

**THE DETERMINATION OF
SOME COMMON ALLOYING ELEMENTS
IN ALUMINUM AND ITS ALLOYS**

William Zimmerman, III

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Dr. O. T. Marzke, Superintendent, Metallurgy Division**

September 30, 1947



NAVAL RESEARCH LABORATORY

COMMODORE H. A. SCHADE, USN, DIRECTOR

WASHINGTON, D.C.

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PREFACE

This report publishes procedure for aluminum alloy analysis which results from experiences of the Metallurgy Division over a period of several years.

ABSTRACT

A method is proposed for the determination of silicon, copper, silver, lead, titanium, iron, nickel, and zinc in aluminum and its alloys using a single sample weight.

Silicon is dehydrated with perchloric acid; copper, lead, and silver are precipitated as the sulphides, ignited, fused, dissolved and electroplated; an aliquot of the sulphide filtrate is used for the titanium; iron is determined in the balance of the filtrate by titration with ceric sulphate following expulsion of hydrogen sulphide; zinc is precipitated in a formic acid solution with hydrogen sulphide and nickel is determined by precipitation with dimethylglyoxime in the filtrate from the zinc determination.

THE DETERMINATION OF SOME COMMON ALLOYING ELEMENTS IN ALUMINUM AND ITS ALLOYS

INTRODUCTION

In order to systematize the chemical analysis of aluminum and its alloys and to provide for greater economy of reagents, time, and effort, several different attempts to develop a sequential analytical procedure have been made in this laboratory. Many other sequential procedures have been proposed; the earliest of which were developed by Richards *, Regelsberger † and Moissan ‡. Later methods have been developed by Alcoa § and Balco ** and from a study of the ASTM methods ††, other sequential procedures may be devised. Alcoa has developed a sequence for the determination of copper, silicon, iron and titanium on a single sample weight in commercially pure aluminum. Balco has developed several procedures of limited scope or for special alloys: a) the determination of silicon, copper and iron on a single sample weight of duralumin; b) the determination of antimony, copper and iron in B.A. 35; and c) the determination of copper, manganese, magnesium and nickel following an acid attack on aluminum alloys.

The above methods are limited in scope and cannot be used for general routine laboratory analysis. The ASTM procedure provides for the development of sequential procedures for the determination of silicon, copper, lead, iron, zinc and titanium in a sulphuric acid solution.

The proposed method provides for the determination of the above elements but in a perchloric acid solution and, in addition, provides for the determination of nickel and silver when present. Except for chromium, manganese and magnesium, which, it has been the experience of the author, are best determined on separate samples, the proposed method provides a procedure which permits accurate determinations of all of the common alloying elements of aluminum and its alloys on a single sample weight. This is of particular importance when the amount of sample available is limited.

The dehydration of silica with perchloric acid has been used for many years in this laboratory in iron and steel analyses and the method has proved so efficient that the same medium was tried with aluminum alloys. Although certain precautions must be taken during dehydration, it has proved a very efficient and easy medium with which to work and has been used with aluminum alloys in this laboratory for the past four years.

* Richards, J. W., "Aluminium" 2nd Edition, 469-487, (1890)

† Regelsberger, F., "Z. Angew. Chem.," 4, 360-363, 442-446, 473-478 (1891)

‡ Moissan, H., "Compt. Rend." 121, 851-856, (1895)

§ Aluminum Company of America, "Chemical Analysis of Aluminum," (1941)

** British Aluminum Company, Limited, "Analysis of Aluminum and its Alloys," (1941)

†† ASTM, "Methods of Chemical Analysis of Metals," p. 130 ff. (1943).

In the proposed method, copper, lead, and silver are precipitated from the silica filtrate with hydrogen sulphide. Following the expulsion of hydrogen sulphide, an aliquot is taken for the determination of titanium with peroxide and the reduced iron is titrated with ceric sulphate in the balance of the solution. Zinc is precipitated with hydrogen sulphide in a buffered formic acid solution following the titration of the iron and the addition of citric acid. Nickel is finally precipitated with dimethylglyoxime in the filtrate from the zinc determination following expulsion of hydrogen sulphide. Copper, lead and silver are determined electrolytically using platinum gauze electrodes. Copper and silver are stripped from the cathode and the silver is then determined as the chloride.

