But now, since the main source of error seems to have been overcome, there appears to be no reason why the volumetric determination of uranium in minerals should present any difficulty.

THE SEPARATION OF TIN AND ANTIMONY.

BY LEROY W. MCCAY.

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The action of hydrogen sulphide on hydrofluoric acid solutions of arsenic, antimony, tin, and other heavy metals, has been studied by Arthur A. Noyes.[1] He found that although hydrogen sulphide has no action on a solution of stannic fluoride containing free hydrofluoric acid, it does precipitate antimony partially from a similar solution of antimony fluoride. He says nothing about the action of the gas on hydrofluoric acid solutions of arsenic, antimony and tin, *when these elements are present in their different states of oxidation.* His experimental work led him to conclude that it is not possible to separate quantitatively tin and antimony in hydrofluoric acid solution with hydrogen sulphide. My experimental work goes to show that when the hydrofluoric acid solution contains all the tin in the stannic, and all the antimony in the antimonious state, it is possible, by a proper regulation of the conditions, to separate the two elements quantitatively with hydrogen sulphide.

When a current of hydrogen sulphide is passed into (1) a moderately dilute solution of antimonious fluoride, containing some free hydrofluoric acid, or into (2) a moderately dilute solution of an antimonious compound which has been rendered alkaline with sodium hydroxide and then strongly acidified with hydrofluoric acid, the antimony is *almost* completely precipitated as antimonious sulphide. If, however, either solution be mixed with large amounts of sodium acetate, the hydrogen sulphide precipitates the antimony as antimonious sulphide so completely that mere traces of the element remain dissolved. Some colorimetric determinations based on the observation that hydrogen sulphide produces in exceedingly dilute solutions of antimonious compounds a light yellow color, the intensity of which is proportional to the amount of the metal present, indicate that the filtrate from the antimonious sulphide, precipitated from a hydrofluoric acid solution in which large amounts of sodium acetate have been dissolved, contains approximately four-tenths of a milligram of antimony per liter. The determinations were made as follows:

The fluorides in the filtrates from the antimonious sulphide were converted into sulphates by evaporation with concentrated sulphuric acid, and from a solution of the latter salts the traces of antimony were re-

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[1] A System of Qualitative Analysis, including nearly all the Metallic Elements, Part II, *Tech. Quart.*, **17**, 214 (1904).

moved with hydrogen sulphide. The precipitates remained suspended in the solutions for days. Indeed, it was only after the lapse of about a week that they had settled so completely as to leave the supernatant liquids clear and limpid. They were light yellow in color and composed for the greater part of sulphur, which was extracted with alcohol and carbon bisulphide. In each case the unstained part of the filter paper was cut away and the remainder moistened with a few drops of concentrated hydrochloric acid; a small crystal of Rochelle salt was added, the solution warmed, diluted and filtered into a Nessler cylinder. After introducing 10 cm^3. of water saturated with hydrogen sulphide and diluting to exactly 100 cm^3., the yellow color was matched in the ordinary way. Five drops (0.25 cm^3.) of a N/100 solution of tartar emetic were always more than enough to produce in the standard of comparison, a corresponding yellow tint.

Hydrogen sulphide produces no change in solutions of antimonic fluoride, either before or after the dissociation of the free acid has been repressed by the addition to the solution of a large amount of sodium acetate.

When a current of hydrogen sulphide is passed into (1) a moderately dilute solution of stannous fluoride containing free hydrofluoric acid, or into (2) a moderately dilute solution of a stannous compound which has been made alkaline with sodium hydroxide and then strongly acidified with hydrofluoric acid, stannous sulphide is precipitated. The precipitation of tin as stannous sulphide by hydrogen sulphide also takes place in either solution after it has been mixed with large amounts of sodium acetate. The precipitation seems to be only partial.[1] Hydrogen sulphide produces no change when passed into a solution of stannic fluoride containing free hydrofluoric acid, either before or after the dissociation of the free acid has been repressed by the addition of large amounts of sodium acetate.

The behavior of hydrofluoric acid solutions of arsenious and arsenic compounds toward hydrogen sulphide appears to be analogous to that observed in the case of similar solutions of the corresponding antimony compounds. There is, however, this difference: The interaction of hydrogen sulphide and a solution of arsenic fluoride gives rise to the formation of sulphoxy-compounds, and ultimately a yellow precipitate, which is in all probability a mixture of arsenious sulphide, arsenic sulphide and sulphur.

