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DETERMINATION OF TIN IN NONFERROUS METALS BY DISTILLATION AS BROMIDE AND PRECIPITATION WITH CUPFERRON

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ABSTRACT

A gravimetric method is described for the determination of tin in copper-base and lead-base alloys. The procedure involves separation of the tin by distillation, precipitation with cupferron, and ignition to stannic oxide. Results obtained by applying the method to known amounts of tin and to a number of nonferrous alloys show that an accuracy to ± 0.2 mg can be expected for amounts of tin ranging from 0.05 to 0.24 g.

CONTENTS

	Page
I. Introduction.....	307
II. Procedure for copper-base and lead-base alloys.....	308
1. Distilling apparatus.....	308
2. Preparation of the solution.....	310
3. Removal of arsenic, antimony, and excess hydrochloric acid.....	310
4. Distillation of tin.....	311
5. Precipitation of tin.....	311
III. Discussion of procedure and results.....	312
IV. References.....	314

I. INTRODUCTION

In the analysis of nonferrous alloys, tin is usually determined by titration of stannous chloride with an iodine or iodate solution. The reduction of tin to stannous chloride is effected in acid solution by means of a metal. Lead, nickel, aluminum, antimony, and iron have been used for this purpose. The method is subject to certain limitations, which have been discussed frequently in the literature. Molybdenum [1] * and vanadium [1] are partially reduced and cause high results. Tungsten [1] interferes by reason of its color. Copper [2], antimony [2], arsenic [3], iron [3], titanium [4], and potassium iodide [4] have been stated to interfere under certain conditions. In order to overcome the effect of these impurities, Scherrer [5] separated the tin by distilling as stannic tetrabromide prior to reduction and titration.

It has been claimed that oxygen [4] dissolved in the oxidizing reagent also causes erroneous results. When an iodine solution

*Figures in brackets indicate the literature references at the end of this paper.

is standardized with tin, the titer of the solution is slightly higher than that obtained by standardization with arsenious oxide. This effect is apparently not directly proportional to the oxygen concentration, hence it is impractical to compensate for it by adjusting the blank correction. To decrease this oxygen error, it has been recommended that potassium iodate [3] be used instead of iodine. An apparatus [4] designed to prepare oxygen-free iodine solutions has been recommended, but this apparatus does not appear to be convenient for everyday use. It is evident that the iodometric method for the determination of tin is subject to limitations in work of high accuracy, although the errors involved may be small and not prohibitive for most commercial work.

Kling and Lassieur [6] first proposed the use of cupferron for the quantitative determination of tin in the hydrofluoric acid filtrate obtained after separation of antimonous sulfide by the method described by McCay [7]. The cupferron is added in the presence of a large excess of boric acid, used to form a slightly dissociated complex with the free hydrofluoric acid present. The tin-cupferron compound is ignited to stannic oxide. Subsequently these authors stated that for rapid work they preferred an electrolytic method for tin.

Furman [8] also studied this combination of the McCay method with the cupferron precipitation of tin, and separated tin from antimony, zinc, manganese, cobalt, and nickel. The use of hydrofluoric acid is an obvious disadvantage of this method.

Pinkus and Claessens [9] precipitated tin with cupferron in the presence of antimony, arsenic, and zinc. This separation requires that antimony be in the quinquevalent state. The valences of the tin and arsenic are immaterial.

In the proposed method the sample is decomposed with nitric acid¹ and the tin separated as impure stannic oxide. This precipitate, which contains in the usual case all the arsenic and antimony, is dissolved in nitric and sulfuric acids, and the solution treated with hydrazine sulfate to reduce the arsenic and antimony to the trivalent state. The solution is transferred to a distilling apparatus, and the arsenic and the bulk of the antimony removed by distillation, phosphoric acid having been added to retain the tin. The tin is now distilled into a separate receiver by the use of diluted hydrobromic acid, and the distillate treated with potassium permanganate to oxidize traces of antimony. After proper adjustment of the acidity, tin is precipitated with cupferron, filtered, and ignited to stannic oxide.

