Solutions of pure potassium nitrate were used, 1 gram of potassium nitrate in 250 cc. of water at 20°. Ten cubic centimeters of this solution are equivalent to 8.86 cc. of nitric oxide at 0° and 760 mm.

Considering the average volume 10.61 cc. of NO as being equivalent to 8.86 cc. of NO at 0° and 760 mm. the factor 0.835 was deduced with which the column of corrected volumes was obtained.

If there is a doubt as to whether the nitrate used for standard is pure, or whether all the gas is being driven over it is a simple matter to transfer the gas to a Hempel burette, and measure it under atmospheric pressure.

The direct comparison of gas volumes not only simplifies calculations, but also introduces the safeguards of a duplicate test against error.

The method of analysis has been in use at this laboratory for more than a year, and the article is published with permission of the E. I. du Pont de Nemours Powder Co.

EXPERIMENTAL STATION.
E. I. DU PONT DE NEMOURS POWDER CO.,
WILMINGTON, DELAWARE.

THE ANALYSIS OF TIN-ANTIMONY ALLOYS.

BY LEROY W. MCCAY.

Received August 9, 1910.

The fact that hydrogen sulphide precipitates the antimony only from a dilute hydrofluoric acid solution containing tin in the higher and antimony in the lower stage of oxidation serves as an excellent means for the quantitative separation of these two elements.[1] If the solution be a hydrochloric or sulphuric acid one, the addition of hydrofluoric acid converts the metals into their fluorides, and the solution can then be diluted indefinitely without becoming turbid. The mixture of stannic sulphide, antimonious and antimonic sulphides and free sulphur obtained in the regular course of analysis was, until recently,[2] always dissolved in warm concentrated hydrochloric acid in a small platinum dish, hydrofluoric acid added, the solution filtered into a large platinum dish holding about 500 cc., and from the diluted solution the antimony precipitated in the cold with hydrogen sulphide as antimonious sulphide. The objection, however, to this method of dissolving the tin and antimony sulphides is that the accompanying sulphur, along with that which separates from the pentasulphide, forms, or seems to form, a protecting coating about some of the antimonious sulphide, so that it remains unattacked by the hydrochloric acid. Even after two extractions with the warm, concentrated acid antimony can generally be detected in the sulphur.

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[1] THIS JOURNAL, 31, 373 (1909).

[2] The neutralization of the solution with sodium hydroxide and the addition to it, after introducing the hydrofluoric acid, of an excess of sodium acetate has proved unnecessary. See original paper, *loc. cit.*

If the treatment of the sulphides with the acid be carried out in a small flask attached to a reflux condenser, the reaction is soon complete, for here the acid can be boiled and kept boiling without there being any danger of antimonious chloride escaping. However, such a method for bringing the antimony into solution is far too tedious. The difficulty is avoided if concentrated sulphuric acid heated to strong fuming be employed as the solvent. The reaction goes on smoothly and rapidly, and is complete in from twenty to thirty minutes. The tin is converted into stannic, the antimony into antimonious sulphate. During the reaction, sulphur dioxide escapes along with the fumes of sulphur trioxide, and considerable sulphur volatilizes, a part of which condenses upon the clock-glass covering the dish in which the solution is made. The sulphur which remains is in the form of yellow or brown globules. I have tested it again and again for antimony, but have never found that it contained more than a trace. In each case the washed globules were dried and rubbed to a fine powder in an agate mortar, the mass was extracted with warm, concentrated hydrochloric acid, the solution filtered and hydrogen sulphide passed into the filtrate. Some attempts made to determine the antimony colorimetrically go to show that it never amounts to a tenth of a milligram. When the solution of the sulphates as above obtained is cool, it, together with the sulphur, is transferred to a small platinum dish with a minimum amount of water, the hydrofluoric acid added, the liquid heated, cooled, diluted and filtered (paraffined funnel) into the large platinum dish where the precipitation of the antimony with hydrogen sulphide is made. A platinum or paraffined glass tube is used for introducing the gas into the solution. The antimonious sulphide precipitated from a sulphuric acid solution containing hydrofluoric acid is pure, barring a trace of sulphur which can be rapidly and completely extracted with a mixture of equal parts of absolute alcohol and carbon disulphide.[1] Dried at 110° it is free from water, nor does it after such drying suffer any loss when heated to blackness in a current of carbon dioxide. The sulphide is not absolutely insoluble in the liquid from which it is thrown down. The solubility, however, is very small, and can in most cases be neglected. Some experiments made with Kahlbaum's purest antimony indicate that the filtrates from the sulphide contain on an average 0.0004 gram antimony.[2] The solubility seems to increase with the quantity of hydrofluoric acid employed. When just enough of the latter (8–10 drops of a 48 per cent. solution) is added to prevent hydrolysis, the precipitation of the antimony by hydrogen sul-

