.927	axial	spectrum	3	3	ABC	auto	Y
Sr	421.552	axial	spectrum	3	3	ABC	auto	Y
Ti	334.941	axial	spectrum	3	3	ABC	auto	Y
V	292.401	axial	spectrum	3	3	ABC	auto	Y
Zn	206.200	axial	spectrum	3	3	ABC	auto	Y

Results and Discussion

Method development for analyzing electrolytic etching solutions was performed by applying different calibration strategies: calibration against aqueous standards (A) and standard addition calibration (B). A matrix-matched quantitative calibration is not applicable due to the diversity of acidic composition as well as varying contents of matrix elements such as phosphorus, sodium, zink, manganese and nickel.

Consistency of the obtained results was tested by applying two dilution factors for each calibration strategy.

Table 4: Results obtained by aqueous calibration without matrix matching (A) and standard-addition calibration (B) for two dilutions

Element	Specified content [mg/L]	1: 200				1:50				LOQ[5] [µg/L]	QC recovery[6] [%]
		A [mg/L]	RSD[1] [%]	B [mg/L]	RSD [%]	A [mg/L]	RSD [%]	B [mg/L]	RSD [%]		
Ag	< 1	< DL[2]	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.87	101.4
Al	≤ 1	0.48	6.12	0.74	3.5	0.61	2.59	0.662	1.8	1.68	100.8
B	1	0.98	2.03	n.d.	–	1.33	1.5	n.d.	–	1.41	99.2
Ba	< 1	0.10	0.47	0.01	4.43	0.02	0.64	0.002	10.5	0.03	96.6
Ca	≤ 1	0.81	0.17	1.10	1.22	0.78	0.45	1.01	1.68	0.21	102.4
Cd	< 1	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.24	102.2
Co	1	1	1.48	0.99	3.13	1.06	2	1.06	0.81	0.66	102.7
Cr	< 1	< DL	< DL	(0.10)[3]	12.7	0.10	1.99	0.09	2.64	0.42	102.6
Cu	< 1	< DL	< DL	< DL	< DL	(0.02)[3]	30.9	0.03	1.9	0.54	100.8
Fe	16	16.8	0.88	16.8	0.97	16.5[4]	1.16	17.5	1.71	0.27	99.7
K	2	3.15	0.53	2.44	2.33	3.85	0.67	2.43	0.16	1.92	98.2
Li	< 1	0.33	0.44	0.08	0.88	0.09	0.28	0.02	0.26	0.06	103.8
Mg	< 1	0.34	0.29	0.30	0.31	0.28	0.04	0.29	1.07	0.02	100.8

Element	Specified content [mg/L]	1: 200				1:50				LOQ[5] [µg/L]	QC recovery[6] [%]
		A [mg/L]	RSD[1] [%]	B [mg/L]	RSD [%]	A [mg/L]	RSD [%]	B [mg/L]	RSD [%]		
Mn	1400	1350	0.84	1463	0.84	1052[4]	0.17	9964	0.36	0.12	99.3
Mo	< 1	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	2.19	101.2
Na	2400	2280	0.39	2220	2.38	2239[4]	0.4	2284	0.58	0.18	101.0
Ni	1100	1061	3.25	1119	1.48	1074[4]	0.66	1063	0.16	5.16	98.9
P	6000	5940	1.99	5713	0.38	5908[4]	0.81	5843	0.37	11.2	100.7
Pb	< 1	< DL	< DL	(0.18)[3]	27.8	(0.14)[3]	14.7	(0.17)[3]	15.9	3.36	97.8
Si	7	< DL	< DL	7.58	1.31	< DL	< DL	7.27	0.98	2.04	103.4
Sn	< 1	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.48	99.5
Sr	< 1	0.07	0.04	< DL	< DL	0.023	0.52	0.01	2.33	0.03	95.1
Ti	< 1	0.24	1.08	0.07	3.38	0.11	0.84[4]	0.07	0.48	0.15	97.2
V	< 1	(0.03)[3]	28.4	(0.04)[3]	28.2	(0.02)[3]	12.2	(0.02)[3]	11.1	0.36	102.6
Zn	1400	1385	0.39	1506	0.54	1357	0.09	1540	1.18	0.60	100.5

1 ... RSD values for three replicate measurements
2 ... value below detection limit (DL)
3 ... value in the range of detection limit (RSD value are effected by noise)
4 ... value outside calibration range
5 ... method-specific limit of quantification (LOQ) with LOQ equals 3 x DL (DL obtained from calibration curve method)
6 ... recovery rates of 50 µg/L QC sample prepared from 'EPA method 200.7 calibration standard' by HIGH-PURITY STANDARDS (proof of method robustness)

The results for different calibration strategies and dilution factors revealed pronounced matrix-effects; hence, standard-addition calibration to a 1:50 dilution is recommended if quantification of trace impurities is desired. However, all matrix constituents can be determined from aqueous standard calibration without matrix-matching and superb specification limits for all trace impurities can be realized. RSD values of 0.5% to 2% and spike recovery in the range of 95% to 104% of an EPA 200.7 standard solution demonstrate method robustness and precision.

Figures 1-6 present a selection of high-resolution spectra for 1:50 dilution (blue) and 1:200 dilution (grey); automatic baseline fit (ABC, green).

