

Analytical Methods: Hexavalent Chromium Plating Solutions

Mary C. Traficante, Atotech USA Inc., Rock Hill, SC

This is a brief review of accepted analytical methods for chromium plating solutions. The relative standard deviation (RSD) of certain methodologies is presented. Normal concentrations for each component and consequences of operating outside these concentrations are discussed. Analytical methods for CrO₃, SO₄, F and impurities are included.

For more information contact:

Mary C. Traficante

Manager

Technical Service & QC Lab

Atotech USA

1750 Overview Dr.

Rock Hill, SC 29731

(803) 817-3585

mtraficant@atousa.com

Introduction:

Hexavalent chromium electrolytes contain chromic acid and sulfuric acid. The electrolyte may also be formulated using a fluoride based or a non-fluoride (proprietary) secondary catalyst. The concentrations of these components will determine how the bath will perform, and how it should be used (decorative vs. functional or hard chrome).

As with any plating process, the process parameters should be defined and the components of the electrolyte analyzed to ensure process control. A variety of analytical methods are available that enable the analyst to determine the concentration of all components of the bath, which is the subject of this paper.

Typically, the plater has a laboratory that is equipped to handle the basic analytical needs of the plant. These companies rely on independent or suppliers' laboratories to analyze the more complex components of the plating solution.

Many suppliers offer a prescribed amount of routine analytical service to their customers and are available to help resolve issues with chemistry. Testing by an outside lab should not be used to control the daily operation of the bath, but rather as a means to check and control the in-house analytical results.

The suppliers' laboratory will typically analyze many thousands of samples per year representing hundreds of different and diverse customers. Computer programs are necessary to manage the magnitude of samples received from a variety of surface finishing companies.

How are samples handled by a supplier?

- Sample received (typically delivered by Fed-Ex) and unpackaged.
- Sample given an ID number and logged in computer with:
 - Company name
 - Process name, tank number and gallonage
 - Date sampled and date received by supplier
- Samples separated by solution type and delivered to appropriate analyst
- Analyst organizes into subgroups and logs into notebook using sample ID number
- Samples analyzed
- Raw results are entered into computer program that calculates final results and additions needed to adjust chemistry to optimum process parameters.
- Program tracks analytical results of the particular tank; large changes since last analysis are noted
- Laboratory report printed and faxed to customer.

Even though the suppliers' laboratory may be well equipped with sophisticated instrumentation and trained analytical chemists, it is unrealistic to expect the supplier to become intimately familiar with any one particular tank. It is up to the plater to know and understand the operation of the plating tank and entire line. This is why it is so important for the plater to assess what his analytical needs are in order to control the chemistry of a bath on a daily basis and set up to do so. The function and operating ranges of each component in a hexavalent chromium solution are outlined below (Table I), this will aid in assessing analytical needs.

Needs Assessment:

Chromium

Hexavalent chromium solutions are rather simple in that the metal comes solely from the chromic acid in solution, insoluble lead anodes are used. The chromium consumption is calculated based upon ampere-hours, if drag out is kept to a minimum the calculation can give a very accurate consumption rate. If the chromic acid is added based upon this calculation, it will be possible to control the solution by only a periodic analytical determination of chromic acid.

Sulfate:

Sulfate is introduced to the electrolyte in the form of sulfuric acid. Sulfate is not consumed during chrome plating, loss is through drag out. The absolute value of sulfate is not critical, rather the ratio between the chromic acid and sulfate concentration is the controlling factor of the electrolyte.

Increases in sulfate concentration can usually be traced to the water source and/or drag in. Deionized water is recommended to prevent the introduction of both sulfates and chlorides into the chrome solution. Drag in of a sulfuric acid dip or a nickel plating solution will add sulfate to the chrome plating bath. Fortunately, sulfate may be precipitated from a hexavalent chrome electrolyte using barium carbonate. (2 parts of BaCO_3 are needed to ppt. 1 part of SO_4 as BaSO_4).

Secondary Catalysts:

Fluoride catalysts even though not consumed during the plating process are volatile therefore the concentration needs to be determined and controlled. Fluoride catalysts will also form tight complexes with impurities (Fe, B, Al) that might be present in the bath. If the fluoride is complexed it will be ineffective as a catalyst. Analytical procedure for fluoride must be capable of testing for active fluoride rather than total fluoride.

