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NRL Report 6357

Procedures for the Chemical Analysis of Copper-Base Alloys

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March 10, 1966

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Procedures for the Chemical Analysis of Copper-Base Alloys

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Two sets of sequence procedures are presented, each with its own recommended application, that will quickly resolve a great number of analytical problems that may be encountered in the chemical characterization of many common and unusual copper-base alloys. One procedure provides for the precipitation of tin, as metastannic acid, with nitric acid when alloy compositions are such that no appreciable tin-contamination problems arise; the second provides for the retention of tin in solution with hydrofluoric acid when tin-contamination problems are present. By the use of the appropriate procedure, rapid access to the greatest possible amount of analytical information on individual samples, and results comparable in accuracy to standard methods, will be obtained.

INTRODUCTION

The methods discussed in this report for the analysis of familiar alloy types have emerged under the pressure of a heterogeneous work load involving the need for composition information on both the materials of research and the materials supporting research. The procedures have been designed to provide rapid access to the greatest possible amount of analytical information on individual samples and to yield results comparable in accuracy to those obtained by standard or even umpire methods.

For assistance in broadening the scope of usefulness of this report, two sets of methods are provided that will give a rapid approach to a great number of analytical problems that may be encountered in copper-base alloy work. Both are sequence methods in which a number of possible alloying elements are determined in the electrolyte, following the removal of copper and lead. The first method provides for the precipitation of tin, as metastannic acid, with nitric acid when alloy compositions are such that no appreciable tin-contamination problems arise; the second provides for the retention of tin in solution with hydrofluoric acid when tin-contamination problems are present.

Two tables of analytical data are provided for assistance in choosing the appropriate method for a particular alloy and as a ready reference guide to the level of accuracy that may be expected from the application of the method. Table 1 lists a selected group of copper-base alloy types with nominal composition data. A dagger in the table indicates the types of alloys that may be analyzed with the first, or nitric acid, sequence. The unmarked, and analytically more complex, alloys should be approached with the nitric-hydrofluoric acid sequence.

Table 2 lists a series of National Bureau of Standards (NBS) standard samples, along with their certified analyses. Accompanying each set of certified data are two sets of analytical data obtained by the proposed two methods, to be outlined below. These data not only show the merits of the methods properly applied, but show dramatically the magnitude of the errors that may be expected by the improper choice of method.

NITRIC ACID SEQUENCE METHOD

Principle

The tin, as metastannic acid, is separated from the hot HNO_3 solution of the sample. Copper and lead are removed electrolytically. Nickel, iron, manganese, and aluminum are determined photometrically on aliquots of the spent electrolyte.

Determination of Tin

Procedure—Transfer a carefully weighed 1-g sample to a 100-ml beaker. Carry a reagent blank through the entire procedure, using the same amounts of all reagents, to serve as a reference

NRL Problem M01-20 and Project RR 007-01-46-5422. This is a final report on one phase of the problem; work on other phases is continuing. Manuscript submitted September 24, 1965.

TABLE 1
Percentage Composition of Representative Copper-Base Alloys

Alloy Name*	Elements								
	Cu	Zn	Pb	Sn	Si	Ni	Al	Fe	Other
Gilding Metal†	95‡	5							
Red Brass†	85	15							
Malleable Brass†	75	25							
Cartridge Brass†	70	30	0.07m¶						
Free Cutting Brass†	61.5	35.5	3						
Leaded Red Brass†	85	5	5	5					
Leaded Yellow Brass†	66	30	3	1					
Naval Brass†	60	39.25	0.20m	0.75					
Silicon Brass†	77	22			1				
Aluminum Bronze†	89						10	0.75	0.25 Mn
Beryllium Bronze†	98								2 Be
Leaded Bronze (Silver Bearing)	70		29						1 Ag
Manganese Bronze	58.5	39.0	0.20m	1				1.4	0.1 Mn
Manganese Bronze	62	26.5					5	3	3.5 Mn
Phosphor Bronze	90			10					0.25 P
Silicon Bronze	96				3				1.0 Mn
Nickel-Silver (German Silver)†	57	20	9	2		12			
Nickel-Silver (German Silver)†	64	8	4	4		20			

*Alloy types selected from Van Nostrand's Scientific Encylopedia, 3rd ed., p. 223.
†These alloys may be analyzed by the nitric acid sequence, described in the report.
‡The numbers in the table are in percent.
¶"m" indicates maximum permissible percentage.

solution in subsequent photometric determinations. (This latter is optional, and the need for a blank should be determined by the degree of analytical accuracy required.) Add 10 ml of water, cover with a watch glass, and add 10 ml of HNO_3. After the initial vigorous reaction subsides, digest on a hot plate until the sample is completely dissolved, bring to a gentle boil, and continue boiling for several minutes after the brown fumes have been expelled. Remove from the hot plate, dilute to 50 ml with hot water, place on an asbestos pad on a hot plate, and maintain the temperature of the solution just below boiling for 1 hr. Filter the hot solution through a Whatman-42 9-cm paper containing pulp.* Transfer the precipitate quantitatively to the paper and wash 3 times with hot 1% HNO_3, then 5 times with hot water, each time being careful to play the stream of water on the precipitate, then around the top of the filter paper. Reserve the filtrate for "Determination of Copper and Lead" (in next section of the report). Transfer the filter paper and contents to a porcelain crucible, place in a cold furnace, and gradually (over 2 hr) raise the temperature to about 800°C. Remove the crucible, cool, and weigh the ignited SnO_2†. The SnO_2-to-Sn factor is 0.788.