II. PROCEDURE FOR COPPER-BASE AND LEAD-BASE ALLOYS

1. DISTILLING APPARATUS

An all-glass distilling apparatus, similar to that designed by Scherrer [5] was used in this work. Small modifications were made as to size and compactness.

¹ Throughout this paper whenever acids are mentioned, nitric acid will refer to the concentrated acid of sp gr 1.42; sulfuric acid, the concentrated acid of sp gr 1.84; phosphoric acid, the acid containing 85 percent of H_3PO_4 ; and hydrobromic acid, the acid containing 48 percent of HBr. Diluted acids will be designated as follows: For example, diluted nitric acid (1+2) will mean 1 part of nitric acid diluted with 2 parts of water.

In figure 1, *A* is a constricted tube having a capacity of about 60 ml. All solutions are added through this tube. It is sealed to a stopcock having a straight 3-mm bore. The tube extending from *A* into *B* has a diameter of not over 4-mm in order to maintain a column of liquid in it. The side tube in *B* is for the purpose of introducing a stream of carbon dioxide. *B* is sealed to the top of the flask neck, and should

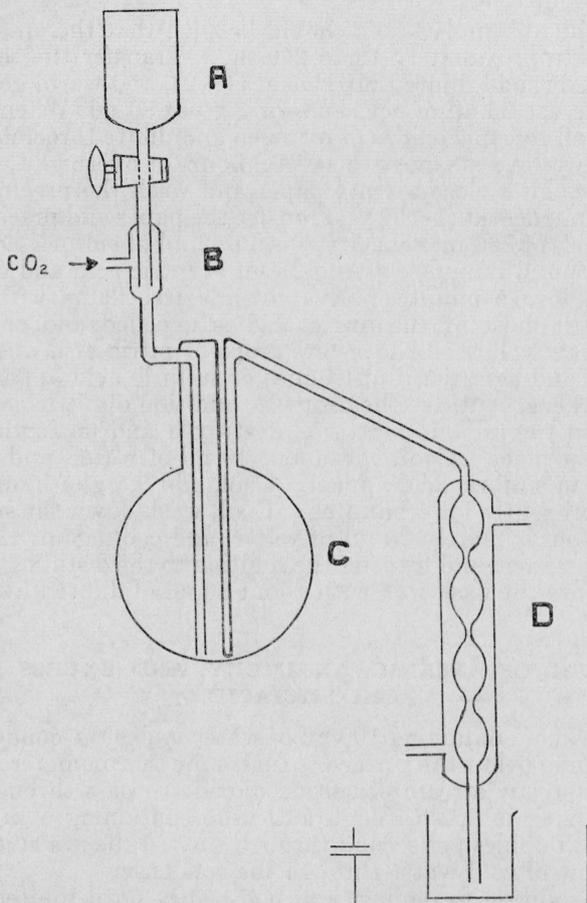


FIGURE 1.—Distilling apparatus.

extend as close to the bottom (without touching) as possible, say 1 to 2 mm. This is to minimize bumping.

The boiling flask, *C*, has a capacity of 1,000 ml. It is provided with a delivery tube leading to a condenser, and a thermometer-well closed at the bottom. The thermometer-well is sealed to the top of the flask neck, and reaches nearly to the bottom of the flask. The distance between the bottom of the flask and the delivery tube is 16 to 17 cm. The flask, *C*, rests on an asbestos board having a round hole about 4 cm in diameter to receive the burner flame. The apparatus is fastened to a large ring stand by a clamp at *D*.

The distillate is collected in a beaker containing 100 ml of cold distilled water so placed that the tip of condenser *D* is slightly immersed. An evaporating dish with a side exit tube is provided to hold the beaker and also to catch the condenser water which is permitted to flow into it.

