surface of the solution. A single cc. of the solution is ample for the determination. The thoroughly mixed solution is brought to the temperature of 25° in the jacketed cell of the instrument and the index is determined. The necessity of precise control of the temperature is to be emphasized, since a variation of 0.1° in temperature changes the index about 0.00002. From the index of the mixture and those of the pure, single chlorides in 20% solution, the composition of the mixture is calculated by simple proportion. Thus the index of the 20% solution of a certain mixture was found to be 1.36244. The indices of the 20% potassium and sodium chloride solutions are, respectively, 1.35992 and 1.36829 (the first and last values of Table II), whence,

$$\frac{1.36829 - 1.36244}{1.36829 - 1.35992} = \frac{\%\ \text{KCl}}{100}.$$

The total difference in refractive indices of 20% sodium chloride and 20% potassium chloride is only 0.00837. A change, then, of 1% in the relative concentration of a salt mixture will change the index only 0.00008, whereas a variation of 0.1% in total salt concentration changes the index about 0.00018. Because of these facts, and because of the marked variation of the index of refraction with variation of temperature, the method is not of high accuracy. Owing, however, to its comparative rapidity and to its avoidance of costly reagents, there may be instances in which it will prove of use.

Table III gives the results of several trial analyses.

TABLE III.

Actual composition (% KCl).	Index.	Composition calculated from index (% KCl).
69.44	1.36244	69.3
43.09	1.36463	43.7
28.95	1.36582	29.0
00.42	1.36820	1.1

BURLINGTON, VERMONT.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI.]

A NEW METHOD FOR THE SEPARATION OF THE COPPER GROUP FROM THE ARSENIC GROUP, WITH ESPECIAL REFERENCE TO THE IDENTIFICATION OF ARSENIC.

BY M. CANNON SNEED.

Received October 25, 1917.

In qualitative chemical analysis, yellow ammonium sulfide is universally employed for the separation of the copper from the arsenic group. This method is not entirely satisfactory, because some copper sulfide dissolves as well as the sulfides of arsenic, antimony, and tin.[1] To obviate

---

[1] Rössing, *Z. anorg. allgem. Chem.*, **25**, 407 (1900); *Z. anal. Chem.*, **41**, 1 (1902); Noyes, THIS JOURNAL, **29**, 170 (1907).

this difficulty, Welsh and Weber[1] recommend the use of a solution of ammonium polysulfide containing about 5% of sodium hydroxide. Mercuric sulfide, however, is quite soluble in sodium sulfide,[2] which must be present in their reagent.[3]

Furthermore, the methods of qualitative analysis usually employed to separate the copper and arsenic groups lead the analyst into many difficulties. Colloidal suspensions interfere, free sulfur increases the complexities, the use of yellow ammonium sulfide is undesirable, and the whole procedure is not clean-cut, so that, unquestionably, much improvement is needed at this particular point in the scheme of analysis of the cations. This paper is written with a view of presenting a more desirable method of analysis for these two groups.

Procedure.

After mercurous mercury, silver, and lead have been removed by the addition of hydrochloric acid in the usual way, heat the filtrate to 90°, and saturate it with hydrogen sulfide by means of a *rapid* stream of the gas passed long enough to insure the complete precipitation of arsenic.[4] Without removing any precipitate which may form, add a volume of water equal to that of the solution, and again pass hydrogen sulfide. In case an excess of acid is still present,[5] filter the solution and evaporate the filtrate to dryness. Dissolve the residue in a solution prepared by adding 3 or 4 cc. of dilute hydrochloric acid to 75 or 100 cc. of water. Treat the resulting solution with hydrogen sulfide, and if any precipitate is produced, collect it on a filter, together with the previous one, and wash the combined precipitates with hydrogen sulfide water containing about 2% of ammonium nitrate.[6]

Prepare a special reagent as follows: Saturate a 12% solution of sodium hydroxide with hydrogen sulfide. Add to each liter of this solution 400 cc. of a 40% solution of sodium hydroxide.[7] Digest the combined precipitates of the copper and arsenic groups with this reagent. Mercuric, arsenous, arsenic, antimonous, antimonic, stannous and stannic sulfides dissolve, while lead, bismuth, copper and cadmium sulfides settle quickly, leaving above them a clear, almost colorless liquid, which is

---

[1] This Journal, 38, 1011 (1916).

[2] Gmelin-Kraut, "Handbuch d. anorg. Chem.," Ed. 7, 5, 1059 (1909).