*It is good practice to complete the filtration of the metastannic acid (H_2SnO_3) precipitate while the solution is still hot because H_2SnO_3 is slightly more soluble in a cold solution.

Determination of Copper and Lead (by Electrolysis)

Electrolysis Apparatus—For heavy work loads a special electrolysis panel, with stationary electrode holders connected in parallel to a heavy-duty

†Arsenic and antimony, if present, are quantitatively precipitated with the tin. And for samples containing appreciable amounts of tin, phosphorus is almost quantitatively precipitated (90-95%). Varying amounts of iron, silicon, and manganese are also retained or precipitated. Iron in the ignited precipitate is usually indicated by the presence of the reddish Fe_2O_3 color; however, if phosphorus is present in appreciable amounts, the color due to iron is completely masked. Iron also tends to prevent the complete precipitation of tin as metastannic acid. Should appreciable amounts of iron and tin be present in the same sample, it is advisable to use the nitric-hydrofluoric acid sequence procedure. Refer to Table 2.

Depending upon the amounts of the above contaminants present in high-tin samples, dissolution and subsequent filtration of the sample may be difficult. Under such conditions, as much as 4 mg of copper may be retained in the metastannic acid precipitate.

TABLE 2
Comparison of NBS Certificate Values with HNO_3 Procedure and HNO_3-HF Procedure Values

NBS Sample	Type of Analysis	Elements										
		Cu	Zn	Sn	Pb	Ni	Fe	Mn	Al	P	Si	Sb
37b	NBS Cert.	70.36*	27.09	0.99	0.90	0.45	0.21					
	HNO_3-HF	70.29			0.94	0.45	0.20(a)					
	HNO_3	70.37		1.01	0.92	0.46	0.18(a)					
52b	NBS Cert.	88.25	2.96	8.00	0.011	0.72	0.032	0.005		0.002		
	HNO_3-HF	88.25				0.72	0.03					
	HNO_3	88.17		8.11		0.72	0.01					
62b	NBS Cert.	57.39	37.97	0.96	0.28	0.27	0.82	1.29	0.97		0.048	0.005
	HNO_3-HF	57.42			0.27(b)	0.27	0.83(a)	1.30	1.00			
	HNO_3	57.41		1.00	0.27(b)	0.29	0.77(a)	1.27	0.98			
63b	NBS Cert.	77.94	0.71	9.78	9.36	0.33	0.47		0.05	0.44	0.12	0.54
	HNO_3-HF	77.91			9.30	0.33	0.47		0.05			
	HNO_3	77.76		11.51(c)	9.42	0.32	0.29(d)		0.06			
124a	NBS Cert.	85.01	5.21	4.82	4.89	0.001	0.004		0.006			
	HNO_3-HF	84.99			4.93		0.005(e)					
	HNO_3	84.95		4.87	4.89							
158	NBS Cert.	90.85	2.07	0.97	0.003		1.48	1.31	0.54		2.72	
	HNO_3-HF	90.85				0.01	1.48	1.32	0.55			
	HNO_3(f)	90.52		2.74(g)			0.18	1.36	0.56		2.31(f)	
162	NBS Cert.	28.93				66.38	0.34	2.34	0.23		0.67	
	HNO_3-HF	28.92				65.0(h)	0.34(a)	2.36	0.31(i)			
	HNO_3(f)	28.92					0.31(a)	2.36	0.33(i)		0.64	

*The numbers in the table are in percent.

(a) Obtained photometrically after separating Fe from Zn or Ni. See "Determination of Iron," page 6.

(b) The first anodic coating was stripped, then replated in the presence of about 0.2 g of Cu. See "Determination of Copper and Lead," page 2.

(c) No correction applied for the Fe, Sb, As, P, and Cu precipitated or occluded with the metastannic acid.

(d) Depending on sample composition, much of the Fe may be precipitated with Sn. Based on a 1-g sample of NBS sample 63b, 0.0018 g of Fe was recovered from the metastannic acid precipitate. See footnote, page 2 (right-hand column)

(e) Since relative photometric errors increase at high transmittances, results obtained below the recommended procedural limits should be considered approximations.

(f) Sample dissolved with HNO_3, then taken to fumes with $HClO_4$ before filtration. Note the low value of silicon on sample 158.

(g) Correction applied for SiO_2 but not for Fe and Cu.

(h) Value obtained photometrically using a dilution factor of 2500.

(i) No correction applied for the presence of Ni.

direct-current source, is recommended. Each set of electrode holders should be connected to an individual current regulating device.

For light work loads, any of the commercially available electroanalyzers may be used. These instruments usually have a rotating holder for the inner electrode.

Electrodes for Electroanalysis – Preferences regarding electrode dimensions* and types vary. Cylindrical electrodes, fabricated from reinforced platinum gauze, are most common. Provision is usually made for rotation of the inner electrode.

In the electrolytic deposition of copper and lead, the rotating or inner electrode is generally made the anode. It is especially recommended that the electrodes be sandblasted. Even under optimum plating conditions, high-lead samples are prone to flake-off during electrolysis. This condition becomes more pronounced as the dimensions of the anode decrease.

Reagents – The reagents used are: hydrochloric acid (1%), and copper nitrate solution made by dissolving 100 g of $Cu(NO_3)\cdot 5H_2O$ in 1 liter of 5% HNO_3.

