change in the concentration of the hydroxyl ion in extreme dilutions of an acid.

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SEPARATION OF THE METALS OF THE TIN GROUP.[1]

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The customary methods for the separation of arsenic, antimony and tin for qualitative purposes depend, in principle, either on the relative strength of the acids of these elements (for instance, the ammonium carbonate separation of arsenic from antimony and tin), or upon the difference in the solubilities of their sulfides in acids.[2] Of these principles the latter is perhaps the one most made use of in present practice.

Thus, in the procedure outlined by A. A. Noyes and W. Bray,[3] the three elements are separated from each other by the use of graded concentrations of hydrochloric acid. In the hands of a practiced operator this method leaves little to be desired, and is one of the most satisfactory methods described. When, however, the method was employed by persons of less manipulative expertness, such as students entering for the first time into qualitative work, the results were by no means as satisfactory as might have been anticipated. The statistics collected[4] show tin as giving the greatest trouble, it being missed in 20.2% of the cases considered. Arsenic was overlooked in 18% of the cases, while antimony was very rarely missed (less than 1%).

According to the method of Noyes, the sulfides of the second group are precipitated and then separated by treatment with ammonium polysulfide in much the usual manner, As_2S_5, Sb_2S_5 and SnS_2 being thrown out from the resulting polysulfide filtrate upon acidification with hydrochloric acid. Up to this point no particular difficulty is encountered, except occasionally with copper, which dissolves to a slight extent in ammonium polysulfide. This will be referred to again under the description of the new procedure.

The precipitated tin group sulfides, superficially dried, are then treated with exactly 10 cc. of concentrated hydrochloric acid (sp. gr. 1.20), and warmed for 10 minutes on the steam bath. Arsenic sulfide remains

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[1] Presented as thesis for the degree of B.S. by J. M. Welch to the College of Liberal Arts and Sciences, University of Illinois.

[2] A separation based upon the precipitation of antimony as the pyroantimonate of sodium has been proposed by Hahn, *Z. anorg. Chem.*, **92**, 168 (1915).

[3] THIS JOURNAL, **29**, 137 (1907).

[4] From reports of the students in qualitative analysis first semester 1914–1915. About 200 reports were examined.

behind, and antimony and tin go into solution as $SbCl_3$ and $SnCl_4$, respectively.

Up to this point the method here proposed follows the lines laid out by Noyes and Bray,[1] but from here on the procedure is modified. In the original method the filtrate containing the antimony and tin is diluted so that 50 cc. of solution contain 10 cc. of concentrated hydrochloric acid. Hydrogen sulfide is then passed into the solution, *which meanwhile should be kept at 90°.* If no precipitate is formed, further 5 cc. of water are added and hydrogen sulfide is again passed into the solution. If antimony sulfide has been formed it is removed by filtration, the tin is then precipitated as the sulfide from the cold solution, after dilution to 70 cc.

If these steps are carried out with proper attention to the essential details the results are very satisfactory. The limits of dilution are not very wide, however, and in addition the temperature must be controlled. Errors at this point of the procedure will cause the formation of a "brown precipitate," as has been noted by Noyes and Bray. As a matter of experience, this error was a very common one on the part of numerous students using the method. Aside from the fact that the characteristic color of antimony sulfide is masked, producing corresponding uncertainty in the interpretation of the results, large quantities of tin are lost with the antimony. Unless the precipitate is again treated by a special procedure, tin may be, and often is, overlooked entirely.

Experimental.

In the literature very little is to be found concerning the nature of the brown precipitate formed when antimony and tin sulfides are precipitated together. Its color in no way corresponds to that of a mixture of the two sulfides, and in view of the regularity and ease with which it is formed it is strange that so little mention is made of it. Of the well-known texts on qualitative analysis, that of A. A. Noyes, and one or two others, are the only ones which mention it. No reference is found in the general literature. Pouget[2] has described a number of compounds which are possibly of the same nature. By precipitating salts of the metals with solutions containing K_3SbS_3 he obtained compounds of the type Me_3SbS_3 and Me_2KSbS_3. For the heavy metals, these are brown to black precipitates of constant composition. The alkali-earth compounds are white to yellow, the manganese salt is rose colored. The mineral pyrargyrite, Ag_3SbS_3, is a naturally occurring example of these thioantimonites. The tin thioantimonite has not been described.

It is possible that the brown precipitate is of the same general character as the compounds described by Pouget. It is formed whenever

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[1] *Loc. cit.*

[2] *Compt. rend.*, **124**, 1445, 1518 (1897); **126**, 1144, 1792 (1898); **129**, 103 (1898).

tin and antimony sulfides are precipitated together from a dilute hydrochloric acid solution. When equivalent portions of nearly neutral solutions of sodium thioantimonite and stannic chloride are mixed (molar solutions), a muddy black precipitate is formed at once, which darkens on standing. With excess of antimony the color is shifted somewhat to the red, while with corresponding excess of tin the yellow predominates more and more. Occasionally, when much antimony is present, its sulfide may be observed to form first on passing hydrogen sulfide into the solution and as the precipitation proceeds the characteristic drab-colored compound is formed. The preparation of a definite tin thioantimonite has so far not been undertaken, but the characteristic way in which such solutions reacted led to an investigation of the reliability of the behavior as an indication of tin and antimony.