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[1] Thiele, *Z. anal. Chem.*, 30, 479.

[2] The volume of the solution from which the antimony was in each case precipitated amounted to roughly 450 cc. The solution contained 8–10 cc. concentrated sulphuric acid and 5 cc. hydrofluoric acid.

phide is complete.[1] The sulphide is best collected in a Neubauer crucible and washed with water saturated with hydrogen sulphide and strongly acidified with acetic acid. The filtrate is evaporated in platinum on the sand bath, heated to fuming, and the thick liquid poured into a liter of water:

$$Sn(SO_4)_2 + 4H_2O = H_4SnO_4 + 2H_2SO_4.$$

Before weighing, the stannic oxide should be strongly ignited in the presence of ammonium carbonate.

Concentrated sulphuric acid heated to fuming or, if necessary, to boiling is also admirably adapted for decomposing the alloys of tin and antimony. Unless the amount of lead in such an alloy be very great it remains behind as pure lead sulphate which, after diluting the solution somewhat, adding hydrofluoric acid and then water and alcohol, can be filtered off, washed, dried and weighed. The advantage of separating and determining the lead at this stage of the analysis, and in such a simple manner, will be evident to all familiar with the difficulties ordinarily encountered in separating lead from antimony. The filtrate is caught in a paraffined beaker, one of ceresin,[2] or in the large platinum dish placed under a bell-jar resting on a ground-glass plate, and furnished with the necessary adjustments for filtering by suction. The hot sulphuric acid converts the tin into stannic, the antimony into antimonious sulphate. The alloy should be in the form of filings or very fine borings, and the treatment with the acid carried out in a covered porcelain or quartz dish, heated on the sand bath. Half an hour after the acid commences to fume strongly the decomposition is ordinarily complete, and the contents of the dish are then transferred to one of platinum in which 5 cc. of hydrofluoric acid[3] diluted with 20 cc. of water have been placed. The stannic and antimonious sulphates are converted into fluorides, while the lead sulphate remains undissolved. When hard leads and type metal containing over 50 per cent. of lead are treated in this way the resulting lead sulphate is apt to be gray and contain several milligrams of antimony. In such a case the lead sulphate should, after drying, be mixed with six times its weight of a mixture of equal parts of sulphur and sodium carbonate, and fused in a covered porcelain crucible at a barely red heat for fifteen minutes. In making this fusion I find it best to use a small burner flame about 5 cm. long. The ring carrying the triangle and crucible is lowered until the tip of the flame not only touches

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[1] This observation and the fact that the antimonious sulphide when dry is free from all foreign matter have led me to undertake a revision of the determination of the equivalent of antimony.

[2] Baker Chem. Co., Phillipsburg, N. J.

[3] The amount of hydrofluoric acid necessary will depend, of course, on the quantities of tin and antimony present. For all of the alloys which I have thus far examined 5 cc. of the 48 per cent. acid have proved sufficient.

the bottom of the crucible but spreads out so as to lick the sides to some extent. The mixture of sulphur and antimony sulphides obtained by acidifying the sulpho-salt solution is dried, dissolved in a small amount of hot, concentrated sulphuric acid, diluted somewhat, a little hydrofluoric acid added (small platinum dish), and the filtrate from the sulphur combined with the main tin and antimony solution. The lead sulphide is then converted into the sulphate and weighed as such.

