CONTROL, ANALYSIS, AND TESTING

CHEMICAL ANALYSIS OF PLATING SOLUTIONS

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Plating solutions must be routinely analyzed in order to maintain the recommended bath formulation and to preempt the occurrence of problems related to improper levels of bath constituents. Contaminant levels in the solutions must also be monitored. Manufacturers of plating systems establish optimum specifications to ensure maximum solution efficiency and uniformity of deposits. The various factors that cause the concentrations of bath constituents to deviate from their optimum values are as follows:

1. drag-out;
2. solution evaporation;
3. chemical decomposition; and
4. unequal anode and cathode efficiencies.

A current efficiency problem is recognized by gradual but continuous changes in pH, metal content, or cyanide content (see Table I).

The techniques employed for the quantitative analysis of plating solutions are classified as volumetric (titrimetric), gravimetric, and instrumental. Volumetric and gravimetric methods are also known as "wet" methods. The analyst must select the method that is best suited and most cost effective for a particular application.

The wet methods outlined here are simple, accurate, and rapid enough for practically all plating process control. They require only the common analytical equipment found in the laboratory, and the instructions are sufficiently detailed for an average technician to follow without any difficulty. The determination of small amounts of impurities and uncommon

Table I. Problems Caused by Unequal Anode and Cathode Efficiencies

Problem	*Cause*
High pH	High anode efficiency
Low pH	High cathode efficiency
High metal content	High anode efficiency
Low metal content	High cathode efficiency
High free cyanide	Low anode efficiency
Low free cyanide	High anode efficiency

metals should be referred to a competent laboratory, as a high degree of skill and chemical knowledge are required for the determination of these constituents.

Hull cell testing (see the section on plating cells elsewhere in this *Guidebook*) enables the operator to observe the quality of a deposit over a wide current density range.

VOLUMETRIC METHODS

When titrants composed of standard solutions are added to a sample that contains a component whose concentration is to be quantitatively determined, the method is referred to as a volumetric method. The component to be determined must react completely with the titrant in stoichiometric proportions. From the volume of titrant required, the component's concentration is calculated. The simplicity, quickness, and relatively low cost of volumetric methods make them the most widely used for the analysis of plating and related solutions.

Volumetric methods involve reactions of several types: oxidation-reduction, acid-base, complexation, and precipitation. Indicators are auxiliary reagents, which usually signify the endpoint of the analysis. The endpoint can be indicated by a color change, formation of a turbid solution, or the solubilization of a turbid solution.

Some volumetric methods require little sample preparation, whereas others may require extensive preparation. Accuracy decreases for volumetric analyses of components found in low concentrations, as endpoints are not as easily observed as with the components found in high concentrations.

Volumetric methods are limited in that several conditions must be satisfied. Indicators should be available to signal the endpoint of the titration. The component-titrant reaction should not be affected by interferences from other substances found in the solution.

GRAVIMETRIC METHODS

In gravimetric methods, the component being determined is separated from other components of the sample by precipitation, volatilization, or electroanalytical means. Precipitation methods are the most important gravimetric methods. The precipitate is usually a very slightly soluble compound of high purity that contains the component. The weight of the precipitate is determined after it is filtered from solution, washed, and dried. Gravimetric methods are used to supplement the available volumetric methods.

Limitations of gravimetric methods include the requirement that the precipitated component has an extremely low solubility. The precipitate must also be of high purity and be easily filterable.

Species that are analyzed gravimetrically include chloride, sulfate, carbonate, phosphate, gold, and silver.

INSTRUMENTAL METHODS

Instrumental methods differ from wet methods in that they measure a physical property related to the composition of a substance, whereas wet methods rely on chemical reactions. The selection of an instrument for the analysis of plating solutions is a difficult task. Analysts must decide if the cost is justified and if the analytical instrument is capable of analyzing for the required substances with a high degree of accuracy and precision. Instruments coupled to computers can automatically sample, analyze, and record results. Mathematical errors are minimized and sample measurements are more reproducible than with wet methods. Instrumental methods are also extremely rapid when compared with wet methods.

Unlike humans, instruments cannot judge. They cannot recognize improper sample preparation or interfering substances. Erroneous results are sometimes produced by electronic and mechanical malfunctions.

Analytical instruments frequently used in the analysis of plating solutions can be categorized as spectroscopic, photometric, chromatographic, and electroanalytical. Spectroscopic methods (flame photometry, emission spectrometry, X-ray fluorescence, mass spectrometry, and inductively coupled plasma) are based on the emission of light. Photometric methods (spectrophotometry, colorimetry, and atomic absorption) are based on the absorption of light. Chromatographic methods (ion chromatography) involve the separation of substances for subsequent identification. Electroanalytical methods (potentiometry, conductometry, polarography, amperometry, and electrogravimetry) involve an electric current in the course of the analysis.

The instrumental methods, comprehensively reviewed below, are most applicable to plating environments.

SPECTROSCOPIC METHODS

Spectroscopy is the analysis of a substance by the measurement of emitted light. When heat, electrical energy, or radiant energy is added to an atom, the atom becomes excited and emits light. Excitation can be caused by a flame, spark, X-rays, or an AC or DC arc. The electrons in the atom are activated from their ground state to unstable energy shells of higher potential energy. Upon returning to their ground state, energy is released in the form of electromagnetic radiation.

Because each element contains atoms with different arrangements of outermost electrons, a distinct set of wavelengths is obtained. These wavelengths, from atoms of several elements, are separated by a monochromator such as a prism or a diffraction grating. Detection of the wavelengths can be accomplished photographically (spectrograph) or via direct-reading photoelectric detectors (spectrophotometers). The measurement of intensity emitted at a particular wavelength is proportional to the concentration of the element being analyzed.

An advantage of spectroscopy is that the method is specific for the element being analyzed. It permits quantitative analysis of trace elements without any preliminary treatment and without prior knowledge as to the presence of the element. Most metals and some nonmetals may be analyzed. Spectroscopic analysis is also useful for repetitive analytical work.

Disadvantages of spectroscopic analysis include the temperature dependence of intensity measurements, as intensity is very sensitive to small fluctuations in temperature. The accuracy and precision of spectrographic methods is not as high as some spectrophotometric methods or wet analyses. Spectrographic methods are usually limited to maximum element concentrations of 3%. Additionally, sensitivity is much smaller for elements of high energy (e.g., zinc) than for elements of low energy (e.g., sodium).

Applications of spectroscopy include the analysis of major constituents and impurities in plating solutions, and of alloy deposits for composition.

Flame Photometry

In flame photometry (FP), a sample in solution is atomized at constant air pressure and introduced in its entirety into a flame as a fine mist. The temperature of the flame (1,800–3,100˚K) is kept constant. The solvent is evaporated and the solid is vaporized and then dissociated into ground state atoms. The valence electrons of the ground state atoms are excited by the energy of the flame to higher energy levels and then fall back to the ground state. The intensities of the emitted spectrum lines are determined in the spectrograph or measured directly by a spectrophotometer.

The flame photometer is calibrated with standards of known composition and concentration. The intensity of a given spectral line of an unknown can then be correlated with the amount of an element present that emits the specific radiation.

Physical interferences may occur from solute or solvent effects on the rate of transport of the sample into the flame. Spectral interferences are caused by adjacent line emissions when the element being analyzed has nearly the same wavelength as another element. Monochromators or the selection of other spectral lines minimize this interference. Ionization interferences may occur with the higher temperature flames. By adding a second ionizable element, the interferences due to the ionization of the element being determined are minimized.

An advantage of FP is that the temperature of the flame can be kept more nearly constant than with electric sources. A disadvantage of the method is that the sensitivity of the flame source is many times smaller than that of an electric arc or spark.

FP is used for the analysis of aluminum, boron, cadmium, calcium, chromium, cobalt, copper, indium, iron, lead, lithium, magnesium, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, tin, and zinc.

Emission Spectrometry

In emission spectrometry (ES), a sample composed of a solid, cast metal or solution is excited by an electric discharge such as an AC arc, a DC arc, or a spark. The sample is usually placed in the cavity of a lower graphite electrode, which is made positive. The upper counterelectrode is another graphite electrode ground to a point. Graphite is the preferred electrode material because of its ability to withstand the high electric discharge temperatures. It is also a good electrical conductor and does not generate its own spectral lines.

The arc is started by touching the two graphite electrodes and then separating them. The extremely high temperatures (4,000–6,000˚K) produce emitted radiation higher in energy and in the number of spectral lines than in flame photometry. Characteristic wavelengths from atoms of several elements are separated by a monochromator and are detected by spectrographs or spectrophotometers. Qualitative identification is performed by using available charts and tables to identify the spectral lines that the emission spectrometer sorts out according to their wavelength. The elements present in a sample can also be qualitatively determined by comparing the spectrum of an unknown with that of pure samples of the elements. The density of the wavelengths is proportional to the concentration of the element being determined. Calibrations are done against standard samples.

ES is a useful method for the analysis of trace metallic contaminants in plating baths. The “oxide” method is a common quantitative technique in ES. A sample of the plating bath is evaporated to dryness and then heated in a muffle furnace. The resultant oxides are mixed with graphite and placed in a graphite electrode. Standards are similarly prepared and a DC arc is used to excite the sample and standards.

X-ray Fluorescence

X-ray fluorescence (XRF) spectroscopy is based on the excitation of samples by an X-ray source of sufficiently high energy, resulting in the emission of fluorescent radiation. The concentration of the element being determined is proportional to the intensity of its characteristic wavelength. A typical XRF spectrometer consists of an X-ray source, a detector, and a data analyzer.

Advantages of XRF include the nondestructive nature of the X-rays on the sample. XRF is useful in measuring the major constituents of plating baths such as cadmium, chromium, cobalt, gold, nickel, silver, tin, and zinc. Disadvantages of XRF include its lack of sensitivity as compared with ES.

X-ray spectroscopy is also used to measure the thickness of a plated deposit. The X-ray detector is placed on the wavelength of the element being measured. The surface of the deposit is exposed to an X-ray source and the intensity of the element wavelength is measured. A calibration curve is constructed for intensity against thickness for a particular deposit. Coating compositions can also be determined by XRF.

Mass Spectrometry

In mass spectrometry (MS), gases or vapors derived from liquids or solids are bombarded by a beam of electrons in an ionization chamber, causing ionization and a rupture of chemical bonds. Charged particles are formed, which may be composed of elements, molecules, or fragments. Electric and magnetic fields then separate the ions according to their mass to charge ratios (*m/e*). The amount and type of fragments produced in an ionization chamber, for a particular energy of the bombarding beam, are characteristic of the molecule; therefore, every chemical compound has a distinct mass spectrum. By establishing a mass spectrum of several pure compounds, an observed pattern allows identification and analysis of complex mixtures.

The mass spectrum of a compound contains the masses of the ion fragments and the relative abundances of these ions plus the parent ion. Dissociation fragments will always occur in the same relative abundance for a particular compound.

MS is applicable to all substances that have a sufficiently high vapor pressure. This usually includes substances whose boiling point is below 450˚C. MS permits qualitative and quantitative analysis of liquids, solids, and gases.

Inductively Coupled Plasma

Inductively coupled plasma (ICP) involves the aspiration of a sample in a stream of argon gas, and then its ionization by an applied radio frequency field. The field is inductively coupled to the ionized gas by a coil surrounding a quartz torch that supports and encloses the plasma. The sample aerosol is heated in the plasma, the molecules become almost completely dissociated and then the atoms present in the sample emit light at their characteristic frequencies. The light passes through a monochromator and onto a detector.

The high temperature (7,000˚K) of the argon plasma gas produces efficient atomic emission and permits low detection limits for many elements. As with atomic absorption (AA), ICP does not distinguish between oxidation states (e.g., Cr^{3+} and Cr^{6+}) of the same element—the total element present is determined. Advantages of ICP include complete ionization and no matrix interferences as in AA. ICP allows simultaneous analysis of many elements in a short time. It is sensitive to part-per-billion levels.

Disadvantages of ICP include its high cost and its intolerance to samples with greater than 3% dissolved solids. Background corrections usually compensate for interferences due to background radiation from other elements and the plasma gases. Physical interferences, due to viscosity or surface tension, can cause significant errors. These errors are reduced by diluting the sample. Although chemical interferences are insignificant in the ICP method, they can be greatly minimized by careful selection of the instrument's operating conditions, by matrix matching, or by buffering the sample.