Chromium, manganese and magnesium are determined on separate samples; chromium and manganese, because they may be determined with no preliminary separations; and magnesium because a caustic attack eliminates the necessity of filtering a large mass of gelatinous aluminum hydroxide.

The following procedure has been in use in this laboratory except for minor changes for the past two years for all routine analysis.

PROCEDURE

Step I a - The Determination of Silicon (Less than 1%)

Weigh out a 2.000 gram sample of millings or drillings to the nearest milligram, place in a 400 ml pyrex beaker, add 30 ml HNO₃ (1-1), place on a medium hot plate until solution is complete (add additional HNO₃ (1-1) to complete solution if necessary). When solution is complete or nearly so, cautiously add 40 ml HClO₄ (70-72%) and evaporate to fumes of HClO₄. Caution: As the sample dehydrates, there is some danger of spattering which may be minimized by the use of bumping beakers.

After the sample has fumed vigorously for 15-20 minutes, remove from the hot plate and allow to cool slightly. While still hot, remove the cover glass and allow the sample to fume gently in order to remove any Cl₂ formed by the decomposition of the perchloric acid and to prevent the precipitation of AgCl. When cool, dilute to 125-150 ml with hot water, filter through an 11.0-cm #40 Whatman paper, police the beaker thoroughly and transfer the SiO₂ to the paper and wash with warm HClO₄ (1-1000) to remove mineral constituents, finally wash paper and precipitate 3-5 times with warm water to remove the last traces of HClO₄. Reserve the filtrate (solution A). Place the precipitate and paper in a platinum crucible, ignite carefully to remove carbon and finally at 1000°C. Cool in a dessicator and weigh. Add sufficient H₂SO₄ (1-4) to moisten the impure SiO₂ and add 5-10 ml HF. Evaporate to dryness, heat cautiously to drive off SO₃, finally at 1000°C, then cool and reweigh.
$$\frac{\text{Difference in weight} \times 46.72}{\text{sample weight}} = \% \text{Si.}$$

Step I b.- Determination of Silicon (more than 1%)

For silicon content between 1% and 3% use a 2.000-g sample, above 3% use a 1.000-g sample, weighed accurately to the nearest milligram. Place the sample in a platinum dish, add 15 ml water and then slowly add 8-g NaOH pellets (5-6 NaOH for a 1.0-g sample). When the first violent reaction subsides, heat to boiling, then cool somewhat, add 1-2 ml H₂O₂ (30%) dropwise, heat to boiling a second time, repeat the addition of peroxide until no more oxidation takes place, dilute to about 50 ml and pour into a 400-ml pyrex beaker, scrub out the dish thoroughly and wash well, first with water, then with dilute HNO₃, add sufficient HNO₃ to the solution to neutralize the excess NaOH and to

dissolve any unattacked metals. Heat to boiling to remove any oxides of nitrogen, cool somewhat, then cautiously add 40 ml HClO_4 (35 ml for a 1.000-g sample). Evaporate to fumes of HClO_4 and continue as in Ia above, observing the same precautions.

If the ignited SiO_2 appears dark, fuse the impure SiO_2 with a minimum amount of Na_2CO_3 , dissolve the melt in hot water, neutralize with HNO_3 (1-1), add 30-35 ml HClO_4 and repeat the dehydration, etc. It is best to test the filtrate for other elements to be determined, although they are usually absent.

Step II. - Determination of Silver, Copper and Lead

Heat the filtrate from the silicon determination (solution A) to boiling and saturate with H_2S , allow the precipitated sulphides to settle and filter through an 11.0-cm #42 Whatman paper, wash with H_2SO_4 (1-100) saturated with H_2S . Place the precipitate and paper into a fused-quartz or porcelain crucible and ignite at 550-600°C. Reserve the filtrate (solution B). Fuse the ignited oxides with a minimum amount of $\text{K}_2\text{S}_2\text{O}_7$ at as low a temperature as possible and dissolve the fused melt in 25 ml of water and 5 ml HNO_3 . Scrub out the crucible and place the solution in a 250 or 400-ml beaker for electrolysis, dilute sufficiently to cover the electrodes, heat to 40°C, and add 1 ml H_2O_2 (30%). Electrolyze for one-half hour with a current of one ampere, using weighed sand-blasted platinum gauze electrodes. Add additional peroxide as necessary to prevent deposition on the anode. When copper begins to plate out on the cathode, make no more peroxide additions and allow the electrolysis to continue for 15 minutes, then add 4 ml H_2SO_4 and continue electrolysis until deposition is complete as shown by rinsing the sides of the beaker with a jet of distilled water and noting the lack of additional deposition on the freshly immersed platinum. When deposition is complete,, the electrodes are raised, and a beaker of distilled water is substituted for the electrolyte. Remove the electrodes from the electrolysis outfit, dip into fresh-distilled water then into alcohol and dry in the oven at 110°C. Allow the cathode to dry for two to three minutes, but dry the anode with the PbO_2 deposit, for a longer period. (A thirty-minute drying period is recommended but this may be shortened to five minutes for the amount of lead usually found in aluminum alloys.)