[3] An appreciable quantity of HgS dissolves in ammon. polysulfide. It has been shown by Volhard, *Ann.*, 255, 255 (1889), that the presence of ammonium salts renders mercuric sulfide less soluble in the sulfide of sodium.

[4] Foster, This Journal, 38, 52 (1916).

[5] Stieglitz, "Qualitative Analysis, Laboratory Manual," 1916, p. 31.

[6] The use of the ammonium nitrate solution is recommended to prevent, as far as possible, any of the sulfides of these two groups from going into the colloidal condition, and thus reduce the likelihood of error in the analysis.

[7] Do not use sodium polysulfide.

easily filtered.[1] Wash the residue thoroughly with hydrogen sulfide water, and dissolve it in the smallest possible amount of boiling, dilute[2] nitric acid. Probably a little free sulfur will remain. To the acid solution add two or three drops of dilute sulfuric acid, and evaporate it almost to dryness. Cool and treat the residue with water and a little dilute sulfuric acid. Collect any solid material on a filter paper and test it for lead, if lead has not been found previously; otherwise, it is discarded.[3] The filtrate may be tested for bismuth, copper and cadmium according to any standard scheme of analysis.

To the filtrate which contains the arsenic group, add sufficient ammonium carbonate[4] to precipitate the mercury completely.[5] When this precipitate is boiled with dilute hydrochloric acid containing a few crystals of potassium chlorate, it dissolves. Confirm the presence of mercury by adding this solution, which has been boiled to remove chlorine, to one of stannous chloride. Treat the solution, from which mercury was removed, with enough dilute hydrochloric acid to precipitate entirely the sulfides of arsenic, antimony and tin.[6] Collect the precipitate, and treat it with 10 to 20 cc. of concentrated hydrochloric acid; then warm the mixture until the vigorous evolution of hydrogen sulfide ceases. The

---

[1] Stannous sulfide dissolves rather slowly in the special reagent even at a temperature of 90°. If the solution be boiled, a part of the tin separates in the metallic form while the remainder is oxidized to the stannic condition: $2Sn^{++} \longrightarrow Sn + Sn^{++++}$. It is, therefore, advisable to digest the combined precipitates of the copper and arsenic groups for five to ten minutes at a temperature of 100° with the sodium sulfide reagent, in which it dissolves (Gmelin-Kraut, *Handbuch d. anorg. Chem.*, Ed. 7, 4, 289 (1911)):

$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + H_2$$

Unless stannous tin is present, the precipitates need be digested only two or three minutes. The prolonged treatment required to dissolve SnS may be avoided by boiling the solution, after the removal of the silver group, with sufficient nitric acid to oxidize the tin. The amount of acid required for this purpose is usually very small. After the oxidation is complete, the copper and arsenic groups should be precipitated with H_2S in the usual way. Stannous tin is not commonly met with in mixtures prepared for analysis.

[2] Dilute nitric acid, 6 *N*. Dilute hydrochloric acid, 6 *N*. Dilute sulfuric acid, 6 *N*.

[3] Sometimes basic bismuth sulphate is present in this residue.

[4] If trivalent antimony is present, add enough sulfur to change it to the pentavalent condition before ammonium carbonate is used, otherwise some antimonous sulfide will be precipitated.

[5] Volhard, *Loc. cit.*

[6] Another method for separating mercury from arsenic, antimony and tin is as follows: Mercuric sulfide may be precipitated by dilute HCl together with the sulfides of arsenic, antimony, and tin. When these sulfides are treated with concentrated HCl, mercuric sulfide remains undissolved with the sulfides of arsenic. HgS may be separated from As_2S_3 and As_2S_5 by dissolving the latter in concentrated ammonium hydroxide.

sulfides of antimony and tin dissolve, while those of arsenic do not. Tin and antimony may be identified by various standard methods. Treat the residue, which consists of the sulfides of arsenic, and free sulfur, with 5 or 6 cc. of concentrated ammonium hydroxide. Arsenic, in either the tri- or pentavalent state, dissolves readily, leaving a residue of sulfur. First, neutralize the solution with concentrated nitric acid. If a yellow precipitate results, the presence of arsenic is indicated. Without filtering, treat the mixture with a moderate excess of concentrated nitric acid and boil it until a clear liquid results. Treat the hot solution, in a test tube, with an excess of ammonium molybdate.[1] Allow the contents of the tube to stand for several minutes at a temperature of 85 to 90°. If a large quantity of arsenic is present, an immediate yellow precipitate forms; but if there is only a trace of arsenic, half an hour may be required to obtain conclusive evidence of it. By this method, arsenic at a dilution of one part of 225,000 parts of water may be identified by using only 50 cc. of such a solution.