Procedure – To the solution reserved for the determination of copper and lead, add one drop of 1% HCl to promote better plating conditions for copper.† Mount the electrodes on the electroanalyzer, with the rotating electrode as the anode. If stationary electrodes are used, air stirring, at the rate of 2 bubbles/sec, will shorten the electrolysis time. Immerse the electrodes in the electrolyte so that they just clear the bottom of the electrolysis beaker, and dilute with just enough water to cover the platinum gauze cylinders. Cover the beaker with split watch glasses, and electrolyze for 90 min at a current of 1 to 2 amp. Dilute the electrolyte sufficiently to raise the liquid level approximately 3 mm, and continue electrolysis 15 min longer. If no copper deposit appears on the freshly immersed portion of the cathode stem, the electrodeposition is complete.

While lowering the beaker, containing the spent electrolyte, away from the electrodes (with the current still flowing), play a gentle stream of rinse water from a wash bottle on both electrodes. Reserve the electrolyte. Further dilute the acid solution on the deposits by quickly immersing them in a beaker containing fresh rinse water. Release the electrodes into this beaker, and wash several times more by immersion in beakers containing fresh tap water, taking care to prevent loss of any loosely adhering PbO_2 deposit on the anode.‡ A final dip of the electrodes into alcohol will facilitate drying.

Dry the anode in an oven at 120°C for 20-30 min. The cathode may be dried at room temperature, or in an oven for a few minutes; longer heating should be avoided. Cool and weigh the electrodes. For greater accuracy, strip the deposits from the electrodes in HNO_3, rinse, dry, and reweigh. Multiply the PbO_2 weight by 0.866 for lead (some laboratories prefer the empirical factor 0.844).

NOTE: For samples containing manganese, it is well to strip the lead oxide from the anode with 10 ml of HNO_3 and 2 ml of 3% H_2O_2. Rinse the stripped electrode thoroughly, catching the rinsings in the stripping beaker. Boil to destroy the excess H_2O_2 and evaporate to a volume of about 5 ml. Add one drop of 1% HCl and 10 ml of the 10% $Cu(NO_3)_2$ solution. Proceed as in the electrolysis of copper and lead. The electrolyte from the second lead electrolysis should be reserved if the second anode weight is appreciably different from the first. In this case evaporate the second electrolyte to a volume of about 3 ml and oxidize with KIO_4 (see procedure for the colorimetric determination of manganese).

Transfer the reserved spent electrolyte from the first electrolysis to a 250-ml volumetric flask, dilute to the mark, and mix. (If an electrolyte containing HF is being treated, immediately transfer it to a clean, dry polyethylene bottle

*Without exceeding the limits of compatibility of the electrolysis apparatus, the authors prefer large-type electrode pairs for either a stationary or rotating electrode system. For commercially available electroanalyzers with a rotating center electrode, the preference is as follows: diameter and height of gauze barrel of outer electrode, 52 mm and 50 mm, respectively; diameter and height of the gauze barrel of inner electrode, 15 mm and 50 mm, respectively; stem diameter, 1.6 mm; overall height of barrel plus stem, 125 mm.

†The presence of small amounts of chloride ion facilitates the plating process. In its absence, poor platings occur frequently. J.S. Scherrer, R.K. Bell, and W.S. Mogerman, *J. Res. Natl. Bur. Std. (USA)* **22**:697 (1939).

‡At the completion of the electrolysis, the process of removing and rinsing the electrodes requires special care, principally to prevent partial loss of the PbO_2 coating on the anode. Loss will be experienced more frequently with very low or very high PbO_2 platings. A deposit that contains less than 0.2% lead often does not form a very adherent coating on the anode, and hence may be partially lost during the rinsing process. Leads higher than 5% are prone to flake-off during electrolysis and the subsequent rinsing process. These percentages are nominal and will vary in different laboratories, depending on plating and accessory equipment.

and cap it to prevent loss due to evaporation.) Reserve for the determination of nickel, iron, manganese, and aluminum.

Preliminary Tests for Iron, Aluminum, Manganese, and Nickel

If the sample is known to contain iron, aluminum, manganese, or nickel, omit the pertinent preliminary test or tests outlined below and proceed directly with the indicated required photometric determinations.

If specification information regarding the composition of an alloy is not available, the presence or absence of these elements may be established quickly as follows: From the 250-ml volumetric flask containing the reserved spent electrolyte, transfer a 100(±5)-ml portion to a beaker and add NH_4OH until the solution is distinctly ammoniacal. Cover, place the beaker on a hot plate, boil 1 min, and remove from the heat. The formation of a flocculent precipitate indicates the presence of iron or aluminum, or both; a brownish precipitate indicates a preponderance of iron, a whitish precipitate indicates a preponderance of aluminum. Add a few crystals of $(NH_4)_2S_2O_8$ and replace the beaker on the hot plate. Again boil for 1 min and remove from the heat. The formation of a blackish precipitate indicates the presence of manganese. In the presence of $Fe(OH)_3$, small amounts of manganese are detected with difficulty. Hence, if the presence of manganese is suspected, the manganese should be determined photometrically.

Should iron, aluminum, or manganese be present as determined by the formation of their respective precipitates, they may be determined as described subsequently under the appropriate photometric procedure, using a proper aliquot of the reserved spent electrolyte.

To establish the presence or absence of nickel in a solution which contains iron, aluminum, or manganese, add HCl to dissolve the precipitate, then add sufficient citric acid to complex these ions. Again make the solution ammoniacal and add 10 ml of dimethylglyoxime solution (1 g of dimethylglyoxime dissolved in 100 ml of ethanol) to precipitate the nickel.*

*Small amounts of nickel precipitate very slowly. If a precipitate does not form immediately, allow the solution to stand overnight.