It goes without saying that the above reactions can be employed for detecting antimonious and antimonic, stannous and stannic, and arsenious and arsenic compounds, respectively, where present together.

The fact that hydrogen sulphide precipitates from a hydrofluoric

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[1] This may be due to the oxidizing action of the air.

acid solution of antimonious and stannic compounds, after the dissociation of the free acid has been repressed by the addition of large amounts of sodium acetate, the antimony only, and that, too, practically completely, serves as a basis for an accurate and reliable quantitative method for separating these elements.[1]

Since in the regular course of analysis, antimony and tin are obtained in the form of sulphides, and since these sulphides are soluble in concentrated hydrochloric acid with the formation of antimonious and stannic chlorides, no difficulty is encountered in obtaining a solution containing the antimony in the lower, the tin in the higher state of oxidation. Moreover, sulphurous acid reduces antimonic to antimonious compounds, but has no action on stannic compounds.

The degree of completeness of the separation of the two elements by this method, involving the behavior of hydrogen sulphide toward antimonious and stannic compounds in hydrofluoric acid solution, will be evident from the figures given below.

The preliminary measurements were made as follows:

At first known weights of recrystallized tartar emetic were dissolved in measured volumes of carefully analyzed stannic chloride solutions. To each solution, diluted somewhat and contained in a large platinum dish holding 500 cm^3., a drop of methyl orange, sodium hydroxide to distinct alkaline reaction and then 5 cm^3. of 48 per cent. hydrofluoric acid[2] were added. After about half an hour, 10 grams of sodium acetate were dissolved in the solution,[3] it was diluted to 300 cm^3. and treated with a rapid current of hydrogen sulphide for one hour. The rubber tubing from the gas generator was slung over the arm of a ring stand so that the paraffined delivery tube hung directly above the centre of the dish and could be lifted or lowered until the end under the solution was about a centimeter above the bottom of the dish. By introducing the gas into the solution in this way there was no splashing, little sulphide adhered to the dish, and the delivery tube served as a convenient stirrer. The antimonious sulphide was filtered off *at once*, and washed with water containing acetic acid and saturated with hydrogen sulphide.[4] A glass

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[1] If we assume that Noyes' solutions contained both antimonious and antimonic fluorides we can see at once why his attempts to separate the element from tin were not more successful. The assumption is a reasonable one, for on merely treating antimony with concentrated nitric acid and evaporating to dryness we obtain, not antimonic acid, but a mixture of antimonious and antimonic oxides, or one composed of antimonious oxide and antimony tetroxide. A. Rose, *Pogg.*, **53**, 161 (1841).

[2] The amount of hydrofluoric acid necessary will depend of course on the quantities of tin and antimony present. Thus far 5 cm^3. have proved to be sufficient.

[3] The color of the solution changes from pink to yellow. The fluorides which sometimes separate out here dissolve immediately on diluting the solution.

[4] Water containing a little ammonium acetate and acetic acid seems to serve the purpose equally well.

funnel well paraffined was used, and the filtrate caught in cups made by cutting off the tops of old paraffin bottles which had contained hydrofluoric acid. Such cups are far superior to beakers coated with paraffin, for the paraffin coating in places frequently becomes loose and scales off. The filtrate was poured into the large platinum dish, 20 cm³. of concentrated sulphuric acid were added and the solution was evaporated on the water bath. The dish was left on the bath until the residue was free from hydrofluoric acid. I found that a constant and thorough stirring with a platinum spatula of the thick, syrupy residue served to promote the escape of the last traces of hydrofluoric acid. In no case was the residue heated until fumes of sulphuric anhydride escaped, for it was feared that by so doing, traces of platinum would dissolve and subsequently interfere with the determination of the tin. The residue in the dish was then dissolved in water, the solution poured into a large beaker, diluted to about 500 cm³. and the tin precipitated with hydrogen sulphide as stannic sulphide. The latter was converted into the oxide by roasting, all the details given by Rose and Fresenius being carefully observed. Since the stannic sulphide, in spite of a thorough washing, is apt to retain a few tenths of a milligram of sodium sulphate, the resulting oxide was, after it had been ignited to constant weight in the presence of ammonium carbonate, extracted a number of times in the crucible with boiling water. After each addition of water the liquid was stirred, the oxide allowed to settle and the clear liquid decanted through a very small filter paper which was washed and burned, the ash being added to the contents of the crucible. A reignition of the oxide gave the weight from which the amount of tin was calculated.

