# IMPROVED METHOD FOR DETERMINATION OF ALUMINUM IN CERTAIN NONFERROUS MATERIALS BY USE OF AMMONIUM AURINTRICARBOXYLATE

By John A. Scherrer and William D. Mogerman

## ABSTRACT

The difficulties encountered in using existing colorimetric methods for the determination of small amounts of aluminum in nonferrous materials are discussed. A method is proposed for obviating these difficulties. If the method is combined with a preliminary electrolysis in a mercury cathode cell, from 0.02 to 0.08 mg of aluminum can be determined quickly and accurately, without a colorimeter. The use of the mercury cathode cell and the effect of interfering substances are also discussed.

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## I. INTRODUCTION

The determination of small amounts of aluminum has become a matter of considerable importance in the nonferrous and other metal industries. The undesirable effect of this element, even in very small amounts, in solders, bearing metals, and similar products makes it necessary for the buyer to limit the aluminum content rigorously. Thus, Federal Specification QQ-S-571, Tin-Lead Solder, Grade A, requires that the aluminum content shall be "none" on a 5-g sample. Federal Specification QQ-M-161, Anti-friction Metal, Grade 1, requires that the aluminum content shall be "none" on a 20-g sample. The increasing use of reclaimed metal has made these restrictions more necessary than ever.

Probably the best-known reagent for determining very small amounts of aluminum is ammonium aurintricarboxylate. The outstanding advantage which it has over other organic reagents for small amounts of aluminum is the almost complete absence of color when added in excess under the conditions of test. Thus, complicated formulas for correcting the determination are obviated.

Ever since this reagent was first recommended by Hammett and Sottery,[1] the method has been the subject of considerable research. Nevertheless, serious difficulties remain and have stood in the way of its general acceptance. The difficulties encountered in trying to apply the method to the routine requirements of a busy nonferrous analytical laboratory led to the work embodied in this paper.

The first difficulty is that the ammonium aurintricarboxylate generally available on the market is not satisfactory.[2] Scherrer and Smith[3] have eliminated this defect by preparing the reagent in a new way, but there still remains a serious drawback. Even with a good reagent, standards prepared by the usual procedures vary considerably and fade rapidly, duplicates disagree, blanks are not uniform, and results are generally inconsistent. It is, for instance, not at all uncommon to have a standard prepared from 0.03 mg of aluminum look darker than one prepared from 0.05 mg. Other investigators[4] have pointed out some of these defects, but the methods that have been proposed to overcome them are uncertain, complicated, and decidedly exacting.

The advantages of the method now proposed are speed, accuracy, extreme simplicity, and the use of no special apparatus. It consists essentially in subjecting a dilute sulfuric acid solution of the material to a treatment in a mercury cathode cell to remove interfering elements, and then determining aluminum colorimetrically in the filtered electrolyte.

## II. MERCURY CATHODE CELL

The bulk of all interfering elements must be removed before the colorimetric test can be made. Removal by use of hydrogen sulfide or other chemical means is obviously undesirable because, with the small amounts of aluminum in question, effects such as adsorption and coprecipitation may cause loss of most of it in the preliminary work. Electrolysis in a mercury cathode cell was decided upon as the best way to remove many of the interfering elements. A modified Melaven cell[5] with a motor stirrer, as shown in figure 1, was used. Vigorous stirring of the mercury and solution are essential for rapid deposition. About 50 ml (650 g) of mercury and a current of 3 to 5 amperes was found suitable. Of course, the current permissible will vary with the size and shape of the cell, but in general, the highest current density which will not cause boiling of the solution and excessive spray may be used. Under these conditions 1 g of copper or of iron can be deposited completely in the mercury cathode in 35 to 45 minutes. Tin, antimony, lead, zinc, etc., take longer, but, depending upon the condition of the mercury, electrolysis for 2 to 3 hours will remove 1 g of any of these metals.

