



505 S Maple Road – Ann Arbor, MI 48103 – USA
TEL (800) 422-2558 – FAX (734) 665-9099

www.Eberbachlabtools.com



E1000.00 Electro Analysis Apparatus
INTRODUCTION TO METHODS

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The following information is a product of research carried on at Battelle Memorial Institute, Columbus, Ohio under the sponsorship of Eberbach Corporation. It is intended to serve as an introduction to the use of electrolytic methods in quantitative analysis.

Electroanalysis, as used in this text, is a process of plating an element on an electrode which is weighed before and after deposition. Elements are plated on the cathode as metals or, in some cases, on the anode as hydrated oxides. Most electrolyses are made in dilute mineral acid solutions. Some elements require special electrolytes such as ammonium hydroxide, cyanides, and organic acids.

Although a number of elements are deposited under ordinary conditions, it is possible to effect specific determinations in many systems with a minimum of chemical preparation. Metals may be replated to effect additional purification. When the ratio of electrode weight to deposited-metal weight is unfavorable, the metal is dissolved from the electrode and determined by chemical or other procedures. In some instances, electroanalysis is used to advantage in the removal of interfering ions.

Copper and lead as metals or in alloys such as brasses, bronzes, etc., are particularly well suited to electroanalytical techniques. This discussion will be confined to these two elements. However, numerous references to the literature are included, covering other elements and special electroanalysis procedures.

GENERAL CONDITIONS FOR PLATING, COPPER AND LEAD

Electroanalysis provides a convenient method for the simultaneous or individual determination of copper and lead. Copper may be electrolytically separated from lead, cadmium, zinc, and other metals having an electrode potential near, or more positive than, copper (Table 1). In some cases, it is necessary to separate copper and/or lead from interfering ions. For instance, copper may be precipitated as the sulfide or thiocyanate⁽²⁾ and then be determined electrolytically after appropriate chemical treatment.

TABLE 1. ELECTROMOTIVE SERIES

Element	E _o , Volts
Li	-3.02
K	-2.92
Ba	-2.90
Sr	-2.89
Ca	-2.87
Na	-2.71
Mg	-2.34
Al	-1.67
Mn	-1.05
Zn	-0.76
Cr	-0.71
Fe	-0.44
Cd	-0.40
Co	-0.28
Ni	-0.25
Sn	-0.14
Pb	-0.13
H	0.00
Sb	0.15
As	0.24
Bi	0.32
Cu	0.34
Ag	0.80
Hg	0.80
Au	1.42

In the electroanalysis of copper, the ideal electrolyte would consist of 3 per cent H₂SO₄ and 2 per cent (or less) of HNO₃. The nitric acid serves as a depolarizing agent to prevent the discharge of hydrogen at the cathode, and also assists in producing a more dense and coherent copper plate. The concentration of nitric acid should be kept low because of its tendency to dissolve the plated copper or retard its electrodeposition⁽²³⁾.

For the highest efficiency, the volume of electrolyte should be just sufficient to cover the electrodes. Many analysts insist that when plating copper, the temperature of the electrolyte should not be permitted to rise above 40°C. When more than one ampere of current is supplied to the cell, the electrolyte should be stirred to prevent the polarization due to ion starvation at the electrode surface.

When plating lead alone as the dioxide on the anode, the nitric acid concentration of the electrolyte should be high. Fifteen to thirty per cent (v/v) yields the best results⁽¹⁰⁾. The addition of a few drops (0.25 ml.) of H₂SO₄ produces a more dense and adherent "lead dioxide plate"^(10, 18). The lead solution should be heated nearly to boiling at the start of the electrolysis. It may be allowed to cool during the plating process; in fact, better recovery is attained when the last few milligrams plate from a cool solution.

Large amounts of copper, ten grams or more, can readily be plated in electroanalysis. However, a sample containing more than one gram is seldom justified. Samples to be analyzed for lead should contain 0.05 to 0.150 gram of the metal. Larger amounts of lead may produce a plate that is loosely adherent to the anode, so that washing the plate may result in mechanical loss of the lead dioxide.