2. PREPARATION OF THE SOLUTION

The weight of sample taken should be such that the amount of tin ranges from approximately 10 to 200 mg. Transfer the sample to a covered beaker, add diluted nitric acid (1+2), and warm gently. For a 1-g sample use 25 ml of acid and for 5 g use 80 ml. When solution is complete, boil to expel oxides of nitrogen and dilute threefold with hot water. Digest on a steam bath several hours or overnight. Filter the solution through a close-texture paper and wash the precipitate with hot diluted nitric acid (1+99). Transfer the paper and precipitate to a Kjeldahl flask of 300 ml capacity.² Add 12 ml of sulfuric acid and let stand for about 15 minutes. Add 25 ml of nitric acid and digest on a steam bath for 15 minutes. Heat over a free flame with constant rotation until most of the nitric acid is expelled and the solution becomes straw yellow. Add a few drops of nitric acid and continue the heating and agitation until fumes of sulfuric acid appear. If the solution darkens, continue the dropwise addition of nitric acid and the heating until the organic matter is destroyed and no further change of color takes place. Cool, add about 10 ml of water, and evaporate until fumes of sulfuric acid appear. Cool, add 0.5 g of hydrazine sulfate, and boil gently for 5 minutes.³ Cool, wash down the sides of the flask with approximately 25 ml of water, and cool again. Add 10 ml of hydrochloric acid and transfer the solution to the distilling apparatus (fig. 1). Rinse the flask well with about 80 ml of diluted hydrochloric acid (1+1).

3. REMOVAL OF ARSENIC, ANTIMONY, AND EXCESS HYDROCHLORIC ACID

Place a beaker containing 100 ml of water under the condenser with the end dipping below the surface. Insert the thermometer in the well and allow a steady stream of carbon dioxide to pass through the apparatus, passing it first through a U-tube containing a little water. About 2 to 3 bubbles per second through the U-tube is a suitable rate. Start the flow of cold water through the condenser.

Heat the solution to boiling, and boil gently until the temperature rises to approximately 110° C. Add 10 to 12 ml of phosphoric acid, and increase the rate of heating. When the temperature reaches 155° C, add 25 ml of hydrochloric acid⁴ dropwise at a rate of 30 to 40 drops per minute, maintaining the temperature at 160° ± 5° C. Discontinue the heating, lower the receiver, and rinse the condenser tip.

² Some copper-base alloys contain an appreciable amount of iron, which exerts a solvent action on meta-stannic acid. In analysis of the highest accuracy, or if more than 5 mg of iron is present, the dissolved tin must be recovered. Add diluted ammonium hydroxide (1+1) to the filtrate until it is strongly alkaline, boil, filter, wash with diluted ammonium hydroxide (1+10), and finally with water. Add the paper and precipitate to the Kjeldahl flask containing the first precipitate.

³ This step, intended to reduce arsenic and antimony, is necessary for separation of these elements by volatilization. However, if they are known to be absent or very low in amount the operation can be omitted.

⁴ This amount of hydrochloric acid will usually suffice to remove the most of any antimony present. Complete removal requires considerably more hydrochloric acid and is not essential.

4. DISTILLATION OF TIN

Allow the solution in *C* to cool to about 150° C and place in position a new receiver containing 100 ml of water. Transfer hydrobromic acid mixture ⁵ to *A*, and allow it to drop into *C* at a rate of 30 to 40 drops per minute. Resume distillation ⁶ by raising the temperature quickly to 180° C. Maintain the temperature between 180° and 185° C until all the acid has been added. Then cut off the heat and the flow of carbon dioxide, and rinse the inside as well as outside of the condenser tip.⁷

5. PRECIPITATION OF TIN

Dilute ⁸ the distillate with water until the concentration of hydrobromic acid is approximately 6 percent by volume and then add 1 *N* potassium permanganate solution dropwise and with vigorous stirring until an amber color appears. Shake up the filter paper, that was used as a cover, with a little water and add the pulp to the solution. Add sufficient sulfuric acid to make the concentration 4 percent by volume after the necessary volume of cupferron solution has also been added.

Chill the solution in ice water and add chilled cupferron solution (6 g per 100 ml of water) in a slow stream, while stirring vigorously. For amounts of tin up to 10 mg, use 10 ml of reagent, for 50 mg use 40 ml, and for 200 mg use 110 ml. Avoid a large excess of reagent. Precipitation is complete immediately. Stir vigorously to coagulate the precipitate and filter through a close-texture paper containing a small amount of paper pulp. It is important to wash out halogen acids completely. Wash the paper and precipitate thoroughly with cold diluted cupferron wash solution (25 ml of 6-percent cupferron solution diluted to 1,000 ml). Amounts of tin up to 80 mg should be washed 12 times with 8- to 10-ml portions of wash solution; larger amounts, such as 200 mg, should be washed at least 20 times.