ICP is applicable to the analysis of major components and trace contaminants in plating solutions. It is also useful for waste-treatment analysis.

PHOTOMETRIC METHODS

Photometric methods are based on the absorption of ultraviolet (200–400 nm) or visible (400–1,000 nm) radiant energy by a species in solution. The amount of energy absorbed is proportional to the concentration of the absorbing species in solution. Absorption is determined spectrophotometrically or colorimetrically.

The sensitivity and accuracy of photometric methods must be frequently checked by testing standard solutions in order to detect electrical, optical, or mechanical malfunctions in the analytical instrument.

Spectrophotometry and Colorimetry

Spectrophotometry involves analysis by the measurement of the light absorbed by a solution. The absorbance is proportional to the concentration of the analyte in solution. Spectrophotometric methods are most often used for the analysis of metals with concentrations of up to 2%.

Spectrophotometers consist of a light source (tungsten or hydrogen), a monochromator, a sample holder, and a detector. Ultraviolet or visible light of a definite wavelength is used as the light source. Detectors are photoelectric cells that measure the transmitted (unabsorbed) light. Spectrophotometers differ from photometers in that they utilize monochromators, whereas photometers use filters to isolate the desired wavelength region. Filters isolate a wider band of light.

In spectrophotometric titrations, the cell containing the analyte solution is placed in the light path of a spectrophotometer. Titrant is added to the cell with stirring, and the absorbance is measured. The endpoint is determined graphically. Applications of this titration include the analysis of a mixture of arsenic and antimony and the analysis of copper with ethylene diamine tetra acetic acid (EDTA).

The possibility of errors in spectrophotometric analyses is increased when numerous dilutions are required for an analysis.

Colorimetry involves comparing the color produced by an unknown quantity of a substance with the color produced by a standard containing a known quantity of that substance. When monochromatic light passes through the colored solution, a certain amount of the light, proportional to the concentration of the substance, will be absorbed. Substances that are colorless or only slightly colored can be rendered highly colored by a reaction with special reagents.

In the standard series colorimetric method, the analyte solution is diluted to a certain volume (usually 50 or 100 ml) in a Nessler tube and mixed. The color of the solution is compared with a series of standards similarly prepared. The concentration of the analyte equals the concentration of the standard solution whose color it matches exactly. Colors can also be compared to standards via a colorimeter (photometer), comparator, or spectrophotometer.

The possible errors in colorimetric measurements may arise from the following sources: turbidity, sensitivity of the eye or color blindness, dilutions, photometer filters, chemical interferences, and variations in temperature or pH.

Photometric methods are available for the analysis of the following analytes:

Anodizing solutions: Fe, Cu, Mn
Brass solutions: Fe
Cadmium solutions: Fe, Ti, Zn, Cu, Ni
Chromium solutions: Cr, Fe, Ni, Cu, Se
Acid copper solutions: Cl, Fe
Alkaline copper solutions: Fe, Se
Gold solutions: Au, Ni, In, Co, Cu, Fe, PO_4
Iron solutions: Mn, NH_3
Lead and tin-lead solutions: Pb
Nickel solutions: Cr, Cu, Zn, Fe, Co, NH_3
Palladium solutions: Pd, Cr, NH_3
Platinum solutions: Pt
Rhodium solutions: Rh
Silver solutions: Ni, Cu, Sb
Acid tin solutions: Fe, Cu
Alkaline tin solutions: Cu, Pb, Zn

Acid zinc solutions: Cu, Fe
Alkaline zinc solutions: Cu, Fe
Wastewater: Cr^{6+}, Ni, Cu, Fe, Zn, Pb, Al, B, NO_3, NO_2, PO_4, Cl, CN, wetting agents.

Atomic Absorption

Metals in plating and related solutions can be readily determined by AA spectrophotometry. Optimum ranges, detection limits, and sensitivities of metals vary with the various available instruments.

In *direct-aspiration atomic absorption* (DAAA) analysis, the flame (usually air-acetylene or nitrous oxide-acetylene) converts the sample aerosol into atomic vapor, which absorbs radiation from a light source. A light source from a hollow cathode lamp or an electrodeless discharge lamp is used, which emits a spectrum specific to the element being determined. The high cost of these lamps is a disadvantage of the AA method. A detector measures the light intensity to give a quantitative determination.

DAAA is similar to flame photometry in that a sample is aspirated into a flame and atomized. The difference between the two methods is that flame photometry measures the amount of emitted light, whereas DAAA measures the amount of light absorbed by the atomized element in the flame. In DAAA, the number of atoms in the ground state is much greater than the number of atoms in any of the excited states of the spectroscopic methods. Consequently, DAAA is more efficient and has better detection limits than the spectroscopic methods.

Spectral interferences occur when a wavelength of an element being analyzed is close to that of an interfering element. The analysis will result in an erroneously high measurement. To compensate for this interference, an alternate wavelength or smaller slit width is used.

When the physical properties (e.g., viscosity) of a sample differ from those of the standard, matrix interferences occur. Absorption can be enhanced or suppressed. To overcome these interferences, matrix components in the sample and standard are matched or a release agent, such as EDTA or lanthanum, is added.

Chemical interferences are the most common interferences encountered in AA analysis. They result from the nonabsorption of molecularly bound atoms in the flame. These interferences are minimized by using a nitrous oxide-acetylene flame instead of an air-acetylene flame to obtain the higher flame temperature needed to dissociate the molecule or by adding a specific substance (e.g., lanthanum) to render the interferant harmless. Chemical interferences can also be overcome by extracting the element being determined or by extracting the interferant from the sample.

The sensitivity and detection limits in AA methods vary with the instrument used, the nature of the matrix, the type of element being analyzed, and the particular AA technique chosen. It is best to use concentrations of standards and samples within the optimum concentration range of the AA instrument. When DAAA provides inadequate sensitivity, other specialized AA methods, such as graphite furnace AA, cold vapor AA, or hydride AA, are used.

In *graphite furnace AA* (GFAA), the flame that is used in DAAA is replaced with an electrically heated graphite furnace. A solution of the analyte is placed in a graphite tube in the furnace, evaporated to dryness, charred, and atomized. The metal atoms being analyzed are propelled into the path of the radiation beam by increasing the temperature of the furnace and causing the sample to be volatilized. Only very small amounts of sample are required for the analysis.

GFAA is a very sensitive technique and permits very low detection limits. The increased sensitivity is due to the much greater occupancy time of the ground state atoms in the optical path as compared with DAAA. Increased sensitivity can also be obtained by using larger sample volumes or by using an argon-hydrogen purge gas mixture instead of nitrogen. Because of its extreme sensitivity, determining the optimum heating times, temperature, and matrix modifiers is necessary to overcome possible interferences.

Interferences may occur in GFAA analysis due to molecular absorption and chemical effects. Background corrections compensate for the molecular absorption interference. Specially coated graphite tubes minimize its interaction with some elements. Gradual heating helps to decrease background interference, and permits determination of samples with complex mixtures of matrix components.

The GFAA method has been applied to the analysis of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin.

Cold vapor atomic absorption (CVAA) involves the chemical reduction of mercury or selenium by stannous chloride and its subsequent analysis. The reduced solution is vigorously stirred in the reaction vessel to obtain an equilibrium between the element in the liquid and vapor phases. The vapor is then purged into an absorption cell located in the light path of a spectrophotometer. The resultant absorbance peak is recorded on a strip chart recorder.

The extremely sensitive CVAA procedure is subject to interferences from some organics, sulfur compounds, and chlorine. Metallic ions (e.g., gold, selenium), which are reduced to the elemental state by stannous chloride, produce interferences if they combine with mercury.

Hydride atomic absorption (HAA) is based on chemical reduction with sodium borohydride to selectively separate hydride-forming elements from a sample. The gaseous hydride that is generated is collected in a reservoir attached to a generation flask, and is then purged by a stream of argon or nitrogen into an argon-hydrogen-air flame. This permits high-sensitivity determinations of antimony, arsenic, bismuth, germanium, selenium, tellurium, and tin.

The HAA technique is sensitive to interferences from easily reduced metals such as silver, copper, and mercury. Interferences also arise from transition metals in concentrations greater than 200 mg/L and from oxides of nitrogen.

Ion Chromatography

In ion chromatography (IC), analytes are separated with an eluent on a chromatographic column based on their ionic charges. Because plating solutions are water based, the soluble components must be polar or ionic; therefore, IC is applicable to the analysis of plating and related solutions.

Ion chromatographs consist of a sample delivery system, a chromatographic separation column, a detection system, and a data handling system.

IC permits the rapid sequential analysis of multiple analytes in one sample. The various detectors available, such as UV-visible, electrochemical, or conductivity, allow for specific detection in the presence of other analytes. IC is suitable for the analysis of metals, anionic and cationic inorganic bath constituents, and various organic plating bath additives. It is also used for continuous on-line operations.

Interferences arise from substances that have retention times coinciding with that of any anion being analyzed. A high concentration of a particular ion may interfere with the resolution of other ions. These interferences can be greatly minimized by gradient elution or sample dilution.

IC has been applied to the analysis of the following analytes in plating and related solutions:

Metals: Aluminum, barium, cadmium, calcium, trivalent and hexavalent chromium, cobalt, copper, gold, iron, lead, lithium, magnesium, nickel, palladium, platinum, silver, tin, zinc.

Ions: Ammonium, bromide, carbonate, chloride, cyanide, fluoborate, fluoride, hypophosphite, nitrate, nitrite, phosphate, potassium, sodium, sulfate, sulfide, sulfite.

Acid Mixtures: Hydrofluoric, nitric, and acetic acids.

Organics: Brighteners, surfactants, organic acids.

ELECTROANALYTICAL METHODS

Electroanalytical methods involve the use of one or more of three electrical quantities—current, voltage, and resistance. These methods are useful when indicators for a titration are unavailable or unsuitable. Although trace analysis may be done quite well by spectroscopic or photometric methods, electroanalytical methods offer ease of operation and relatively lower costs of purchase and maintenance.

Potentiometry

Potentiometry involves an electrode that responds to the activity of a particular group of ions in solution. Potentiometric methods correlate the activity of an ion with its concentration in solution.

In potentiometric titrations, titrant is added to a solution and the potential between an indicator and reference electrode is measured. The reaction must involve the addition or removal of an ion for which an electrode is available. Acid-base titrations are performed with a glass indicator electrode and a calomel reference electrode. The endpoint corresponds to the maximum rate of change of potential per unit volume of titrant added.

Advantages of potentiometric titrations include its applicability to colored, turbid, or fluorescent solutions. It is also useful in situations where indicators are unavailable.

The sensitivity of potentiometric titrations is limited by the accuracy of the measurement of electrode potentials at low concentrations. Solutions that are more dilute than 10^{-5} N cannot be accurately titrated potentiometrically. This is because the experimentally measured electrode potential is a combined potential, which may differ appreciably from the true electrode potential. The difference between the true and experimental electrode potentials is due to the residual current, which arises from the presence of electroactive trace impurities.

The direct potentiometric measurement of single ion concentrations is done with ion selective electrodes (ISEs). The ISE develops an electric potential in response to the activity of the ion for which the electrode is specific. ISEs are available for measuring calcium, copper, lead, cadmium, ammonia, bromide, nitrate, cyanide, sulfate, chloride, fluoride, and other cations and anions.

Cation ISEs encounter interferences from other cations, and anion ISEs encounter interferences from other anions. These interferences can be eliminated by adjusting the sample pH or by chelating the interfering ions. ISE instructions must be reviewed carefully to determine the maximum allowable levels of interferants, the upper limit of the single ion concentration for the ISE, and the type of media compatible with the particular ISE.