Should iron, aluminum, and manganese be absent, add 10 ml of dimethylglyoxime solution directly to the ammoniacal solution under test. The formation of the characteristic reddish flocculent precipitate indicates the presence of nickel.* If present, the nickel may be determined photometrically on an aliquot of the reserved spent electrolyte as described in the next subsection.

In the analysis of copper-base alloys, zinc is frequently determined by difference (*i.e.,* subtracting the sum of the percentages of the determined constituents from 100 percent).

Photometric Determinations of Iron, Aluminum, Manganese, and Nickel

General Consideration – These tests are conducted with aliquots of the reserved spent electrolyte contained in the 250-ml volumetric flask.

The apparatus used for these procedures is a filter photometer, or spectrophotometer, and accessory items such as cells, filters, *etc.,* depending upon the requirements of the instrument to be used.

The calibration curve may be prepared from NBS standard samples, or from composites of NBS standard samples that closely approximate the compositions of the samples to be analyzed. Alternatively, the curve may be prepared with appropriate aliquots of a standard solution containing the element to be determined. Caution: For curves prepared from standard solutions, careful attention must be given to interfering elements.

After a curve has been established, it is good practice to include a reagent blank and an aliquot from at least one NBS standard sample. The reagent blank and standard sample should be carried through the entire procedure, using the same amounts of all reagents. Solutions thus prepared and used carefully will provide sufficient blank and standard sample aliquots to last through many sets of analyses.

Each photometric procedure will include the percentage limits through which the curve may be applied. It should be kept in mind that the relative error increases very rapidly at transmittances above 80% and below 10%. Should it become desirable to determine percentages that fall near or outside these limits, new curves and

procedural modifications may be required. Generally, the upper concentration limit of a curve may be doubled by taking a sample aliquot half as large as that recommended in the procedure. Extending the lower concentration limit of a curve may be more difficult, due to the increased concentration of interfering constituents in larger aliquots if evaporation is required. Much depends also upon the element to be determined, the pH requirements, *etc.* Suggestions will be made where appropriate in individual procedures.

Determination of Nickel—Proceed as follows:

REAGENTS—The reagents used are: citric acid (20%), made by dissolving 100 g of citric acid in water and diluting to 500 ml; bromine water (saturated); dimethylglyoxime (ammoniacal), made by dissolving 5 g of dimethylglyoxime in 500 ml of concentrated NH_4OH; and a standard nickel solution, made by dissolving 0.1 g of high-purity nickel in 10 ml of HNO_3 (boil gently to expel brown fumes, cool, and dilute to 500 ml in a volumetric flask and mix). This nickel stock solution contains 200 μg of Ni per ml. From it, prepare a dilute standard solution containing 20 μg of Ni per ml.

PREPARATION OF CALIBRATION CURVE—The calibration curve may be prepared from NBS standard samples, or from composites of these that closely resemble the sample to be analyzed. Alternatively, the curve may be prepared with appropriate aliquots of the dilute standard nickel solution. To prepare a curve for alloys containing between 0.10 and 2% nickel, transfer aliquots of the dilute standard nickel solution containing 20, 100, 200, 300, and 400 μg of nickel, respectively, to five 100-ml volumetric flasks, and adjust the volume of each to 20 ml. To a separate 100-ml volumetric flask, add 20 ml of water to serve as a reference solution.

COLOR DEVELOPMENT AND PHOTOMETRY—Add the following reagents to each flask, with mixing after each addition: 5.0 ml of 20% citric acid solution, 10 ml of saturated bromine-water, and 6 ml of 1% dimethylglyoxime (ammoniacal) solution. Dilute to 100 ml and mix.

After 10 min, transfer a suitable portion of the reference solution to an absorption cell and adjust the photometer to the initial setting,* using a wavelength of 530 mμ. Maintaining this adjustment, take the photometric readings of the calibration solutions.

Plot the photometric readings against the respective microgram quantities of nickel used for color development.

PROCEDURE—Transfer a 5-ml aliquot†‡ of the sample solution from the 250-ml volumetric flask, containing the reserved spent electrolyte, to a 100-ml volumetric flask. To a separate 100-ml volumetric flask, add 5 ml of the reagent blank solution (in less exacting work, 5 ml of water will suffice). Proceed with each as directed under the previous subsection entitled "Color Development and Photometry."

CALCULATION—Convert the photometric reading of the sample aliquot to micrograms of nickel by means of the calibration curve. Calculate the percentage of nickel as follows:

$$\text{Nickel (percent)} = (A/B) \times 100$$

where A is the micrograms of nickel found in the sample aliquot, and B is the micrograms of sample represented by the sample aliquot.

Determination of Iron—Proceed as follows:

REAGENTS—The reagents used are: (a) Buffered hydroxylamine, made by dissolving 100 g of ammonium acetate in a liter of water, adding 8 g of hydroxylamine hydrochloride, and then 70 ml of HCl. Dilute to 2 liters and mix (pH $\approx$ 4.2). (If used infrequently, prepare as needed.) (b) 1,10-phenanthroline, made by dissolving 1.5 g of 1,10-phenanthroline in 150 ml of water at 80-90°C.

*This setting will correspond to 100% transmission, or zero absorbance, depending upon the equipment used or the preference of the operator.

