Challenge

Routine analysis of high and low concentrated elements in galvanic baths, chemical baths, and wastewater from the electroplating industry.

Solution

Easy and reliable analysis of main and minor elements even in strong matrices with the contrAA 800 F and autosampler AS-FD with automatic dilution function.

Elemental Analysis During the Electroplating Process with contrAA 800

Introduction

In the electroplating industry many different galvanic and chemical baths must be controlled regularly for their chemical composition to achieve the best quality for coated workpieces in a cost-efficient operation. The analysis accompanying the electroplating process is carried out in a separate laboratory or directly in the production hall. In addition, strict regulations must be considered regarding the concentration of toxic elements in wastewater from the plating processes. The required analytical instrument should be easy to use, reliable, and cost efficient, as well as robust in the vicinity of chemical baths. At the same time, sample matrices with high concentrations of salts, metals, and acids or bases are demanding regarding the analytical performance of the instrument. Besides the typical metals used to create functional or decorative coatings, e.g., Au, Ag, Cr, Cu, Fe, Ni, Pb, Rh, Sn, Zn, or Zr, and electrolytes like alkali or alkaline earth metals, also metalloids or non-metals such as boron (B) or phosphorous (P) have to be analyzed. Boron is often used in the form of boric acid as a pH buffer, while phosphorous is used in certain plating processes, such as phosphate conversion coating or electroless nickel-phosphorous plating. The concentrations of these analytes reach values from the percentage range (for main components) down to the low mg/L range (for minor components) and even to the µg/L range (in wastewater).

The contrAA 800 flame atomic absorption spectrometer meets all these requirements with outstanding performance. With its continuous light source offering a spectral range from 185 to 900 nm, all elements relevant to the electroplating process can be analyzed in one analytical run without lamp exchange. The high intensity of this xenon short-arc lamp allows lowest detection limits even for metalloids or non-metals such as boron or phosphorus, for which the analysis by hollow cathode lamps is limited. The CCD array detects the analyte line with best resolution and provides additional information about the spectral vicinity. Integrated software tools correct spectral interferences and provide further software functions like a side pixel evaluation to decrease the sensitivity of the analyte line for highly concentrated elements. In addition, the AS-FD autosampler offers an automatic dilution function that significantly reduces the need for manual pipetting. Calibrations can be performed automatically starting from a stock standard. Samples can be diluted up to a factor of 500, and the automatic overrange dilution function automatically dilutes samples that are outside the calibration range and repeats the measurement. When a high sample throughput is required, the fast-sequential mode of the contrAA 800 with flame atomization can reduce the analysis time by a factor of 3 compared to conventional line-source AAS.

In this application note Au, B, Cr, Cu, Fe, K, Ni, P, Pb, Rh, Sn, Zn, and Zr have been determined in ten different chemical and galvanic baths as well as in wastewater from electroplating processes to demonstrate the performance of the contrAA 800 F in typical applications of the electroplating industry.

Materials and Methods

Samples and reagents

- Samples of different galvanic baths and wastewater from galvanic processes
- HCl (36%, traceSELECT, Fluka)
- Certificated stock solutions of the individual analytes (1,000 mg/L)
- CsCl ionization buffer (100 g/L CsCl = 10%)
- HF (≥ 48%, puriss p.a., Sigma-Aldrich)
- NH_4F (20% (w/w))
- Al solution (5% (w/w), as $Al(NO_3)_3 \cdot 9\ H_2O$)

The samples were diluted with 1% HCl according to the dilution factors given in Table 3 (see page 6). For gold (Au), 5% HCl was necessary for stabilization. For easily ionizable elements such as potassium (K), 0.1% (w/w) CsCl was added as ionization buffer. For the quantification of zirconium (Zr), a sample aliquot of 45 mL was mixed with 2.5 mL HCl, 1 mL NH_4F (20%), and 0.5 mL of each HF, CsCl (10%) and Al (5%). To avoid a precipitation of AlF_3, the volume of HCl was added first.

Instrumentation

The instrument settings applied in this application, with short explanations of the instrument settings, are shown in Table 1. The method parameters applied for the individual analytes are listed in Table 2.