Some of the solutions that can be analyzed by potentiometric methods are:

Anodizing solutions: Al, H_2SO_4, $C_2H_2O_4$, CrO_3, Cl
Brass solutions: Cu, Zn, NH_3, CO_3
Bronze solutions: Cu, Sn, NaOH, NaCN, Na_2CO_3
Chromium solutions: Cr, Cl
Cadmium solutions: Cd, NaOH, NaCN, Na_2CO_3
Acid copper solutions: Cl
Alkaline copper solutions: NaOH, NaCN, Na_2CO_3
Gold solutions: Au, Ag, Ni, Cu
Lead and tin/lead solutions: Pb, Sn, HBF_4
Nickel solutions: Co, Cu, Zn, Cd, Cl, H_3BO_3
Silver solutions: Ag, Sb, Ni
Acid tin solutions: Sn, HBF_4, H_2SO_4
Alkaline tin solutions: Sn, NaOH, $NaCO_3$, Cl
Zinc solutions: Zn

Conductometry

Electrolytic conductivity measures a solution's ability to carry an electric current. A current is produced by applying a potential between two inert metallic electrodes (e.g., platinum) inserted into the solution being tested. When other variables are held constant, changes in the concentration of an electrolyte result in changes in the conductance of electric current by a solution.

In conductometric titrations, the endpoint of the titration is obtained from a plot of conductance against the volume of titrant. Excessive amounts of extraneous foreign electrolytes can adversely affect the accuracy of a conductometric titration.

Conductometric methods are used when wet or potentiometric methods give inaccurate results due to increased solubility (in precipitation reactions) or hydrolysis at the equivalence point. The methods are accurate in both dilute and concentrated solutions, and they can also be used with colored solutions.

Conductometric methods have been applied to the analysis of Cr, Cd, Co, Fe, Ni, Pb, Ag, Zn, CO_3, Cl, F, and SO_4.

Polarography

In polarography, varying voltage is applied to a cell consisting of a large mercury anode (reference electrode) and a small mercury cathode (indicator electrode) known as a dropping mercury electrode (DME). Consequent changes in current are measured. The large area of the mercury anode precludes any polarization. The DME consists of a mercury reservoir attached to a glass capillary tube with small mercury drops falling slowly from the opening of the tube. A saturated calomel electrode is sometimes used as the reference electrode.

The electrolyte in the cell consists of a dilute solution of the species being determined in a medium of supporting electrolyte. The supporting electrolyte functions to carry the current in order to raise the conductivity of the solution. This ensures that if the species to be determined is charged, it will not migrate to the DME. Bubbling an inert gas, such as nitrogen or hydrogen, through the solution prior to running a polarogram, will expel dissolved oxygen in order to prevent the dissolved oxygen from appearing on the polarogram.

Reducible ions diffuse to the DME. As the applied voltage increases, negligible current flow results until the decomposition potential is reached for the metal ion being determined. When the ions are reduced at the same rate as they diffuse to the DME, no further increases in current occur, as the current is limited by the diffusion rate. The half-wave potential is the potential at which the current is 50% of the limiting value.

Polarograms are obtained by the measurement of current as a function of applied potential. Half-wave potentials are characteristic of particular substances under specified conditions. The limiting current is proportional to the concentration of the substance being reduced. Substances can be analyzed quantitatively and qualitatively if they are capable of undergoing anodic oxidation or cathodic reduction. As with other instrumental methods, results are referred to standards in order to quantitate the method.

Advantages of polarographic methods include their ability to permit simultaneous qualitative and quantitative determinations of two or more analytes in the same solution. Polarography has wide applicability to inorganic, organic, ionic, or molecular species.

Disadvantages of polarography include the interferences caused by large concentrations of electropositive metals in the determination of low concentrations of electronegative metals. The very narrow capillary of the DME occasionally becomes clogged.

Polarographic methods are available for the following solutions:

Anodizing solutions: Cu, Zn, Mn
Brass solutions: Pb, Cd, Cu, Ni, Zn
Bronze solutions: Pb, Zn, Al, Cu, Ni
Cadmium solutions: Cu, Pb, Zn, Ni

Table II. Reactions That Can Be Analyzed by Amperometry

Analyte	*Titrant*	*Supporting Electrolyte*
Fluoride	Lead nitrate	Potassium chloride
Gold	Hydroquinone	Sulfuric acid
Nickel	Dimethylglyoxime	Chloride
Lead	Sodium fluoride	Chloride
Bromide	Silver nitrate	Nitric acid
Calcium	EDTA	Ammonia
Cadmium	EDTA	Ammonia
Chloride	Silver nitrate	Nitric acid
Indium	EDTA	Weak acid

EDTA, ethylene diamine tetra acetic acid.

Chromium solutions: Cu, Ni, Zn, Cl, SO_4
Acid copper solutions: Cu, Cl
Alkaline copper solutions: Zn, Fe, Pb, Cu
Gold solutions: Au, Cu, Ni, Zn, In, Co, Cd
Iron solutions: Mn
Lead and tin-lead solutions: Cu, Cd, Ni, Zn, Sb
Nickel solutions: Cu, Pb, Zn, Cd, Na, Co, Cr, Mn
Palladium solutions: Pd, Cr^{3+}, Cr^{6+}
Rhodium solutions: Rh
Silver solutions: Sb, Cu, Cd
Acid tin solutions: Sn^{4+}, Cu, Ni, Zn
Alkaline tin solutions: Pb, Cd, Zn, Cu
Acid zinc solutions: Cu, Fe, Pb, Cd
Alkaline zinc solutions: Pb, Cd, Cu
Wastewater: Cd, Cu, Cr^{3+}, Ni, Sn, Zn

Amperometry

Amperometric titrations involve the use of polarography as the basis of an electrometric titration. Voltage applied across the indicator electrode (e.g., DME or platinum) and reference electrode (e.g., calomel or mercury) is held constant and the current passing through the cell is measured as a function of titrant volume added. The endpoint of the titration is determined from the intersection of the two straight lines in a plot of current against volume of titrant added. Polarograms are run to determine the optimum titration voltage.

Amperometric titrations can be carried out at low analyte concentrations at which volumetric or potentiometric methods cannot yield accurate results. They are temperature independent and more accurate than polarographic methods. Although amperometry is useful for oxidation-reduction or precipitation reactions, few acid-base reactions are determined by this method.

Some of the reactions that can be analyzed by amperometric methods are given in Table II.

Electrogravimetry

In electrogravimetry, the substance to be determined is separated at a fixed potential on a preweighed inert cathode, which is then washed, dried, and weighed. Requirements for an accurate electrogravimetric analysis include good agitation, smooth adherent deposits, and proper pH, temperature, and current density.

Table III. Molarities and Normalities of Standard Solutions

Standard Solution	*Formula*	*Normality*	*Molarity*
EDTA	$C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O$	0.2	0.1
Ferrous ammonium sulfate	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	0.1	0.1
Hydrochloric acid	HCl	1.0	1.0
Iodine	I_2	0.1	0.1
Potassium dichromate	$K_2Cr_2O_7$	0.1	0.02
Potassium iodide-iodate	KI-KIO3	0.1	0.0167
Potassium permanganate	$KMnO_4$	0.1	0.02
Potassium thiocyanate	KSCN	0.1	0.1
Silver nitrate	$AgNO_3$	0.1	0.1
Sodium hydroxide	NaOH	1.0	1.0
Sodium thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	0.1	0.1

EDTA, ethylene diamine tetra acetic acid.

Advantages of electrogravimetry include its ability to remove quantitatively most common metals from solution. The method does not require constant supervision. Disadvantages include long electrolysis times.

Some of the metals that have been determined electrogravimetrically are cadmium, cobalt, copper, gold, iron, lead, nickel, rhodium, silver, tin, and zinc.

SAMPLING

Analyses are accurate only when the sample is truly representative of the solution being analyzed. Each tank should have a reference mark indicating the correct level for the solution, and the bath should always be at this level when the sample is taken. Solutions should be stirred before sampling. If there is sludge in the tank, the solution should be stirred at the end of the day and the bath allowed to stand overnight, taking the sample in the morning.

Solutions should be sampled by means of a long glass tube. The tube is immersed in the solution, the thumb is placed over the upper open end, and a full tube of solution is withdrawn and transferred to a clean, dry container. The solution should be sampled at a minimum of 10 locations in the tank to ensure a representative sample. A quart sample is sufficient for analysis and Hull cell testing, and any remaining solution can be returned to its tank.

STANDARD SOLUTIONS, REAGENTS, AND INDICATORS FOR WET METHODS

Standard solutions, reagents, and indicators can be purchased ready-made from laboratory supply distributors. Unless a laboratory has the experience and high degree of accuracy that is required in preparing these solutions, it is recommended that they be purchased as prepared solutions. Preparations for all the solutions are given here to enable technicians to prepare or recheck their solutions.

A standard solution is a solution with an accurately known concentration of a substance used in a volumetric analysis. Standardization of standard solutions requires greater accuracy than routine volumetric analyses. An error in standardization causes errors in all analyses that are made with the solution; therefore, Primary Standard Grade chemicals should be used to standardize standard solutions.

The strengths of standard solutions are usually expressed in terms of normality or molarity. Normalities of standard solutions and their equivalent molarities are listed in Table III. The methods to standardize all the standard solutions required for the analysis of plating and related solutions are listed in Table IV.

Indicators are added to solutions in volumetric analyses to show color change or onset of turbidity, signifying the endpoint of a titration. The indicators required for all of the analyses and their preparations are listed in Table V. Analytical Grade chemicals should be used in preparing analytical reagents (Table VI) and Reagent Grade acids should be used (Table VII). When chemicals of lesser purity are used, the accuracy of the results will be diminished.

Tables VIII through XII provide specific methods for testing the constituents of electroplating, electroless, and anodizing baths, as well as acid dips and alkaline cleaners.

SAFETY

As with any laboratory procedure, the accepted safety rules for handling acids, bases, and other solutions should be followed. Acids are always added to water, not the reverse. Mouth pipettes should not be used for pipetting plating solutions. Safety glasses should always be worn, and care should be exercised to avoid skin and eye contact when handling chemicals. A fume hood should be used when an analytical method involves the liberation of hazardous or annoying fumes. Laboratory staff should be well versed in the first-aid procedures required for various chemical accidents.

DETERMINATION OF CATHODE EFFICIENCY

The procedure for determining cathode efficiency, using the setup pictured in Fig. 1, is as follows:

1. Connect the copper coulometer in series with the test cell.
2. The copper coulometer solution should contain 30 oz/gal copper sulfate pentahydrate and 8 oz/gal sulfuric acid.
3. Use the same anodes, temperature, and agitation in the test solution that are used in the plating bath.
4. Plate at 0.4 A (30 A/ft^2) for a minimum of 10 minutes.
5. Rinse both cathodes, dry in acetone, and weigh.

$$\% \text{ Cathode Efficiency} = \frac{\text{weight in grams of test metal} \times \text{valence of test metal in bath} \times 3177}{\text{weight in grams of copper metal} \times \text{atomic weight of test metal}}$$

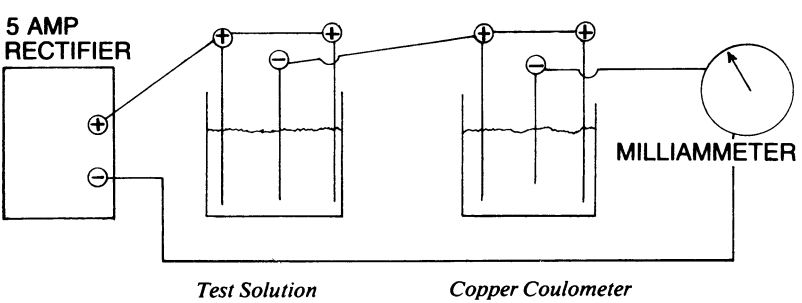

Fig. 1. Test setup for determination of cathode efficiency. Use 500-ml beakers and 1 × 2-in. brass cathodes. The anodes for the test solution should match that used in the plating bath. Use copper anodes for the coulometer.