†For samples containing less than 0.10% nickel, proceed as follows: Transfer a 10-ml aliquot of the sample solution to a beaker. To a second beaker, add 10 ml of water to serve as a blank. To a third beaker, add 40 μg of nickel (calibrating solution) at a volume of 10 ml. To each beaker add the following carefully measured reagents, with swirling after each addition: 5 ml of 20% citric acid solution, 5 ml of saturated bromine-water, and 5 ml of ammoniacal dimethylglyoxime. Allow to stand for 10 min, adjust the photometer to the initial setting at 530 mμ with the blank, and take the photometric readings for the calibrating and sample solutions. Plot the curve and convert the photometric reading for the sample solution to micrograms of nickel.

‡Interfering elements must not be ignored in taking larger aliquots. For example, the presence of manganese tends to produce high nickel results. Trouble due to interferences may be overcome by extraction of the nickel as follows: Add 5 ml of 10% hydroxylamine hydrochloride to the color complex. Mix and extract with 15 ml of chloroform in a separatory funnel. Transfer the chloroform layer to a second separatory funnel and shake with 10 ml of 0.5N HCl. Discard the chloroform layer. Now develop the nickel dimethylglyoxime color complex in the acid layer using 5 ml of saturated bromine-water and 5 ml of ammoniacal dimethylglyoxime solution, mixing after each addition. Blank and standard solutions should be carried through the same procedure.

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Dilute to one liter. (c) A standard iron solution, made by dissolving 0.1000 g of iron wire (99.9% pure) with 25 ml of (3:2) HNO_3. Boil gently to expel brown fumes, cool, transfer to a 500-ml volumetric flask, dilute to the mark, and mix. This stock solution contains 200 μg of iron per ml. And (d) prepare dilute standard iron solutions containing 2 and 20 μg of iron per ml, respectively.

PREPARATION OF CALIBRATION CURVE – The calibration curve may be prepared with NBS standard samples, or from composites of these that closely resemble the sample to be analyzed. Alternatively, the curve may be prepared with appropriate aliquots of the dilute standard iron solution. To prepare a curve for alloys containing between 0.03 and 0.80% iron,* transfer 6, 60, 100, and 160 μg of iron, respectively, to four 50-ml volumetric flasks (each addition should be less than 10 ml). To a separate 50-ml volumetric flask, add 8 ml of water to serve as a reference solution.

COLOR DEVELOPMENT AND PHOTOMETRY – Add to each flask, with mixing after each addition, 30 ml of the buffered hydroxylamine solution and 10 ml of the 1,10-phenanthroline solution. Dilute to the mark and mix.

Transfer a suitable portion of the reference solution to an absorption cell, and adjust the photometer to the initial setting,† using a wavelength of 490 mμ. Maintaining this adjustment, take the photometric readings of the calibration solutions. Plot the photometric readings against respective microgram quantities of iron used for color development.

PROCEDURE‡ – Transfer a 5-ml aliquot of the sample solution from the 250-ml volumetric flask, containing the reserved spent electrolyte, to a 50-ml volumetric flask.

To a separate 50-ml volumetric flask, add 5 ml of the reagent blank solution (in less exacting work, 5 ml of water will suffice). Proceed with each as directed under "Color Development and Photometry" above.

NOTE: The presence of appreciable amounts of zinc or nickel tends to produce low (sometimes very low) iron results. In such cases it is recommended that the iron be separated as the hydroxide. In this case, proceed as follows: Transfer a 25-ml aliquot of the sample solution from the 250-ml volumetric flask, containing the reserved spent electrolyte, to a 250-ml beaker. Add 5 g of NH_4Cl and a solution containing about 0.002 g of manganese, if manganese is not already present. Dilute to 100 ml and add an excess of NH_4OH. Boil 1 min, remove from heat, and carefully add a few crystals of $(NH_4)_2S_2O_8$. Again boil 1 min, remove from the heat, and filter through a fast paper. Wash several times with hot water, remove the filtrate, and place the precipitation beaker under the funnel. Dissolve the precipitate by washing the paper successively with 3% H_2O_2 (added dropwise), hot 10% HCl, and hot water. Repeat these washings until the precipitate has been completely dissolved, then wash with hot water. Add 5 ml of HNO_3 to the beaker and evaporate the contents to near dryness (1 ml or less). Transfer the solution to a 25-ml volumetric flask and dilute to the mark. Begin with a 5-ml aliquot of this solution as directed in the procedure.

CALCULATION – Convert the photometric reading of the sample aliquot to micrograms of iron by means of the calibration curve. Calculate the percentage of iron as follows:

$$\text{Iron (percent)} = (A/B) \times 100$$

where A is the micrograms of iron found in the sample aliquot, and B is the micrograms of sample represented by the sample aliquot.

Determination of Manganese – Proceed as follows:

REAGENTS – The reagents used are: (a) Potassium periodate, made by dissolving 13.6 g of KIO_4 in 800 ml of hot water. Add 268 ml of 85% phosphoric acid, and dilute to 2 liters. (b) Sodium hydroxide solution, made by dissolving 100 g of NaOH in 100 ml of water. Cool, dilute to 200 ml, and store in a polyethylene bottle. And (c) a standard manganese solution, made by dissolving 0.2000 g of electrolytic manganese (99.9% pure) with 40 ml of (1:1) HNO_3. Boil to expel the brown fumes, cool, and dilute to 2 liters in a volumetric flask. This solution contains 100 μg of manganese per ml.

Prepare a dilute manganese solution (1 ml = 10 μg Mn) by diluting 100 ml of the strong manganese solution to 1 liter in a volumetric flask.

PREPARATION OF CALIBRATION CURVE – The curve may be prepared with NBS standard

*Generally, the upper limit (0.80%) for iron may be extended to 1.6% by merely diluting an aliquot of the iron color-complex with an equal volume of water and measuring the new transmittance. However, it is preferable to start anew with a smaller sample aliquot.