After weighing the combined silver and copper plate, the deposit is stripped from the electrode with as little dilute HNO_3 (1-3) as possible. Boil off the oxides of nitrogen and precipitate the silver as the chloride, using 0.1 N HCl . Allow the precipitated AgCl to settle and coagulate overnight, filter through a weighed glass-frit or Gooch crucible, wash with 0.01 N HCl and dry at 150°C. Weigh as AgCl , calculate to Ag and subtract from the combined weight of silver and copper.

Step III. - The Determination of Iron

Transfer the filtrate from the sulphide precipitation (solution B) to a 600-ml beaker and rapidly heat to a hard boil. Boil until a test with lead acetate paper is negative for H_2S (20-30 minutes). Cool in a water bath, transfer to a 200-ml volumetric flask, make up to volume, take a 100- ml aliquot for the determination of titanium. Transfer the balance of the solution to a beaker and titrate with a standard $\text{Ce}(\text{SO}_4)_2$ solution, equivalent to 2 mg Fe per ml. Use either o-phenanthroline as an indicator, and subtract an indicator blank, or use a potentiometer to determine the end point. Reserve the iron solution for determination of zinc and nickel (Solution C).

Step IV. - The Determination of Titanium

Evaporate the aliquot taken above to about 50 ml and transfer to a 100-ml volumetric flask, filtering if necessary. Add 2 ml H_3PO_4 (1-1) and 2 ml H_2O_2 (30%) and dilute to

the mark. Record the transmission with a Klett colorimeter, using a #42 filter and a standard colorimeter test tube. Calculate the percentage of titanium present from a graph made by recording the transmission through standards of known concentration.

Step V. - The Determination of Zinc

To the solution from the iron determination (solution C) add 30 ml of a 20% solution of citric acid, neutralize with NH_4OH using methyl red as an indicator. Add 30 ml formic acid solution (200 ml formic acid, 30 ml ammonium hydroxide, and water to make one liter), heat to boiling, gas with H_2S , filter through an 11.0-cm #42 Whatman paper, wash well with a formic acid wash solution (10 ml of formic acid solution diluted to one liter and saturated with H_2S). Dissolve the precipitated ZnS by placing paper and precipitate in the original beaker and adding 40 ml HCl (1-3), dilute to 150 ml, add 10 ml citric acid solution, neutralize with NH_4OH , add 30 ml formic acid solution, heat, gas, filter as before and ignite in a weighed porcelain crucible at $700-750^\circ\text{C}$. Weigh as ZnO . Reserve the filtrates.

Step VI. - The Determination of Nickel

Combine the filtrates from the determination of zinc, boil out the H_2S , evaporate somewhat, filter on a #40 paper, add 2-3 ml HNO_3 to oxidize the iron, neutralize the solution, which is now about 400 ml, with NH_4OH , using methyl red as an indicator, make just acid with HCl , add 20 ml of an alcoholic 1% solution of dimethylglyoxime (or 20 ml of a 3% water solution of the sodium salt of dimethylglyoxime) for a nickel content up to 0.02 g and add an additional 5 ml for each additional 0.01 g of nickel present. Make the solution just ammoniacal, then add 3-4 drops NH_4OH in excess, coagulate the precipitated nickel dimethylglyoxime at 80°C for one-half hour, allow to cool, and proceed as in either (a) or (b) below.

(a) Filter the nickel precipitate on a weighed glass-frit or Gooch crucible, wash well with cold water, dry at 110°C , cool, and weigh as nickel dimethylglyoxime containing 20.32% nickel.