In the case of alloys such as solders, bearing metals, and bronzes, it was at first thought advisable to remove those metals which form peroxides (lead, bismuth, manganese) by depositing them on the anode instead of in the mercury cathode. To accomplish this a large platinum gauze anode was used. It was subsequently found that by using

1 J. Am. Chem. Soc. **47**, 142 (1925).
2 Under the conditions of test, a satisfactory reagent gives a definite pink color with 0.02 mg of aluminum and a slightly straw-colored blank with no aluminum in 50 ml of solution.
3 J. Research NBS **21**, 113 (1938) RP1118.
4 Winter, Thrun, and Bird, J. Am. Chem. Soc. **51**, 2721 (1929); also Cox, Schwartze, Hann, Unangst and Neal, Ind. Eng. Chem. **24**, 403 (1932).
5 Ind. Eng. Chem., Anal. Ed. **2**, 180 (1930).

a platinum wire as anode (about 0.10 cm in diameter), which projected about 12 cm into the solution, a sufficiently high current density was established to prevent deposition of lead and bismuth as peroxides, and to cause them finally to collect in the mercury cathode. Under these conditions, much of the manganese is likewise deposited in the cathode.

It is known that iron, copper, nickel, cobalt, zinc, gallium, germanium, silver, cadmium, indium, tin, antimony, chromium, molybdenum, lead, bismuth, arsenic, selenium, tellurium, rhenium, osmium, thallium, mercury, gold, platinum, iridium, rhodium, and palladium can be completely deposited or removed electrolytically. Manganese is not removed entirely, but the small amount left in solution does no harm in the subsequent colorimetric test. Beryllium, phosphorus, vanadium, alkaline earths, and rare earths are not removed; their effect will be discussed later. No loss of aluminum was ever observed as a result of subjecting a solution to electrolysis in a mercury cathode cell.[6]

When contamination of the mercury by deposited metals reaches about 1 percent, further deposition is retarded, and the mercury should



FIG. I

FIGURE 1.—*Modified mercury cathode cell.*

be cleaned.[7]  Furthermore, if mercury which is too badly contaminated is used, there is danger that metals already deposited, will redissolve.
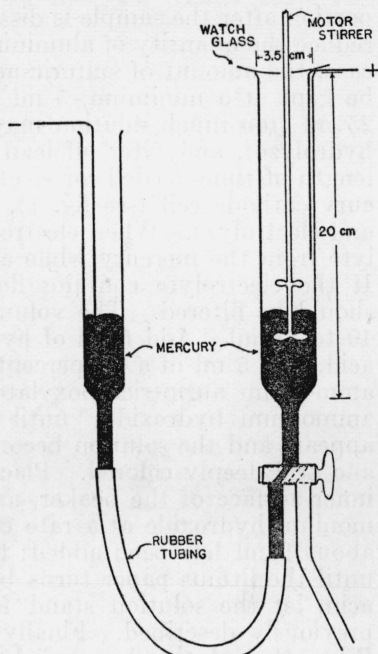
## III. PROCEDURE

The range in which this method has been applied in this laboratory is from 0.02 to 0.08 mg of aluminum. All tests with the "aurin" reagent were made in a volume of from 40 to 75 ml, because after electrolysis in the mercury cathode cell the volume normally falls within these limits. However, if smaller volumes were used, the test would undoubtedly be applicable to amounts of aluminum below 0.02 mg.

Dissolve a convenient weight of sample in an appropriate acid.[8] Many nonferrous alloys can be dissolved in sulfuric acid directly, but

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[6] For example, two determinations of aluminum in NBS Standard Sample Manganese Bronze 62, containing lead, copper, manganese, zinc, etc., in addition to 1.13 percent of aluminum, gave values of 1.12 and 1.14 percent by precipitation by ammonium hydroxide after preliminary mercury cathode separation. There is evidently no loss of aluminum even when the amount present is much greater than is ordinarily determined by the "aurin" method.

[7] The mercury is accumulated and 10 to 20 pounds cleaned at one time. It is cleaned well enough for further use as a cathode by covering it in a large thick-walled spherical flask with 10 times its volume of 10-percent nitric acid, and mixing vigorously by means of a jet of air or by suction until no further cloudiness or discoloration of the acid layer takes place. A water aspirator can be used. The flask is provided with a two-holed stopper. Through one hole a long tube leads to the bottom of the mercury; in the other hole a short tube leads to the aspirator. Depending upon the amount of contamination, 10 to 20 hours' mixing are required. Three portions of acid are usually sufficient, and about one-half of the mixing time should be devoted to the first portion.