†See footnote on p. 6, left-hand column.

‡William Goodman, *Anal. Chem.* **19**:141 (1947).

samples, or from composites of these that closely resemble the sample to be analyzed. Alternatively, the curve may be prepared with appropriate aliquots of the two standard manganese solutions. To prepare a curve for alloys containing between 0.04 and 2.0% manganese, transfer 40, 1000, and 2000 μg of manganese, respectively, to three 100-ml volumetric flasks. To a separate 100-ml volumetric flask, add 25 ml of water to serve as a reference solution.

COLOR DEVELOPMENT AND PHOTOMETRY—To each flask, add 15 ml of KIO_4 solution and insert a long stirring rod to promote smoother boiling. Boil gently for 3 min. (If color does not develop in a given flask, remove it from the heat and very cautiously add 1 ml of the NaOH solution. Return it to the hot plate and again boil for 3 min.) Place each flask in a hot water bath for 30 min, cool, dilute to the mark, and mix.

Transfer a suitable portion of the reference solution to an absorption cell, and adjust the photometer to the initial setting,* using a wavelength of 525 mμ.† Maintaining this adjustment, take the photometric readings of the calibration solutions.

Plot the photometric readings against respective microgram quantities of manganese used for color development.

PROCEDURE—Transfer a 25-ml aliquot of the sample solution from the 250-ml volumetric flask, containing the reserved spent electrolyte, to a 100-ml volumetric flask. To a separate 100-ml volumetric flask, add 25 ml of water to serve as a reference solution. Proceed with each as directed under "Color Development and Photometry" above.

CALCULATION—Convert the photometric reading of the sample aliquot to micrograms of manganese by means of the calibration curve. Calculate the percentage of manganese as follows:

$$\text{Manganese (percent)} = (A/B) \times 100$$

where A is the micrograms of manganese found in the sample aliquot, and B is the micrograms of sample represented by the sample aliquot.

*See footnote on p. 6, left-hand column.

†Chromium is not apt to be present, but if it is, determine the transmittance or absorbance at 575 mμ. Convert the photometric reading to micrograms of manganese from a standard curve prepared from appropriate standards containing chromium and read at 575 mμ.

Determination of Aluminum—Proceed as follows:

REAGENTS‡—The reagents used are: (a) Ammonium acetate (stock solution), made by dissolving 350 g of ammonium acetate in water and diluting to 1 liter. (b) Buffered ammonium acetate solution, made by transferring 200 ml of the stock ammonium acetate solution to a 1-liter beaker and adding 400 ml of water. Add 25 ml of thioglycolic acid (purified), then 18 ml of NH_4OH, and dilute to 1 liter. Adjust to pH 6 with NH_4OH, using a pH meter. (Prepare several hours before use. Store in a dark glass-stoppered bottle in a dark place. The solution lasts one week.) (c) Eriochrome cyanine-R (0.1% solution), made by dissolving 1 g of eriochrome cyanine-R in 800 ml of water in a 1-liter volumetric flask. Add 10 ml of 1N HCl and dilute to 1 liter with water. Mix and store in a dark place. Prepare fresh monthly. (d) A standard aluminum solution (stock solution), made by dissolving 0.1000 g of Al (99.9% pure) with 10 ml of HCl (1:1) and 2 ml of HNO_3. Boil gently for several minutes, cool, and dilute to 1 liter in a volumetric flask. This solution contains 100 μg of aluminum per ml. And (e) reference and dilute aluminum standard solutions, which are made, using matched pipettes, by transferring 2-, 4-, 8-, and 12-ml aliquots of the stock aluminum solution to four 30-ml quartz crucibles. To each, and to a fifth quartz crucible, the latter to serve as a reference solution, add 3 ml of H_2SO_4 (1:1). Without boiling, evaporate the contents of each crucible to white fumes of H_2SO_4. Cool and dilute each cautiously with 10 ml of water. Transfer to separate 200-ml volumetric flasks, dilute to the mark, and mix. In increasing order, these flasks contain 0, 1, 2, 4, and 6 μg of Al per ml.

PREPARATION OF CALIBRATION CURVE—The curve may be prepared from NBS standard samples, or from composites of these that closely resemble the compositions of the samples to be analyzed. These samples should be carried through the entire procedure beginning with the nitric or nitric-hydrofluoric dissolution of the sample, as required. Since the curve does not follow Beer's Law, the NBS standard samples should be composited to provide about five or six points at appropriately-spaced curve intervals to cover the range of aluminum to be determined.

‡See Charles Dozinel, *Chim. Anal.* (Paris) **38**:244-9 (1956).

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Alternatively, the curve may be prepared with appropriate aliquots of the dilute aluminum standard solutions. To prepare a curve for alloys containing between 0.1 and 1.5% aluminum, transfer 2-ml aliquots of the reference solution and dilute aluminum standard solutions to five 100-ml beakers so that these beakers contain, respectively, 0, 2, 4, 8, and 12 μg of aluminum.

LAKE DEVELOPMENT AND PHOTOMETRY – Add exactly 20 ml of buffered ammonium acetate solution to each beaker and swirl. Using a blow-out pipette, add 2 ml of eriochrome cyanine-R solution and swirl. Transfer each solution to a separate absorption cell. Adjust the photometer to its initial setting with the cell containing the reference solution, using a wavelength of 535 mμ.* Then, without changing the initial adjustment, quickly read and record the photometric measurements for the calibration and unknown sample solutions.

