



Analysis of Phosphating Baths using ICP-OES

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Phosphating is used for passivation to improve resistance to corrosion of painted surfaces. Prior to the phosphating step, several steps occur such as: Degreasing using a hot alkaline solution to remove dirt, oil, grease, shop oil and soluble markings; Pickling using dilute solutions of either hydrochloric or sulfuric acid to remove surface rust and mill scale to provide a chemically clean metallic surface; Fluxing using a salt solution to remove oxides and to prevent oxidation. Monitoring the level of elements in baths is crucial to ensure an efficient process. Both major elements and trace of contaminants have to be monitored and ICP-OES is an excellent tool due to its capability to analyze major and trace elements with a multi-element analysis capability and a reduced sample preparation time.

Due to its sensitivity, its Far UV capability and its ability to analyze a large variety of samples, the Ultima 2 ICP-OES instrument was used for this application.

Sample preparation

Due to the high content of some elements and the viscosity of some samples, the standard addition technique was used so as matrix effects can be minimized. The samples were diluted 1000 times for the analysis of major elements and 10 times for the analysis of trace elements. All standard solutions were prepared using Spex CertiPrep single element standard solution.

Samples analyzed are listed below:

- Sample 1** Degreasing bath - NaOH 5g/L, KOH 20g/L, silicic acid and potassium salt 10 to 20 g/L,
- Sample 2** Pickling bath - Fe < 25 g/L and H₃PO₄ 20%,
- Sample 3** Prephosphating bath - H₃PO₄ around 1%, Ni(NO₃)₂ around 0.1%,
- Sample 4** Phosphating bath - H₃PO₄ around 1%, Ni(NO₃)₂ around 0.1%,
- Sample 5** Electrolysis stripping bath - CrO₃ around 150 g/L, H₂SO₄ 1.5 g/L,
- Sample 6** Electrolysis stripping bath - H₂SO₄ 250 g/L,
- Sample 7** Chrome plating bath - CrO₃ around 300 g/L, H₂SO₄ 3 g/L,
- Sample 8** Electrolytic polishing bath - H₃PO₄ around 900 g/L, H₂SO₄ 300 g/L, CrO₃ 100 g/L,
- Sample 9** Degreasing bath - H₃PO₄ around 20 g/L,
- Sample 10** Pickling bath - NaOH > 20g/L,
- Sample 11** De-oxidation bath - HNO₃ 7 to 10 g/L, Fe₂(SO₄)₃ 35 to 40 g/L,
- Sample 12** Anodic oxidation bath - H₂SO₄ 200 g/L,
- Sample 13** Anodic oxidation bath - H₂SO₄ 200 g/L,
- Sample 14** Water with unknown salt < 1 g/L



Figure 1: ULTIMA 2 High Resolution ICP-OES

Operating conditions

All characteristics of the Ultima 2 ICP-OES instrument used are given in Table 1.

Table 1. Characteristics of ULTIMA 2 ICP-OES Spectrometer

Optical mounting	Czerny-Turner
Focal length	1 meter
Far UV Option	YES
Gratings	2400 g/mm
Resolution	5 pm for 120-320 nm
(specification)	10 pm for 320-800 nm
Thermoregulation	32 ± 0.1°C
RF Generator	40.68 MHz solid state, water cooled
Torch	Vertical with Radial Viewing and Total plasma View*

* Total Plasma View: Measurement of the whole Normal Analytical Zone for enhanced sensitivity and reduced matrix effects



A parallel flow nebulizer and cyclonic double pass spray chamber were used to ensure a good stability even with viscous samples. The 3 mm injector and the sheath gas device that are unique to HORIBA Scientific ICP-OES instruments help to avoid memory effects between samples and ensure shortest stabilization time.

All details of the introduction system are given in Table 2.

Table 2. Specification of the sample introduction system

Nebulizer	Parallel flow
Spray chamber	Glass cyclonic double pass
Sample uptake	1 mL/min
Injector tube inner diameter	3 mm
Pump tubing	Black-black pump tubing for sample Grey-grey pump tubing for drain

All plasma parameters were optimized for sensitivity and robustness and are given in table 3.