Table IV. Standardization of Standard Solutions

Solution	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant; wt-sample in grams)*
0.1 M EDTA 37.0 g $Na_2EDTA{\cdot}2H_2O$ per liter H_2O	5.0 g $CaCO_3$ dissolved in 1:3 HCl and diluted to 500 ml in a volumetric flask. Pipette 20-ml sample, add 100 ml H_2O,[a] 10 ml pH 10 buffer, and EBT powder.	EDTA	Red-blue	M EDTA = (wt $CaCO_3$ × ml sample)/(ml EDTA × 50.05)
0.1 N HCl 9 ml 36% HCl per liter H_2O	0.2 g Na_2CO_3, 125 ml H_2O, and bromocresol green.	HCl	Blue-green	N HCl = (wt Na_2CO_3)/(ml × 0.05299)
1.0 N HCl 89 ml 36% HCl per liter H_2O	2.0 g Na_2CO_3, 125 ml H_2O, and bromocresol green.	HCl	Blue-green	N HCl = (wt Na_2CO_3)/(ml × 0.05299)
0.1 N I_1 12.7 g I_2, 24.0 g Kl per liter H_2O	0.2 g As_2O_3, 20 ml 1.0 N NaOH, gently heat until As_2O_3 dissolves, cool, add phenolphthalein, 1.0 N HCl added from pink to colorless, 100 ml H_2O, 1 ml conc. HCl, 2 g bicarbonate added slowly, and starch solution.	I_2	Colorless-blue	N I_2 = (wt As_2O_3/(ml × 0.04946)
0.01 N $Hg(NO_3)_2$ 1.083 g HgO, 5 ml 50% HNO_3 per liter H_2O	7.5 g KCl dissolved in H_2O and diluted to 1,000 ml in a volumetric flask. Pipette 2-ml sample, add 100 ml H_2O, and 15 ml 20% trichloroacetic acid.	$Hg(NO_3)_2$	Colorless-purple	N $Hg(NO_3)_2$ = (wt KCl × ml sample)/(ml $Hg(NO_3)_2$ × 74.56)
0.1 N KI-KIO_3 3.6 g KIO_3, 1.0 g NaOH, 10.0 g KI per liter H_2O	In 500-ml flask add 0.20 g Sn, 100 ml conc. HCl, 2 drops $SbCl_3$ solution, let stand at room temperature till dissolved. Add 180 ml H_2O, 5-in. folded "U"-shaped nickel strip, and 5.0 g reduced iron powder. Stopper flask with rubber stopper fitted with ¼-in. glass tube immersed into a saturated $NaHCO_3$ solution. Heat solution on hot-plate to boil for 20 minutes and then place in cooling tank and allow to cool to room temperature. Make sure glass outlet tube is immersed in the $NaHCO_3$. Remove stopper and add starch solution.	KI-KIO_3	Colorless-blue	N KI-KIO_3 = (wt Sn)/(ml × 0.059345)

Table IV. Standardization of Standard Solutions *(cont.)*

Solution	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant; wt-sample in grams)*
0.1 N $KMnO_4$ 3.2 g $KMnO_4$ per liter H_2O	Heat $KMnO_4$ solution to near boiling for 30 minutes and let stand overnight. Filter through a sintered glass crucible. Then, to standardize: add 0.2 g $Na_2C_2O_4$, 200 ml H_2O, 30 ml 20% H_2SO_4, heat to 185–195°F.	$KMnO_4$	Colorless-pink	N $KMnO_4$ = (wt $Na_2C_2O_4$)/(ml × 0.0670)
0.1 N KSCN 9.7 g KSCN per liter H_2O	0.3 g Ag, 15 ml 50% HNO_3, 100 ml H_2O, and FAS.	KSCN	Colorless-red	N KSCN = (wt Ag)/(ml × 0.10787)
0.1 $AgNO_3$ 17.0 g $AgNO_3$ per liter H_2O	0.2 g NaCl, 125 ml H_2O, and K_2CrO_4.	$AgNO_3$	Yellow-red	N $AgNO_3$ = (wt NaCl)/(ml × 0.05845)
0.1 N NaOH 4.0 g NaOH per liter H_2O	0.5 g potassium hydrogen phthalate ($KHC_8H_4O_4$), 125 ml H_2O, and phenolphthalein.	NaOH	Colorless-pink	N NaOH = (wt $KHC_8H_4O_4$)/(ml × 0.20422)
1.0 N NaOH 40.0 g NaOH per liter H_2O	4.0 g potassium hydrogen phthalate ($KHC_8H_4O_4$), 125 ml H_2O, and phenolphthalein indicator.	NaOH	Colorless-pink	N NaOH = (wt $KHC_8H_4O_4$)/(ml × 0.20422)
0.1 N $Na_2S_2O_3$ 25.0 g $Na_2S_2O_3 \cdot 5H_2O$ per liter H_2O	Add 0.1 g Na_2CO_3 to $Na_2S_2O_3$ solution and let stand for 24 hours. To standardize: add 0.12 g KIO_3, 2 g KI, 25 ml H_2O, and 8 ml 10% HCl. Titrate to light yellow with $Na_2S_2O_3$ and add 2 ml starch solution.	$Na_2S_2O_3$	Blue-colorless	N $Na_2S_2O_3$ = (wt KIO_3)/(ml × 0.03567)
0.1 N $Th(NO_3)_4$ 14.0 g $Th(NO_3)_4 \cdot 4H_2O$ per liter H_2O	5.0 g NaF dissolved in H_2O and diluted to 1,000 ml in a volumetric flask. Pipette 10-ml sample, add 100 ml H_2O, alizarin indicator, 2% HNO_3, dropwise from pink to yellow, and 3 ml fluoride buffer.	$Th(NO_3)_4$	Yellow-pink	N = (wt NaF per liter)/(ml × 4.1998)

EDTA, ethylene diamine tetra acetic acid.
[a]Use deionized or distilled water for all solutions.

Table V. Indicators for Analyses

Alizarin	1.0 g sodium alizarin sulfonate, 1,000 ml H_2O.
Bromocresol Green	0.4 g bromocresol green, 1,000 ml H_2O, 0.5 ml 1.0 N NaOH.
Bromocresol Purple	0.4 g bromocresol purple, 1,000 ml H_2O, 1.0 ml 1.0 N NaOH.
EBT Powder	2.0 g Eriochrome Black T, 198 g NaCl.
EBT Solution	5.0 g Eriochrome Black T, 150 ml methanol, 100 ml triethanolamine.
FAS	50 g ferrous ammonium sulfate, 950 ml H_2O, 10 ml conc. HNO_3.
K_2CrO_4	20 g K_2CrO_4, 980 ml H_2O.
Methyl Orange	1.0 g methyl orange (sodium salt), 1,000 ml H_2O.
Murexide	2.0 g murexide, 198 g NaCl.
PAN	1.0 g peroxyacetal nitrate, 1,000 ml methanol.
Phenolphthalein	1.0 g phenolphthalein, 500 ml ethanol, 500 ml H_2O.
Starch Solution	10.0 g starch, 1,000 ml hot H_2O, 0.5 ml formaldehyde.
Sulfo Orange	100 ml sulfo orange, 100 g NaCN, 845 ml H_2O.

Note: Use deionized or distilled water for preparation of all solutions.

Table VI. Reagents for Analyses

Ammonium Oxalate Solution	40 g ammonium oxalate, 960 ml H_2O.
Dimethylglyoxime Solution	10 g dimethylglyoxime, 1,000 ml ethanol.
Fluoride Buffer	Dissolve 40 g monochloroacetic acid in 400 ml H_2O and divide the solution in two equal parts. Add phenolphthalein to one part and titrate with 1.0 N NaOH from colorless to pink. Mix both parts and add H_2O to 1,000 ml.
KF Solution	100 g KF dissolved in 1,000 ml H_2O. Neutralize to pH 7.0 with 1.0 N NaOH.
NaCN Solution	100 g NaCN, 900 ml H_2O.
Na_2SO_4 Solution	135 g Na_2SO_4, 950 ml H_2O.
pH 10 Buffer	350 ml conc. NH_4OH, 54 g NH_4Cl, 625 ml H_2O.
Reducing Solution	100 ml conc. HCl, 250 ml conc. $HC_2H_3O_2$, 200 ml ethanol, 450 ml H_2O.
Rochelle Solution	200 g Rochelle salts, 800 ml H_2O.
$SbCl_3$ Solution	2.0 g $SbCl_3$, 100 ml 50% HCl.
Silver Nitrate Solution	10 g $AgNO_3$, 95 ml H_2O.
Sodium Sulfite Solution	100 g sodium sulfite, 950 ml H_2O. Adjust to pH 9.0 with 1.0 N NaOH or 1.0 N HCl. Solution has a 1-week shelf life.
Tartaric Acid Solution	150 g tartaric acid, 950 ml H_2O.

Note: Use deionized or distilled water for preparation of all reagents.

Table VII. Properties of Reagent Grade Acids

Acid	*Formula*	*Wt %*	*Specific Gravity (60˚F)*	*Pounds/Gallon*
Acetic	$HC_2H_3O_2$	99.0	1.050	8.76
Fluoboric	HBF_4	48.0	1.365	11.38
Formic	$HCHO_2$	98.0	1.220	10.17
Hydrobromic	HBr	48.0	1.490	12.43
Hydrochloric	HCl	36.0	1.183	9.87
Hydrofluoric	HF	70.0	1.256	10.48
Nitric	HNO_3	70.0	1.420	11.84
Phosphoric	H_3PO_4	85.0	1.690	14.09
Sulfuric	H_2SO_4	93.0	1.835	15.30