	Tartar emetic. Gram.	Tin taken. Gram.	Tin found. Gram.	Tin. Per cent.
1	0.3047	0.1250	0.1242	99.36
2	0.3326	0.1480	0.1481	100.06
3	0.4679	0.1480	0.1476	99.73
4	0.5100	0.1500	0.1498	99.87

I next determined electrolytically, according to the directions given by Classen,[1] the amount of antimony present in the sample of recrystallized tartar emetic.

	Tartar emetic. Gram.	Antimony found. Gram.
1	0.5100	0.1912
2	0.5100	0.1911

These figures are markedly higher than theory demands.[2] However, as will be seen below, they agree very well with those found on deter-

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[1] Potassium cyanide instead of sodium sulphite was used to do away with the disturbing influence of the polysulphides.

[2] Expressed in percentages they agree quite well with the results of Classen, who used tartar emetic as a standard substance in testing his electrolytic method for determining antimony. See Classen, *Quant. Analyse durch Electrolyse*, **1897**, 193.

mining in the same way the antimony in the antimonious sulphide obtained in the separation of the element from tin.

	Tartar emetic. Gram.	Tin taken. Gram.	Antimony found. Gram.	Tin found. Gram.
1	0.5100	0.1500	0.1905	0.1501
2	0.5100	0.1500	0.1912	0.1497

The coatings of antimony dissolved completely in concentrated nitric acid containing some Rochelle salt. They were free from tin, for when 0.2 gram of pure antimony, to which a little granule of tin, weighing about a milligram, had been added, was treated with concentrated nitric acid containing some Rochelle salt, a small residue of stannic oxide remained. I could not detect antimony with certainty in the oxide of tin. It was, in each case, converted into the sulphide by fusing it with sulphur and sodium carbonate, dissolving the sulpho-salt in water and acidifying the solution with sulphuric acid. The well washed sulphide was then dissolved in concentrated hydrochloric acid, the solution warmed and filtered into a small platinum dish, where it was permitted to act on a roll of pure iron wire, at a gentle heat, for several hours. At the end of this period the dish was still bright, the solution being of a light green color. To convince myself of the delicacy and reliability of the test I now added to the solution three drops of a N/100 solution of tartar emetic. In less than ten minutes the surface of the dish was covered with a distinct brown stain.

Since it is well known that the electrolytic method for determining antimony yields results which are generally high, I do not insist on the accuracy of the above figures. However, as I have already intimated, they do show that the separation of antimony and tin according to the course of procedure under discussion is practically complete. That the results for the tin are satisfactory is evident at a glance.

It seemed best at this point to discard the tartar emetic and start out with pure metallic antimony, also to determine the antimony by another method.

A standard solution of antimony was prepared by dissolving about 5 grams of the purest antimony I could obtain in concentrated hydrochloric acid with the addition of potassium chlorate, heating the solution on the water bath until all free chlorine was expelled, adding a considerable amount of tartaric acid and diluting to one liter. The antimony in 25 cm³. of this solution was then carefully determined according to the directions given by Fresenius, with the exception that the mixture of antimonic and antimonious sulphides and sulphur was collected in a Gooch crucible over asbestos, and heated at about 300° to blackness in a Henz furnace,[1] and in a current of carbon dioxide. Three determinations were made.

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[1] *Z. anorg. Chem.*, **37**, 10.

	Found. Gram.
1	0.1225
2	0.1228
3	0.1224
Average,	0.1226 Sb.

25 cm³. = 0.1226 gram, 20 cm³. = 0.0981 gram.

I also prepared for this series of separations a new tin solution by dissolving exactly 6 grams of Kahlbaum's purest tin in concentrated hydrochloric acid with addition of potassium chlorate. After getting rid of all the free chlorine by warming the solution on the water bath, 20 grams of tartaric acid dissolved in a little water were added and the solution was diluted to a liter. Here, too, the tin was determined in 25 cm³. It was precipitated from a volume of about 600 cm³. with hydrogen sulphide as stannic sulphide, which, after a thorough washing with water containing ammonium acetate and acetic acid and drying, was converted into the oxide by roasting.