Table 1: Applied instrument settings

Parameter	Specifications used in this application	Comments
Instrument	contrAA 800 F/D	Flame or Duo (flame + graphite furnace) instruments can be used.
Burner head	50 mm or 100 mm	The 50 mm burner head can be used for both, C_2H_2/air and C_2H_2/N_2O flame. The 100 mm burner head can be used for the C_2H_2/air flame with higher sensitivity.
Burner head angle	0° (most elements) or 90° (K and highly concentrated Zn)	Usually, the burner head is positioned straight in the beam path (0°). For very sensitive or highly concentrated elements, like K or highly concentrated Zn in a Zn bath, the burner head can be rotated by 90°. This has the same effect as a dilution by a factor of approx. 10 for the 100 mm burner or by a factor of approx. 5 for the 50 mm burner.
Flame type	C_2H_2 /air or C_2H_2/N_2O	Easily atomizable elements can be analyzed with the C_2H_2/air flame. For refractory elements, e.g., B, Cr, Sn, or Zr, the hotter C_2H_2/N_2O flame is applied.
Additional oxidant flow	Off, 75 L/h or 150 L/h	To eliminate matrix interferences, an additional oxidant flow of 75 L/h or 150 L/h can be applied, which is often used for the analysis of Fe.
Gas flow and burner height	Automatical optimization	The ideal gas flow rate and burner height for each element and each sample matrix can be automatically determined using the automatic flame optimization procedure.

Parameter	Specifications used in this application	Comments
Autosampler	AS-FD	Automatic sample dilution up to factor 500, automatic overrange dilution and automatic calibration from stock standards are possible.
Injection switch	SFS 6	The injection switch SFS 6 allows a continuous rinsing of the sample path and thus reduces carry-over effects.
Replicates	3	Usually, three measurement replicates are sufficient.
Read time	3–5 s	A longer read time can lead to higher precision. Usually, a read time of 3 s is sufficient.
Evaluation pixel	3–7	Usually, three evaluation pixels are used, more pixels can improve the signal evaluation.
Background correction mode	IBC	The iterative baseline correction (IBC) adjusts and smoothes the baseline.
Rinsing solution	1–5% HCl or HNO_3	In this application, mostly 2% HCl was used. Precious metals such as Au require higher concentrations of HCl (5%).

Table 2: Applied method parameters for the individual analytes

Element	Wavelength [nm]	Burner head [mm]	Flame type
Au	242.7950	50	C_2H_2/air
B	249.7733	50	C_2H_2/N_2O
Cr	359.3488	50	C_2H_2/N_2O
Cu	324.7540	100	C_2H_2/air
Fe	248.3270	50	C_2H_2/air
K	766.4908	50 (90°)	C_2H_2/air
Ni	232.0030	50	C_2H_2/air
P	213.6175	50	C_2H_2/N_2O
Pb	217.0005	100	C_2H_2/air
Rh	343.4893	100	C_2H_2/air
Sn	224.6050	50	C_2H_2/N_2O
Zn	213.8570	50	C_2H_2/air
Zn (Zn bath)	213.8570	50 (90°)	C_2H_2/air
Zr	360.1193	50	C_2H_2/N_2O

Calibration

All analytes were calibrated using aqueous standards in an appropriate concentration range. The calibration standards were prepared automatically with 2% HCl and 0.1% (w/w) CsCl by the AS-FD autosampler starting from a suitable stock standard (for Zr, the calibration standards should be prepared separately according to the sample preparation (see chapter "Samples and Reagents" on page 2). The obtained calibration curves were evaluated either by a linear or a non-linear rational fit and obtained a coefficient of determination of R^2(adj.) > 0.998. Figure 1 shows an example of a linear and a non-linear rational calibration curve, respectively.

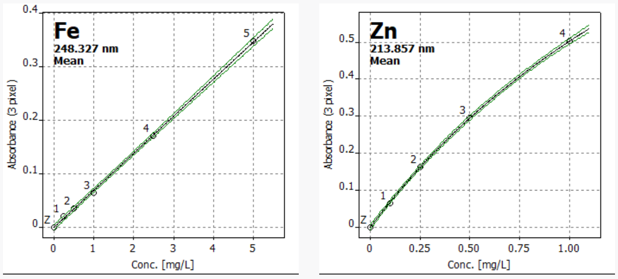

Figure 1: Linear calibration curve of Fe, R^2(adj.) = 0.9993, and non-linear calibration curve of Zn, R^2(adj.) = 0.9998.