Table VIII. Test Methods for Electroplating Solutions

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Brass					
CuCN (Method I)	2 ml	15 ml conc. HNO_3, heat to blue color, 100 ml H_2O,[a] conc. NH_4OH to deep blue, heat to 140°F, and add PAN.	0.1 M EDTA	Purple-green	CuCN (oz/gal) = 2.985 × M × [2 × CuCN ml − 0.8 × $Zn(CN)_2$ ml]
CuCN (Method II)	2 ml	100 ml H_2O, 15 ml conc. HNO_3, heat to blue color and disappearance of brown fumes, NH_4OH to deep blue, acetic acid to light blue, 5 g KI. Titrate with $Na_2S_2O_3$ to pale yellow, add 5 ml starch solution, continue titrating to colorless.	0.1 N $Na_2S_2O_3$	Blue-colorless	CuCN (oz/gal) = ml × 5.971 × N
$Zn(CN)_2$	5 ml	100 ml H_2O, 10 ml pH 10 buffer, EBT powder, and 15 ml 10% formaldehyde.	0.1 M EDTA	Red-blue	$Zn(CN)_2$ (oz/gal) = ml × 3.131 × M
NaCN or KCN	5 ml	100 ml H_2O and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	NaCN (oz/gal) = ml × 2.614 × N KCN (oz/gal) = ml × 3.473 × N
NaOH or KOH	5 ml	25 ml H_2O and 5 ml sulfo-orange.	1.0 N HCl	Orange-yellow	NaOH (oz/gal) = ml × 1.067 × N KOH (oz/gal) = ml × 1.496 × N
Na_2CO_3 or K_2CO_3	10 ml	100 ml hot H_2O, 35 ml 10% $Ba(NO_3)_2$, allow to settle, filter, wash filter twice with hot H_2O, transfer filter paper and precipitate to a beaker, add 100 ml H_2O, and methyl orange.	1.0 N HCl	Orange-pink	Na_2CO_3 (oz/gal) = ml × 0.707 × N K_2CO_3 (oz/gal) = ml × 0.921 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
$KNaC_4H_4O_6 \cdot 4H_2O$	5 ml	25 ml 20% H_2SO_4, filter, wash flask and filter paper twice each with H_2O, and boil the collected filtrate 5 minutes.	0.1 N $KMnO_4$	Colorless-pink	$KNaC_4H_4O_6 \cdot 4H_2O$ (oz/gal) = ml × 1.250 × N
Bronze					
Cu (Method I)	2 ml	15 ml conc. HNO_3, heat to blue color, 100 ml H_2O, conc. NH_4OH to deep blue, heat to 140°F and add PAN.	0.1 M EDTA	Purple-green	Cu (oz/gal) = ml × 4.236 × M
Cu (Method II)	2 ml	100 ml H_2O, 15 ml conc. HNO_3, heat to blue color and disappearance of brown fumes, NH_4OH to deep blue, acetic acid to light blue, 5 g KI. Titrate with $Na_2S_2O_3$ to pale yellow, add 5 ml starch solution, continue titrating to colorless.	0.1 N $Na_2S_2O_3$	Blue-colorless	Cu (oz/gal) = ml × 4.236 × N
Sn	5 ml	100 ml H_2O, 50 ml conc. HCl, 3.0 g iron powder in 500-ml flask. Stopper flask with stopper fitted with a glass tube immersed in a beaker filled with saturated bicarbonate solution. Heat gently till iron dissolves. Cool to room temperature, making sure outlet tube is immersed in bicarbonate solution. Add 10 ml starch solution and bicarbonate during titration.	0.1 N KI-KIO_3	Clear-blue	Sn (oz/gal) = ml × 1.583 × N
NaCN or KCN	5 ml	100 ml H_2O and 10 ml 10KI.	0.1 N $AgNO_3$	Clear-turbid	NaCN (oz/gal) = ml × 2.614 × N KCN (oz/gal) = ml × 3.473 × N
NaOH or KOH	5 ml	25 ml H_2O and 5 ml sulfo-orange.	1.0 N HCl	Orange-yellow	NaOH (oz/gal) = ml × 1.067 × N KOH (oz/gal) = ml × 1.496 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Na_2CO_3 or K_2CO_3	10 ml	100 ml hot H_2O, 35 ml 10% $Ba(NO_3)_2$, allow to settle, filter, wash filter twice with hot H_2O, transfer filter paper and precipitate to a beaker, add 100 ml H_2O and methyl orange.	1.0 N HCl	Orange-pink	Na_2CO_3 (oz/gal) = ml × 0.707 × N K_2CO_3 (oz/gal) = ml × 0.921 × N
$KNaC_4H_4O_6 \cdot 4H_2O$	5 ml	25 ml 20% H_2SO_4, filter, wash flask and filter paper twice each with H_2O, and boil the collected filtrate 5 minutes.	0.1 N $KMnO_4$	Colorless-pink	$KNaC_4H_4O_6 \cdot 4H_2O$ (oz/gal) = ml × 1.250 × N
Cadmium Cyanide					
Cd	2 ml	100 ml H_2O, 10 ml pH 10 buffer, EBT powder, and 15 ml 10% formaldehyde.	0.1 M EDTA	Red-blue	Cd (oz/gal) = ml × 7.493 × M
Total and Free NaCN	5 ml	100 ml H_2O, 15 ml conc. NH_4OH, and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	Total NaCN (oz/gal) = ml × 2.614 × N Free NaCN (oz/gal) = Total NaCN − 1.744 × Cd
NaOH	5 ml	25 ml H_2O and 5 ml sulfo-orange.	1.0 N HCl	Orange-yellow	NaOH (oz/gal) = ml × 1.067 × N
Na_2CO_3	10 ml	100 ml hot H_2O, 35 ml 10% $Ba(NO_3)_2$, allow to settle, filter, wash filter twice with hot H_2O, transfer filter paper and precipitate to a beaker, add 100 ml H_2O and methyl orange.	1.0 N HCl	Orange-pink	Na_2CO_3 (oz/gal) = ml × 0.707 × N
Cadmium Fluoborate					
Cd	2 ml	100 ml H_2O, 10 ml pH 10 buffer, EBT powder, and 15 ml 10% formaldehyde.	0.1 M EDTA	Red-blue	Cd (oz/gal) = ml × 7.493 × M

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
NH_4BF_4	5 ml	50 ml H_2O, boiling chips, 50 ml 20% NaOH in Kjeldahl flask. Attach flask to the distillation apparatus with the collection tube from the condenser immersed in a beaker containing 100 ml saturated H_3BO_3 solution. Boil flask till 20 ml remain in still. Remove beaker and add methyl orange.	0.1 N HCl	Yellow-red	NH_4BF_4 (oz/gal) = ml × 2.795 × N
Cadmium Sulfate					
Cd	2 ml	100 ml H_2O, 10 ml pH 10 buffer, EBT powder, and 15 ml 10% formaldehyde.	0.1 M EDTA	Red-blue	Cd (oz/gal) = ml × 7.493 × M
H_2SO_4	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-yellow/green	100% H_2SO_4 (oz/gal) = ml × 0.654 × N
Chromium					
$CrO_3(Cr^{6+})$	10 ml of stock	10-ml sample into 500-ml volumetric flask. Pipette 10 ml of stock, add 100 ml H_2O, 2 g ammonium bifluoride, 15 ml conc. HCl, 10 ml 10% KI, and starch solution. (See Table XIII for alternate methods.)	0.1 N $Na_2S_2O_3$	Blue to colorless	CrO_3 (oz/gal) = ml × 22.219 × N
Cr^{3+}	10 ml of stock	10-ml sample into 500 ml volumetric. Pipette 10 ml of stock, add 200 ml H_2O, 0.25 g Na_2O_2, boil gently 30 minutes, maintain volume at 200 ml with H_2O. Cool, add 2 g ammonium bifluoride, 15 ml conc. HCl, 10 ml 10% KI, and starch solution.	0.1 N $Na_2S_2O_3$	Blue to colorless	Cr^{3+} (oz/gal) = (ml × 22.219 × N − Cr^{6+}) × 0.520

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
SO_4	25 ml	100 ml H_2O, 100 ml reducing solution, boil 30 minutes, remove from heat, add 50 ml 10% $Ba(NO_3)_2$, 100 ml hot H_2O. Allow solution to stand for 3–4 hours, heat solution to boiling. Filter in tared Gooch crucible, wash precipitate with hot H_2O, dry in oven at 110°C, cool in desiccator and weigh.			SO_4 (oz/gal) = (weight in grams of precipitate) × 2.195
F	5 ml	100 ml H_2O, 1.0 N NaOH to pH 7.5, using a pH meter previously standardized to pH 7.0. Add 10% $AgNO_3$ solution until the disappearance of the yellow color after settling of the precipitate, filter, wash precipitate, save filtrate. Add Alizarin indicator, 2% HNO_3 till color of solution changes from pink to yellow. Add 3 ml fluoride buffer.	0.1 N $Th(NO_3)_4$	Yellow-pink	F (oz/gal) = ml × 0.507 × N
Copper Cyanide					
CuCN (Method I)	2 ml	15 ml conc. HNO_3, heat to blue color, 100 ml H_2O, conc. NH_4OH to deep blue, heat to 140°F, and add PAN.	0.1 M EDTA	Purple-green	CuCN (oz/gal) = ml × 5.971 × M
CuCN (Method II)	2 ml	100 ml H_2O, 15 ml conc. HNO_3, heat to blue color and disappearance of brown fumes, NH_4OH to deep blue, acetic acid to light blue, 5 g KI. Titrate with $Na_2S_2O_3$ to pale yellow, add 5 ml starch solution, continue titrating to colorless.	0.1 N $Na_2S_2O_3$	Blue-colorless	CuCN (oz/gal) = ml × 5.971 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
NaCN or KCN	5 ml	100 ml H_2O and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	NaCN (oz/gal) = ml × 2.614 × N KCN (oz/gal) = ml × 3.473 × N
NaOH or KOH	5 ml	25 ml H_2O and 5 ml sulfo-orange.	1.0 N HCl	Orange-yellow	NaOH (oz/gal) = ml × 1.067 × N KOH (oz/gal) = ml × 1.496 × N
Na_2CO_3 or K_2CO_3	10 ml	100 ml hot H_2O, 35 ml 10% $Ba(NO_3)_2$, allow to settle, filter, wash filter twice with hot H_2O, transfer filter paper and precipitate to a beaker, add 100 ml H_2O, and methyl orange.	1.0 N HCl	Orange-pink	Na_2CO_3 (oz/gal) = ml × 0.707 × N K_2CO_3, etc K_2CO_3 (oz/gal) = ml × 0.921 × N
$KNaC_4H_4O_6 \cdot 4H_2O$	5 ml	25 ml 20% H_2SO_4, filter, wash flask and filter paper twice each with H_2O, and boil the collected filtrate 5 minutes.	0.1 N $KMnO_4$	Colorless-pink	$KNaC_4H_4O_6 \cdot 4H_2O$ (oz/gal) = ml × 1.250 × N
Copper Fluoborate					
Cu (Method I)	2 ml	100 ml H_2O, conc. NH_4OH to deep blue, heat to 140°F, and add PAN.	0.1 M EDTA	Purple-green	Cu (oz/gal) = ml × 4.236 × M $Cu(BF_4)_2$ (oz/gal) = Cu × 3.73
Cu (Method II)	2 ml	100 ml H_2O, NH_4OH to deep blue, acetic acid to light blue, 5 g KI. Titrate with $Na_2S_2O_3$ to pale yellow, add 5 ml starch solution, continue titrating to colorless.	0.1 N $Na_2S_2O_3$	Blue-colorless	Cu (oz/gal) = ml × 4.236 × N
HBF_4	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-green	100% HBF_4 (oz/gal) = ml × 1.171 × N
Copper Pyrophosphate					
Cu (Method I)	2 ml	100 ml H_2O conc. NH_4OH to deep blue, heat to 140°F and add PAN.	0.1 M EDTA	Purple-green	Cu (oz/gal) = ml × 4.236 × M

