Chromium plating bath

Chromium plating baths consist of a solution of about 250 g/l of CrO_3 in 1 – 2% H_2SO_4. Trace of Iron, Lead and Copper increase themselves, step by step, during the life of the bath.

Iron accumulate in the bath during the first phase of the chromium plating process and also after a first anodic attack on the surface of the objects. Usually an iron concentration of 7 – 8 g/l is considered acceptable, while at 15 – 20 g/l the plating become dull.

The corrosion of the anodes causes the solubilization of lead. Usually lead precipitate as chromate and its concentration is generally low.

Corrosion of electrical circuits in contact with the bath brings copper in solution. Usually when the sum of iron and copper concentration is higher than 10 – 12 g/l the bath has to be renewed.

Trivalent chromium is originated from addition of organic substances to the bath or from the reduction of Cr(VI) nearby the cathodes. In a optimised bath Cr(III) is re-oxidised at the anode; so its concentration is re-equilibrated. Best concentration of Cr(III) is under 3 g/l.

The general effect of high concentrations of Cr (III), Fe and Cu cause also a decreasing of the electrical conductivity of the bath. In this way electrical current has to be increased and the running cost become higher.

Usually the concentration of CrO_3 is measured by means of a simple titration, while other metals are analysed by means of Flame atomic Adsorption spectrophotometry (FAAS), but the same metals can be analysed by means of an equivalent analytical technique, with the same performances but more inexpensive: Voltammetry.

Voltammetry necessitate only a little nitrogen gas cylinder for the deaeration of the solutions and usual glassware and reagents.

All the procedures are simple and are reported on the operator manual. In the next pages the sheets of the following analysis of chromium bath are reported:

- Cr (VI), Total Cr, Fe and Cu by means of DPV
- Pb and Cd by means of DPS

Analysis of chromium (VI)

Pour 10 ml of 0.1 M NaOH (4 g of NaOH in 1 litre of distilled water) in the cell.
Add 300 µl of 0.1 M EDTA.
Deareate for 5 minutes
Scan blank voltammogram.
Add 100 µl of 1+999 diluted sample in distilled water.
Scan sample voltammogram. If a shoulder appear on the peak at –820 mV, add 100 µl of EDTA again. Repeat the EDTA addition until the shoulder disappears.
Add known volumes of standard solution and scan the voltammograms.
Standard solution for the additions: 100 mg/l Cr (VI)
Volume of the additions: 100 µl
Technique: DPV/a with point to point blank subtraction.
Start potential: -500 mV
End potential: -1350 mV
Scanning speed: 30 mV/sec

Analysis of total chromium (as Cr 3+)

Pour 10 ml of 20 g/l KSCN solution in the cell
Deareate for 5 minutes
Scan blank voltammogram.
Add 100 µl of 1+999 diluted sample in 7% hydroxylamine chlorhydrate solution .
Scan sample voltammogram.
Add known volumes of standard solution and scan the voltammograms.
Standard solution for the additions: 100 mg/l Cr (VI) in 7% hydroxylamine chlorhydrate solution
Volume of the additions: 100 µl
Technique: DPV/a with point to point blank subtraction.
Start potential: -500 mV
End potential: -1000 mV
Scanning speed: 20 mV/sec

Analysis of iron

Pour 10 ml of 0.15 TEA / 0.1 M NaOH buffer (2.25 g of triethanolamine + 0.4 g of NaOH in 100 ml of distilled water) in the cell.
Deareate for 5 minutes
Scan blank voltammogram. Check that peak at –1000 mV is very low.
Add 100 – 400 µl of 1+999 diluted sample in distilled water.
Scan sample voltammogram.
Add known volumes of standard solution and scan the voltammograms.
Standard solution for the additions: 10 mg/l Fe
Volume of the additions: 100 µl
Technique: DPV/a with point to point blank subtraction.

