

ON A VOLUMETRIC METHOD OF GENERAL APPLICABILITY FOR THE DETERMINATION OF COMBINED SULPHURIC ACID.*

BY LAUNCELOT W. ANDREWS.

OF the volumetric methods at present in use for the determination of sulphuric acid, none can be considered entirely satisfactory, although some of them are very useful for technical purposes. Several of these methods involve a double titration, some require three standard solutions, and others are only applicable in the absence of bases precipitable by sodium carbonate.

The author believes, therefore, that the presentation of a new method, applicable in the presence of magnesium, calcium, aluminum, zinc, manganese, iron (ferric), nickel, cobalt, and silver, which requires but one standard solution with a single titration, and which in precision is at least equal to the ordinary gravimetric determination as barium sulphate, while demanding much less time for its execution, will not be thought superfluous.

The process depends upon the following series of reactions: First, to the solution of a sulphate is added an excess of a solution of barium chromate in hydrochloric acid; second, the solution is neutralised with ammonia or calcium carbonate, and filtered; third, the filtrate is acidified with hydrochloric acid, potassium iodide added, and the free iodine titrated with decinormal sodium thiosulphate solution (1 c.c. = 12.654 mg. iodine = 2.662 mg. SO_3).

The barium chromate employed may contain barium sulphate, but must be completely freed from soluble chromates and from barium carbonate, nitrate or chloride, by prolonged washing, first with boiling water slightly acidified with acetic acid, finally with hot distilled water, until the washings give no precipitate with sulphuric acid, and (in a quantity of 100 c.c.) a barely perceptible reaction with hydrochloric acid, potassium iodide and starch paste.†

A suitable solution of the barium chromate is prepared by digesting it with hydrochloric acid containing 36 grms. acid in the litre. This solution will contain from 2 to 4 per cent. of barium chromate, according to the temperature at which it was prepared.

The reagent being ready, the analysis is performed as follows:—

The sulphate to be determined is diluted, if necessary, until it does not contain more than 2 per cent., at most, of sulphuric anhydride, is made approximately neutral, and is heated to boiling. While boiling hot, an excess of the barium chromate solution is gradually introduced, and the boiling continued one minute, or longer, if carbonates were present.

The precipitate of barium sulphate is always yellow from the barium chromate which is carried down with it, provided sufficient excess of the latter reagent was added.

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† When barium chloride is precipitated with an excess of potassium chromate, the water with which the precipitate is washed well, for a long time, show a yellow colour. This is not, as has been supposed, due to the solubility of BaCrO_4 , but to the fact that it obstinately retains soluble chromate. According to the author's observation, barium chromate is not sufficiently soluble in water to impart any colour to the latter. According to the mean of four concordant determinations, one million parts of water dissolve 15 parts barium chromate at 18°C .

Calcium carbonate, which must be entirely free from barium or strontium carbonates or calcium sulphate, is then thrown in small portions into the still hot liquid until no further evolution of carbonic anhydride is observed, and the boiling continued one or two minutes. The solution is filtered while hot, and the precipitate is washed with a small quantity of hot water until the washings are colourless, and a little longer. Under these conditions, the barium chromate has no tendency to run through the filter or to retain any soluble chromate. 75 c.c. of water will usually be found more than sufficient to effect the washing.

If, on the other hand, the solution is allowed to stand over night with the precipitate in it, calcium chromate will be retained and a longer washing becomes necessary. In this case the results may come somewhat too high, in consequence of the necessarily large amount of wash-water dissolving an appreciable quantity of barium chromate. Under normal conditions the error from this source is quite insignificant.

The filtrate, after cooling, is treated with a sufficient amount of crystals of potassium iodide (free from iodate) and with 5 to 7 c.c. fuming hydrochloric acid for each 100 c.c. of liquid. This amount of acid is enough to induce a prompt and complete reduction of the chromate, but not enough to decompose the starch paste. It is advisable to run in the decinormal sodium thiosulphate from a burette until the brown colour of the iodine is nearly discharged before adding the starch, and then to continue the titration slowly, with constant stirring, until the turning point is reached.

