

**THE CHEMICAL ANALYSIS
OF
ELECTROPLATING SOLUTIONS**

A Theoretical Approach

by

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.....dedicated to
my parents, without whose realization
of the value of education, this book
would never have been written.

INTRODUCTION

The author feels that there is need for a book that not only describes the mechanical procedures of analysis, which are to be found in the literature, but also presents the subject in its proper perspective, devoting space also to the underlining theories. The modern analyst must be made aware of the fact that, for example, the procedure for the determination of the chloride content of his plating solution is the classical Mohr titration devised in 1856. He should know that this technique is based upon the formation of two insoluble precipitates of different color.

Electrodeposition of metals and alloys is no longer, if it ever was, a black art. Electroplating is a science and has a definite place in the vast realm of chemistry. For the desired results, the plating baths must be chemically analyzed in order to control, within proper limits, the concentration of the pertinent constituents.

It is the intention of this book to equip the chemist with the tools he needs to do his job well. It should be noted that the analytical chemist can do his job by following the methods that are to be found in the chemical literature, but to do his job *well* he must also understand the process that he is performing. He should know why a certain reagent is used in a certain analysis at a particular time. When this is known, the critical steps or hazards become apparent. Possible sources of error will be pointed out, so that if an analysis fails or yields unreasonable results, the analyst may search for the causes of failure and find the problem.

If you wish only to do the job, this book will be of no great advantage; but if you want to know what is happening so you can do your job well, this book will be of help. It should also be borne in mind that chemical control is not a substitute for good housekeeping in the plating shop!

SPECIAL ACKNOWLEDGEMENTS

A number of references were used so extensively in this writing that grateful acknowledgement is in order.

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1. ANALYTICAL TECHNIQUES

The Scope of Analytical Chemistry

Analytical chemistry is concerned with finding out what something is made of and what the percentage of each constituent present is. In short, “what?” and “how much?” To determine what is present is the work of qualitative analysis and determining how much is present is the work of quantitative analysis.

Since we know from what a plating solution is made, we are concerned only with the problem of how much is present. Quantitative analysis is further subdivided according to the methods available to the chemist. These methods are as follows:

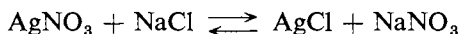
1. Gravimetric
The weight of some compound is determined at some point in the analysis.
2. Volumetric
From the volume of reactant required, the species concentration in question is mathematically calculated.
3. Instrumental
Some sort of instrument, such as a spectrophotometer, is used to measure the species concentration.

The first two subdivisions are referred to as “classical” or “wet” techniques. The third is a much more recent approach.

This book covers specific details about analyses using the first two methods. The third method is dealt with in principle only.

The Theory of Titration—The Equivalent

Early in the development of analytical chemistry it was realized that a certain amount of one substance was chemically equivalent to a certain amount of another substance. For example. Consider the following reaction:



This reaction tells us that one mole of silver nitrate reacts with one mole of sodium chloride to produce one mole of silver chloride and one mole of sodium nitrate. This means that 169.89 grams of silver nitrate react with exactly 58.46 grams of sodium chloride. From these fundamental statements it is seen that if 169.89 grams of silver nitrate are dissolved in water and diluted to a total volume of one liter and the 58.46 grams of sodium chloride treated in a similar manner, two solutions that are chemically equivalent to one another are produced. A new term was therefore introduced, "normality", being defined as the number of equivalents of a substance per liter of solution. Therefore, these two solutions prepared above are one normal (abbreviated 1 N) silver nitrate and 1 N sodium chloride.

Now, for example, it can be seen that a liter of 0.1 N sulfuric acid solution is chemically equivalent to 1/10 liter of 1 N sodium hydroxide solution.

A shortcut method of calculating volumes of solutions that are equivalent to one another when they have different normalities is to use the following equation:

$$V_1N_1 = V_2N_2$$

For example, 500 ml of 7 N phosphoric acid would be completely neutralized by how many milliliters of 0.5 N potassium hydroxide?

$$N_1 = 0.5 \text{ liters}$$

$$V_1 = 7$$

$$N_2 = 0.5$$

$$V_2 = ?$$

$$V_2 = \frac{V_1N_1}{N_2} = \frac{(0.5)(7)}{(0.5)} = 7 \text{ liters of } 0.5\text{N KOH}$$

The equivalent (abbreviated eq.) is a quantity of a substance. One thousandth of that quantity is called a milliequivalent, (abbreviated meq.).

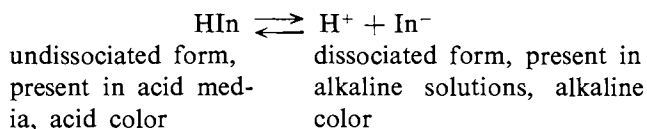
Endpoints and Indicators

In volumetric analysis, a solution containing the unknown is treated with an appropriate reagent whose strength is known. The latter is

added until the amount added is chemically equivalent to the amount of unknown substance present. This point at which equivalent amounts of the two reagents are present is called the equivalence point or endpoint. An auxiliary reagent known as an indicator is usually added to the solution to show the point at which equivalent quantities are present. This indicator signal can take the form of, for example, a color change or the formation of a turbid or suddenly clear solution.