Stirring the solution during electrolysis markedly increases the rate of deposition^(9,23). Stirring is especially important in the deposition of lead because only the ions in contact with the anode are oxidized to the tetravalent state. The tetravalent ion then reacts with water to produce the dioxide (PbO_2^-), which is held to the anode by electrical attraction (anaphoresis)^(3,4,9).

INTERFERENCES IN THE DETERMINATION OF COPPER

THE NOBLE METALS

Gold, mercury, and silver will deposit with copper unless they are removed. Silver may be removed as the chloride. It is important then to remove the residual chloride by fuming the sample with sulfuric acid.

SELENIUM, TELLURIUM, ARSENIC, AND LEAD

Selenium and tellurium will interfere by plating with the copper unless they are oxidized and kept in the hexavalent state during electrolysis. An ammoniacal solution of the sample is boiled with a gram of potassium persulfate which will oxidize both selenium and tellurium. The solution can then be made acid and electrolyzed as usual. The addition of another portion of persulfate after start of the electrolysis may be necessary to keep the tellurium oxidized. When lead is not being determined at the same time as the copper, a strong oxidizing condition to prevent interference from tellurium can be maintained the addition of ten milligrams of manganese nitrate. The electrically generated permanganate will effectively prevent the interference also of arsenic and antimony⁽⁸⁾. Note that because selenium has a lower decomposition potential than copper, it must first be oxidized with persulfate as above and the manganese nitrate added before the electrolyzing is begun.

TIN, TUNGSTEN, BISMUTH, AND MOLYBDENUM

Tin may be removed from a copper sample by precipitating it as the metastannic acid in nitric acid. If the sample is dissolved in fuming nitric acid, the metastannic acid formed will be granular, easily filtered and washed, and will occlude little, if any, copper⁽²⁶⁾. Tungsten as the trioxide will also separate from solution with this treatment.

Bismuth will deposit along with the copper. It may then be dissolved from the cathode with the copper and determined separately. Molybdenum also plates with copper to produce a dark-colored plate. When a very small quantity (6 mg.) is present, the addition of a milligram of sodium chloride will prevent its deposition^(26, 19).

IRON, CHROMIUM AND MANGANESE

Iron, chromium, or manganese may interfere in the copper determination because copper is appreciably soluble in solutions of salts of metals having two states of oxidation. More than 0.05 gram of iron in the sample⁽²⁶⁾ will result in incomplete recovery of the copper. The separation of copper from iron may be accomplished by plating the copper from an electrolyte containing phosphate or fluoride. The latter materials sequester the iron so that it will not affect the copper deposit. This is an especially valuable technique when the copper content of steel is to be determined^(17, 22). Iron is reduced to the ferrous state at the cathode and then can convert nitric to nitrous acid. If this occurs, the copper already deposited is rapidly redissolved because of the ease with which it is attacked by nitrous acid. Manganese and chromium in amounts less than 0.05 gram do not interfere with the quantitative removal of the copper⁽²⁶⁾. When more than 0.05 gram of these metals is present, two ammonia separations are required to separate them from the copper.

THE HALOGENS

Chlorides, bromides, and iodides must be removed by fuming the sample with sulfuric acid. Even milligram amounts of the halides may cause the copper plate to be spongy or loosely crystalline. Although a drop of 0.1 N HCl is often added to a nitrate electrolyte⁽²⁾, it is undesirable and unnecessary in the mixed nitrate-sulfate solution (26).

NITROUS ACID

It is imperative that all nitrogen oxides be boiled from the electrolyte before attempting to plate copper. Copper will not deposit completely from a solution containing nitrous acid and any deposited copper may redissolve at once. Urea or sulfamic acid may be added to combine with any nitrous acid that may be produced during electrolysis. Sulfamic acid is the preferred reagent. The addition of urea may produce erroneous results because of the possible occlusion of organic matter in the copper plate⁽²⁶⁾.*

INTERFERENCES IN THE DETERMINATION OF LEAD

Silver, bismuth, manganese, antimony, arsenic, mercury, tin, chromate, chlorine, and phosphate all interfere with the deposition of lead on the anode as dioxide⁽¹⁰⁾. If significant amounts of these are present, they must be removed by appropriate chemical treatment before lead can be plated as the dioxide. Silver, bismuth, and manganese will co-deposit as oxides on the anode with lead. Chromate, arsenic, antimony, tin, phosphate, and chlorine either hinder the deposition of the lead dioxide or contaminate the deposit. Mercury will cause part of the lead to co-deposit on the cathode as a lead amalgam⁽¹⁸⁾.