The above process must be modified in the presence of ferric, nickel, or zinc salts by using ammonia instead of calcium carbonate to neutralise the acid liquid. The solution in this case is to be made distinctly alkaline, and the excess of ammonia boiled nearly away before filtering. The necessity for this modification arises from the fact that if a ferric or nickel or zinc salt is boiled with a chromate and calcium carbonate, basic chromates of iron and nickel are precipitated, from which the chromic acid cannot be removed, or only with difficulty, by washing. Barium chromate, when precipitated from its acid solution by ammonia, does not possess the agreeable properties which it shows when thrown down by calcium carbonate. It is much more finally divided than in the latter case, tends to run through the filter, which must therefore be double or of very dense paper, and requires a longer washing to remove the soluble chromates which it more tenaciously retains; consequently, ammonia is only to be used when the employment of calcium carbonate is inadmissible. It is not practicable to precipitate the excess of barium chromate with sodium acetate from hydrochloric acid solution. Numerous experiments, the details of which it is not worth while to give, show that barium chromate is so soluble in hot dilute acetic acid that the results fall 3 to 5 per cent too high, while if precipitated cold and allowed to stand, the results are too low.*

The following analyses show the applicability of the method :—

I. Taken 10 c.c. of a solution containing 20.8984 grams. pure and dry ammonium sulphate per litre. Diluted to 50 c.c., treated with 15 c.c. BaCrO_4 solution with CaCO_3 , as described above.

*The method cannot be used in the presence of phosphoric acid, and, of course, all reducing agents, as well as bismuth and copper salts, must be excluded.

Required 47.60 c.c. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol. = .1267 gram. SO_3 found. Calculated, .1266 gram. SO_3 ; 100.08 per cent. found.

II. Taken 10 c.c. of the same ammonium sulphate solution and treated as in No. I. Required 47.60 c.c. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol.

The volume of the solution before titration was 300 c.c. 100.08 per cent. found.

III. 20 c.c. of the same ammonium sulphate solution, treated as before, required 95.50 c.c. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol.

Total volume of the solution, 400 c.c.; 100.37 per cent. found.

IV. Taken .2980 gram. $\text{CuSO}_4 + 5\text{H}_2\text{O}$, small crystals obtained by triple recrystallisation of a commercial sample. The copper was precipitated from boiling sol. with $(\text{NH}_4)_2\text{S}$ (free from sulphate), solution boiled with acetic acid to expel H_2S , filtered and filtrate treated as above.

35.95 c.c. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol. required = .0957 gram. SO_3 = 32.11 per cent. found. Theoretical per cent. = 32.09.

V. Taken 10 c.c. $(\text{NH}_4)_2\text{SO}_4$ solution (see 1) containing .20898 gram., diluted to 100 c.c., treated with 20 c.c. BaCrO_4 sol. as above and neutralised with ammonia. Required 47.30 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol. = .1260 gram. SO_3 instead of .1266 gram. Found 99.52 per cent.

VI. Taken .6485 gram. $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$. Treated as No. V. Required 80.65 c.c. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol. = .2147 gram. SO_3 . Calculated .2153 gram. SO_3 . Found 33.11 per cent. SO_3 . Theory 33.20 per cent.

VII. *a.* Taken 100 c.c. of the Iowa City water supply. Treated as No. V. Required 2.10 c.c. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol.

b. Taken 200 c.c. ditto, ditto. Required 4.30 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol.

Found 56 mg. and 57 mg. SO_3 per litre. A gravimetric analysis gave 58 mg. SO_3 per litre.

It seems probable that an indirect determination of sodium and potassium would be possible by weighing these elements as sulphates and determining the sulphuric anhydride volumetrically as described. Experiments to test this are now in progress. If feasible, it is evident that it would often be more convenient than the usual indirect determination as chlorides, while free from some of the well-known sources of error involved in the gravimetric determination of sulphuric acid in the presence of alkalies.

It is both a duty and a pleasure for me to take this opportunity to express publicly my thanks to Mr. F. W. Spanutius, instructor in chemistry here, for the zeal and skill with which he has assisted me in the experimental part of this investigation. Some of the test analyses given above were performed by him.