Start potential: -700 mV
End potential: -1300 mV
Scanning speed: 30 mV/sec

Analysis of Lead

Pour 10 ml of supporting electrolyte (0.35 g of hydroxylamine chlorhydrate + 0.5 ml of 37% HCl in 50 ml of distilled water) in the cell.
Deareate for 5 minutes
Scan blank voltammogram.
Add 2 ml of 1+99 diluted sample in distilled water.
Scan sample voltammogram.
Add known volumes of standard solution and scan the voltammograms.
Standard solution for the additions: 10 mg/l Pb
Volume of the additions: 200 µl
Technique: DPS/a with point to point blank subtraction.
Start and deposition potential: -800 mV
End potential: -200 mV
Scanning speed: 20 mV/sec

Analysis of Copper

Pour 10 ml of supporting electrolyte (0.35 g of hydroxylamine chlorhydrate + 0.5 ml of 37% HCl in 50 ml of distilled water) in the cell.
Deareate for 5 minutes
Scan blank voltammogram.
Add 50 µl of 1+99 diluted sample in distilled water.
Scan sample voltammogram.
Add known volumes of standard solution and scan the voltammograms.
Standard solution for the additions: 10 mg/l Cu
Volume of the additions: 100 µl
Technique: DPS/a with point to point blank subtraction.
Start potential: +100 mV
End potential: -300 mV
Scanning speed: 20 mV/sec

Analysis of Cadmium

Pour 10 ml of supporting electrolyte (0.35 g of hydroxylamine chlorhydrate + 0.5 ml of 37% HCl in 50 ml of distilled water) in the cell.
Deareate for 5 minutes
Scan blank voltammogram.
Add 2 ml of 1+99 diluted sample in distilled water.
Scan sample voltammogram.
Add known volumes of standard solution and scan the voltammograms.
Standard solution for the additions: 10 mg/l Pb
Volume of the additions: 200 µl
Technique: DPS/a with point to point blank subtraction.
Start and deposition potential: -800 mV
End potential: -200 mV
Scanning speed: 20 mV/sec

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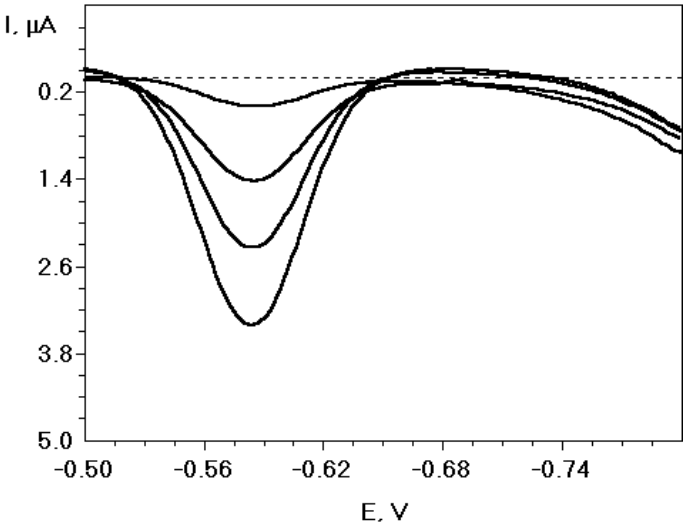
Typical results of voltammetric and FAAS analysis of a chromium plating bath.

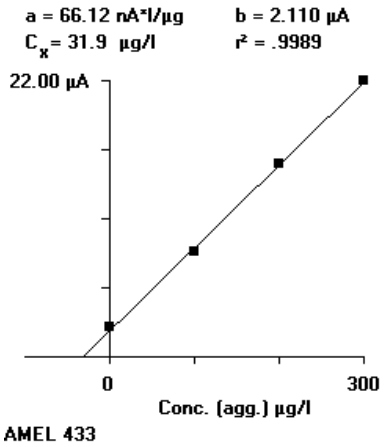
Metal	Voltammetry (g/l)	FAAS (g/l)
Cd	0.0032	ND
Pb	0.043	ND
Fe	8.7	8.9
Cu	2.3	2.2
Cr tot	137	135
Cr VI	124	ND