CAUTION: Since reference, calibration, and unknown sample solutions undergo a continuous fading process following the addition of eriochrome cyanine-R, it is recommended that lake development for all solutions be completed and the photometer readings be taken as quickly as possible.

NOTE: Instead of making the initial setting at 100% transmittance or zero absorbance, choose some nominal figure such as 90% transmittance, or 0.05 absorbance. By so doing, it is possible to obtain a second on-scale reading for the reference solution after a complete set of readings has been taken. If a set of readings is taken within a period of 5 min, the increase in transmittance due to fading in the reference solution is generalley less than 1%.

PROCEDURE – Transfer 20-ml aliquots from the 250-ml volumetric flasks, containing the reserved spent electrolyte and the reagent blank solution, to separate 30-ml quartz crucibles. Add 3 ml of H_2SO_4 (1:1) to each and evaporate, without boiling, to white fumes of H_2SO_4. Cool and dilute each cautiously with 10 ml of water. Transfer to separate 200-ml volumetric flasks, dilute to the mark, and mix.

Transfer 2-ml aliquots of each to separate 100-ml beakers and proceed as directed under "Lake Development and Photometry" above.

*This procedure has been written for a cell having a 1-cm light path. Cells having other dimensions may be used, provided that suitable adjustments can be made in the amounts of sample and reagents used.

CALCULATION – Convert the photometric readings for unknown sample and reagent blank to micrograms of aluminum. Calculate the percentage of aluminum as follows:

$$\text{Aluminum (percent)} = (A/B) \times 100$$

where A is the micrograms of aluminum represented in the final solution, and B is the micrograms of sample represented in the final solution.

NOTES: (a) To determine aluminum percentages greater than 1.5%, alter the procedure by evaporating appropriately smaller aliquots of the reserved spent electrolyte with 3 ml of H_2SO_4 (1:1). (b) To determine aluminum percentages less than 0.1% in a given alloy, a separate calibration curve must be prepared. This may be accomplished by transferring two 20-ml aliquots of the reference solution to separate 100-ml beakers, one to serve as a reference solution, the other (after the addition of 8 μg of Al) to serve as a calibration solution. To a third 100-ml beaker, transfer a 20-ml aliquot of the solution under test. Neutralize each with NH_4OH until just slightly acid to congo red paper. With swirling after each addition, add 25 ml of buffered ammonium acetate solution, 3 ml of eriochrome cyanine-R solution, and dilute to 50 ml. Adjust the photometer and take readings as previously directed.

NITRIC-HYDROFLUORIC ACID SEQUENCE METHOD

Principle

The sample is completely dissolved in nitric and hydrofluoric acids. Copper and lead are removed electrolytically. Nickel, iron, manganese, and aluminum are determined photometrically on aliquots of the spent electrolyte. Tin is determined volumetrically on a separate sample.

Apparatus

Polyethylene beakers (250-ml) and polyethylene beaker covers.

Procedure

Transfer a carefully weighed 1-g sample to a 250-ml polyethylene beaker and cover with a

polyethylene beaker cover. (If aluminum is not determined, vycor beakers are satisfactory. In this case, the brown fumes may be expelled by boiling for several minutes after the sample has been dissolved.) Add 15 ml of water, 1 ml of HF, and 10 ml of HNO_3. Allow to stand for a few minutes for the vigorous action to subside. Rinse the cover and inner wall of the beaker with water from a wash bottle, then place the beaker on a steam bath for 30 min. Cool, rinse down, and dilute to 150 ml with water. Determine copper and lead electrolytically as directed in the nitric acid sequence. Reserve the electrolyte for photometric determination of nickel, iron, manganese, and aluminum as directed in the nitric acid sequence.

Determination of Tin

Since no provision was made for the determination of tin in the analytically more complex copper-base alloys which were initially dissolved with HNO_3—HF, a method is included for the separate determination of tin in these alloys. This method is a volumetric procedure in which the tin is separated, reduced to the divalent state, then oxidized to the tetravalent state with a standard KIO_3 solution.

Apparatus—A 500-ml Erlenmeyer flask is fitted with a one-hole rubber stopper attached to an L-shaped glass tube. When assembled for the tin reduction, the free end of the tube extends to near the bottom of an adjacent 250-ml beaker, which contains about 75 ml of saturated $NaHCO_3$ solution. This insures the exclusion of air during the reduction and subsequent cooling process.

Reagents—The reagents used are: ferric chloride solution (1%), made by dissolving 10 g of $FeCl_3 \cdot 6H_2O$ in 500 ml of water, adding 10 ml of HCl, and diluting to 1 liter; antimony chloride solution (2%), made by dissolving 2 g of $SbCl_3$ in 50 ml of HCl and diluting to 100 ml with water; aluminum rods for tin reduction, made by cutting aluminum welding rod material (S-2 grade, diam = 3/32 in.) into 3.2-in. lengths; a starch solution, made by adding a paste, containing 1 g of soluble starch in 5 ml of water, to 100 ml of boiling water, stirring and cooling; a potassium iodide solution (10%), made by dissolving 10 g of KI in 100 ml of water (prepare fresh as needed); sodium bicarbonate pills (~0.65 g each); sodium bicarbonate solution (saturated); and a standard potassium iodate solution (0.1N), made by dissolving 3.567 g of KIO_3 in 200 ml of a water solution containing 1 g of NaOH and 10 g of KI, then diluting to 1 liter in a volumetric flask. (The tin-equivalent of this solution may be established by carrying a 0.1000-g sample of mossy tin (99.9%) throughout the procedure.)