Non-fluoride secondary catalyst (proprietary) is extremely stable and is not consumed by electrolysis. A confidential method for the proprietary catalyst exists; the supplier will quantitatively analyze the catalyst as necessary.

Contaminants:

Contamination of the chromium solution is most commonly introduced by the substrate being plated and drag in of the previous plating solution. It is not uncommon to find a considerable amount of iron in "hard" or functional chromium solutions that are used to plate chromium directly on steel. Likewise it is common for decorative chromium solutions to be contaminated with nickel from drag in of the bright nickel electrolyte. Other contaminants are copper, aluminum, zinc, chloride, nitrate, phosphate and trivalent chromium.

Table 1: Functions of Constituents of a Hexavalent Chromium Electrolyte

COMPONENT	FUNCTION	OPERATING RANGES		EFFECT OF OPERATING OUTSIDE RANGE
		Decorative	Functional	
Chromic Acid	Provides metal ions	20 - 40 oz/gal	30-50 oz/gal	Too low causes higher resistance, too high not detrimental but wasteful.
Sulfate	Primary Catalyst: allows chromium to be plated out of solution as a bright metal deposit.	0.01 - 0.02 oz/gal	0.30-0.50 oz/gal	The ratio of chromic acid:sulfate is the defining parameter for good operation. Too low SO ₄ (high ratio) will cause burning. To high SO ₄ (low ratio) will cause poor chrome coverage.
Fluoride	Secondary Catalyst: provides brightness, hardness, increased efficiency, increased micro-cracking	0.4 - 1.25 g/l	2.0 - 4.5 g/l	Too low causes lower efficiency, fewer microcracks, and poor activation of nickel causing whitewashing. Too high will decrease covering power of the chrome & cause excessive etching of the parts.
Non-Fluoride Catalysts	Secondary Catalyst: provides brightness, hardness, increased efficiency, increased micro-cracking	90-125% of suppliers optimum content	90-125% of suppliers optimum content	Too low or too high will cause decreased efficiencies, decreased hardness and dull deposits.
Ratio CrO₃ : SO₄	Determines covering power, ability to plate at proper current densities w/o burning.	175-225:1	80-125:1	Low ratio will cause decreased chrome coverage. High ratio will cause HCD burning & even inability to plate chrome at all.
Trivalent Chrome	Natural product of oxidation/ reduction reactions of electroplating. Small amount of Cr+3 beneficial for coverage of Cr.	<0.5 oz/gal	<0.5 oz/gal	If > 0.5 oz/gal the trivalent is considered a contaminant and will cause increased resistivity, increased tendency to burn, dark banded deposit at chrome leave-off, and poor coverage.
Chloride	Contaminant brought in by water or from drag in of nickel plating solution.	0.003-0.009 oz/gal 25 ppm - 70 ppm	0.003-0.009 oz/gal 25 ppm - 70 ppm	From 25 -70 ppm coverage will be reduced. At > 75 ppm there will be severe reduction of coverage, reduced efficiency and possible cathodic etching of work.
Metals: Cu, Fe, Zn, Ni, B, Al	Metals are introduced into chrome solutions in many ways, Ni from drag in, Cu & Al from bussing, Fe from substrate	< 1.0 oz/gal total	< 1.0 oz/gal total	If > 1.0 oz/gal there could be increased resistivity, roughness, hazy deposits, reduced covering power, decreased bright range and interference with F catalyst

Methods:

Chromic Acid:

There are two (2) methods that are widely used throughout the industry for the determination of chromic acid in chromium plating solutions: density and titrimetric.

The density of the solution may be measured using a hydrometer or by weighing an accurate volume of the solution. The resultant Specific Gravity or Baume is related to the chromic acid concentration using published charts. This technique is fast, easy and generally precise. There are two (2) factors that greatly influence the accuracy. First, the temperature of the solution influences the density. It is important that the temperature of the solution is measured and recorded at the time of the density reading, when referring to the chart the temperature must be corrected for. A general rule is “ for every 10 degrees F increase in temperature the Baume will decrease by 0.3 degrees.