[8] Throughout this paper whenever acids are mentioned, sulfuric acid will mean the concentrated acid of specific gravity 1.84; hydrochloric acid, the concentrated acid of specific gravity 1.18; and glacial acetic acid, the concentrated acid of approximately 99.5 percent. Ammonium hydroxide will mean the concentrated solution of specific gravity 0.90.

if another acid has been used, convert the sample to sulfate by gentle fuming with sulfuric acid.[9] Particular care must be taken to remove nitric acid completely. It is sometimes practicable to take an aliquot portion after the sample is dissolved and diluted to volume, and thus reduce the quantity of aluminum to within the proper range. In any case, the amount of sulfuric acid in the solution to be tested should be kept at a minimum, 5 ml or less. Dilute the solution to about 25 ml (too much dilution may cause tin and possibly antimony to hydrolyze), and filter off lead sulfate, if it is desired to reduce the length of time needed for electrolysis. Wash the filtrate into a mercury cathode cell (see fig. 1), if hydrolysis takes place disregard it, and electrolyze. When electrolysis is complete, separate the electrolyte from the mercury while at least part of the current is kept on. If the electrolyte contains floating particles of loose amalgam, it should be filtered. The volume of the solution should now be from 40 to 75 ml. Add 5 ml of hydrochloric acid, 5 ml of glacial acetic acid, and 5 ml of a 0.2-percent aqueous solution of a tested sample of ammonium aurintricarboxylate. Mix well while cautiously adding ammonium hydroxide [10] until the cloudy appearance of the dye disappears and the solution becomes clear, although still acid to litmus and still deeply colored. Place a piece of litmus paper against the inner surface of the beaker, and, while stirring constantly, add ammonium hydroxide at a rate of about 1 drop every 2 seconds until about 2 ml has been added; then add 1 drop every 3 or 4 seconds until the litmus paper turns blue. Now add 5 ml of glacial acetic acid, let the solution stand for 10 minutes, and neutralize it as previously described. Finally, add 5 ml of ammonium hydroxide. When the solution has cooled to room temperature, compare the color obtained with that of solutions of known aluminum content which have been similarly prepared. If the comparison is made in 150-ml beakers against a white background, a difference of 0.01 mg of aluminum can be readily distinguished.

## IV. EXPERIMENTAL RESULTS AND DISCUSSION OF PROCEDURE

Although such observations as were made in this laboratory concerning the sensitivity of this method of determining aluminum, and of the effect of temperature, ripening period and excess of reagents, confirm the work of Yoe and Hill,[11] nevertheless the procedure which they proposed has the drawbacks mentioned earlier in this paper. In attempting to find the source of difficulty it was noticed that the rate of addition of ammonium hydroxide affected the results sharply. Two samples having the same aluminum content differed markedly when one was neutralized slowly and the other quickly. Duplicate samples sometimes differed even when ammonium hydroxide was added apparently at the same speed. It was noticed, however, that whenever a pair of these differing duplicates was reacidified with acetic acid, allowed to stand 10 to 15 minutes, and then neutralized again with ammonium hydroxide at any moderate rate, they "evened up" and did not fade subsequently. This observation formed the

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[9] Just how much of any aluminum occurring as oxide is caught in this method is not known, for this would depend upon the solubility of the oxide in the dissolving acids. In any event, the total aluminum can be obtained by examining any residue left after decomposition of the sample.
[10] If the presence of rare earths or alkaline earths is suspected, ammonium hydroxide saturated with ammonium carbonate should be used throughout.
[11] J. Am. Chem. Soc. 49, 2395 (1927).

basis for the modified procedure recommended in this paper. The reliability of the procedure as modified was confirmed by numerous tests with solutions which contained only the reagents involved and known amounts of aluminum. Since the method is designed for the determination of small quantities of aluminum, between the limits of 0.02 and 0.08 mg, the amounts of aluminum taken were 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, and 0.08 mg, respectively. By following the recommended procedure, the identical quantities of aluminum which had been added were again found. When no aluminum was added, no color was developed by the reagent.