Transfer the paper and precipitate to a weighed porcelain crucible large enough to hold the paper comfortably and dry at 45° C ⁹ for 4 to 5 hours or preferably overnight. Place in a cold muffle furnace and raise the temperature very gradually until smoking has ceased. Generally, about 2 or 3 hours are required. It is then safe to raise the temperature gradually to 1,000° C. Ignite for 30 minutes at this temperature, cool in a desiccator for 1 hour, and weigh as SnO₂. Ignite again to check for constant weight. Subtract the weight of the residue obtained in a blank carried through all the steps of the procedure. The weight of the blanks obtained in the experiments listed in tables 1 to 3 ranged from 0.1 to 0.3 mg and averaged 0.2 mg. The corrected weight of SnO₂ multiplied by 78.77 and divided by the weight of sample represents the percentage of tin.

⁵ This mixture consists of diluted hydrobromic acid (1+2) containing 5 ml of hydrochloric acid per 100 ml of solution. For 10 mg of tin use 30 ml of this mixture, for 50 mg use 60 ml, and for 200 mg use 140 ml.

⁶ Cover the receiver with a filter paper having a center hole for the condenser outlet, and use this paper afterward for pulp by shaking it up with a little water.

⁷ When dealing with materials of unknown tin content, it is advisable to test for completeness of distillation by distilling with an additional 25-ml portion of acid mixture, catching the distillate in a new receiver, and treating the second distillate with cupferron separately.

⁸ The solution is diluted to the proper acidity rather than neutralized with ammonium hydroxide because ammonium bromide is apparently adsorbed by the precipitate, cannot be washed out completely, and causes loss of tin during ignition.

⁹ This operation is conveniently done on top of a drying oven. Too rapid drying at higher temperatures will cause the precipitate to liquefy and spatter.

III. DISCUSSION OF PROCEDURE AND RESULTS

The separation of tin by distillation prior to precipitation appears to have definite advantages over other methods. Experiments on the precipitation of tin as the hydroxide, sulfide, and cupferron compound indicated that the last-named method was the most suitable for gravimetric work under the conditions following distillation. A number of interfering elements not removed by the McCay method are eliminated by distillation, as for example, iron, titanium, zirconium, gallium, and vanadium. In addition, distillation eliminates the danger of error caused by co-precipitation.

In the method described in this paper the distillation procedure of Scherrer [5] is modified and combined with the cupferron method for tin. As the volatile elements arsenic and antimony are frequently associated with tin, directions for the removal of arsenic and the bulk of the antimony are included. The removal of all the antimony is not sought as this requires considerable time, involves danger of loss of a small amount of tin by volatilization, and is, moreover, unnecessary as quinquevalent antimony in moderate amount (not over 20 mg) is not co-precipitated with tin by cupferron. Trivalent antimony is precipitated by cupferron.

In the absence of an excessive quantity of lead, it is possible to conduct the distillation without the preliminary separation of the tin as hydrated oxide. Lead in amounts sufficient to produce a heavy precipitate of lead sulfate causes bumping during distillation. More than 200 mg of lead cannot be handled in the apparatus.

Repeated trials have shown that approximately a sixfold excess of cupferron over stoichiometric requirements must be used to precipitate tin completely; a four-fold excess is insufficient. On the other hand, a too-generous excess must be avoided as the excess reagent precipitates in part and increases the danger of loss by spattering during the drying of the precipitate. This precipitate requires more than ordinary care in drying.

As stannic bromide is extremely volatile on ignition, particular care must be exercised in washing the paper and precipitate free from hydrobromic acid. Depending upon the size of the precipitate, 10 to 20 thorough washings on the filter paper with cold diluted cupferron solution (0.15 percent) are necessary. Large precipitates should be filtered and washed with the aid of moderate suction.

The results shown in table 1 indicate the accuracy that can be expected if tin is precipitated with cupferron under the conditions that would prevail after distillations as in the recommended procedure.