Secondly, metal contaminants will increase the density of the solution, which will yield a false high chromic acid concentration. If the metal contamination content is known a correction factor can be applied to improve the accuracy of the method.

A titrimetric analysis is the generally accepted procedure to determine the chromic acid concentration in plating solutions. There are 2 widely used titrimetric methods. One uses standard ferrous ammonium sulfate as the titrant, the other uses standard sodium thiosulfate (iodide method).

The ferrous ammonium sulfate titration involves acidifying the sample with phosphoric acid and titrating with standard ferrous ammonium sulfate solution using Ferroin indicator. Phosphoric acid is used to prevent color interference from ferric ions however the endpoint is still not very sharp. A benefit of this method is that copper does not interfere with this titration as with the sodium thiosulfate titration method.

The sodium thiosulfate titration method (iodide) involves adding ammonium bifluoride to an acidified sample to prevent interference of iron. An excess of iodide is added and the liberated iodine titrated with sodium thiosulfate, using starch indicator. Copper gives a positive error and should be corrected for by subtracting from the calculated result (for chromic acid) $\frac{1}{2}$ of the copper concentration found.¹ The RSD (relative standard deviation) of the iodide method has been determined to be 1.1% in our lab. Therefore reported results should be good to +/- 1.1%. (i.e.: a reported result of 36 oz/gal confidence is 35.6 – 36.4).

Sulfate

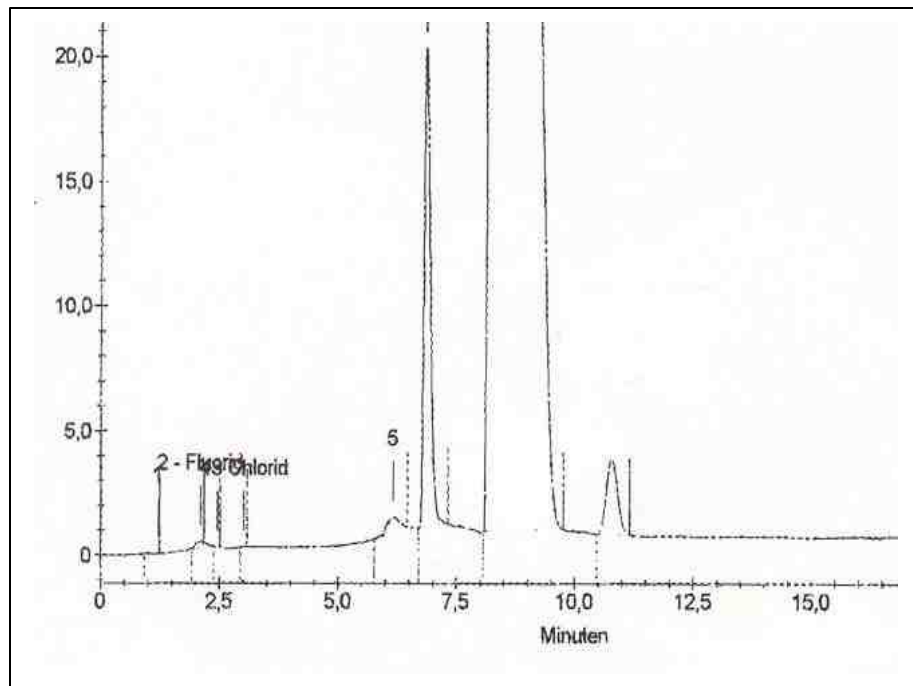
There are several methods used for the determination of sulfate in chromic acid plating solutions: gravimetric, centrifuge and ion chromatography.

The gravimetric method involves precipitation of barium sulfate using a solution of barium chloride. The precipitate is filtered from solution, washed, dried and weighed.

The gravimetric method will yield accurate results, however gravimetric techniques are not commonly used to analyze plating solutions due to dependence upon operator skill and time limitations. Precipitation, filtration, collection and solid handling steps require great care to insure accuracy. Replicates are always necessary and a single analysis will take several hours.²

The centrifuge method is quick and relatively easy. It is based upon measuring the volume of barium sulfate precipitated upon adding a solution of barium chloride. The precipitate is compacted by centrifuging at a specific speed (rpm) and time (min.). The volume of precipitate is measured directly in oz/gal from graduated centrifuge tubes.³ The relative standard deviation (RSD) of this method was measured in our lab to be approximately 4.5% (Table 2).