Further experiments were made with five specimens of bronze which contained small quantities of aluminum. In this instance, the aluminum content was first determined gravimetrically in 5-g portions of the alloys. The percentages so obtained were 0.006, 0.018, 0.025, 0.03, and 0.05. The aluminum was then determined in the alloys according to the colorimetric procedure recommended in this paper. The results obtained were identical with those determined gravimetrically, and it is to be particularly noted that only 0.1 g of the alloy was required as a sample. To eliminate the personal equation, an additional operator independently repeated the colorimetric determinations, and obtained the same results as those given above.

To make certain that the aluminum in an alloy can be accurately determined by the recommended procedure, known quantities of aluminum were added to solutions of various types of alloys which either contained no aluminum or less than 0.001 percent, and subsequently recovered. The results of such experiments are given in table 1.

A comparison was also made of the recommended procedure with those of previous investigators. Unless the modified procedure as recommended in this paper was followed, erroneous results were obtained. For instance, a solution containing 0.05 mg of aluminum appeared to contain more aluminum than one to which 0.08 mg had been added, and a blank solution appeared to contain 0.03 mg of aluminum.

With the recommended procedure, no starch or other protective colloid is needed, and the time required to complete the determination, after removal of the electrolyzed solution from the mercury cathode cell, is from 20 to 30 minutes. The procedure has been successfully and satisfactorily applied for over 2 years to the routine determination of small amounts of aluminum in a large variety of nonferrous materials.

TABLE 1.—*Recovery of aluminum added to nonferrous alloys*

| Material | Sample | Al added | Al found |
|---|---|---|---|
| | g | mg | mg |
| Antifriction metal; approx. composition: 63.7% Pb, 20.5% Sn, 14.0% Sb, 1.6% Cu_____ | 1.00<br>1.00<br>1.00<br>1.00 | None<br>0.03<br>.05<br>.08 | None<br>0.03<br>.05<br>.08 |
| Lead-base bearing metal No. 53; approx. composition: 79% Pb, 11% Sn, 10% Sb_____ | 1.00<br>0.50<br>.50 | None<br>0.10<br>.10 | <0.001<br>a .10<br>.10 |
| Solder; approx. composition: 50% Pb, 50% Sn_____ | 1<br>3<br>1 | None<br>None<br>0.05 | None<br>None<br>a 0.05 |

a PbSO₄ filtered off before electrolysis.

## V. REMOVAL OF INTERFERING SUBSTANCES

Fortunately, most of the elements likely to be contained in non-ferrous materials which would interfere with the determination of aluminum by forming colored lakes or hydroxide precipitates are completely or nearly completely removed by a careful electrolysis of the solution in the mercury cathode cell. Hammett and Sottery [12] have contributed information of a qualitative nature as to the effect of some of the common and some of the less common elements that interfere. Corey and Rogers [13] and Middleton [14] contributed additional information concerning the less common elements. Although many of these latter elements are not ordinarily encountered in non-ferrous work, some tests of their effect were made, mainly because it was suspected that the "aurin" reagent used in this laboratory may not have been the same as that used by other investigators.

### 1. BEHAVIOR OF ELEMENTS THAT CAN BE REMOVED BY MERCURY CATHODE TREATMENT

Of the list of elements given in section II of this paper as completely removable by electrolysis, only iron, copper, nickel, cobalt, zinc, gallium, germanium, thallium, silver, cadmium, indium, tin, antimony, chromium, molybdenum, lead, bismuth, arsenic, and mercury are likely to be encountered in nonferrous materials. Ordinarily, these will all have been removed before the "aurin" test is made, but failure to remove very small amounts is of consequence only in the case of iron. Iron must be completely removed because it gives a red color much like that produced by aluminum even when extremely small amounts of it are present. Mercury cathode treatment can be made to remove iron completely, but with samples of high iron content great care must be taken to wash down spray which carries iron up above the solution.