Found, 25 cm³. = 0.1502 gram Sn.

This figure agrees well with the calculated amount, 0.1500 gram.

The separations were made as follows: 20 cm³. of the antimony and 25 cm³. of the tin solution were pipetted into a beaker holding about a liter, the mixture was diluted to 600 cm³. and the metals were precipitated as sulphides with hydrogen sulphide. In each case, the gas was passed for one hour. After standing over night in a warm place, the dark brown precipitate was filtered off and washed with water containing ammonium acetate and a little acetic acid. In the first two cases (separations 1 and 2) each precipitate was dried at 70°–75°, as much of it as possible transferred to a clock glass and what remained adhering to the filter paper dissolved in a few drops of yellow ammonium sulphide, the solution and washings being caught in a small beaker. After evaporating this solution to dryness on the water bath, the main portion of the precipitate was brushed into the beaker, the latter covered with a watch glass, the precipitate moistened with a few drops of water and treated with 5 cm³. of concentrated hydrochloric acid. The beaker was placed on the simmering water bath, and allowed to remain there until all the hydrogen sulphide had been expelled. The solution was then diluted with a little water containing tartaric acid, filtered into the large platinum dish, neutralized with pure caustic soda and acidified with 5 cm³. of 48 per cent. hydrofluoric acid. To repress the dissociation of the hydrofluoric acid, the same amount of sodium acetate was used as was employed in the former separations. The solution was now diluted to 300 cm³. and the antimony precipitated with hydrogen sulphide as already described. Since the results for the tin were a trifle low, and an examination of the residues of sulphur proved that the extractions were not complete, the mixture of the sulphides in each of the next experiments (separations 3 and 4) was not dried, but, after as much water as possible had been removed with the filter-pump, treated at once with concentrated hydrochloric acid. This was accomplished by cutting away the unstained half of the filter paper and submitting the other half carrying the precipitate to the action of the acid. A beaker of 100 cm^3. capacity was employed. It was covered with a watch glass and gently heated on the water bath until the hydrogen sulphide was expelled. During the digestion on the bath the paper was kneaded to a fine pulp with a glass rod. When the last traces of hydrogen sulphide had disappeared, two grams of tartaric acid dissolved in 5 cm^3. of water were added, the solution was diluted to about 20 cm^3. and filtered into the platinum dish. Since even in these circumstances the paper pulp was found to retain traces of antimony and tin, it was dried, extracted with carbon bisulphide and again treated with concentrated hydrochloric acid. In this case, however, only about 1 cm^3. of the acid was used. If very accurate results are required, this second treatment with the acid should not be omitted. Whether the sulphur forms a protecting coating about some of the sulphides, or whether small amounts of difficultly soluble sulphochlorides are formed during the action of the hydrochloric acid is a matter which has not yet been cleared up.

The antimonious sulphide was collected in a large platinum Gooch crucible over a disk of hardened filter-paper, the filtrate being caught in a paraffin cup, placed under a bell-jar resting on a ground glass plate, and provided with the necessary adjustments for filtering by suction. To avoid splashing the cup was covered with a paraffined clock glass with a hole in the center through which the lower end of the paraffined crucible support was passed. After washing the precipitate with water containing ammonium acetate and acetic acid, then with water and finally with alcohol it was dried to constant weight at 110°. The weight of the crucible and disk, also dried at 110°, having been previously determined, the weight of the amorphous, red sulphide was obtained. The greater part of it was then heated to blackness in a little porcelain boat in a current of carbon dioxide gas, according to the directions given by Fresenius. The weight of the crucible and disk along with the rest of the precipitate was determined, and from the various data the amount of antimony calculated.

This method for filtering off the sulphide and determining the antimony works admirably, and leaves little to be desired. That the antimony in the red precipitate can be determined at once by dissolving the latter in concentrated hydrochloric acid alone, or in concentrated hydrochloric acid with the addition of potassium chlorate, and making use of the volumetric methods of Mohr or Weller will be evident to all analysts.

The tin in the filtrate was determined according to the process outlined above. Owing to the charring action of the sulphuric acid on the tartaric acid the solution of the tin is of a marked brown color, but no difficulty has been experienced in effecting a complete precipitation of the metal with hydrogen sulphide. The stannic sulphide appears to act as a mordant, for in settling it extracts the brown coloring matter from the solution, leaving the supernatant liquid, when subsidence is complete, perfectly colorless.