*Any sample containing organic matter must be treated by controlled ignition at low temperatures, or by a "wet ashing process" to destroy the organic materials.

ANALYSIS FOR BRASS** FOR COPPER AND LEAD

Many electrolytic procedures are described in the literature for the analysis of brass, bronze, and other copper-containing alloys. The following method is intended to illustrate the techniques used for the assay of copper and lead in a typical brass.

Wash the sample in ether or benzene to remove any traces of oil or grease. Place 1-gram sample in a 150-ml. beaker with a watch-glass cover. Add 15 ml. of nitric acid*** slowly to prevent too violent a reaction. Permit the solution to evaporate at a temperature somewhat below the boiling point until the solution volume is about 5 ml. (Never evaporate to dryness.) Slow evaporation (about 1 hour) will insure precipitation of the tin as metastannic acid. Dilute the solution to 50 ml. and heat for half an hour to insure solution of all soluble salts. Add some paper pulp to assist in collecting the metastannic acid, and filter (No. 42 Whatman or equivalent) the solution into a 250-ml. beaker. Wash with 1 per cent nitric acid. Reserve filtrate.

To recover copper and lead that may have been occluded by the metastannic acid, use either of the two following procedures:⁽²⁴⁾

A. Transfer the filter paper and contents to the original beaker and add 15 ml. of H_2SO_4 and 25 ml. of HNO_3 . Heat until all organic matter is decomposed (H_2SO_4 fumes). Transfer solution to a 400-ml. beaker and dilute to 250 ml. Make the solution alkaline with 25 per cent NaOH to dissolve the metastannic acid. Add 20 ml. of 25 per cent Na_2S and digest the solution on the steam bath until the supernatant liquid is clear. Cool the solution to room temperature and filter through a fine textured paper, washing with 2 per cent Na_2S . Dissolve the residue in a few milliliters of 1:1 HNO_3 and add it to the filtrate reserved above.

**Per cent composition: Cu 55.0 to 90.0, Sn 0.0 to 5.0, Pb 0.0 to 5.0, P 0.0 to 0.1, As 0.0 to 0.1, Sb 0.0 to 0.1, Fe under 0.25, Ni under 0.25, Zn remainder.

***Solution of the sample in fuming nitric acid and subsequent boiling after diluting to 50 ml. is said to yield a metastannic acid that is crystalline, easily filtered, and will hold up little, if any copper or lead⁽²⁶⁾.

B. Place filter paper containing the metastannic acid in the original beaker and add 20 ml. of HNO_3 and 15 ml. of $HClO_4$. Heat to copious white fumes to destroy organic matter.* Cool beaker and wash cover glass and sides of beaker, then add 15 to 25 ml. of HBr . Heat to copious fumes to volatilize tin, arsenic, and antimony. If the solution is not clear, repeat the treatment with HBr . Evaporate the solution nearly to dryness, dissolve the residue in a few ml. of 1:1 HNO_3 , and add it to the original filtrate.

Heat the combined filtrate containing the copper and lead almost to boiling and place it on the electroanalyzer. Add sufficient water to cover the electrodes. Add five drops of sulfuric acid and electrolyze with a current of 1.0 to 2.0 amperes for half an hour. Increase current to 4.0 amperes, and add six ml. of H_2SO_4 to the electrolyte.

Ten minutes after the solution has lost its blue color, some water is added to raise the level of the solution on the stem of the cathode. If no copper deposits on the freshly exposed surface during the next ten minutes, the copper may be assumed to have been quantitatively plated from the solution.

With the current on, the beaker containing the electrolyte is lowered rapidly away from the electrodes and replaced with a beaker of water. After the electrodes are rinsed thoroughly with water, they are rinsed with acetone and dried at 100° C. for 20 to 30 minutes and then weighed.