Table 3. Operating conditions

Power	1000 W
Plasma gas	12 L/min
Auxiliary gas	0 L/min
Sheath gas	0.2 L/min
Nebulizer flow	0.8 L/min
Pump speed	15 rpm

Acquisition was done using 3 replicates with Max mode and 2s integration time for analyte and background correction. 20 µm/15 µm slit combination was used for all wavelengths.

Results

Lines used for analysis are given in Table 4 below.

Table 4. List of lines used for the analysis

Wavelength (nm)	Wavelength (nm)
Al 396.152	Na 589.995
Cl 134.724	Ni 231.604
Cr 206.164	P 213.618
Cu 327.396	S 180.676
Fe 259.940	Si 251.611
Mg 285.213	Ti 337.280
Mn 259.373	Zn 206.200

All results are given in Tables 5a and 5b for trace elements and Tables 6a and 6b for major elements. Results are all corrected from the dilution factor. The sample description is given in the sample preparation part. All concentrations are given with two significant figures and for each value.

Table 5a. Trace elements concentrations

mg/L	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Cl	61	180	44	63	23	207	10
Cr	10	54	3.1	1.3	-	-	-
Cu	0.50	4.9	0.03	0.1	68	127	71
Fe	-	953	-	-	-	-	-
Mn	0.07	-	-	-	-	-	-
Ni	-	-	753	-	-	-	-
S	248	285	-	-	514	-	-
Si	-	60	59	157	-	-	-

Table 5b. Trace elements concentrations

mg/L	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12	Sample 13	Sample 14
Al	-	24	-	86	-	-	0.56
Cl	0.94	15.2	41	59	37	38	24
Cr	-	0.66	5.2	9.3	27	12	-
Cu	1.6	0.93	4.8	37	131	77	-
Fe	-	0.31	18	-	146	91	0.27
Mg	-	7.2	30	50	285	219	-
Mn	-	0.67	27	71	20	12	-
P	-	-	66	-	-	-	-
S	-	80	421	-	-	-	26
Si	8.7	8	133	20	17	17	-
Ti	-	0.2	2.7	1	4.9	4.4	-
Zn	-	3.3	18	126	385	58	-

Table 6a. Major elements concentrations

g/L	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Cr	-	-	-	-	77	2.2	177
Fe	-	-	0.90	1	3.2	15	4.1
Mn	-	1.7	6.9	11	-	-	-
Na	3.1	-	-	-	-	-	-
Ni	-	-	-	1.5	-	-	-
P	1.7	96	11	10	-	-	-
S	-	-	0.5	0.92	-	81	1.1

Table 6b. Major elements concentrations

g/L	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12	Sample 13	Sample 14
Al	-	-	13	-	6.4	16	-
Cr	39	-	-	-	-	-	-
Fe	1.7	-	-	12	-	-	-
Na	-	-	37	-	-	-	-
P	285	6.9	-	-	-	-	-
S	79	-	-	13	73	90	-

The stability of the ICP-OES was evaluated on two days on Sample 2. Between each measurement, the plasma was switched off. Measurement was performed without any recalibration after 15 minutes pre-heat time. Results are given in Table 7.

Table 7: Stability test results on Sample 2.

	Day 1 - 14:40	Day 2 - 11:00	Day 2 - 15:00
Cr (mg/L)	56	58	55
Cu (mg/L)	4.9	5.1	4.9
Si (mg/L)	60	61	60
S (mg/L)	281	283	283

Conclusion

Thanks to the reduced matrix of the ULTIMA 2, trace elements can be measured in samples containing high concentrations of other elements, such as Samples 2, 8, 12 or 13, with a minimized dilution so as sensitivity and accuracy of measurement is ensured for the undiluted bath.

This performance is mainly due to the combination of the 3 mm i.d. injector and the radial viewing mode using the Total Plasma view concept that reduces matrix effects and increases residence time of the sample in the plasma, thus enhances sensitivity.

The analysis of such complex samples with large variations of concentrations is easy to handle thanks to the robustness of the plasma allowing the use of standard plasma conditions and ensuring a perfect stability over days thanks to its dynamic range.

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