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Cu (Method II)	2 ml	100 ml H_2O, NH_4OH to deep blue, acetic acid to light blue, 5 g KI. Titrate with $Na_2S_2O_3$ to pale yellow, add 5 ml starch solution, continue titrating to colorless.	0.1 N $Na_2S_2O_3$	Blue-colorless	Cu (oz/gal) = ml × 4.236 × N
Total P_2O_7	5 ml	100 ml H_2O, 1.0 N HCl dropwise to pH 3.8 (use pH meter standardized at pH 4.0), back-titrate with 1.0 N NaOH if pH 3.8 is overshot, stir 5 minutes and make sure pH is 3.6–3.8, add 50 ml 20% $ZnSO_4$ (adjusted to pH 3.8) and stir 10 minutes. Titrate slowly with stirring using 1.0 N NaOH to pH 3.8 (note these ml NaOH used for calculation).	1.0 N NaOH		Total P_2O_7 (oz/gal) = ml × 2.32 × N + Cu × 1.37 Ratio = [Total P_2O_7 (oz/gal)]/Cu (oz/gal)
NH_3	10 ml	200 ml H_2O, boiling chips, 50 ml 20% NaOH in Kjeldahl flask. Attach flask to the distillation apparatus with the collection tube from the condenser immersed in a beaker containing 100 ml saturated H_3BO_3 solution. Boil flask and distill over 100 ml. Remove beaker and add methyl orange.	0.1 N HCl	Yellow-red	29% NH_3 (oz/gal) = ml × 0.80 × N
Copper Sulfate					
Cu (Method I)	2 ml	100 ml H_2O, conc. NH_4OH to deep blue, heat to 140°F, and add PAN.	0.1 M EDTA	Purple-green	Cu (oz/gal) = ml × 4.236 × M $CuSO_4 \cdot 5H_2O$ (oz/gal) = Cu × 3.93
Cu (Method II)	2 ml	100 ml H_2O, NH_4OH to deep blue, acetic acid to light blue, 5 g KI. Titrate with $Na_2S_2O_3$ to pale yellow, add 5 ml starch solution, continue titrating to colorless.	0.1 N $Na_2S_2O_3$	Blue-colorless	Cu (oz/gal) = ml × 4.236 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Cu (Method III)		(See Table XIV)			
H_2SO_4	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-green	100% H_2SO_4 (oz/gal) = ml × 0.654 × N
Cl	50 ml	50 ml H_2O, 25 ml 50% HNO_3, 5 drops 0.1 N $AgNO_3$. Note: For chloride analysis, carbon-treat the solution prior to analysis.	0.01 N $Hg(NO_3)_2$	Turbid-clear	Cl (ppm) = ml × 709.1 × N
Acid Gold					
Au	20 ml	25 ml conc. H_2SO_4, heat to white fumes, cool, add 10 ml 30% H_2O_2, heat to white fumes. Repeat H_2O_2 and heating until Au sponge coagulates and solution clears. Cool, add 100 ml H_2O, heat at 140°F for 5 minutes. Filter through Gooch crucible containing fiberglass filter paper, wash Au sponge with hot H_2O, dry crucible in oven at 110°C, cool in desiccator and weigh.			Au (g/L) = (weight of gold precipitate) × 50.0
Gold Cyanide					
Au	20 ml	Procedure as above for acid gold.			As above for acid gold.
NaCN or KCN	5 ml	100 ml H_2O, 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	NaCN (g/L) = ml × 19.605 × N KCN (g/L) = ml × 26.048 × N
Na_2CO_3 or K_2CO_3	10 ml	100 ml hot H_2O, 35 ml 10% $Ba(NO_3)_2$, allow to settle, filter, wash filter twice with hot H_2O, transfer filter paper and precipitate to a beaker, add 100 ml H_2O, and methyl orange.	1.0 N HCl	Orange-pink	$NaCO_3$ (g/L) = ml × 5.303 × N K_2CO_3 (g/L) + ml × 6.908 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Indium Cyanide					
In	2 ml	100 ml H_2O, 50 ml Rochelle solution, 10 ml pH 10 buffer, heat to 140˚F, and add EBT powder.	0.1 M EDTA	Red-blue	In (oz/gal) = ml × 7.655 × M
Total KCN	5 ml	100 ml H_2O, 20 ml 20% NaOH, and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	Total KCN (oz/gal) = ml × 3.473 × N
Free KCN	5 ml	100 ml H_2O and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	Free KCN (oz/gal) = ml × 3.473 × N
KOH	5 ml	25 ml H_2O and 5 ml sulfo-orange.	1.0 N HCl	Orange-yellow	KOH (oz/gal) = ml × 1.496 × N
Indium Fluoborate					
In	2 ml	100 ml H_2O, 50 ml Rochelle solution, 10 ml pH 10 buffer, heat to 140˚F, and add EBT powder.	0.1 M EDTA	Red-blue	In (oz/gal) = ml × 7.655 × M
NH_4BF_4	5 ml	50 ml H_2O, boiling chips, 50 ml 20% NaOH in Kjeldahl flask. Attach flask to the distillation apparatus with the collection tube from the condenser immersed in a beaker containing 100 ml saturated H_3BO_3 solution. Boil flask till 20 ml remain in still. Remove beaker and add methyl orange.	0.1 N HCl	Yellow-red	NH_4BF_4 (oz/gal) = ml × 2.795 × N
Iron Chloride					
Fe^{2+}	5 ml	100 ml H_2O, 25 ml 20% $ZnSO_4$, and 50 ml 10% H_2SO_4.	0.1 N $KMnO_4$	Colorless-pink	Fe^{2+} (oz/gal) = ml × 1.489 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Total Fe	5 ml	100 ml H_2O, 5 g Cd flakes, boil 5 minutes, cool and decant liquid into 500-ml flask, wash Cd residue with H_2O and add to flask, add 25 ml 20% $ZnSO_4$, and 50 ml 10% H_2SO_4.	0.1 $KMNO_4$	Colorless-pink	Total Fe (oz/gal) = ml × 1.489 × N Fe^{3+} (oz/gal) = Total Fe − Fe^{2+}
HCl	25 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-yellow/green	36% HCl (oz/gal) = ml × 0.540 × N
Iron Fluoborate					
Fe^{2+}	5 ml	100 ml H_2O, 25 ml 20% $ZnSO_4$, and 50 ml 10% H_2SO_4.	0.1 $KMnO_4$	Colorless-pink	Fe^{2+} (oz/gal) = ml × 1.489 × N
Total Fe	5 ml	100 ml H_2O, 5 g Cd flakes, boil 5 minutes, cool and decant liquid into 500-ml flask, wash Cd residue with H_2O and add to flask, add 25 ml 20% $ZnSO_4$, and 50 ml 10% H_2SO_4.	0.1 N $KMnO_4$	Colorless-pink	Total Fe (oz/gal) = ml × 1.489 × N Fe^{3+} (oz/gal) = Total Fe − Fe^{2+}
NaCl	5 ml	100 ml H_2O, 5 ml 30% H_2O_2, boil for 10 minutes, filter, wash precipitate with hot H_2O, and add K_2CrO_4 to filtrate.	0.1 N $AgNO_3$	Yellow-red	NaCl (oz/gal) = ml × 1.558 × N
Lead Fluoborate					
Pb	1 ml	100 ml H_2O, 25 ml Rochelle solution, 20 ml conc. NH_4OH, and EBT solution.	0.1 M EDTA	Red-blue	Pb (oz/gal) = ml × 27.625 × M
HBF_4	10 ml	100 ml H_2O.	1.0 N NaOH	Clear-turbid	100% HBF_4 (oz/gal) = ml × 1.171 × N
Black Nickel					
Zn	2 ml	100 ml H_2O, 10 ml pH 10 buffer, EBT powder, and 15 ml 10% formaldehyde.	0.1 M EDTA	Red-blue	Zn (oz/gal) = ml × 4.358 × M

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Ni	2 ml	100 ml H_2O, 10 ml conc. NH_4OH, and murexide powder.	0.1 M EDTA	Orange-purple	Ni (oz/gal) = (ml EDTA for Ni − ml EDTA for Zn) × 3.914 × M
NaSCN	10 ml	100 ml H_2O, 15 ml 20% H_2SO_4, and FAS indicator.	0.1 N $AgNO_3$	Red-colorless	NaSCN (oz/gal) = ml × 1.081 × N
Nickel Fluoborate					
Ni	2 ml	100 ml H_2O, 10 ml conc. NH_4OH, and murexide powder.	0.1 M EDTA	Orange-purple	Ni (oz/gal) = ml × 3.914 × M
H_3BO_3	10 ml	25 ml H_2O, 5.0 g mannitol, and bromocresol purple.	1.0 N NaOH	Green-purple	H_3BO_3 (oz/gal) = ml × 0.824 × N
Nickel Strike					
Ni	2 ml	100 ml H_2O, 20 ml conc. NH_4OH, and murexide powder.	0.1 M EDTA	Orange-purple	Ni (oz/gal) = ml × 3.914 × M
HCl	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-yellow/green	36% HCl (fl oz/gal) = ml × 1.115 × N
Nickel Sulfamate					
Ni	2 ml	100 ml H_2O, 20 ml conc. NH_4OH, and murexide powder.	0.1 M EDTA	Orange-purple	Ni (oz/gal) = ml × 3.914 × M
$NiBr_2$	5 ml	100 ml H_2O and K_2CrO_4.	0.1 N $AgNO_3$	Yellow/green-red	$NiBr_2$ (oz/gal) = ml × 2.914 × N
$NiCl_2 \cdot 6H_2O$	20 ml	100 ml H_2O and K_2CrO_4.	0.1 N $AgNO_3$	Yellow/green-red	$NiCl_2 \cdot 6H_2O$ (oz/gal) = ml × 0.792 × N
H_3BO_3	10 ml	25 ml H_2O, 5.0 g mannitol, and bromocresol purple.	1.0 N NaOH	Green-purple	H_3BO_3 (oz/gal) = ml × 0.824 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
SO_4	10 ml	100 ml H_2O, 5 ml 50% HCl, 25 ml $Ba(NO_3)_2$, allow solution to stand 4 hours, filter in tared Gooch crucible, wash precipitate with H_2O, dry in oven at 110°C, cool in desiccator, and weigh.			SO_4 (oz/gal) = (weight in grams of precipitate) × 5.488
Watts Nickel					
Ni	2 ml	100 ml H_2O, 20 ml conc. NH_4OH, and murexide powder.	0.1 M EDTA	Orange-purple	Ni (oz/gal) = ml × 3.914 × M
$NiCl_2 \cdot 6H_2O$	1 ml	100 ml H_2O, 1 ml K_2CrO_4 (if pH is below 4.0, add 1.0 g $CaCO_3$).	0.1 N $AgNO_3$	Yellow/green-red	$NiCl_2 \cdot 6H_2O$ (oz/gal) = ml × 15.847 × N $NiSO_4 \cdot 6H_2O$ (oz/gal) = 4.5 (Ni − 0.247 × $NiCl_2 \cdot 6H_2O$)
H_3BO_3	10 ml	25 ml H_2O, 5.0 g mannitol, and bromocresol purple.	1.0 N NaOH	Green-purple	H_3BO_3 (oz/gal) = ml × 0.824 × N
Nickel-Iron					
Ni	2 ml	100 ml H_2O, 20 ml conc. NH_4OH, and murexide powder.	0.1 M EDTA	Orange-purple	Ni (oz/gal) = ml × 3.914 × M
Fe^{2+}	5 ml	100 ml H_2O, 25 ml 20% $ZnSO_4$, and 50 ml 10% H_2SO_4.	0.1 N $KMnO_4$	Colorless-pink	Fe^{2+} (oz/gal) = ml × 1.489 × N
Total Fe	5 ml	100 ml H_2O, 5 g Cd flakes, boil 5 minutes, cool and decant liquid into 500-ml flask, wash Cd residue with H_2O and add to flask, add 25 ml 20% $ZnSO_4$, and 50 ml 10% H_2SO_4.	0.1 $KMNO_4$	Colorless-pink	Total Fe (oz/gal) = ml × 1.489 × N Fe^{3+} (oz/gal) = Total Fe − Fe^{2+}
H_3BO_3	10 ml	25 ml H_2O, 5.0 g mannitol, and bromocresol purple.	1.0 N NaOH	Green-purple	H_3BO_3 (oz/gal) = ml × 0.824 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Palladium					
Pd	10 ml	10 ml conc. HNO_3, heat until syrupy, 10 ml conc. HNO_3, heat to onset of boiling. Add 250 ml H_2O, cool, slowly add 40 ml dimethylglyoxime solution, allow solution to stand at least 2 hours, filter through No. 3 porosity tared crucible, wash precipitate with H_2O. Dry in oven at 110°C, cool in desiccator, and weigh.			Pd (g/L) = (weight in grams of precipitate) × 31.67
Platinum					
Pt	10 ml	10 ml conc. HCl, heat until syrupy, 100 ml H_2O, 5 g sodium acetate, 1 ml conc. formic acid, heat at 140°F for 5 hours, filter, wash precipitate with hot H_2O. Place filter paper and Pt precipitate in tared porcelain crucible, dry slowly with Bunsen burner, char filter paper, dry Pt precipitate at high temperature for 30 minutes. Cool in desiccator and weigh.			Pt (g/L) = (weight in grams of precipitate) × 100.0
Rhodium					
Rh	25 ml	2 g Mg turnings, conc. HCl dropwise. When all Mg dissolves, add 0.5 g Mg turnings and HCl dropwise to ensure complete precipitation of Rh. Filter solution in tared Gooch crucible containing fiberglass filter paper, wash precipitate with hot H_2O, dry in oven at 110°C, cool in desiccator and weigh.			Rh (g/L) = (weight in grams of precipitate) × 40.0
H_2SO_4 or H_3PO_4	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-yellow/green	100% H_2SO_4 (g/L) = ml × 4.904 × N 100% H_3PO_4 (g/L) = ml × 9.800 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Ruthenium					
Ruthenium cannot be easily determined by volumetric or gravimetric methods. It is usually determined by emission spectroscopy and its analysis should be referred to a competent laboratory.					
Silver Cyanide					
Ag	5 ml	15 ml conc. H_2SO_4, 5 ml conc. HNO_3, heat until the disappearance of orange fumes, cool, add 100 ml cold H_2O, and FAS indicator.	0.1 N KSCN	Colorless-red	Ag (oz/gal) = ml × 2.877 × N AgCN (oz/gal) = Ag × 1.241
NaCN or KCN	5 ml	100 ml H_2O and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	NaCN (oz/gal) = ml × 2.614 × N KCN (oz/gal) = ml × 3.473 × N
Na_2CO_3 or K_2CO_3	10 ml	100 ml hot H_2O, 35 ml 10% $Ba(NO_3)_2$ allow to settle, filter, wash filter twice with hot H_2O, transfer filter paper and precipitate to a beaker, add 100 ml H_2O and methyl orange.	1.0 N HCl	Orange-pink	Na_2CO_3 (oz/gal) = ml × 0.707 × N K_2CO_3 (oz/gal) = ml × 0.921 × N
Tin Fluoborate					
Sn^{2+}	2 ml	100 ml H_2O, 25 ml 50% HCl, 10 ml starch solution, add bicarbonate during titration.	0.1 N KI-KIO_3	Colorless-blue	Sn^{2+} (oz/gal) = ml × 3.956 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Sn^{4+}	2 ml	In 500-ml flask add sample, 100 ml conc. HCl, 2 drops $SbCl_3$ solution. Add 180 ml H_2O, 5-in. folded "U"-shaped nickel strip and 5.0 g reduced iron powder. Stopper flask with rubber stopper fitted with ¼-in. glass tube immersed into a saturated $NaHCO_3$ solution. Heat solution on hot plate to boil for 20 minutes and then place in cooling tank and allow to cool to room temperature. Make sure glass outlet tube is immersed in the $NaHCO_3$. Remove stopper and add starch solution.	0.1 N KI-KIO_3	Colorless-blue	Sn^{4+} (oz/gal) = ml × 3.956 × N − Sn^{2+}
HBF_4	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Clear-turbid	100% HBF_4 (oz/gal) = ml × 1.171 × N
Free H_3BO_3	10 ml	100 ml H_2O, 10 ml Na_2SO_4 solution. Titrate to pH 7.0, using a pH meter previously standardized to pH 7.0. Add 5 g mannitol, titrate from pH 7.0 to pH 8.0 (ml NaOH required for this step are used for the calculation).	1.0 N NaOH		H_3BO_3 (oz/gal) = ml × 0.824 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Tin Stannate					
$K_2SnO_3 \cdot 3H_2O$ $Na_2SnO_3 \cdot 3H_2O$	5 ml	100 ml H_2O, 50 ml conc. HCl, 3.0 g iron powder in 500-ml flask. Stopper flask with stopper fitted with a glass tube immersed in a beaker filled with saturated bicarbonate solution. Heat gently till iron dissolves. Cool to room temperature, making sure outlet tube is immersed in bicarbonate solution. Add 10 ml starch solution and bicarbonate during titration.	0.1 N KI-KIO_3	Colorless-blue	$K_2SnO_3 \cdot 3H_2O$ (oz/gal) = ml × 3.986 × N $Na_2SnO_3 \cdot 3H_2O$ (oz/gal) = ml × 3.556 × N
KOH NaOH	5 ml	25 ml H_2O and 5 ml sulfo-orange	1.0 N HCl	Orange-yellow	KOH (oz/gal) = ml × 1.496 × N NaOH (oz/gal) = ml × 1.067 × N
Tin Sulfate					
$SnSO_4$	5 ml	100 ml H_2O, 25 ml 50% HCl, 10 ml starch solution, add bicarbonate during titration.	0.1 N KI-KIO_3	Colorless-blue	$SnSO_4$ (oz/gal) = ml × 2.863 × N Sn^{2+} (oz/gal) = $SnSO_4$ × 0.553
Sn^{4+}	2 ml	In 500-ml flask add sample, 100 ml conc. HCl, 2 drops $SbCl_3$ solution. Add 180 ml H_2O, 5-in. folded “U”-shaped nickel strip and 5.0 g reduced iron powder. Stopper flask with rubber stopper fitted with ¼-in. glass tube immersed into a saturated $NaHCO_3$ solution. Heat solution on hot-plate to boil for 20 minutes and then place in cooling tank and allow to cool to room temperature. Make sure glass outlet tube is immersed in the $NaHCO_3$. Remove stopper and add starch solution.	0.1 N KI-KIO_3	Colorless-blue	Sn^{4+} (oz/gal) = ml × 3.956 × N − Sn^{2+}