Finally, sulfate in a chrome solution may be measured using ion chromatography. The method is based upon separating the components of the chromium solution using a specific separation column. Chromatography isolates the components of a sample according to their individual affinity to a solid ion exchange resin, packed within a column. After the components are separated and eluted from the separation column some physical or chemical property is measured. In the case of ion chromatography the conductivity is measured.^{4,5} (Figure 1)



- Sulfate: 6 min.RT

Figure 1:

Dionex DX500, Gradient operation, 10 ml/min. Ionpac AS4A-SC, Sensitivity 10 us

Table 2: Sulfate readings using Kocour ppt. method (SO4 value = 0.33 oz/gal)

Smple #	SO4	Smple #	SO4	Smple #	SO4
1	0.34	11	0.33	21	0.33
2	0.31	12	0.35	22	0.30
3	0.35	13	0.36	23	0.33
4	0.32	14	0.36	24	0.32
5	0.37	15	0.33	25	0.30
6	0.33	16	0.33	26	0.30
7	0.36	17	0.35	27	0.35
8	0.36	18	0.31	28	0.35
9	0.35	19	0.36	29	0.34
10	0.32	20	0.35	30	0.33
Mean = 0.336 Estimated Std Deviation = 0 .0147 (4.5%)					

Fluoride Catalyst

Fluoride ion can be determined by specific ion electrode, ion chromatography or aluminum wire etch method.

The specific ion electrode (SIE) method is fast, relatively easy and generally reliable. This analytical method will measure the total fluoride anion present in the chromium solution as opposed to the active fluoride ion. Iron, aluminum and boron will complex with the fluoride rendering it inactive as a catalyst for the chromium solution. The SIE method is better suited for decorative chrome solutions, as there are generally far less iron and aluminum present in decorative chromes than functional or hard chromes.⁶

The aluminum wire etch method is based on dissolution of aluminum by free silica fluoride ions. A designated length of aluminum wire is cleaned, micro-etched, dried and weighed. The wire is immersed in a specific volume of the chrome solution to be tested for a defined time and temperature (+/- 2 degrees F). The wire is removed, rinsed, dried and weighed. The weight loss is converted to g/l of silicofluoride by relating to a standard graph. This method will determine the active fluoride only. Metal contaminants do not interfere with the method.

The ion chromatographic method for fluoride will detect the total fluoride present in the solution. For chromium plating solutions that are not contaminated with complexing metals the IC method is possible.

Non F Secondary Catalyst

A proprietary Ion Chromatographic method exists for the determination of the non-fluoride chromium catalyst. This catalyst is extremely stable therefore should not be necessary to analyze more than 1/month. The suppliers lab will analyze and recommend adjustments if needed.

An indirect plating method to determine catalyst level is available. In this procedure the cathode current efficiency is measured, this current efficiency is related to concentration of catalyst via a standard graph.

Trivalent Chromium

There are 3 methods that are widely used to determine the amount of trivalent chromium in a hexavalent chrome solution: visual, spectrophotometric and titrimetric.

The visual method may be used to approximate the quantity of trivalent chrome present. In most cases an approximation is all that is needed because trivalent chromium is present in all hexavalent chromium solutions and is only considered an impurity when the level is > 0.5 oz/gal. The visual test will clearly distinguish between quantities greater or less than 0.5 oz/gal. The visual method is based upon the fact that hexavalent chrome solutions have a reddish-orange color if trivalent chrome is absent. When trivalent chrome is present the color of the solution becomes darker and brownish in color. As the trivalent concentration increases the darkness or brownness intensifies. The test is simple; a sample of the solution is diluted and compared to previously prepared and diluted (to the same volume) standards of known trivalent concentration. The standards are prepared by adding a specific quantity of sucrose (table sugar) to a hexavalent chrome solution. (0.42 grams of sucrose will produce 1 gram of trivalent chromium).