In order to determine the limits between which this substance would reveal its presence, varying quantities of stannic tin and trivalent antimony were mixed and diluted to 70 cc., with an acid content of 10 cc. of hydrochloric acid. These solutions were then precipitated at ordinary temperatures by means of hydrogen sulfide. The relative concentrations of the two metals in the test solutions are given in Table I.

TABLE I.

Composition of Solutions for the Investigation of the "Brown Precipitate."

Solution.	Sb per cc. (mg.).	Sn per cc. (mg.).	Ratio. Sb/Sn.	Solution.	Sb per cc. (mg.).	Sn per cc. (mg.).	Ratio. Sb/Sn.
A........	6.30	0.32	20/1	N........	2.24	1.28	7/4
B........	5.98	0.32	19/1	O........	1.92	1.60	6/5
C........	5.66	0.32	18/1	P........	1.60	1.92	5/6
D........	5.34	0.32	17/1	Q........	1.28	2.24	4/7
E........	5.02	0.32	16/1	R........	0.96	2.56	3/8
F........	4.70	0.32	15/1	S........	0.64	2.88	2/9
G........	4.38	0.32	14/1	T........	0.32	3.20	1/10
H........	4.06	0.32	13/1	U........	0.32	3.52	1/11
I........	3.74	0.32	12/1	V........	0.32	3.74	1/12
J........	3.52	0.32	11/1	W.......	0.32	4.06	1/13
K........	3.20	0.32	10/1	X........	0.32	4.38	1/14
L........	2.88	0.64	9/2	Y........	0.32	4.70	1/15
M........	2.56	0.96	8/3				

Solutions "A" to "K" gave red to red-brown precipitates, "K" to "S" were decidedly brown, while the precipitates from solutions "R" to "Y" varied from clay-brown to yellow-brown.

With the ratio of the antimony content to the tin content varying as given in solutions "I" to "U" the brown color was easily recognized, being most sharply defined in the region indicated by solutions "K" to "S," inclusive. When the antimony was present in greater proportion than is indicated in "I," it was difficult to discover a marked difference between the color of the precipitate and that of a precipitate of antimony sulfide alone. When the proportion of the tin exceeded that given in solution "U" the yellow color of tin sulfide predominated, so that there could be no doubt as to its presence. The presence of antimony was indicated under these conditions by the red precipitate first formed when hydrogen sulfide was passed into the solution.

It was found that, within the limits indicated, not only was the characteristic brown precipitate obtained, but also that a colorimetric estimate of the relative proportions of the two constituents, tin and antimony, was possible. In order to show this the precipitates listed in Table I were renumbered so as not to suggest their composition and beginners from the laboratory were asked to arrange them in the order of the color gradations from red through brown to yellow. This was repeated a number of times and in every case the precipitates from "K" to "S," inclusive, were arranged in the order of decreasing antimony-tin ratio.

From this it would appear that when the ratio of antimony and tin in a mixture lies between 12/1 and 1/12, the color of the precipitate formed by the action of hydrogen sulfide in a solution containing the equivalent of 10 cc. of concentrated hydrochloric acid to a volume of 70 cc. is a very valuable indication of the presence of tin.

Treatment of the Precipitate.—If a separation of the antimony and tin is not desired the precipitate is ready for the procedure devised by Pertusi and Gastaldi.[1] According to this method the sulfides are suspended in a little water and shaken with metallic magnesium powder. The tin compound is reduced to the metal and is after reduction dissolved in dilute hydrochloric acid. The solution is allowed to run through a filter into mercuric chloride solution, the $SnCl_2$ revealing its presence by the production of mercurous chloride. The antimony does not interfere with the reaction, and in the case of all mixtures listed in Table I satisfactory tests were obtained for tin by this method. No particular account is taken of antimony in this process, however, and it seemed advisable to include a positive confirmation of this element in the steps taken, particularly to take care of the extreme mixtures where antimony or tin predominates very largely.

One of the most satisfactory tin and antimony separations is that of F. W. Clarke,[2] which is used for the quantitative separation of these two elements. A series of tests of this method was made, for the purpose directly in view, with solutions similar to those given in Table I. In these the proportion of antimony to tin ranged from 20/1 to 1/20, and in every instance both elements were recognized without difficulty. The conditions of the separation are that the combined weight of the two

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[1] *Rend. soc. chim. ital.*, **4**, 83 (1914).

[2] *Chem. News*, **21**, 124 (1870).

metals shall not exceed 0.3 g., that for each 0.1 g. there should be present 5 g. of oxalic acid, and that the tin should be in the stannic form. These conditions are readily met in the ordinary qualitative separation.