TABLE 1.—*Precipitation of tin with cupferron in diluted HBr-HCl-H₂SO₄ solution followed by ignition to SnO₂*

Tin		
Present	Found	Difference
<i>g</i>	<i>g</i>	<i>mg</i>
0.0750	0.0751	+0.1
.0750	.0752	+.2
.2011	.2009	-.2
.2023 ^a	.2025	+.2
.2098 ^a	.2099	+.1
.2583	.2582	-.1
.2587	.2588	+.1

^a In these experiments, 0.0261 g and 0.0207 g of antimony, respectively, were added.

The results in table 2 indicate the accuracy that can be expected if the complete recommended procedure is applied to known amounts of tin.

TABLE 2.—Results obtained by applying the recommended procedure to known amounts of tin

Tin		
Present	Found	Difference
<i>g</i>	<i>g</i>	<i>mg</i>
0.0562	0.0562	±0.0
.0667	.0669	+ .2
.1043	.1041	- .2
.1223	.1222	- .1
.2011 ^a	.2014	+ .3
.2021 ^a	.2022	+ .1
.2070	.2069	- .1
.2083	.2085	+ .2
.2099	.2102	+ .3
.2375	.2377	+ .2

^a In these experiments, 0.0178 g and 0.0280 g of antimony, respectively, were added.

The data in table 3 indicate the results obtained by applying the recommended procedure to copper-base and lead-base alloys.

TABLE 3.—Determination of tin in copper-base and lead-base alloys

Tin		Weight of sample	Material
Present	Found		
<i>Percent</i>	<i>Percent</i>	<i>g</i>	
0.96-----	{ 0.966 .966 .965	5 5 5	} Sheet brass, NBS Standard Sample 37c. ^a
.97-----	{ .973 .971 .968	5 5 5	} Manganese bronze, NBS Standard Sample 62b. ^b
4.69-----	{ 4.68 4.68	2 2	} Ounce metal, NBS Standard Sample 124. ^c
7.83-----	{ 7.81 7.82	1 1	} Cast bronze, NBS Standard Sample 52a. ^d
9.76-----	{ 9.77 9.77	1 1	} Phosphor bronze, NBS Standard Sample 63a. ^e
5.06-----	{ 5.05 5.05 5.05 5.03	1 1 4 4	} Lead-base bearing metal, NBS Standard Sample 53b. ^f
34.88-----	{ 34.88 34.89 34.90 34.90 34.90	0.5 .5 .5 .6 .6	} Solder, NBS Standard Sample 127. ^g

Percentages of other constituents:

- ^a 70 Cu; 27 Zn; 1 Pb; 0.2 Fe.
- ^b 57 Cu; 38 Zn; 0.8 Fe; 0.3 Pb.
- ^c 85 Cu; 5 Zn; 5 Pb.
- ^d 88 Cu; 3 Zn; 0.05 Fe; 0.01 Pb.
- ^e 78 Cu; 9 Pb; 0.6 Zn; 0.6 P; 0.5 Fe; 0.5 Sb; 0.03 As.
- ^f 84 Pb; 10 Sb; 0.2 Cu; 0.04 As.
- ^g 64 Pb; 0.8 Sb; 0.1 As; 0.01 Cu.

This method is applicable to other materials containing tin, such as aluminum alloys, zinc alloys, and steels following preliminary separations, as by the use of hydrogen sulfide when needed. It can be used for tin-base alloys containing 80 to 90 percent of tin and for tin ores, but in these cases, due to the limited amount of cupferron precipitate that can be conveniently handled, a small sample (0.2 to 0.3 g) must be taken, and the resulting accuracy is of the order of approximately 1 part in 800.

The number of elements that may interfere in the recommended procedure is small. Germanium, boron, and molybdenum may accompany tin on digestion with nitric acid, and may distill [10] in part, but of these only molybdenum, which is uncommon in non-ferrous alloys, would be precipitated by cupferron. Scherrer [11] found that with 100 mg of molybdenum originally present, 0.3 mg was found with the tin after one distillation, and only 0.01 mg after a second distillation. It is thus apparent that danger of interference by molybdenum is slight, but should be kept in mind when working with materials containing this element.

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