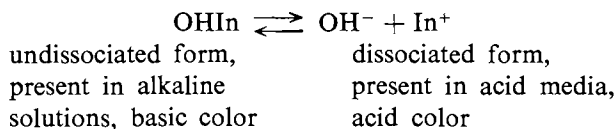
Because indicators are highly complex organic materials, we shall use simply the symbol "In" to denote them. The presentation of their actual molecular structure would serve no purpose here.

In general there are two types of indicators¹, pH sensitive and oxidation—reduction, (redox), indicators. The pH sensitive indicators can be further subdivided into acidic and alkaline subgroups. First consider an acid indicator:



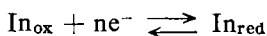
Phenol red is an example of this type of an indicator. Its HIn form is yellow but in a basic solution the formation of the In⁻ ion is spontaneous, (its color is red).

The second category of the pH sensitive indicators is the alkaline subgroup whose general reaction is now given:



Methyl orange is an example of such an indicator. Its color in a solution of pH greater than 4.4 is a yellow—orange while in a more acidic media, where the In⁺ form is prevalent, the solution becomes a brilliant red.

Oxidation—reduction indicators react according to the following general reaction:



¹Excluding adsorption and complex indicator systems that are beyond the scope and intention of this discussion.

where In_{ox} is the oxidized form of the indicator while In_{red} represents the reduced form, the color of one form differing from that of the other. The term ne^- means n number of electrons where n depends on the particular indicator under discussion.

Since a gain or loss of electrons is involved, a certain minimum potential (voltage) must be experienced by the indicator in order for it to accept or release these electrons.

As an example, "ferroin" (o-phenanthroline ferrous complex) is a pale blue in its oxidized form whereas it is red in its reduced form. Its standard reduction potential is 1.06 volts. Thus, the behavior of a true redox indicator depends only upon the change in potential of the system and not specifically on the change in concentration of one of the reagents present.

There is a small group of redox indicators which react specifically with some reagent involved in the redox titration. An example is starch which forms an intensely blue complex with the tri-iodide ion which might be produced or consumed in a redox titration.

For additional information, the following reference books are excellent sources:

I.M. Kolthoff and C. Rosenblum, *Acid-Base Indicators*, The Macmillan Company (1937)

I.M. Kolthoff and V.A. Stenger, *Voljmetric Analysis*, 2d, Vol. I (1942), Vol. II (1947), Interscience Publishers (New York)

See Part Four, Tables I, II & III, for a list of indicators used frequently in analytical chemistry.

Representative Sampling

When a sample of a plating bath is taken it is assumed that the contents of this sample accurately represent the bath's contents.

The term 'sampling' refers to the steps involved in obtaining this representative sample. The sampling of baths requires the observance of a few simple rules so as to insure the collection of a sample whose concentrations are representative. These rules are as follows:

1. If rigorous agitation of the bath is not used the solution should be thoroughly stirred before the sample is taken. Otherwise, the more dense materials in the bath will be nearer the bottom and the sample will thus indicate a lower concentration than is actually present.

2. It is not a good idea to collect a sample from a bath which is being operated. Metal ions are being attracted to the cathode and negative ions are being attracted to the anodes. Thus, it is quite possible to get a variation in the measured concentrations depending upon where the sample was taken with respect to the position of the anodes and cathodes. This effect is minimized when rigorous agitation is being employed such as air or efficient circulation.
3. Just prior to taking the sample the bath should be brought up to operating volume with water. Otherwise the concentration of the solution components will be higher than they actually are under typical operating conditions.

Usually a five or ten ml sample is analyzed. The first step is usually to dilute it to about 200 ml total volume with distilled water. This is done for several reasons. First, by diluting the sample the effect of losing a drop or two is minimized. Second, it is difficult to work with a five or ten ml sample. A diluted sample, rather than a larger full-strength sample is used because a 200 ml sample would require such large volumes of other chemicals during the analysis that it would be not only cumbersome but also expensive.

The Preparation of A Volumetric Solution as A Primary Standard

The preparation of a standard solution in the following pages is illustrated by the following example:

“Weigh to the nearest milligram about 15 grams of reagent grade anhydrous potassium dichromate, $K_2Cr_2O_7$ ”.

To do this, follow this general method:

1. Clean and dry a 50 or 100 ml beaker.
2. Fill it about two-thirds full with reagent grade potassium dichromate.
3. On an analytical balance determine the total weight of beaker and reagent. Record this value to the nearest milligram. For example, 37.017 grams.
4. Place a clean, dry glass funnel (about a three or four inch diameter funnel) in the top of a one liter volumetric flask which must be clean, but not necessarily dry.
5. Carefully pour what you estimate to be about 10–13 grams of the reagent into the funnel. Some of the particles are

bound to adhere to the funnel but do not attempt to shake them into the flask at this time.