The conversion factor commonly used for the lead as dioxide is 0.8640⁽¹⁸⁾, instead of the theoretical 0.8660. The deposit nearly always contains a slight excess of oxygen or combined water.

*It may be necessary to add additional HNO₃.

BIBLIOGRAPHY

1. Trillat, Comp. rend., Vol. 136, p. 1205, 1903.
2. Kolthoff, I. M. and v. d. Meine, G. H., Z. anal. Chem, Vol. 72, p. 337, 1927.
3. Jewett, J. Phys. Chem., Vol. 33, pg. 1024, 1929.
4. Topelman, J. prakt. Chem., Vol. 121, pg. 289 1929.
5. Grendel, F., Pharm. Weekblad; Vol. 67, pp. 913, 1050, 1345, 1930.
6. Lucas, R., and Grassner, F., Mikrochemie (Emrich Festschrift), p. 199, 1930
7. Lucas, R., and Grassner, F., Mikrochemie (Emrich Festschrift), p. 201, 1930.
8. Furman, N. H., Ind. Eng. Chem., Anal. Ed., Vol. 3, p. 217, 1931.
9. Nichols, M. L., Ind. Eng. Chem., Anal. Ed., Vol. 3, p. 384, 1931.
10. Schrenck, W. T., and Delano, Philip H., Ind. Eng. Chem. Anal. Ed., Vol. 3, p. 27, 1931.
11. Von Hevesy, G., and Hobbie, R., Z, anal. Chem., Vol. 88 p. 1, 1932.
12. Stock, A., and Cucuel, F., Naturwissenschaftetf, Vol. 22, p. 390, 1934.
13. Lundell, G. E. F., and Hoffman, J. I. "Outlines of Methods of Chemical Analysis," 1938.
14. Muller, H., Z. anal. Chem., Vol. 113, p. 161, 1938.
15. Stock, A., Ber., Vol. 71, pg. 550, 1938.
16. Scherrer, Bell, Mogerman, J. Research Nat'l. Bur. Standards, Vol. 22, p. 697, 1939.
17. Frediani and Hale, Ind. Eng. Chem., Anal Ed., Vol. 12, p. 763, 1940.
- 11
18. Willard, H. H., and Furman, N. H., "Elementary Quantitative Analysis," 1940.
19. Silverman, Ind. Eng. Chem., Anal. Ed., Vol. 12, p. 343, 1940.
20. Bambach, K., and Cholak, J. Ind. Eng. Chem. Anal. Ed., Vol. 13, p. 504, 1941.
21. Fields, M., New Zealand J. Sci. Tech., Vol. 23B, p. 224, 1942.

22. Silverman, Goodman, Walter, Ind. Eng. Chem., Anal. Ed., Vol. 14, p. 236, 1942.
23. Willard, H. H., Merritt, L. L., and Dean, J. A., "Instrumental Methods of Analysis," 1948.
24. A.S.T.M., "Methods for the Chemical Analysis of Metals," 1950 Ed.
25. Sandell, E. B., "Colorimetric Determination of Traces of Metals," 2nd Ed., 1950.
26. Skowronski, S., A.S.T.M. Bull. No. 174, pp. 60-65, 1951.
27. Salyer, D., and Sweet, T. R., "Determination of Cobalt by Anodic Electrodeposition," Vol. 28, No.1, Anal Chem., January 1956.
28. Salyer, D., and Sweet, T. R., "Determination of Small Amounts of Cobalt in Steels and Nickel Alloys-by the Isotope Dilution-Anodic Deposition Method," Vol. 29, No. 1, Anal. Chem., January 1957.

In addition to the references previously cited, the following are of general interest:

Smith, E. F., "Electroanalysis," 1918.

Furman, "Scott's Standard Methods of Analysis," 5th Ed. 1925.

Classen, Alexander, "Quantitative Analyze durch Electrolyze," 7th Ed., 1927.

Dole, "Principles of Experimental and Theoretical Electrochemistry," 1935.

12

Willard and Diehl, "Advanced Quantitative Analysis," 3rd Ed., 1943.

Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," 1948.