Hydrogen sulphide precipitates from the filtrate from the lead sulphate not only the antimony but any copper which may be present.[1] Their separation is best effected with colorless sodium sulphide or hydrosulphide. Mr. G. W. Thompson uses for this purpose a concentrated solution of potassium hydroxide. Although I prefer the colorless sodium sulphide as a solvent for the antimonious sulphide, the method of Mr. Thompson has given me very satisfactory results. The cupric sulphide can be dissolved in nitric acid and the copper determined electrolytically. To determine the antimony I collect the precipitate from the sulpho-salt solution in a Gooch crucible and heat it to blackness in a current of carbon dioxide. The operation is conducted as follows: The crucible with its contents is placed in a ring on the end of a platinum wire and lowered to the bottom of a large test tube of hard glass. The test tube which is 25 cm. long and 4.2 cm. internal diameter, is clamped at an angle of 45°, so that the lower end is about 35 cm. above the top of the table, and closed with a doubly perforated rubber stopper carrying two tubes. The one through which the carbon dioxide is introduced passes through the center of the stopper and is shoved down until the end is just opposite the mouth of the crucible; the lower end of the other tube, which is short, is flush with the stopper, and simply serves for the escape of the gas. When all the air in the test tube has been displaced by carbon dioxide, the upper part of the full flame of a Bunsen burner is moved briskly around and in contact with the bottom of the tube, and in from fifteen to twenty minutes all the sulphur is driven off. During the operation, I have never noticed the volatilization of any antimonious sulphide due to overheating. The apparatus is exceedingly simple, and the results obtained with it leave little to be desired. The crucible should cool in the current of carbon dioxide. To remove the crucible without having it come in contact with the condensed sulphur, slip a piece of glazed paper down the tube and draw the crucible up over it.[2]

The filtrate from the antimonious and cupric sulphides is heated in a platinum dish on the sand bath, and when the water and most of the

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[1] Bismuth, cadmium and arsenic(ous) are also precipitated. Since the alloys thus far examined by me contain no bismuth or cadmium, and only traces of arsenic, the separation and determination of these elements have not been considered.

[2] Henz, *Z. anorg. Chem.*, 37, 11 (1903).

hydrofluoric acid have evaporated, the remaining liquid is heated more strongly until sulphuric anhydride fumes are given off freely. When the solution has cooled it is poured at once into an excess of water. The hydrolysis of the stannic sulphate can be hastened by neutralizing most of the free acid with ammonia water and heating the solution to boiling. Equally good results can be obtained by precipitating the tin as stannic sulphide and converting this into the oxide by roasting, or by transforming the sulphate into the double oxalate of tin and ammonium and determining the metal electrolytically according to Classen's method.

Since I have received a number of letters requesting information as to the details of the general scheme observed by me in applying this hydrofluoric method to the analysis of tin-antimony alloys, I would say that the following course of procedure will be found satisfactory in most cases. If the directions given are in places not sufficiently full and clear, the reader is referred to the preceding pages.