Gallium, indium, and thallium are closely related to aluminum and might be expected to interfere. Absence of other interfering elements may occasionally make it desirable to apply the test directly to solutions that have not been subjected to electrolysis in the mercury cathode cell. Tests were therefore made to obtain information concerning these elements in such solutions.

If the procedure is applied to a solution containing up to 0.10 mg of gallium by itself, there is no distinguishable difference in appearance between the blank and the solution under test, but larger amounts of gallium (2 mg) impart a deep red color to the solution. This interference can not be overcome by the use of ammonium carbonate solution.

Indium, in amounts up to 2 mg, does not interfere with the determination of small amounts of aluminum (0.05 mg), but larger amounts of indium (20 mg), even in the absence of aluminum, give a pink precipitate immediately upon completion of the test. Smaller amounts (10 mg) do not precipitate immediately, but if the solution is allowed to stand for 30 minutes, a pink precipitate may form. Ammonium carbonate has no effect on this precipitate.

Thallium, in amounts up to 2 mg, does not interfere with the determination of small amounts of aluminum (0.05 mg).

12 J. Am. Chem. Soc. 47, 142 (1925).
13 J. Am. Chem. Soc. 48, 2125 (1926).
14 J. Am. Chem. Soc. 49, 216 (1927).

## 2. BEHAVIOR OF ELEMENTS THAT CANNOT BE REMOVED BY MERCURY CATHODE TREATMENT

Beryllium interferes even in smallest amounts. It gives a color and sometimes a precipitate very similar to that of aluminum, and it therefore must be completely removed. Its separation can be effected with the help of a gathering agent that will in itself not interfere in the subsequent "aurin" test. Thus, a small amount of zirconium (about 40 times that of the aluminum present) as sulphate can be added to the solution containing aluminum and beryllium, and the zirconium and aluminum precipitated with 8-hydroxyquinoline according to the method described by Knowles.[15] Some tests made with this method showed that 2 mg of zirconium will safely gather and separate 0.05 mg of aluminum from 0.05 mg of beryllium. The resulting precipitate, which contains the aluminum and zirconium, is decomposed by nitric and sulfuric acids, gently fumed, and treated with "aurin."

Tests have shown that zirconium is without effect in amounts up to 10 mg, either in the presence or absence of aluminum, provided ammonium carbonate solution is used for neutralization. If ammonium hydroxide without ammonium carbonate is used, a copious red precipitate is formed.

Quadrivalent vanadium by itself (in amounts up to 2 mg) has no effect, but when as little as 0.0001 mg of aluminum is also present a deep color develops, which is soon followed by the formation of a precipitate. However, this precipitate dissolves, and the solution clears in about 15 minutes, leaving a clear blank color.

Quinquevalent vanadium (in amounts up to 1 mg) has no effect either in the presence or absence of aluminum, but larger amounts interfere by imparting a color to the solution.

Calcium, strontium, and barium (in amounts up to 10 mg) have no effect. The same amount of magnesium, however, gives a pink color somewhat similar to that produced by aluminum. This color is not discharged by the use of ammonium carbonate. In alloys containing appreciable amounts of magnesium, aluminum can be separated by twice precipitating with ammonium hydroxide after adding a suitable substance such as zirconium to "gather" the aluminum. The test is then made on the solution of this precipitate.

Scandium, lanthanum, and cerium form red precipitates which are promptly decolorized by ammonium carbonate solution.

Small amounts (1 mg) of uranium or titanium do not interfere, either in the presence or absence of aluminum, but larger amounts (10 mg) yield a slight reddish brown color.

Reasonable amounts of phosphoric acid (up to 25 mg) do not interfere with the test. Larger amounts bleach the color of the lake.

Nitric acid, sulfur dioxide, hydrogen sulfide, and hydrofluoric acid are all harmful to the test because they bleach the color of the lake. These are removed by the prescribed fuming with sulfuric acid.

WASHINGTON, March 15, 1938.

15 J. Research NBS **15,** 87 (1935) RP813.