Separation of Tin—Transfer a 2-g sample to a 500-ml Erlenmeyer flask, add 10 ml of water, 15 ml of HCl, and 15 ml of HNO_3. (Carry a blank throughout the entire procedure.) When solution is complete, boil gently to expel brown fumes. Dilute to 200 ml and add 10 ml of a 1% $FeCl_3$ solution. While swirling, add NH_4OH to the formation of the blue copper-ammonia complex. Boil 1 min and filter through a fast 12.5-cm filter paper containing a little paper pulp. Wash with hot 1% NH_4Cl solution which has been made ammoniacal to litmus. Remove the beaker containing the filtrate, place the original Erlenmeyer flask under the funnel, and dissolve the precipitate by washing alternately with hot HCl (1:1) and hot water. After the precipitate is completely dissolved, wash the paper five times with hot water. Dilute the contents of the flask to 200 ml and reprecipitate the tin and iron as previously directed. Boil 1 min and refilter through the original filter paper, again washing with a hot 1% NH_4Cl solution which has been made ammoniacal to litmus. Return the paper and precipitate to the Erlenmeyer flask and add 75 ml of HCl and 25 ml of water. Swirl to dissolve the precipitate.

Reduction of Tin—Add 2 drops of $SbCl_3$ solution and dilute to 200 ml with water. Assemble the apparatus for tin reduction. Open the flask, add three lengths of the aluminum rods, and restopper the flask tightly. Immerse the free end of the delivery tube in the beaker containing the saturated $NaHCO_3$ solution. Allow the reaction to proceed at room temperature until the aluminum is almost dissolved. (If action is slow starting, apply heat until the aluminum begins to dissolve vigorously.) After the aluminum is almost dissolved, place the flask on a hot plate, with the free end of the L-shaped delivery tube still immersed in the bicarbonate solution. Gradually heat to

boiling (*caution**) as the remainder of the aluminum dissolves, then boil for an additional 3 or 4 min. Ideally the solution should commence to boil gently just before the aluminum is completely dissolved. While the solution is still boiling, quickly lift the flask and transfer the tip of the delivery tube to a beaker containing a fresh supply of $NaHCO_3$ solution. With the delivery tube *continuously* immersed, swirl the flask to clear the inner wall, remove from the heat, and cool in a cold water bath.

Titration — Fill the buret with standard KIO_3 solution and measure out 2 ml of starch solution and 5 ml of KI solution. Remove the rubber stopper from the Erlenmeyer flask and quickly add two $NaHCO_3$ pills, 2 ml of the starch solution, and 5 ml of the KI solution. Immediately titrate with the standard KIO_3 solution until the blue color gives indication of persisting. Continue with the dropwise addition of the KIO_3 until a bluish tint persists for 20-30 sec.

Calculation — Calculate the percentage of tin as follows:

$$\text{Tin (percent)} = [(A-B)C/D] \times 100$$

where A is the milliliters of KIO_3 solution required to titrate the sample, B is the milliliters of KIO_3 solution required to titrate the blank, C is the tin-equivalent of the KIO_3 solution in grams per milliliter, and D is the grams of sample used.

*Too vigorous boiling may liberate excessive amounts of CO_2 from the saturated $NaHCO_3$ solution and thus lessen its effectiveness.

SUMMARY

The foregoing two procedures, or sequence methods, provide rapid access to the analysis of the more common constituents found in many copper-base alloys. Two tables are included to aid the chemist in selecting the appropriate method for a given analysis: Table 1 lists representative copper-base alloys and the recommended analytical scheme to follow for chemically simple or chemically complex alloy systems; Table 2 compares the results obtainable by either sequence method with the National Bureau of Standards certified values assigned to the various alloy constituents. Regarding the latter table, a study of the data reveals analytical pitfalls which require the special attention of the chemist.

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* U.S. Naval Research Laboratory Washington, D.C. 20390	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

Procedures for the Chemical Analysis of Copper-Base Alloys

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

A final report on one phase of the problem.

5. AUTHOR*(S)* *(Last name, first name, initial)*

Gates, O.R., and Mylting, O.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 10, 1966	16	None

8a. CONTRACT OR GRANT NO. NRL Problem M01-20 b. PROJECT NO. RR 007-01-46-5422 c. d.	9a. ORIGINATOR'S REPORT NUMBER*(S)* NRL Report 6357 9b. OTHER REPORT NO*(S)* *(Any other numbers that may be assigned this report)* None

10. AVAILABILITY/LIMITATION NOTICES

Unlimited availability. Available from Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., 22151

11. SUPPLEMENTARY NOTES None	12. SPONSORING MILITARY ACTIVITY Dept. of the Navy (Office of Naval Research)

13. ABSTRACT

Two sets of sequence procedures are presented, each with its own recommended application, that will quickly resolve a great number of analytical problems that may be encountered in the chemical characterization of many common and unusual copper-base alloys. One procedure provides for the precipitation of tin, as metastannic acid, with nitric acid when alloy compositions are such that no appreciable tin-contamination problems arise; the second provides for the retention of tin in solution with hydrofluoric acid when tin-contamination problems are present. By the use of the appropriate procedure, rapid access to the greatest possible amount of analytical information on individual samples, and results comparable in accuracy to standard methods, will be obtained.

DD FORM 1 JAN 64 1473

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Copper Alloys						
Chemical Analysis						
Quantitative Analysis						
(Qualitative Analysis)						
(Photometry)						
Tin						
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