	Sb taken. Gram.	Sb found. Gram.	Sn taken. Gram.	Sn found. Gram.
1	0.0981	0.0987	0.1500	0.1491
2	0.0981	0.0986	0.1500	0.1490
3	0.0981	0.0981	0.1500	0.1502
4	0.0981	0.0987	0.1500	0.1497

The last two separations are most satisfactory, and prove that the second method for dissolving the mixture of the sulphides is to be preferred.

The stannic oxide found in 3 contained a trace of antimony. The oxide was converted into a sulpho-salt, and from its solution the meta was thrown down as stannic sulphide with dilute sulphuric acid. The solution obtained by dissolving the sulphide in concentrated hydrochloric acid was diluted, poured into a small, carefully weighed platinum dish and allowed to act on a roll of pure iron wire for several hours. The dish was covered with a clock glass and heated on the water-bath. A faint brown film which weighed 0.0003 gram appeared on the dish. It dissolved readily in 3 drops of strong hydrochloric acid, and the solution diluted to about 5 cm^3. gave with hydrogen sulphide a red turbidity After standing over night a tiny *brown* precipitate had collected on the bottom of the test tube. The precipitate must have contained then some other sulphide in addition to that of antimony, for on this assumption alone can I account for the pronounced brown color. The question whether antimonic sulphide dissolves in concentrated hydrochloric acid without the formation of traces of antimonic chloride is being investigated. According to Wittstein[1] such traces are always present in the resulting solution. Scherer[2] and Classen,[3] however, state that during the reaction all the antimonic sulphide is converted into antimoniou chloride.

Recently I have made some experiments to determine whether the separation of the two elements cannot be effected without the addi

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[1] *Pharm. Viertelj.*, 18, 534.

[2] *Z. anal. Chem.*, 3, 206.

[3] *Ber.*, 16, 1061.

tion of sodium acetate to their hydrofluoric acid solution. It would appear that the Sb^{III} in such a solution, providing a moderate amount of free hydrochloric acid be present, is as completely precipitated by hydrogen sulphide as it is when the solution is first neutralized with caustic soda, the hydrofluoric acid and then the excess of sodium acetate added and the gas introduced. True, I have as yet made no attempt to determine the amount of antimony present in the filtrate from the antimonious sulphide precipitated from such a solution, but the quantity must be practically negligible, for the figures for the tin and antimony found agree remarkably well with those representing the amounts taken.

The following experiment goes to show the degree of accuracy of this last mode of procedure: 0.4232 gram of recrystallized tartar emetic was placed in the large platinum dish and 25 cm^3. of the tin solution, 5 cm^3. concentrated hydrochloric acid and 5 cm^3. 48 per cent. hydrofluoric acid were added. The liquid was stirred with a platinum spatula until solution was complete, then diluted to 300 cm^3. and the hydrogen sulphide introduced. The antimonious sulphide was filtered off, dried, heated to blackness in a current of carbon dioxide and weighed according to the directions already given. The tin in the filtrate was also determined as above described.

Found: 0.1563 gram Sb = 36.94% and 0.1498 gram Sn = 99.87%.

The percentage of antimony in the sample of tartar emetic was next determined.

Tartar emetic taken. Gram.	Sb_2S_3 found. Gram.	Sb found. Gram.
0.51	0.2632	0.1880

0.1880 Sb = 36.86%.

It may be well to state that solutions of tin and antimony containing hydrofluoric acid can be diluted indefinitely without any basic compounds separating out.

The method is being thoroughly examined, especially as regards its applicability to the analysis of alloys and metallurgical products containing tin and antimony.

PRINCETON, N. J., Dec. 20, 1908.

DETERMINATION OF FERROUS OXIDE IN MAGNETITE.

BY R. B. GAGE.

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The various errors that may occur in the determination of ferrous iron by the Mitscherlich method or those of Pratt and Cooke, their causes and the necessary corrections, are discussed by Hillebrand[1] so thoroughly that it is not necessary to deal with them all here. However, since that

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[1] *U. S. Geological Survey Bulletin, No.* 305 (1907), pp. 131–44.