(b) Filter the nickel precipitate through a #41 Whatman paper, place paper and precipitate back into the beaker, add 15 ml HNO_3 and 10 ml HClO_4 . Evaporate to fumes of HClO_4 , cool, dilute to 100 ml, add 5.0 ml 0.3% AgNO_3 solution, 20 ml citric acid solution (1 lb citric acid, 1 lb ammonium sulphate, 5 grams ammonium chloride, diluted to three liters), titrate with NH_4OH to a clear solution, add 2 ml 20% KI solution and then titrate to a clear solution with NaCN solution (23 g NaCN , 20 g NaOH , diluted to three liters). Subtract a determined blank by titrating the silver nitrate and potassium iodide with no nickel present. Determine the nickel value of the cyanide by titrating against a sample of known nickel content.

EXPERIMENTAL RESULTS

As an indication of the accuracy and precision of the proposed method, some of the results obtained using Bureau of Standard Samples are given in Table I.

It will be noted that when the percentage of the constituent is very small the results are not particularly accurate, for example, the zinc content of B.S. 85a and the titanium content of both B.S. 85a and B. S. 86B. When great accuracy is desired, it is recommended that separate samples be used for these and similar trace elements which are less than 0.05%.

TABLE I
Results of Analysis of Bureau of Standards Aluminum Alloys

Element	Sample No	Found %	Deviation from Certificate %	Certificate %	Element	Sample No	Found %	Deviation from Certificate %	Certificate %			
Silicon	85a	0.117	+0.003	0.114	Copper	85a	2.47	0.01	2.48			
		0.113	-0.001									
		0.112	-0.002									
		0.117	+0.003									
		0.110	-0.004									
	86b	0.449	-0.021	0.47	86b	7.84	-0.04	7.87				
		0.458	-0.012									
		0.476	+0.006									
		0.474	+0.004									
		0.474	+0.004									
Iron	85a	0.206	-0.002	0.208	Titanium	85a	0.017	+0.001	0.016			
		0.214	+0.006									
		0.201	-0.007									
		0.222	+0.014									
		0.228	+0.020									
	86b	1.53	0.00	1.53	86b	0.028	-0.004	0.032				
		1.52	-0.01									
		1.51	-0.02									
		1.54	+0.01									
		1.51	-0.02									
		0.04	+0.021			0.019	Nickel		85a	0.411	-0.001	0.41
		0.06	+0.041									
		0.02	+0.001									
		0.01	-0.009									
		0.01	-0.009									
86b	1.52	+0.02	1.50	86b	0.416	+0.006	0.41					
	1.54	+0.04										
	1.55	+0.05										
	1.53	+0.03										
	1.52	+0.02										

NOTES ON THE PROCEDURE

Procedure in Absence of Silver

When silver is not present, the following modifications in the procedure may be made:

Step I a.- Place sample in 400 ml beaker, add 100 ml HClO_4 (1-6) then slowly add 15 ml HCl (1-1) for each gram of sample. When reaction stops, add 1-2 ml HNO_3 and then 35 ml HClO_4 .

Step I b. - Scrub out dish with HCl instead of HNO_3 but add 1-2 ml HNO_3 before the addition of HClO_4 .

Step II - The precipitated sulphides may best be treated by returning the paper and precipitate to the original beaker, adding 25-30 ml HNO_3 , 5 ml H_2SO_4 , evaporating to fumes of sulphuric acid, taking up to 200 ml adding 8 ml HNO_3 (1-1) and electrolyzing. For the amount of lead usually present in aluminum alloys this procedure is entirely satisfactory, since the solubility of lead sulphate is apparently greater than the solubility of the electrolyzed lead dioxide.

Determination of Silicon

In the determination of silicon, a two-gram sample is frequently preferable to a smaller weight. However, because of the insolubility of aluminum perchlorate, it is recommended that a one-gram sample be used when practical. As the last traces of water and more volatile acids are removed from the solution a heavy precipitate of aluminum perchlorate is formed, and bumping may occur. In order to eliminate the possibility of bumping, two different methods have been used with equal success in this laboratory. The first is to use bumping beakers, which is extremely satisfactory, provided the equipment is available. The second involves careful evaporation of the solution with the use of glass hooks during the preliminary stages and without glass hooks during the final stages of evaporation. It has been found that by using an electric hot plate on high heat with a single layer of asbestos paper separating the beaker and the hot plate, bumping seldom occurs with a two gram sample.