ND = Not determinable

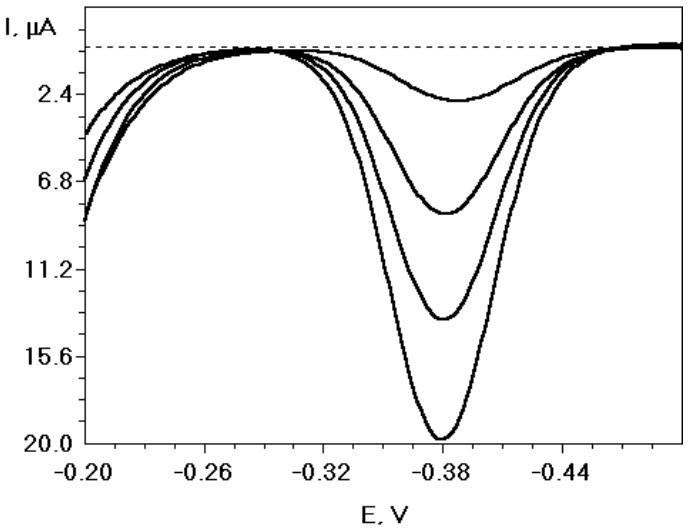
Analysis of other components of the bath:
Fluoride o fluoborate: potentiometry with ISE
Al^{3+}: DPV with calcone
Sulphonates: solvent extraction and IR spectrophotometry.

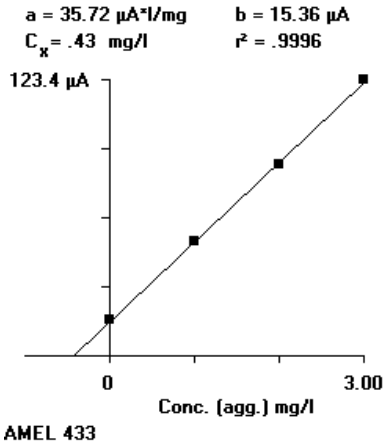
Cadmium (3.2 mg/l - dilution = 100)



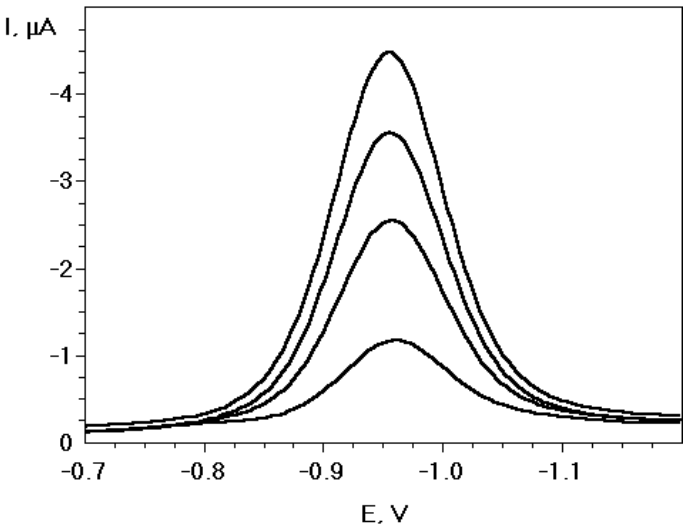


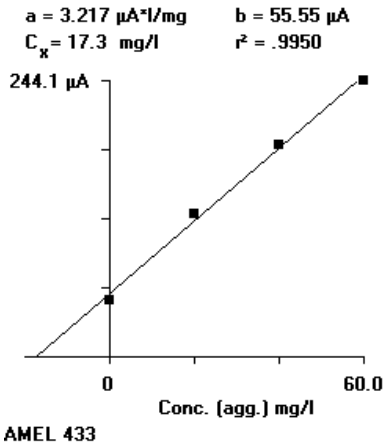
Lead (43 mg/l - dilution = 100)