Place from 0.5–1.0 gram of the alloy, preferably in the form of filings or fine borings, in a quartz or porcelain dish, cover the dish with a clock-glass, and introduce through the lip 10 cc. of concentrated sulphuric acid. Place the dish on the sand bath, heat it rapidly until fumes of sulphuric anhydride begin to escape, and continue the heating for about half an hour. If at the end of this time the solution is clear, and the underlying lead sulphate pure white, remove the dish from the bath, let it cool, and transfer its contents at once to a platinum dish of 250 cc. capacity containing 5 cc. 48 per cent. hydrofluoric acid and 20 cc. of water. Use a rubber-tipped rod and the least possible amount of water for removing the lead sulphate adhering to the porcelain dish. Heat the solution to boiling, stirring all the time with a platinum spatula to prevent bumping. Dilute to 150 cc., cool, add 50 cc. of 95 per cent. alcohol, stir, and let the lead sulphate settle. Collect the lead sulphate in a Neubauer crucible, or on a filter paper fitted in a paraffined funnel, wash thoroughly with water containing one-fourth its volume of alcohol and a little sulphuric acid, dry, ignite, and weigh. If the Neubauer crucible is used, place it in a larger one of porcelain and then ignite. When the alloy contains more than 50 per cent. of lead the sulphate is apt to be gray and contain antimony. In such a case the sulphate should be fused with soda and sulphur according to the directions already given. The filtrate from the lead sulphate, as above obtained, is caught in the large platinum dish placed under the bell-jar provided with the various adjustments for filtering by suction. To avoid splashing it will be found well to cover the dish with a paraffined clock-glass with a hole in the center, through which the end of the stem of the funnel or crucible support is passed. Dilute the filtrate to about 450 cc. and introduce the hydrogen sulphide through a platinum or paraffined tube which is suspended above the center of the dish and lowered until the end in the solution is a centimeter above the bottom of the dish. Let a rapid current of the gas pass through the solution for one hour. Permit the precipitate to subside, filter and wash with water containing acetic acid and saturated with hydrogen sulphide. Suck the precipitate as dry as possible, unfold the filter paper and spread it out in a shallow porcelain dish, add some colorless moderately concentrated sodium sulphide, cover with a clock-glass, and place on the water bath. Add water, filter off the clear fluid, treat the residue again with sodium sulphide, digest a short time, repeat the same operation a third time, bring the residue onto the filter, and wash it with water containing a little sodium sulphide. Dissolve the cupric sulphide in nitric acid and determine the copper electrolytically. Collect the precipitate obtained by acidifying the sulpho-salt solution with sulphuric acid in a Gooch crucible, wash it with water containing hydrogen sulphide, dry and heat it to blackness in a current of carbon dioxide in the apparatus described. The tin in the filtrate from the cupric and antimonious sulphides can be determined according to any one of the three methods mentioned above.

Personally, I prefer to throw down the tin in the form of stannic acid by pouring the thick sulphuric acid solution into an excess of water. The stannic acid so obtained is very pure, barring a little sulphuric acid which, however, is readily expelled by igniting the stannic oxide in the presence of ammonium carbonate.

Mr. G. W. Thompson, of the National Lead Co., has very kindly sent me two alloys which I have analyzed according to the above scheme. Mr. Thompson has also given me the formulas according to which the alloys were prepared, and furnished me the analyses. His process for separating tin from antimony is a modification of the Clarke method.[1] Alloy 2 was also examined by one of our fellows, Mr. H. E. Rankin, who analyzed it according to both the Thompson and hydrofluoric acid methods.

Alloy 1.—Samples taken at random from various parts of the bottle did not give me sufficiently constant results, so I took from the bottom of the mass about five grams which, since the alloy is quite brittle, I ground to a fine powder in an agate mortar. This powder was employed in making the analyses. My results, along with those reported, are given in the following table.

I did not examine the alloy for arsenic. In each case the amount of lead sulphate obtained was too small to weigh. This alloy does not seem to be homogeneous in composition.

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[1] Private communication. See also his paper, "Method of Analysis of Alloys of Lead, Tin, Antimony and Copper," *J. Soc. Chem. Ind.*, 15, 179 (1896).

Constituents.	Formula. Per cent.	Reported.	HF-method.	HF-method.
Lead	..	0.26	trace	trace
Antimony	40	39.32	38.35	38.30
Tin	60	60.42	61.38	61.47
Copper	..	0.13	0.14	0.13
Arsenic	..	trace	....	....
	100	100.13	99.87	99.90

Alloy 2.—The results of both methods agree in a very gratifying way, as will be evident from an inspection of the following table:

			Rankin.		McCay.
Constituents.	Formula. Per cent.	Reported. Per cent.	Thompson-M.	HF-M.	HF-M.
Lead	48	47.38	47.41	47.34	47.43
Antimony	10	10.42	10.45	10.43	10.33
Tin	40	40.30	40.44	40.44	40.42
Copper	2	1.88	1.89	1.73	1.80
Arsenic	..	0.06	....	....	....
	100	100.04	100.19	99.94	99.98

No attempts were made to determine the arsenic. The alloy is undoubtedly very homogeneous in composition.