Spectra

The CCD array detector of the contrAA 800 records the analyte line with its spectral vicinity, as shown in Figures 2a–e. Figure 2a shows as an example the analyte line of chromium (Cr) at 359 nm in the spectral range of 2 nm. In Figure 2b, the analyte line of phosphorous (P) with a secondary line of nickel (Ni) is detected. Due to the high resolution of the spectrometer, the secondary line of Ni is well separated from the analyte line, therefore no spectral interference occurs. In Figure 2c, a spectrum with two analyte lines of boron (B) is shown, the more sensitive line was evaluated. Figure 2d shows the spectrum of zinc (Zn) in a matrix causing spectral interferences. These spectral interferences would influence the result, but can easily be corrected using the CSI tool (CSI = correction of spectral interferences) in the software. The corrected spectrum for the Zn analyte line is shown in Figure 2e.

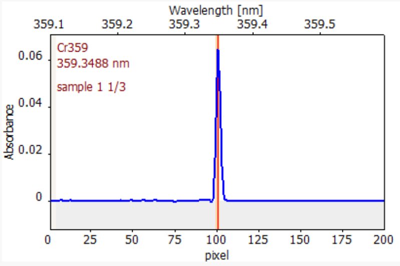

Figure 2a: Spectrum of Cr in a Cr bath

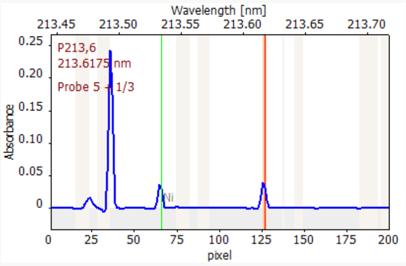

Figure 2b: Spectrum of P in a Ni bath. The analyte line of P is marked orange, the additional lines on the left side are caused by Ni.

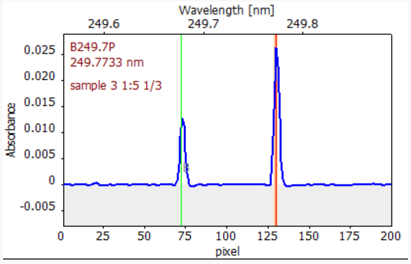

Figure 2c: Spectrum of B in a galvanic bath. Both lines are caused by B, the more intensive line was evaluated (at 249.7733 nm).

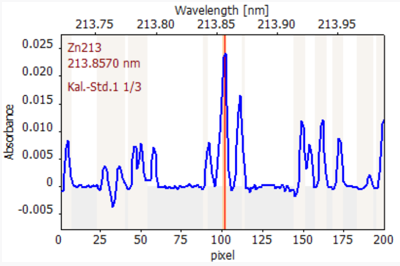

Figure 2d: Spectrum of Zn in matrix causing a spectral interference

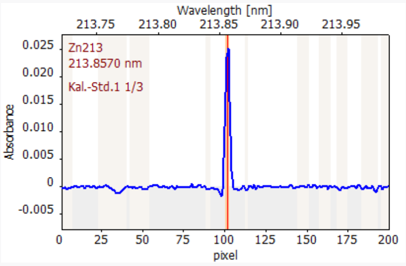

Figure 2e: The same spectrum of Zn after correction using the CSI software tool

Results and Discussion

Exemplary results for the analysis of Au, B, Cr, Cu, Fe, K, Ni, P, Pb, Rh, Sn, Zn, and Zr in different galvanic baths, chemical baths, and wastewater from electroplating processes are shown in Table 3. Some of the samples were spiked with a known analyte concentration to check matrix independency. The obtained recovery rates ranging from 91 to 105% show that no significant matrix effects occurred. The relative standard deviations (RSDs) were below 2.5% for most elements and below 4.5% for all analyzed elements and thus demonstrate the high precision of the measurements. Comparative measurements with the ICP-OES for gold (Au) in a gold bath, iron (Fe) in a copper bath, and phosphorous (P) in a nickel bath confirmed the results and underline the correctness of the AAS results.