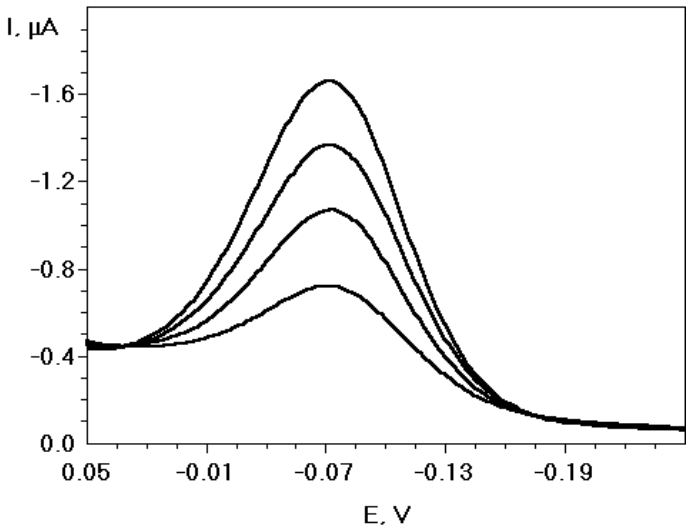


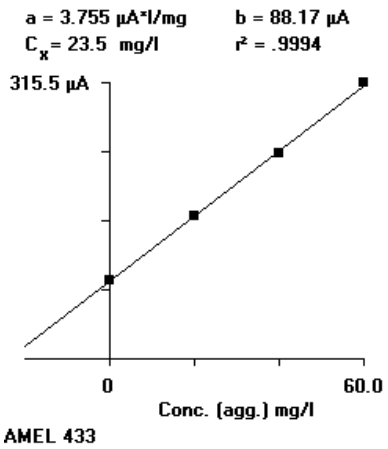
Iron (8.7 g/l - dilution = 500)



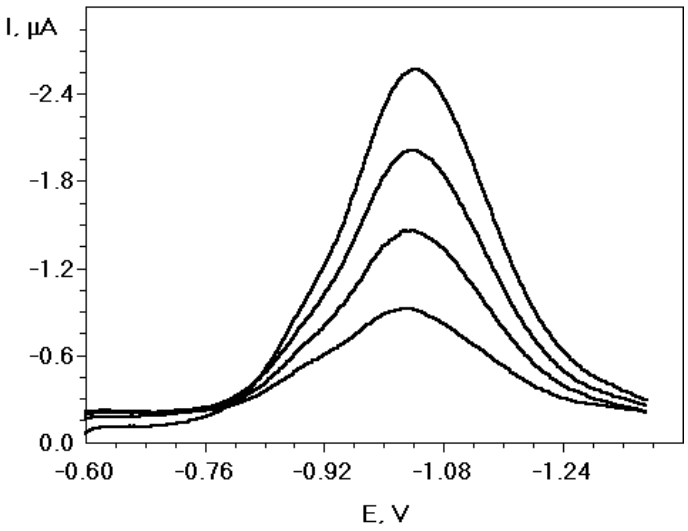


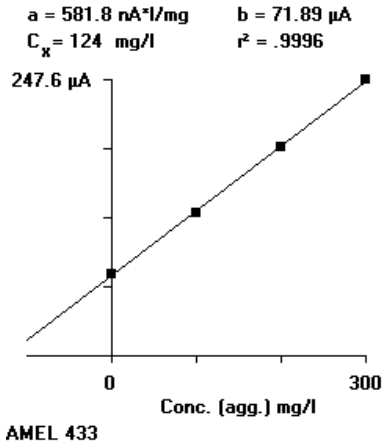
Copper (2.3 g/l – dilution = 100)





Crhromium (VI) (124 g/l Cr (VI) ≡ 238.5 g/l CrO_3 – dilution = 1000)





Total Crhomium (137 g/l Cr ≡ 13 g/l Cr^{3+} – dilution = 1000)