The fact that this method for separating tin from antimony involves the use of a platinum dish holding 500 cc. militates seriously against its general use.[1] I have recently found that the analysis of an alloy can be made in glass vessels, provided one possesses a platinum dish holding 250 cc. in which the lead sulphate can be separated from the tin and antimony with the rather concentrated hydrofluoric acid, and the filtrate from the cupric and antimonious sulphides evaporated to fuming in order to expel the acid. The hydrofluoric acid solutions are so dilute during the other operations that they have little action on good glass, and the salts formed all remain in solution provided one works rapidly. The solution left on evaporating in platinum the filtrate from the cupric and antimonious sulphides contains a little calcium sulphate and possibly some silica; but on diluting the solution the former dissolves and the latter can, if necessary, be filtered off. Of course, the dilution should not be too great, nor should the diluted liquid be heated prior to filtration, for hydrolysis might take place and some stannic acid separate out. I have analyzed both alloys, using an ordinary 250 cc. platinum dish, and Jena beakers, with the following results:

Now these results are fully as good as those obtained by working entirely in platinum. In closing I would say that by first treating alloys very high in lead with dilute nitric acid, evaporating, and then adding concentrated sulphuric acid and heating to fuming, the alloys appear

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[1] O. Brunck, Private communication. Th. Döring, *Chem. Ztg.*, **34**, 747.

to be completely decomposed. Whether in the presence of such large amounts of lead sulphate 5 cc. of 48 per cent. hydrofluoric acid are sufficient to transform all the accompanying stannic and antimonious sulphates into fluorides remains to be seen. Any antimonic acid formed by the nitric acid can be reduced to antimonious oxide by sprinkling some sulphur over the concentrated sulphuric acid, after all the nitric acid has been expelled, and again heating to strong fuming for about fifteen minutes. The reduction is of course effected by the sulphur dioxide formed.

	1. Per cent.	2. Per cent.
Lead	trace	47.41
Antimony	38.30	10.46
Tin	61.30	40.40
Copper	0.12	1.82
Arsenic	....	....
	99.72	100.09

PRINCETON, N. J.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE DETERMINATION OF INDIUM WITH THE USE OF A MERCURY CATHODE.

BY LILY G. KOLLOCK AND EDGAR F. SMITH.

Received July 23, 1910.

Thiel[1] recommends the use of a silver-plated platinum cathode for the deposition of metallic indium. Dennis and Greer[2] found that this metal may be readily precipitated on a rotating platinum dish cathode from solutions of its chloride or nitrate in the presence of pyridine, hydroxylamine or formic acid.

The purpose of the present communication is to offer the results obtained in the electro-analytical behavior of indium toward a mercury cathode.

A solution of indium sulphate (10.15 grams of metal in 500 cc.) containing a small amount of free acid was the electrolyte. A mercury cup of the usual form was employed.[3] The method followed and precautions taken were identical with those described in the determination of other metals with the same apparatus.

With a total dilution of 10 cc., a current varying from 2 to 4 amperes, an e. m. f. of 7.5 to 6.5 volts, and an anode rotating 750 times per minute, the following results were obtained:

0.1013, 0.1008, 0.1010, 0.1013, 0.1011, 0.1010, 0.1011, 0.1011 gram

[1] *Z. anorg. Chem.*, **39**, 119.

[2] *Ber.*, **37**, 75; THIS JOURNAL, **26**, 438.

[3] Smith's *Electro-analysis*, p. 58, 4th Ed.