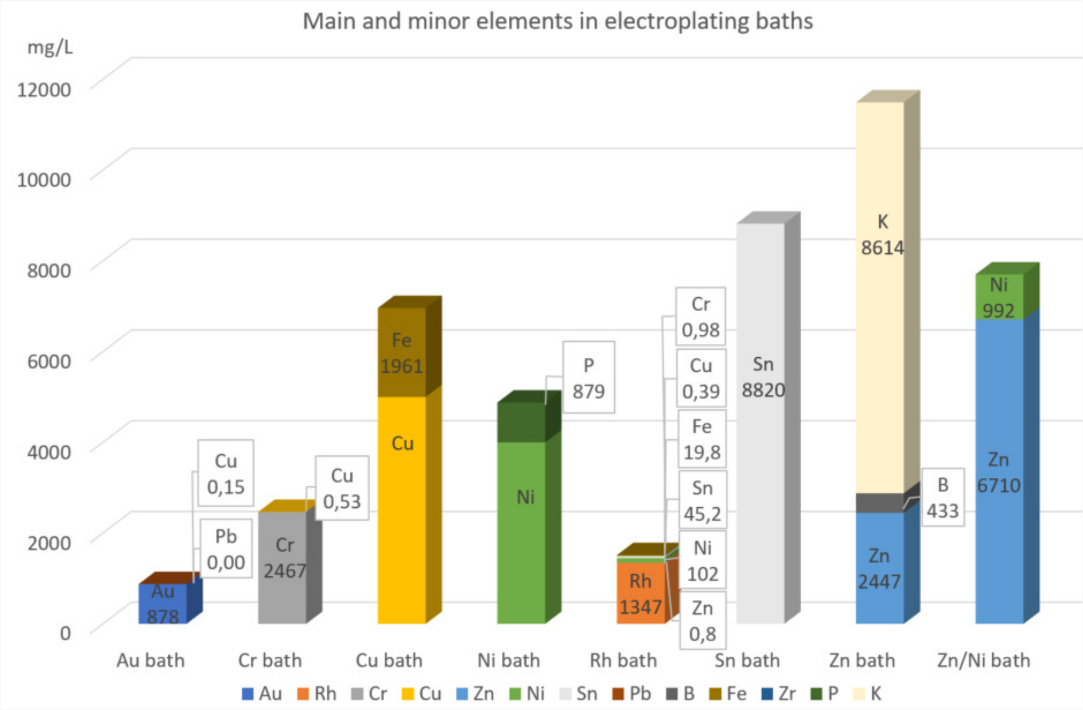

Figure 3: Main and minor elements in electroplating baths (see table 3 for detailed measuring results)

