purpureo ammonio salts of chromium. Recoura,[1] long ago, observed a similar behavior when ordinary green chromic chloride was treated with alkalies. Furthermore, Pfeiffer[2] found that a yellowish green isomer of the above pyridine derivatives was similarly changed into the violet modification by the action of pyridine or ammonia, although none of its chlorine was precipitable with silver nitrate, which in this case, at least, precludes the first sort of hydrolysis.

From this point of view, the color change in pure aqueous solutions of green chromic chloride would become a rather interesting type of reaction. The hydrolysis of the chlorine ions in the green complex would be taking place in a solution whose hydroxyl ion concentration, and consequently whose hydrogen ion concentration, would be governed by the degree of hydrolysis of the green complex ion, ($CrCl_2'$) disappearing, and of the violet ion (Cr''') being formed. If the latter were less hydrolyzed than the former, the hydrogen ion concentration would *decrease* as the color change progressed, and we should have a case of auto-catalysis. If, on the other hand, the latter were more hydrolyzed, the concentration of the hydrogen ion would *increase* and we should have a case of *negative* auto-catalysis.

This color change in solutions of chromic salts is being further investigated experimentally in this laboratory, particularly as regards its velocity and the location of its equilibrium.

THE TECHNICAL ESTIMATION OF ANTIMONY AND ARSENIC IN ORES, ETC.

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The technical estimation of antimony in ores containing also arsenic and possibly tin is frequently a tedious and more or less unsatisfactory operation. Distillation methods may give correct results, but considerable experience in their manipulation is usually required, and perhaps, also, special apparatus not always at the disposal of the technical chemist having only an occasional antimony determination to make. The following method for both antimony and arsenic is free from these objections, and,

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[1] Recoura: Loc. cit.

[2] Pfeiffer: Loc. cit.

in my laboratory, has given results closely checking those obtained by distillation. While it is largely based upon old ideas there are some points of novelty that tend to expedite the work, and the method as a whole is different from any I have seen published. The time required for determining both antimony and arsenic in an ore need not exceed two and one-half hours.

Take 1 gram of the ore in a 150 cc. flask, add 7 grams of potassium acid sulphate, 0.5 gram of tartaric acid and 10 cc. of strong sulphuric acid. Heat over a free flame (manipulating the flask in a holder), cautiously at first, finally with the full power of a Bunsen burner, until any free sulphur is entirely expelled and the separated carbon is completely oxidized, leaving a clean mass or melt with but little free sulphuric acid. Allow to cool with the flask on its side, as otherwise the solidifying cake may break it, or, spread the melt around on the sides while cooling. The object of the tartaric acid in the decomposition is to reduce the arsenic and antimony to the *ous* condition, thus rendering the subsequent solution of the antimony easy and the precipitation of both metals as sulphides rapid and complete. A covered casserole may be employed instead of a flask, if considered more convenient.

After cooling, add 50 cc. of water, 10 cc. of strong hydrochloric acid and 2 or 3 grams of tartaric acid. Heat nearly to boiling for a short time to dissolve everything soluble (especially anhydrous iron sulphate), but do not actually boil for fear of volatilizing some arsenic. Filter, washing with hot water. This filtration is advisable but not a necessity. Dilute the filtrate to about 300 cc. with hot water, maintain the liquid warm and pass in hydrogen sulphide. The arsenic and antimony, being in the *ous* condition, are quickly precipitated, ten minutes being usually sufficient. Filter, washing with hydrogen sulphide water. Rinse the sulphides into a beaker with hot water, using as little as will suffice, add a little colorless potassium sulphide[1] and warm to extract the arsenic and antimony sulphides (also tin sulphide, if present). Pour through the last filter and wash with warm water containing a ittle colorless potassium sulphide. With small amounts of other sulphides present one extraction will usually suffice. Receive the filtrate in a 300 cc. flask. Add to it about 3 grams of potassium acid sulphate and 10 cc. of strong sulphuric

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[1] If sodium sulphide is used a separation of sodium chloride crystals, occluding a little antimony, may occur later.

acid and boil the mixture, finally over a free flame, until the free sulphur is all expelled and the greater part of the free acid also. Allow the clear melt to cool with the flask on its side. When sufficiently cool add 25 cc. of water and 10 cc. of strong hydrochloric acid and warm to effect complete solution, then cool nearly to room temperature under the tap. Now add 40 cc. of strong hydrochloric acid and pass in hydrogen sulphide. The arsenic will be quickly precipitated, being in the *ous* condition. Filter, washing flask and precipitate with a mixture of 2 volumes strong hydrochloric acid and 1 volume of water. Before filtering, moisten the filter with the acid mixture. A double filter supported by a platinum cone will not break under very gentle suction.