The spectrophotometric method is based upon the same color principle as the visual method however the intensity of the color is measured using a spectrophotometer at a defined wavelength. The absorbance of the sample is compared to the absorbance readings of standards at the same wavelength. This method allows for a higher degree of accuracy than the purely visual method.⁷

The titrimetric analysis is run using the same methodology as for hexavalent chromium. The hexavalent chromium is determined as outlined above and an aliquot of the same sample is taken and oxidized. Any trivalent chromium present will be oxidized to the hexavalent state. The sample is titrated once again for hexavalent chrome. The difference in the two titrations represents the amount of trivalent chromium present in the solution at that time. The drawback to this double titration method is that usually the difference between the titrations is very small therefore a relatively small error in either titration can lead to serious error in the reported results of the trivalent chromium concentration.⁸

Chloride

Once again the analyst has several options to choose from to determine the chloride concentration in a chrome plating solution. The choice is largely dependent upon lab capabilities and instrumentation available. There are gravimetric, titrimetric, chromatographic and empirical methods available.

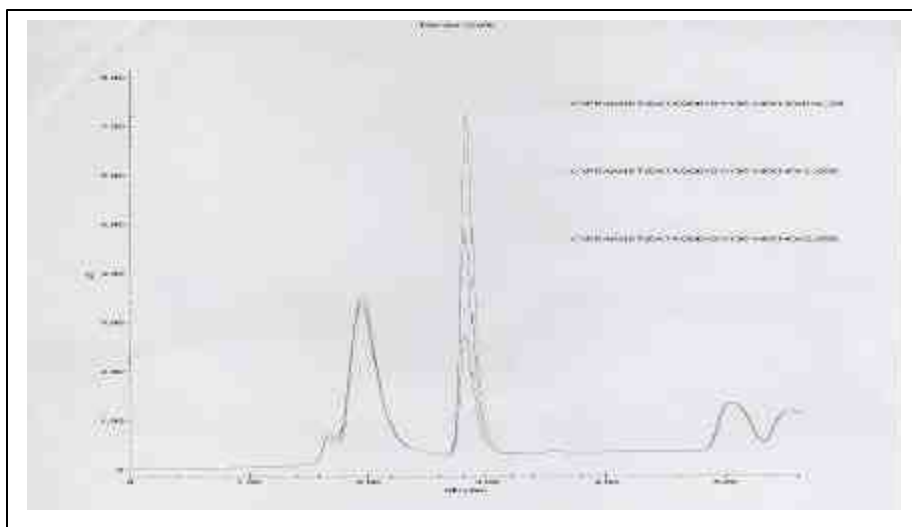
The gravimetric method is rarely used due to the complexity of the test and the fact that the chloride ion can be driven out of the electrolyte by electrolyzing using a large anode

area and small cathode area at relatively high voltage. The gravimetric procedure involves precipitation of the chloride as silver chloride using a solution of silver nitrate. The ppt is then filtered, washed, dried and weighed. As with any gravimetric procedure the test should be run in duplicate to ensure accuracy.⁹

A widely used method is the titration method for chloride. A sample is diluted with chloride free water and acidified with nitric acid, a few drops of a dilute silver nitrate solution is added. If chloride is present the solution will become turbid. The sample is titrated to a clear end-point using a standard mercuric nitrate solution. The end-point is somewhat subjective therefore it is recommended that a blank solution be used for comparison.¹⁰

An empirical method to detect the presence of chloride may be used if a non-fluoride electrolyte is being tested. Simply, a brass panel is immersed into the solution for approx. 1 minute, if the brass becomes etched (yellow) then chloride is present and the solution should be electrolyzed to remove the contamination.¹¹

An ion chromatographic method may be used to determine the chloride concentration in a chrome solution. However a method of standard additions must be used to minimize the error as the relative standard deviation has been determined to be 10%. (Figure 2)



↑ Cl, RT 2.8 min

Figure 2:
Chromatogram of Chloride in Hexavalent Chrome Solutions
Dionex DX500, gradient operation, 1 mil/min, Ionpac AS4-SC

Metal Contaminants

The most common metal contaminants found in hexavalent chrome solutions are iron, copper, nickel, aluminum and zinc. Metallic contamination can be detected and measured accurately by either Atomic Absorption Spectroscopy (AAS) or by Inductively Coupled Plasma (ICP).