In the separation, as ordinarily carried out, H_2S is passed into the hot oxalic acid solution. Antimony sulfide precipitates, of characteristic color and easily filtered, and tin remains in solution. A reversal of the steps was examined for its usefulness, but was found unsatisfactory. It is not possible to achieve a sharp separation of antimony and tin by boiling the mixed sulfides with an oxalic acid solution. Either the tin does not completely dissolve or some of the antimony dissolves with it. It was therefore found necessary to dissolve the antimony-tin mixture completely and then to precipitate the antimony alone. The steps as finally devised will be described under the procedure.

Procedure.

To the precipitated sulfides from the ammonium sulfide separation, after having dried them superficially either by suction or by pressing between filter paper, add exactly 10 cc. of concentrated hydrochloric acid (sp. gr. 1.20) and heat for ten minutes on the steam bath. Arsenic sulfide remains behind and is removed by filtration and examined in the customary manner.

It is assumed that the ammonium sulfide separation from the copper group has been sharp and that neither mercury nor copper is present in this portion of the material. It often occurs that copper dissolves in the ammonium polysulfide (which shows itself in the brown color of the solution). Sodium sulfide does not present this difficulty, but it dissolves mercuric sulfide. If ammonium polysulfide, to which about 5% of NaOH has been added, is used, both difficulties are avoided and a reagent of striking superiority over ammonium polysulfide alone is obtained. To show this, the following mixtures were precipitated: two test tubes each with milligram-mols of mercury, tin and antimony; two, each with milligram-mols of copper, antimony and tin. The precipitates were washed by decantation, and to one of the mercury precipitates and to one of the copper precipitates ammonium polysulfide, containing 5% of NaOH, was added. To the other two precipitates ammonium polysulfide without NaOH was added. All four test tubes were placed in boiling water. The tin group sulfides dissolved immediately in the solvents containing NaOH, and in three minutes the contents of the two tubes consisted of a clear golden yellow solution free from copper or mercury, and a jet-black, dense precipitate of the copper group sulfide at the bottom of the tube. In the comparison tubes, on the other hand, the tin group had not, under the same conditions, dissolved completely after three hours and, furthermore, the ammonium polysulfide had dissolved an appreciable amount of *copper*.

The filtrate from the arsenic, which contains antimony trichloride and tin tetrachloride, is diluted to a volume of 70 cc. and is saturated with H_2S. If the addition of the H_2S takes place while the solution is hot, a portion of the antimony will precipitate first as the red sulfide, but on further addition of H_2S, and as the solution cools, a brown to nearly black precipitate is formed, which is characteristic of tin plus antimony. With practice, the intensity of the coloration may be made the basis of an estimate of the relative quantities of the two constituents. As soon as the formation of this precipitate is observed, the introduction of H_2S is interrupted and the solution and precipitate are heated again until the excess of H_2S is driven off. Five cubic centimeters of hydrogen peroxide solution (3%) are added and the solution is heated until the precipitate has redissolved. Five to ten grams of oxalic acid are now added and H_2S is again passed into the hot solution, which is allowed to cool while it is being saturated. Antimony sulfide precipitates as a bright red, easily filtered precipitate, and is then collected on the filter.

The mixed precipitate may be redissolved by simply evaporating the solution with the precipitate. Upon addition of H_2O_2 the same end is attained without evaporation and in much shorter time. A few drops of bromine water are still more effective in this respect. The excess H_2S is best driven off before adding these oxidizing agents. A large excess should of course not be used, since it would decompose the oxalic acid added later. As antimony sulfide is to be precipitated at the next step, it is not necessary to wait for the last faint red cloud of antimony sulfide to redissolve at this part of the procedure.

The filtrate from the antimony sulfide, which contains the tin, or a portion of the filtrate (10 cc. is usually sufficient), is boiled with 1–2 g. of granulated test lead for two or three minutes. The solution is then chilled (by running water), and filtered into a solution of mercuric chloride. In the presence of tin, white mercurous chloride is formed.

The solution contains tin in the tetravalent state. Upon boiling this with metallic lead this is reduced to stannous tin, which gives the well-known reaction with mercuric chloride. Trials in connection with the method showed that it was reliable with as little as 0.5 mg. of tin. Some of the lead goes into solution during the heating and crystallizes out again upon cooling (as lead chloride). While this precipitate is different in character from the mercurous chloride, errors are avoided by cooling the solution first and filtering from the lead salt.

Summary.

1. It has been shown that when antimony and tin are precipitated together, as sulfides, they form a characteristic brown precipitate (which is possibly a sulfantimonite of tin). Within rather wide limits this is a reliable indication of the presence of these two elements.

2. It was found that the reduction of stannic compounds to stannous compounds by means of metallic lead could be carried out with sufficient ease and accuracy to make it available as a method for the detection of tin.

3. A method for the qualitative analysis of the tin group has been described, which has proven effective in use, particularly in the hands of inexperienced students, and which, it is believed, has some advantages in latitude of conditions, speed, and ease of manipulation.

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