Discussion of the Method.

The method outlined has been used by classes in qualitative analysis with excellent results. They find that the separation of the copper from the arsenic group is precise, and that the identification of the individual ions is usually more conclusive by this than by other schemes. Students, in less than 5% of the cases, have failed to find arsenic, when present, or reported it when their unknowns contained no arsenic. This is exceptional, taking into consideration the fact that by following other methods an error of about 20% is recorded.[2]

By the transference of mercury from the copper group to the arsenic group two equal divisions containing four metals each[3] are obtained, with the further advantage of eliminating the uncertainty of separating completely the sulfides of lead, bismuth, copper and cadmium from mercuric sulfide when solution in nitric acid is depended upon for the separation. Grouping mercury with arsenic does not decrease the ease with which the Hg^{++} is identified.

For many reasons, the use of a mixture of sodium sulfide and sodium hydroxide as a reagent for the group separation, is a decided improvement over yellow ammonium sulfide. It is noteworthy, for example, that all the sulfides which are soluble in ammonium polysulfide, with the exception of copper sulfide, dissolve more readily in the sodium sulfide mixture. Again, as previously noted, the new reagent, unlike yellow ammonium sulfide, effects a complete separation of the groups, and at the same time leaves a solution from which the sulfides of lead, bismuth,

---

[1] A large excess of ammonium molybdate is necessary.

[2] Welsh and Weber, *Loc. cit.*

[3] Gold, platinum and molybdenum omitted.

copper and cadmium separate as a dense residue with a clear, almost colorless, supernatant liquid, free from these sulfides, either suspended or dissolved. Furthermore, it is noted that cadmium sulfide, obtained as a final test for the Cd^{++}, is always of a pure yellow color, and not admixed with any other sulfide.[1] Finally, from a study of the chemical behavior of gold, platinum, and molybdenum it would be expected that the sulfides of these metals would be more readily soluble in a mixture of sodium hydroxide and sodium sulfide than in ammonium polysulfide.

To effect a separation of the copper and arsenic groups Prescott and Johnson[2] recommend the use of sodium sulfide, if mercury be absent, and state that ammonium polysulfide must be employed if tin be present in the stannous condition. But if mercury be transferred to the arsenic group, sodium sulfide must be used. Moreover, mercuric sulfide is more readily soluble in a mixture of sodium sulfide and sodium hydroxide than in sodium sulfide alone; and stannous sulfide dissolves completely in the *mixture* while it often fails to do so in yellow ammonium sulfide.[3] Probably this fact is to be explained by assuming that some salt, *e. g.*, Na_2SnOS, which may be formed under these conditions, possesses a low instability constant which accounts for the suppression of the Sn^{++}, and, therefore, greatly increases the solubility of stannous sulfide. It is true that stannites are much more stable than thiostannites.

Identification of arsenic, as ammonium arsenomolybdate, is readily made by dissolving its sulfides in concentrated ammonium hydroxide, thus freeing it from any sulfur which may be present. The arsenic is then confirmed according to the scheme. This procedure is much more desirable than to dissolve in nitric acid the sulfides of arsenic, together with a large amount of admixed sulfur, which is always present when ammonium polysulfide is used as a reagent. The use of ammonium hydroxide to effect a solution, and the subsequent use of nitric acid to precipitate the sulfides of arsenic and to redissolve them, gives a mixture containing ammonium nitrate and nitric acid, in the presence of which the molybdate test is most sensitive. This method for identifying arsenic is offered as a convenient and reliable wet test, when arsenic is present in concentrations not less than one part of arsenic to 225,000 parts of water, and when at such a dilution the analyst has at least 50 cc. of solution.

CINCINNATI, OHIO.

---

[1] Lead, which is frequently carried through to the point where Cd^{++} is determined, masks the color of cadmium sulfide. This complication arises from the use of too much sulfuric acid or too concentrated nitric acid, both of which dissolve an appreciable amount of lead sulfate. This sulfate, in such acid solutions, is not reprecipitated by ammonium hydroxide, which is employed to precipitate $Bi(OH)_3$, because lead sulfate is soluble in ammonium salts, which makes it possible for lead to be carried over to the point where cadmium is detected.

[2] "Qualitative Analysis," 7th Ed. p. 117 (1917).

[3] Noyes, *Loc. cit.*