Atomic Absorption spectroscopy involves preparing accurate dilutions of a sample. The sample is then aspirated through a small tube into a nebulizer, which forms an aerosol of small droplets. This aerosol is then mixed with an oxidant (air or nitrous oxide) and fuel (acetylene) and burned in a continuous flame. Each element uses a special light source or hollow cathode lamp. The light source or lamp emits energy at a prescribed wavelength. The absorbance of the sample is measured at that wavelength and compared to known standards of that element at the same wavelength. The detection limits are dependent upon the analyte but usually range from ppb to 50 ppm. Samples must be diluted such that the absorbance falls within the linear range.

Inductively coupled plasma (ICP) is atomic emission spectroscopy. Liquids are introduced into the ICP using a nebulizer similar to that used in the AAS. The intensity of the emission at a given wavelength is proportional to the number of atoms emitting and can be expressed as concentration relative to standards. A benefit of the ICP over the AAS is that the ICP is capable of measuring several elements contained in a single sample simultaneously.⁶

Summary:

The chrome plater has a variety of analytical methods to choose from to determine the quantity of all components in a hexavalent chromium solution. The methods chosen will depend upon instrumentation available to the analyst as well as the analyst's capabilities. No matter which method is employed, it is important to know the limitations and capability of the particular method.

The analyst will recommend adjustments to the bath chemistry based upon analytical results; therefore a high level of confidence in the result is needed. The methods used should always be verified by either an outside lab or in-house using known standards. Control of bath chemistry is vital to the plating operation; consistent chemistry will improve overall quality of production, and eliminate one variable when a problem arises. When a plating bath is analyzed and adjusted on a regular basis the history of the solution will be created. The analytical history may be related to the performance of the bath at any given time and thus allow the company to optimize the chemistry for best performance.

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- ¹ Technical Information Sheet No. P-CR-A21, "Determination of Chromium in Chromium Plating Solutions," Atotech USA Inc., Rock Hill, SC 29731 (1985).
- ² Technical Sheet No. P-SM-12, "Simple Methods for Analyzing Plating Solutions", Atotech USA Inc., Rock Hill, SC 29732 (1985) p.6.
- ³ Instructions for test kit Model KSTS, available from: Kocour Co., 4800 South St. Louis, Chicago, IL 60632, (312) 847-1111.
- ⁴ Technical Note 24, "Determination of Chromium", Dionex Corporation, Sunnyvale, California (1987)
- ⁵ Rodgers, Dr. Tim, CEF, "Analytical Review", *Plating and Surface Finishing* Vol. 75 (1988): No's 8,9,10,11, Vol. 76 (1989): No's 1,2,3,4,5. Orlando, FL: American Electroplaters and Surface Finishers Society, 1988, 1989.
- ⁶ Langford, Kenneth E., and Janet E. Parker. *Analysis of Electroplating and Related Solutions*, Fourth Edition. Teddington, Great Britain: Robert Draper, Ltd., 1971. pp 429-432
- ⁷ Langford, Kenneth E., and Janet E. Parker. *Analysis of Electroplating and Related Solutions*, Fourth Edition. Teddington, Great Britain: Robert Draper, Ltd., 1971. pp 380-381
- ⁸ Technical Information Sheet No. P-CR-A21, "Determination of Chromium in Chromium Plating Solutions," Atotech USA Inc., Rock Hill, SC 29731 (1985).
- ⁹ Langford, Kenneth E., and Janet E. Parker. *Analysis of Electroplating and Related Solutions*, Fourth Edition. Teddington, Great Britain: Robert Draper, Ltd., 1971. pp 33,36.
- ¹⁰ Technical Information Sheet No. P-CR-A21, "Determination of Chromium in Chromium Plating Solutions," Atotech USA Inc., Rock Hill, SC 29731 (1985).
- ¹¹ Guernsey, V.E., "Down under Where the Chrome Don't Go, Part III Misplates Related to the Chromium Bath." *Metal Finishing*, Vol 53, No.3. Hackensack, NJ: Metals and Plastics Publications, Inc., 1985. pp 27-30.