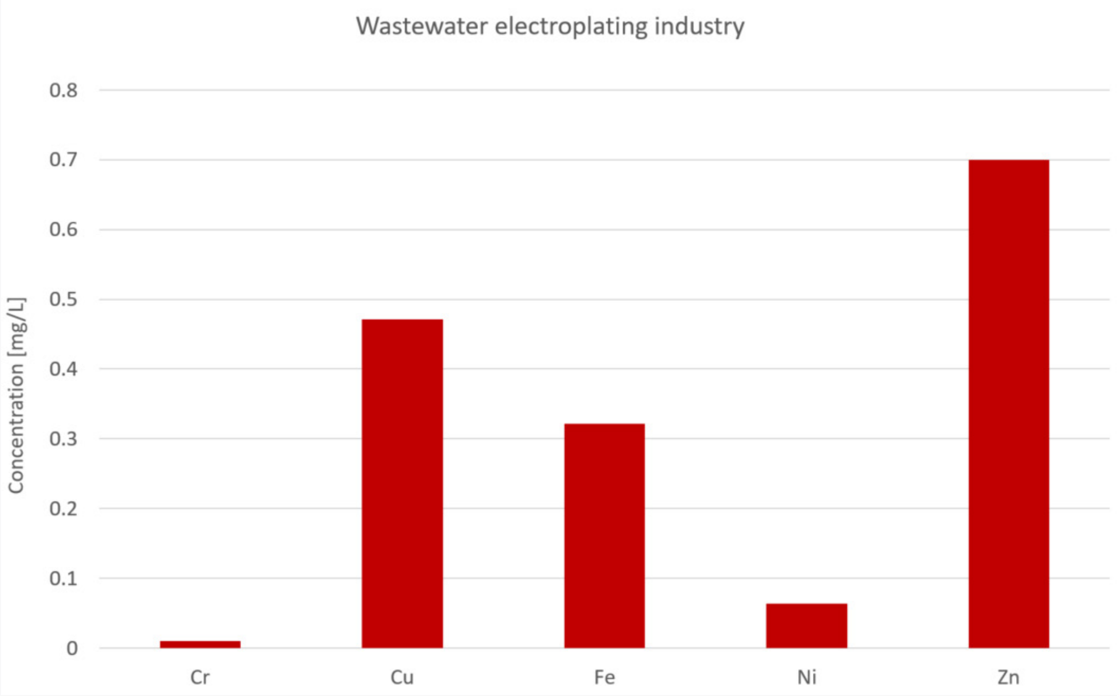

Figure 4: Concentration of the measured analytes in wastewater

Table 3: Measurement results

Sample matrix	Element	Dilution factor	Concentration [mg/L]	RSD[a] [%]	Recovery Rate[b] [%]	Spiked Conc. [mg/L]	LOQ[c] [mg/L]
Au bath	Au	500	878	1.0	100	1.5	0.0105
	Cu	3	0.1545	0.5	93	1.0	0.0042
	Pb	3	< LOD	-	92	1.0	0.0153
Cr bath	Cr	500	2467	2.2	98	1.0	0.0171
	Cu	30	0.533	0.2	93	0.25	0.0042
Cu bath	Fe	1000	1961	0.2	99	1.0	0.0048
Chemical bath	B	5	746	1.5	91	50	8.6
Chemical bath	Zr	3.75	401	1.8	95	40	10.5
Ni bath	P	1	978	1.1	93	2500	28.2
Rh bath	Cr	3	0.984	1.0	-	-	0.0171
	Cu	3	0.391	0.8	103	0.25	0.0042
	Fe	3	19.8	1.0	-	-	0.0048
	Ni	105	102	1.4	-	-	0.0045
	Rh	1000	1347	0.5	-	-	1.8
	Sn	3	45.2	0.9	-	-	117
	Zn	3	0.88	1.1	102	0.25	0.0021
Sn bath	Sn	500	8820	2.1	0.7		117
Zn bath	B	250	4332	1.0	-	-	8.6
	K	20000	86140	1.0	-	-	0.0018
	Zn	20000	24470	2.1	-	-	0.0021
Zn/Ni bath	Ni	500	992	1.1	-	-	0.0045
	Zn	4000	6710	1.1	-	-	0.0021
Wastewater	Cr	2	< LOQ	-	105	0.25	0.024
	Cu	1	0.471	1.3	97	1.0	0.0042
	Fe	2	0.322	1.5	93	1.0	0.009
	Ni	1	0.0639	0.2	103	0.5	0.0045
	Zn	10	0.70	4.1	95	0.5	0.006

[a] RSD = relative standard deviation of 3 replicate measurements

[b] Recovery Rate of the spiked analyte concentration to check for matrix effects

[c] LOQ = Instrumental limit of quantification, calculated by taking 3 times the LOD

Conclusion

A wide range of elements can be determined in different galvanic and chemical baths as well as in wastewater from the electroplating industry using the high-resolution continuum-source flame AAS device contrAA 800 F. Recovery rates from 91 to 105% show that no siginificant matrix interferences occurred, and relative standard deviations below 2.5% for most elements demonstrate the high precision of the measurements. By using a continuum light source, all absorption lines in the spectral range of 185 to 900 nm are accessible for analytical evaluation, so that no lamp-change is necessary. The high intensity of the xenon short-arc lamp results in lowest LODs which easily meet environmental regulations. Even metalloids or non-metals such as boron or phosphorus can be analyzed. The CCD array detector combined with the high-resolution spectrometer visualizes the spectral vicinity of the analyte line, so that possible spectral interferences can be identified and automatically corrected by the software. The autosampler with its automatic dilution function minimizes the effort of manual pipetting. Calibrations can be created automatically. If a sample exceeds the calibration range, the autosampler automatically dilutes the sample and repeats the measurement. The dilution function and, if required, the burner head rotation or side pixel evaluation options enable the analysis of major and minor elements using the same method. The high flexibility of the contrAA 800 flame instrument allows a reliable and easy routine analysis of different matrices, such as electroplating baths and wastewater.

With a dual atomizer system, the contrAA 800 D offers the highest analytical flexibility. It combines the flame and graphite furnace techniques in one device and additionally enables the determination of lowest element concentrations in the ppb range.

This document is true and correct at the time of publication; the information within is subject to change. Other documents may supersede this document, including technical modifications and corrections.

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

Version 1.1 | Author: AnJu
en · 09/2023
© Analytik Jena GmbH+Co. KG | Title image: ©: iStock/Josef Reiter