The arsenic is now all on the filter and the antimony (together with any tin) in the filtrate. Determine the two metals as follows:

Antimony.—Dilute the filtrate with double its volume of warm water and pass in hydrogen sulphide. Filter the antimony sulphide and wash with hydrogen sulphide water sufficiently to remove most of the hydrochloric acid. Rinse the sulphide from the filter into a beaker, add a little ammonium sulphide and warm to effect solution. Pour through the last filter and wash with water containing a little ammonium sulphide. Receive the filtrate in a 300 cc. flask. Small amounts of antimony sulphide may be dissolved directly on the filter. To the filtrate add about 3 to 4 grams of (pure) potassium acid sulphate and 10 cc. of strong sulphuric acid. Boil as previously described to expel, first the water, then all the free sulphur and finally most of the free acid. Cool, add 50 cc. of water and 10 cc. of strong hydrochloric acid. Heat to effect solution and then boil for a few minutes to expel any possible sulphur dioxide. Finally, add 10 cc. more of strong hydrochloric acid, cool under the tap, dilute to about 200 cc. with cold water and titrate with a standard solution of potassium permanganate. The solution ordinarily used for iron titrations will answer. Tin, if present, exists as stannic sulphate and is without influence. The oxalic acid value of the permanganate multiplied by 0.9532 will give the antimony value.

Arsenic.—Thoroughly wash out the hydrochloric acid from the sulphide with hydrogen sulphide water, also rinsing out any sulphide remaining in the flask. Dissolve the sulphide (this may usually be done on the filter) in warm ammonium sulphide solution and wash with the same solution diluted. Receive the filtrate in a 300 cc. flask. Add 2 to 3 grams of potassium acid sulphate and 5 cc. of strong sulphuric acid. Evaporate, boiling to a small bulk, and then manipulate the flask over a free flame until the sulphur is entirely expelled and most of the free acid also. Take up, after cooling, by warming with 50 cc. of water and then boil sufficiently to expel any possible sulphur dioxide. Now drop in a bit of litmus paper as an indicator and then add ammonia until the solution is slightly alkaline. Again acidify slightly with hydrochloric acid and cool to room temperature. Finally add 3 to 4 grams of sodium acid carbonate and a little starch liquor and titrate with standard iodine solution. Pay no attention to a slight discoloration toward the end, but proceed slowly until a single drop of the iodine produces a strong permanent blue color.

The iodine solution may be prepared by dissolving about 11 grams of iodine in a little water with the addition of about 20 grams of potassium iodide and diluting to 1 liter. Standardize with arsenious oxide. Dissolve about 0.150 gram in 5 cc. of strong hydrochloric acid by warming very gently, dilute and neutralize as described above and finally titrate with the iodine solution. One cc. of the latter will equal about 0.003 gram of arsenic.

It is perhaps unnecessary to enumerate a long list of instances showing the accuracy of the above method and I will therefore mention only the following:

	Taken. Gram.	Found. Gram.
As	0.0792	0.0798
Sb	0.0534	0.0531
Sb	0.0516	0.0514
Sb	0.0521	0.0525

With an oxidized ore: As, 0.568 per cent.; Sb, 0.106 per cent. Repeat: Sb, 0.106 per cent.

On this ore Pearce's method (modified) gave As, 0.57 per cent.

The same ore gave, by Knorr's distillation method, Sb, 0.082 per cent.

Ledoux & Co., of New York, reported Sb, 0.081 per cent.

Mr. R. L. Wilder, of El Paso, tested this ore by the new method and found Sb, 0.1005 and 0.0802 per cent.

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