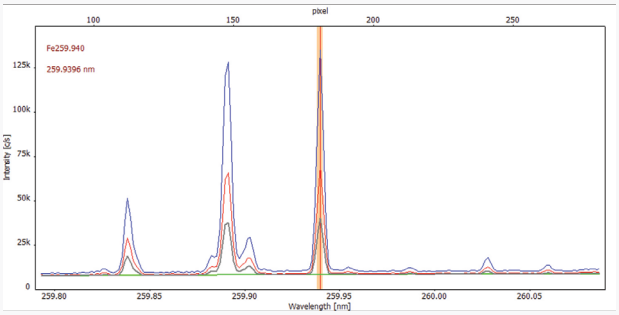

Figure 1: Fe 259.940 nm

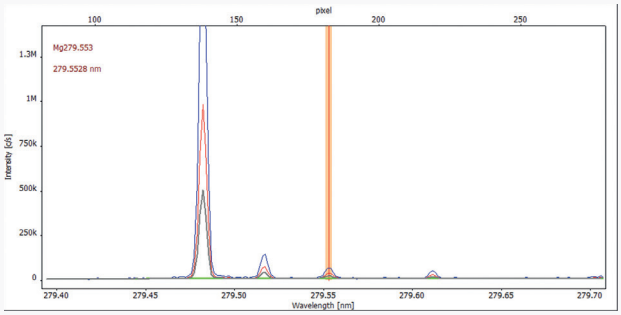

Figure 2: Mg 279.553 nm

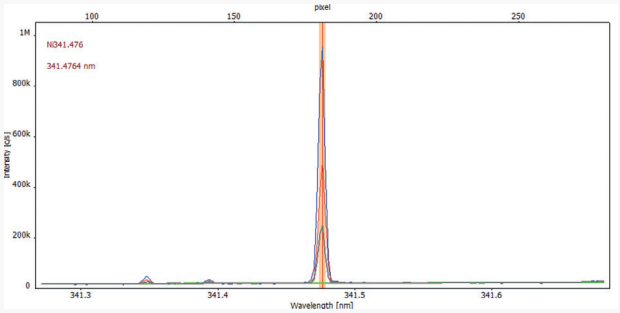

Figure 3: Ni 341.476 nm

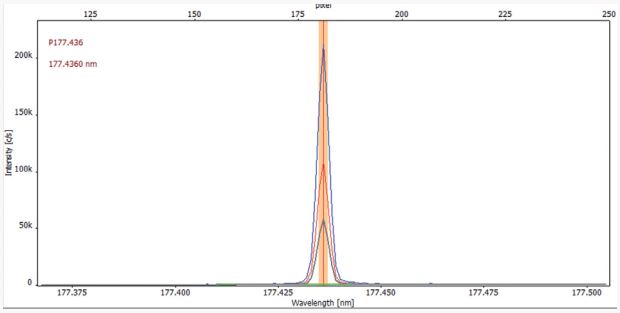

Figure 4: P 177.436 nm

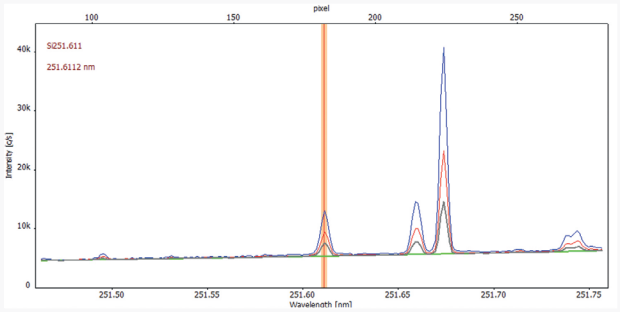

Figure 5: Si 251.611 nm

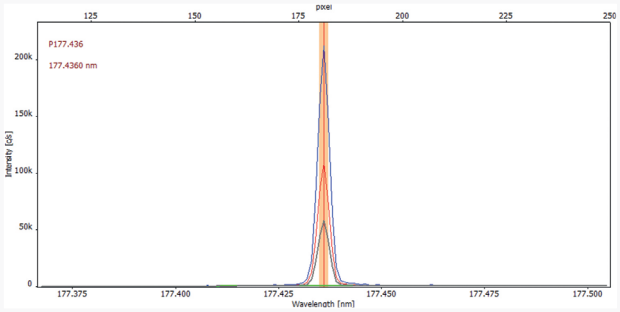

Figure 6: Zn 206.200 nm

Conclusion

Monitoring trace elemental impurities and matrix contents in electrolytic etching solutions that are used for etching and electroplating demonstrates a key task for QC labs in mechanical manufacturing industries such as automotive and aerospace. The level of impurities must be kept at a minimum level while ensuring the correct concentration of the major elemental component of such etching solutions. This analytical task demands a high robustness to handle high matrix containing samples at high analytical precision, the ability to resolve severe spectral interferences, high sensitivity to reduce the specifications for impurities, and a wide working range to measure traces and major components for the same sample run.

The PlasmaQuant 9100 Elite perfectly addresses the demands of this analytical task. The industry-leading high-resolution optical system makes it possible to resolve even severe spectral interferences. Hence, compromises on line selection due to interferences are scarce and most sensitive lines can be used for the quantification of trace impurities. In this application, example limits of quantification of less 1 µg/L with respect to the electrolytic etching solution were achieved for thirteen out of seventeen trace elements, as the most sensitive emission lines are interference-free on the PlasmaQuant 9100 Elite.
In addition, the wide working range of the PlasmaQuant 9100 Elite by the DualView Plus feature and the high robustness ensured by the V-Shuttle Torch and the HF Generator allow for excellent precision and robustness of analytical results in challenging matrices and allow for the quantification of traces and major concentrations from the same run.

Headquarters
Analytik Jena GmbH+Co. KG
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax +49 3641 77 9279

info@analytik-jena.com
www.analytik-jena.com

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