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
H_2SO_4	10 ml	100 ml H_2O, 25 ml ammonium oxalate solution, and methyl orange.	1.0 N NaOH	Red-orange/yellow	100% H_2SO_4 (oz/gal) = ml × 0.654 % v H_2SO_4 = ml × 0.279 × N
Tin-Lead Fluoborate					
Sn^{2+}	100 ml	H_2O, 25 ml 50% HCl, 10 ml starch solution, add bicarbonate during titration	0.1 N KI-KIO_3	Colorless-blue	Sn^{2+} (oz/gal) = ml × 3.956 × N
Sn^{4+}	2 ml	In 500-ml flask add sample, 100 ml conc. HCl, 2 drops $SbCl_3$ solution. Add 180 ml H_2O, 5-in. folded "U"-shaped nickel strip and 5.0 g reduced iron powder. Stopper flask with rubber stopper fitted with ¼-in. glass tube immersed into a saturated $NaHCO_3$ solution. Heat solution on hot-plate to boil for 20 minutes and then place in cooling tank and allow to cool to room temperature. Make sure glass outlet tube is immersed in the $NaHCO_3$. Remove stopper and add starch solution.	0.1 N KI-KIO_3	Colorless-blue	Sn^{4+} (oz/gal) = ml × 3.956 × N − Sn^{2+}
Pb	2 ml	5 ml conc. HNO_3, heat till syrupy, cool and add: 25 ml Rochelle solution, 15 ml conc. NH_4OH, 15 ml 10% NaCN and EBT solution.	0.1 M EDTA	Red-blue	Pb (oz/gal) = ml × 13.813 × M
HBF_4	10 ml	100 ml H_2O.	1.0 N NaOH	Clear-turbid	100% HBF_4 (oz/gal) = ml × 1.171 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Free H_3BO_3	10 ml	100 ml H_2O, 10 ml Na_2SO_4 solution. Titrate to pH 7.0, using a pH meter previously standardized to pH 7.0. Add 5 g mannitol, titrate from pH 7.0 to pH 8.0 (ml NaOH required for this step are used for the calculation).	1.0 N NaOH		H_3BO_3 (oz/gal) = ml × 0.824 × N
Tin-Lead Methane Sulfonate					
Sn^{+2}	5 ml	100 ml H_2O, 25 ml 50% HCl, 10 ml starch solution, add bicarbonate during titration.	0.1 N KI-KIO_3	Colorless blue	Sn^{2+} (g/L) = ml × 11.869 × N
Sn^{4+}	5 ml	In 500-ml flask add sample, 100 ml conc. HCl, 2 drops $SbCl_3$ solution. Add 180 ml H_2O, folded "U"-shaped nickel strip and 5.0 g reduced iron powder. Stopper flask with rubber stopper fitted with ¼-in. glass tube immersed into a saturated $NaHCO_3$ solution. Heat solution on hot-plate to boil for 20 minutes and then place in cooling tank and allow to cool to room temperature. Make sure glass outlet tube is immersed in the $NaHCO_3$. Remove stopper and add starch solution.	0.1 N KI-KIO_3	Colorless-blue	Sn^{4+} (g/L) = ml × 11.869 × N (Sn^{2+})
Pb	25 ml	75 ml H_2O, 3 ml H_2O_2, 50 ml Rochelle solution, 25 ml pH 10 buffer, EBT solution, 15 ml 10% formaldehyde.	0.1 M EDTA	Red-blue	Pb (g/L) = ml × 8.288 × M
Methane sulfonic acid (MSA)	10 ml	100 ml H_2O, phenolphthalein.	1.0 N NaOH	Colorless-pink	100% MSA (g/L) = ml × 9.61 × N

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Tin-Nickel					
Sn	2 ml	100 ml H_2O, 25 ml 50% HCl, 10 ml starch solution, add bicarbonate during titration.	0.1 N KI-KIO_3	Clear blue	Sn (oz/gal) = ml × 3.956 × N
Ni	2 ml	25 ml H_2O, 1 ml 30% H_2O_2, heat gently to boil, cool, add 10 ml tartaric acid solution. Neutralize with conc. NH_4OH to a blue color, add 20 ml pH 10 buffer, 150 ml H_2O, and murexide powder.	0.1 M EDTA	Orange-purple	Ni (oz/gal) = ml × 3.914 × M
NH_4HF_2	10 ml	200 ml H_2O, boiling chips, 50 ml 20% NaOH in Kjeldahl flask. Attach flask to the distillation apparatus with the collection tube from the condenser immersed in a beaker containing 100 ml saturated H_3BO_3 solution. Boil flask and distill over 100 ml. Remove beaker from collection tube before removing heat source. Add methyl orange.	0.1 N HCl	Yellow-red	NH_4HF_2 (oz/gal) = ml × 0.761 × N
Zinc Chloride					
Zn	2 ml	100 ml H_2O, 10 ml pH 10 buffer, EBT powder, and 15 ml 10% formaldehyde.	0.1 M EDTA	Red-blue	Zn (oz/gal) = ml × 4.358 × M
Cl	1 ml	100 ml H_2O, 1 ml K_2CrO_4.	0.1 N $AgNO_3$	Yellow-red	Cl (oz/gal) = ml × 4.727 × N
Zinc Cyanide					
Zn	2 ml	100 ml H_2O, 10 ml pH 10 buffer, EBT powder, and 15 ml 10% formaldehyde.	0.1 M EDTA	Red-blue	Zn (oz/gal) = ml × 4.358 × M

Table VIII. Test Methods for Electroplating Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Total NaCN	1 ml	100 ml H_2O, 20 ml 20% NaOH, and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	Total NaCN (oz/gal) = ml × 13.069 × N
NaOH	5 ml	25 ml H_2O, 5 ml sulfo-orange.	1.0 N HCl	Orange-yellow	NaOH (oz/gal) = ml × 1.067 × N
Na_2CO_3	10 ml	100 ml hot H_2O, 35 ml 10% $Ba(NO_3)_2$, allow to settle, filter, wash filter twice with hot H_2O, transfer filter paper and precipitate to a beaker, add 100 ml H_2O, and methyl orange.	1.0 N HCl	Orange-pink	Na_2CO_3 (oz/gal) = ml × 0.707 × N

EDTA, ethylene diamine tetra acetic acid; PAN, peroxy acetyl nitrate.
[a]Use deionized or distilled water for all solutions.

Table IX. Test Methods for Electroless Plating Solutions

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Copper					
Cu	20 ml	100 ml H_2O,[a] conc. NH_4OH to deep blue, heat to 140°F, and add peroxyacetal nitrate.	0.1 M EDTA	Purple-green	Cu (g/L) = ml × 3.177 × M
NaOH	5 ml	150 ml H_2O. Titrate to pH 10.5, using a pH meter previously standardized to pH 10.0.	0.1 N HCl		NaOH (g/L) = ml × 8.0 × N
HCHO	5 ml	100 ml H_2O. Adjust pH to 9.0, using a pH meter previously standardized to pH 10.0. Add 25 ml sodium sulfite solution, stir 1 minute. Titrate to pH 9.0 (these ml are used for the calculation).	0.1 N HCl		HCHO (g/l) = ml × 16.232 × N
Nickel					
Ni	5 ml	100 ml H_2O, 20 ml conc. NH_4OH, and murexide powder.	0.1 M EDTA	Orange-purple	Ni (oz/gal) = ml × 1.566 × M
$NaH_2PO_2 \cdot H_2O$	5 ml	Use glass-stoppered iodine flask. Add 5 ml conc. H_2SO_4 and 50 ml 0.1 N iodine solution. Swirl to mix, stopper flask, and place in dark for 30 minutes, then add starch solution.	0.1 N $Na_2S_2O_3$	Blue-colorless	$NaH_2PO_2 \cdot H_2O$ (oz/gal) = (ml I_2 × N-I_2 − ml $Na_2S_2O_3$ × N-$Na_2S_2O_3$) × 1.413
Tin					
Sn^{2+}	2 ml	100 ml H_2O, 25 ml 50% HCl, 10 ml starch solution, add bicarbonate during titration.	0.1 N KI-KIO_3	Clear-blue	Sn (oz/gal) = ml × 3.956 × N

EDTA, ethylene diamine tetra acetic acid.
[a]Use deionized or distilled water for all solutions.