When the impure silica appears dark, it is usually caused by the presence of metallic silicon or silicides which resist both the sodium hydroxide-peroxide attack and the perchloric acid attack. If a carbonate treatment is not made, the silicon or silicides may resist the HF attack and leave a black residue which may be fused with carbonate but which is insoluble in a fusion with pyrosulphate. In any case the results for silicon will be low. Whereas, by making the carbonate fusion, accurate results may be attained.

In the presence of large amounts of silver, a slight turbidity may develop upon dilution of concentrated HClO_4 . This seems to have no effect upon the determination since the chloride concentration is too low for the silver chloride to coagulate into large enough particular for retention a #40 paper.

Determination of Silver Copper and Lead

Silver may be precipitated by the addition of 0.1 N HCl directly to the silicon filtrate. In which case, the copper and lead are determined simultaneously.

A rotating electrode apparatus is used for the electrodeposition of copper, lead, and silver; and in the usual case, the stationary electrode is used as the cathode. However, when appreciable amounts of lead are present, it is preferable to reverse the current and plate the lead on the stationary electrode in order to minimize the danger of loss in the lead plate due to flaking.

If both lead and manganese are present, the lead results will tend to be high. Ravner* has shown that this difficulty may be overcome by dissolving the anode plate in dilute nitric acid and replating.

The copper deposit is washed by raising the electrodes and replacing the beaker containing the electrolyte with one containing distilled water without interrupting the flow of current, and then dipping into two separate beakers of alcohol. Previous work done at this laboratory* indicates that this method of washing results in practically no copper loss, and it has the great advantage of not diluting the electrolyte. Although a small amount of the electrolyte is lost in this fashion, it is not sufficient to cause any great error in the results of the succeeding determinations, if any, on the electrolyte. A disadvantage of the copper and silver determination is that it throws any errors in the determination upon the copper results.

Determination of Iron

When permanganate is used to titrate the iron instead of ceric sulphate, the titanium may be determined on the entire sample prior to the determination of zinc and nickel. However, it is advisable to omit the phosphoric acid and set up a special curve for such determinations.

It has been found that if the filtrate from the sulfide precipitation is placed into a 600-ml beaker, then placed on a hot plate which is at a sufficiently high temperature to cause rapid boiling of the solution, it is then unnecessary to maintain a flow of carbon dioxide in order to maintain a non-oxidizing atmosphere. Nor is it necessary to make any special precautions during the cooling of the solution in order to prevent oxidation of the reduced iron despite the presence of perchloric acid. Babson and Johnson† have also shown that, in dilute perchloric acid solutions, hydrogen sulphide gives a quantitative precipitate of copper and lead and also gives a quantitative reduction of the iron.

None of the elements ordinarily present in an aluminum alloy interferes with the determination of iron following the hydrogen sulphide reduction. Lundell and Knowles‡ have stated that polythionic compounds, which may consume the oxidizing agent, may be formed upon treatment with hydrogen sulphide. No difficulty has been experienced at this laboratory in this respect.

Determination of Titanium

The titanium aliquot, as used in the procedure, gives an effective weight of one gram for the determination. It occasionally happens that this is too large a sample for effective determination of the titanium by the colorimetric method and when this is true,

* Ravner, H., "Ind. and Eng. Chem., Anal. Ed.," 17, 41 (1945)

† Babson, E. K., and Johnson, W. W., "Ind. and Eng. Chem., Anal. Ed." 18, 292-293 (1946)

‡ Lundell, G. E. F., and Knowles, H. B., "J. Am. Chem. Soc.," 43, 1560 (1921)

a smaller aliquot should be used. When vanadium or molybdenum are present in the sample, special separations must be made in order to determine the titanium colorimetrically.

Determination of Nickel and Zinc

In the determinations of nickel and zinc there is some danger of ammonium perchlorate contaminating the precipitate, but, by adjusting the volume to above 300 ml for the zinc determination and to about 400 ml for the nickel determination, all traces of perchlorates are removed by the routine washing procedure and there is no contamination of the precipitate.

* * *