6. Place the beaker with its remaining contents back on the balance pan and weigh to the nearest gram. If this weight is between 14.5 and 15.5 grams less than the first weighing, then proceed to determine the weight to the nearest milligram.
7. If the new weighing is not within the above range, repeat step 5 adding about what you think will be necessary.
8. Again determine the weight of the remainder to see if you are within the range.
9. If necessary, continue this adding—weighing cycle until you have added between 14.5 and 15.5 grams.
10. Subtract the final weighing from the first recorded figure found in step 3.
11. With a wash bottle of distilled water, rinse the particles in the funnel down into the flask. This usually requires 30 or 40 ml of water.
12. Lift the funnel almost out of the flask and rinse the outside of the funnel barrel into the flask.
13. Remove the funnel from the flask and rinse the inside neck of the flask into the bottom of the flask. When all of the particles have been rinsed into the bottom of the flask, fill the flask about one half full with distilled water. Swirl or let the flask sit until all of the particles have dissolved.
14. With a wash bottle, dilute the contents to the mark. The bottom of the meniscus should be level with the mark.
15. Calculate the solution strength according to the equation given in the appropriate section.

This weighing method should be followed for all such procedures.

Purity of Laboratory Chemicals

As a general statement, only reagent and primary standard grades of chemicals should be used in the analytical laboratory. The employment of lesser grade chemicals may vitiate the results of the analysis. This problem must also be in proper perspective at the other extreme. That is, cleaning solutions and electrodeposit stripping solutions need not be prepared from anything better than technical or commer-

cial grade materials. A reasonable balance must be struck between considerations of accuracy and those of economics.

Below are listed in order of increasing purity the various chemical grades available.

Technical (or commercial) Grade. This means they are actually of indeterminate quality. Such reagents are not useable in the laboratory except for cleaning solutions.

Purified (or practical) Grade. Here again, an indefinite quality level is implied. Laboratory synthesis is often carried out with this grade of material.

U.S.P. Grade. These reagents conform to standards set by the United States Pharmacopoeia. The specifications are designed to control the presence of contaminants dangerous to health; thus, chemicals passing U.S.P. tests may still be quite heavily contaminated with impurities that are not physiological hazards.

N.F. Grade. Conform to the National Formulary code.

Chemically Pure (C.P.) Grade. The term Chemically Pure has little definite meaning. About all that can be said is that they are more refined than technical grades. They are not suitable for analytical work in general.

Analytical Reagent (Analyzed) Grade. This is the grade of material most commonly employed for use in the analytical laboratory. The labels of such chemicals usually state the percentages of the important impurities present. Analyzed reagents conform to the specifications of the American Chemical Society Committee on Analytical Reagents.

Primary Standard Grade. Relatively few chemicals are obtainable in the extraordinarily pure form required to bear this label. An excellent source for primary standard chemicals is the National Bureau of Standards. Only when they are used, can a standard solution of reliable strength be prepared simply by accurately weighing out a quantity of the material, dissolving it in water, and diluting to the mark in a volumetric flask. Such chemicals have been especially manufactured, controlled and evaluated to be suitable for use as reference standards.

Glassware Cleaning

Naturally all quantitative work demands attention to details, and

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PERIODIC TABLE OF THE ELEMENTS
(Atomic weight values in brackets are for most stable known isotopes)

SERIES	PERIOD	GROUP 0	GROUP 1	GROUP 2	GROUP 3	GROUP 4	GROUP 5	GROUP 6	GROUP 7	GROUP 8					
1		1 H 1.008													
2	1	2 He 4.003	3 Li 6.94	4 Be 9.012	5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 19.00						
3	2	10 Ne 20.183	11 Na 22.990	12 Mg 24.31	13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.064	17 Cl 35.453						
4	3	18 Ar 39.948	19 K 39.102	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71			
5			29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91						
6	4	36 Kr 83.80	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc [99]	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4			
7			47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90						
8	5	54 Xe 131.30	55 Cs 132.91	56 Ba 137.34	57 La 138.91	58-71 See Lanthanide series									
9															
10															
11	6		79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po [210]	85 At [210]	76 Os 190.2	77 Ir 192.2	78 Pt 195.09			
12	7	86 Rn [222]	87 Fr [223]	88 Ra [226]	89 Ac [227]	90-103 See Actinide series									
Lanthanide Series															
		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [147]	62 Sm 150.35	63 Eu 152.0	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide Series															
		90 Th 232.04	91 Pa [231]	92 U 238.03	93 Np [237]	94 Pu [242]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [254]	100 Fm [255]	101 Md [256]	102 No [254]	103 Lw [257]