Table X. Test Methods for Anodizing Solutions

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Chromic					
CrO_3[a]	10 ml of stock	10 ml sample into 500 ml volumetric. Pipette 10 ml of stock, add 100 ml H_2O,[b] 2 g ammonium bifluoride, 15 ml conc. HCl, 15 ml 10% KI, and starch solution.	0.1 N $Na_2S_2O_3$	Blue-colorless	CrO_3 (oz/gal) = ml × 22.219 × N
Free CrO_3	25 ml	100 ml H_2O. Titrate to pH 3.05, using a pH meter previously standardized to pH 4.0.	1.0 N NaOH	Colorless–pink	Free CrO_3 (oz/gal) = ml × 0.533 × N
Sulfuric					
Total H_2SO_4	5 ml	100 ml H_2O and phenolphthalein.	1.0 N NaOH	Colorless-pink	Total H_2SO_4 (oz/gal) = ml × 1.308 × N
Free H_2SO_4	5 ml	100 ml H_2O, 10 ml KF solution, and phenolphthalein.	1.0 N NaOH	Colorless-pink	Free H_2SO_4 (oz/gal) = ml × 1.308 × N
Al					Al (oz/gal) = (ml NaOH for Total H_2SO_4 − ml NaOH for free H_2SO_4) × 0.240 × N

[a]See also alternate method in Fig. 2.
[b]Use deionized or distilled water for all solutions.

Table XI. Test Methods for Acid Dips and Electropolishing Solutions

Bath	Sample Size	Reagents (To be added in order listed)	Titrant	Color Change	Calculations (ml, N, M-titrant)
$HC_2H_3O_2$	10 ml	100 ml H_2O[a] and phenolphthalein.	1.0 N NaOH	Colorless-pink	% wt $HC_2H_3O_2$ (100%) = (ml × 0.6005 × N)/s.g. solution
$H_3C_6H_5O_7 \cdot H_2O$ (Citric acid)	10 ml	100 ml H_2O and phenolphthalein.	1.0 N NaOH	Colorless-pink	% wt $H_3C_6H_5O_7 \cdot H_2O$ = (ml × 0.7005 × N)/s.g. solution
HBF_4	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-yellow/green	% wt HBF_4 (100%) = (ml × 0.8781 × N)/s.g. solution
HCl	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-yellow/green	% wt HCl (100%) = (ml × 0.3646 × N)/s.g. solution
HF	2 g	100 ml H_2O and phenolphthalein. (Note: use plastic labware.)	1.0 N NaOH	Colorless-pink	% wt HF (100%) = (ml × 2.001 × N)/wt
HNO_3	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-yellow/green	% wt HNO_3 (100%) = (ml × 0.6301 × N)/s.g. solution
H_3PO_4	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-yellow/green	% wt H_3PO_4 (100%) = (ml × 0.9800 × N)/s.g. solution
H_2SO_4	10 ml	100 ml H_2O and methyl orange	1.0 N NaOH	Red-yellow/green	% wt H_2SO_4 (100%) = (ml × 0.4904 × N)/s.g. solution
HNO_3 + HF	10 ml 1 ml	100 ml H_2O and methyl orange. 100 ml H_2O, Alizarin, 1.0 N NaOH to pink, 2% HNO_3 dropwise from pink to yellow, 3 ml fluoride buffer.	1.0 N NaOH 0.1 N $Th(NO_3)_4$	Red-yellow/green Yellow-pink	A ml B ml % wt HNO_3 (100%) = [(A ml × N − 10 × B ml × N) × 0.6301]/s.g. solution % wt HF (100%) = (B ml × 20.006 × N)/s.g. solution
H_3PO_4 + H_2SO_4	10 ml	100 ml H_2O and methyl orange. Add phenolphthalein to the solution above.	1.0 N NaOH 1.0 N NaOH	Red-yellow/green Purple-red	A ml B ml % wt H_2SO_4 (100%) = [(A ml − B ml) × 0.4904 × N]/s.g. solution % wt H_3PO_4 (100%) = (B ml × 0.9800 × N)/s.g. solution
H_2SO_4 + H_2O_2 H_2SO_4	10 ml	100 ml H_2O and methyl orange.	1.0 N NaOH	Red-yellow/green	% wt H_2SO_4 (100%) = (ml × 0.4904 × N)/s.g. solution

Table XI. Test Methods for Acid Dips and Electropolishing Solutions *(cont.)*

Bath	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
H_2O_2	2 ml	100 ml H_2O and 25 ml 20% H_2SO_4.	0.1 N $KMnO_4$	Colorless-pink	% wt H_2O_2 (100%) = (ml × 28.345 × N)/s.g. solution
CrO_3 + H_2SO_4 CrO_3	10 ml of stock	10-ml sample into 500 ml volumetric flask. Pipette 10 ml of stock, add 100 ml H_2O, 2 g ammonium bifluoride, 15 ml conc. HCl, 10 ml 10% KI, and starch solution.	0.1 N $Na_2S_2O_3$	Blue-colorless	CrO_3 (oz/gal) = ml × 22.219 × N
H_2SO_4	25 ml	100 ml H_2O, 100 ml reducing solution, boil 30 minutes, remove from heat, add 50 ml 10% $Ba(NO_3)_2$, 100 ml hot H_2O. Allow solution to stand for 3–4 hours, heat solution to boiling. Filter in tared Gooch crucible, wash precipitate with hot H_2O, dry in oven at 110°C, cool in desiccator, and weigh.			100% H_2SO_4 (oz/gal) = (weight in grams of precipitate) × 2.241

[a]Use deionized or distilled water for all solutions.

Table XII. Test Methods for Alkaline Cleaners

Solution	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
Na_2O	25 ml	100 ml H_2O[a] and methyl orange.	1.0 N HCl	Yellow-orange/red	Na_2O (oz/gal) = ml × 0.165 × N
Na_2CO_3 + NaOH	10 ml	100 ml H_2O and sulfo orange.	1.0 N HCl	Orange-yellow	B ml
	10 ml	100 ml H_2O and methyl orange.	1.0 N HCl	Yellow-orange/red	A ml Na_2CO_3 (oz/gal) = (A ml − B ml)× 0.707 × N NaOH (oz/gal) = B ml × 0.533 × N
NaOH + NaCN NaOH	10 ml	100 ml H_2O and sulfo orange.	1.0 N HCl	Orange-yellow	NaOH (oz/gal) = ml × 0.533 × N
NaCN	10 ml	100 ml H_2O and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	NaCN (oz/gal) = ml × 1.307 × N
Na_2CO_3 + NaCN	10 ml	100 ml H_2O and methyl orange.	1.0 N HCl	Yellow-orange/red	A ml
	10 ml	100 ml H_2O and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	B ml NaCN (oz/gal) = B ml × 1.307 × N Na_2CO_3 (oz/gal) = (A ml × N − B ml × N) × 0.707
Na_2CO_3 + Na_3PO_4	10 ml	150 ml H_2O and methyl orange.	1.0 N HCl	Yellow-orange/red	A ml
		Boil above solution 5 minutes, cool, and add phenolphthalein.	1.0 N NaOH	Colorless-pink	B ml Na_3PO_4 (oz/gal) = B ml × 2.186× N Na_2CO_3 (oz/gal) = (A ml × N − 2 × B ml × N) × 0.707
Na_3PO_4 + NaCN + $Na_2SiO_3{\cdot}5H_2O$	10 ml	150 ml H_2O and methyl orange.	1.0 N HCl	Yellow-orange/red	A ml
		Boil above solution 5 minutes, cool, and add phenolphthalein.	1.0 N NaOH	Colorless-pink	B ml
	10 ml	100 ml H_2O and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	C ml Na_3PO_4 (oz/gal) = B ml × 2.186× N NaCN (oz/gal) = C ml × 1.307 × N $Na_2SiO_3{\cdot}5H_2O$ (oz/gal) = (A ml × N − 2 × B ml × N − C ml × N) × 1.414

Table XII. Test Methods for Alkaline Cleaners *(cont.)*

Solution	*Sample Size*	*Reagents (To be added in order listed)*	*Titrant*	*Color Change*	*Calculations (ml, N, M-titrant)*
NaOH + Na_2CO_3 + Na_3PO_4	10 ml	150 ml H_2O and methyl orange.	1.0 N HCl	Yellow-orange/red	A ml
		Boil above solution 5 minutes, cool, and add phenolphthalein. 1.0	1.0 NaOH	Colorless-pink	B ml
	10 ml	100 ml H_2O and phenolphthalein.	1.0 N HCl	Pink-colorless	C ml NaOH (oz/gal) = (2 × C ml − A ml) × 0.533 × N Na_2CO_3 (oz/gal) = (A ml × N − B ml × N − C ml × N) × 1.414 Na_3PO_4 (oz/gal) = B ml × 2.186 × N
NaOH + Na_3PO_4 + NaCN	10 ml	150 ml H_2O and methyl orange.	1.0 N HCl	Yellow-orange/red	A ml
		Boil above solution 5 minutes, cool, and add phenolphthalein. 1.0	1.0 NaOH	Colorless-pink	B ml
	10 ml	100 ml H_2O and 10 ml 10% KI.	0.1 N $AgNO_3$	Clear-turbid	C ml Na_3PO_4 (oz/gal) = B ml × 2.186 × N NaCN (oz/gal) = C ml × 1.307 × N NaOH (oz/gal) = A ml × N − 2 × B ml × N − C ml × N) × 0.533

[a]Use deionized or distilled water for all solutions.

Table XIII. Alternate Method for Chromic Acid

Degrees Baumé	*Oz/gal-CrO_3*	*Degrees Baumé*	*Oz/gal-CrO_3*
1.50	2.1	19.00	29.0
2.00	2.8	19.50	29.8
2.50	3.4	20.00	30.6
3.00	4.1	20.50	31.5
3.50	4.8	21.00	32.4
4.00	5.5	21.50	33.3
4.50	6.2	22.00	34.2
5.00	6.8	22.50	35.1
5.50	7.5	23.00	36.0
6.00	8.2	23.50	37.1
6.50	8.9	24.00	38.2
7.00	9.7	24.50	39.1
7.50	10.4	25.00	40.0
8.00	11.1	25.50	40.9
8.50	11.9	26.00	41.9
9.00	12.6	26.50	42.9
9.50	13.4	27.00	44.0
10.00	14.2	27.50	45.0
10.50	15.0	28.00	46.0
11.00	15.8	28.50	47.1
11.50	16.5	29.00	48.2
12.00	17.3	29.50	49.2
12.50	18.2	30.00	50.2
13.00	19.1	30.50	51.5
13.50	19.8	31.00	52.7
14.00	20.4	31.50	54.0
14.50	21.2	32.00	55.2
15.00	22.0	32.50	56.3
15.50	22.9	33.00	57.5
16.00	23.7	33.50	58.7
16.50	24.5	34.00	60.0
17.00	25.4	34.50	61.2
17.50	26.3	35.00	62.3
18.00	27.2	35.50	63.5
18.50	28.1	36.00	64.8

Procedure: 1. Cool the solution to room temperature after testing.
2. Determine the density of the solution with a Baumé hydrometer.
3. Read the oz/gal of chromic acid (CrO_3) corresponding to this density.

Table XIV. Alternate Method for Copper Sulfate

Baumé	*Copper Sulfate + Sulfuric Acid (oz/gal)*	*Baumé*	*Copper Sulfate + Sulfuric Acid (oz/gal)*
1.5	2.8	14.5	24.7
2.0	3.5	15.0	25.7
2.5	4.3	15.5	26.8
3.0	5.1	16.0	27.8
3.5	5.9	16.5	28.8
4.0	6.7	17.0	29.8
4.5	7.4	17.5	30.8
5.0	8.2	18.0	31.8
5.5	9.0	18.5	32.8
6.0	9.8	19.0	33.8
6.5	10.6	19.5	34.9
7.0	11.5	20.0	35.9
7.5	12.3	20.5	37.0
8.0	13.1	21.0	38.1
8.5	13.9	21.5	39.2
9.0	14.8	22.0	40.4
9.5	15.7	22.5	41.6
10.0	16.6	23.0	42.8
10.5	17.5	23.5	43.9
11.0	18.3	24.0	45.0
11.5	19.2	24.5	46.1
12.0	20.0	25.0	47.3
12.5	21.0	25.5	48.5
13.0	21.9	26.0	49.7
13.5	22.9	26.5	51.0
14.0	23.8	27.0	52.3

Copper sulfate can be determined by taking the Baumé reading. This gives the combined copper sulfate plus sulfuric acid. Subtraction of the ounces of acid leaves the ounces of copper sulfate.
This method of obtaining the concentration of copper sulfate plus sulfuric acid is not accurate if other ingredients such as aluminum sulfate are present or if the solution is contaminated with iron.