

XIV.—*Process for the quantitative estimation of Sulphides, Sulphites, Hyposulphites, and Sulphates, in presence of each other, as adopted in the determination of these salts in "Soda Waste," as obtained from "Black Ash."*

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THIS method is founded upon the decomposition of an alkaline sulphide by carbonate of cadmium; $\text{CdO}, \text{CO}_2 + \text{NaS} = \text{CdS} + \text{NaO}, \text{CO}_2$, and on the changes produced in hyposulphite of silver, and sulphite of silver when heated in water nearly to boiling, which may be expressed thus:— $\text{AgO}, \text{S}_2\text{O}_2 = \text{AgS} + \text{SO}_3$, and $\text{AgO}, \text{SO}_2 = \text{Ag} + \text{SO}_3$. By means of the above reactions, these sulphur salts may be estimated without difficulty, and with positive certainty, as is proved by the subjoined experiments.

To overcome the difficulty of obtaining a sulphide containing a definite proportion of sulphur, 100 measures of a very dilute solution of sulphide of ammonium were taken. In 50 measures, the proportion of sulphur was estimated by precipitating as sulphide of copper. The sulphide was oxidized by nitric acid, and the sulphuric acid precipitated as sulphate of baryta, and yielded 3.7364 grammes $\text{BaO}, \text{SO}_3 = 1.0904$ of protosulphide of ammonium NH_4S . The other half of the solution, of course containing the same amount of sulphide, was reserved for estimation in admixture with the other salts. A similar difficulty arises in obtaining a sulphite of definite composition, and this was overcome in a similar manner. A neutral solution of sulphite of soda was prepared, and 100 measures taken, in half of which the sulphite was estimated—after oxidizing by means of chromate of potassa, and acidifying—by precipitating sulphuric acid with chloride of barium. The weight of BaO, SO_3 obtained was 0.6502 grammes = 0.3516 of sulphite of soda NaO, SO_2 . The other 50 measures, representing the same weight of sulphite, were added to the solution of sulphide of ammonium. Afterwards, 1.146 grammes of crystallized hyposulphite of soda, pulverized, and pressed in bibulous paper, were dissolved and added to the mixture, and lastly 1.213 grammes of anhydrous sulphate of soda. Thus was produced a solution containing 1.0904

grammes NH_4S ; 0·3516 of NaO , SO_2 : 1·146 of NaO , S_2O_2 ; and 1·213 grammes of NaO , SO_3 ; which would afford a mixture, having the following percentage composition:—

Sulphide of ammonium	28·687
Sulphite of soda	9·250
Hyposulphite of soda	30·150
Sulphate of soda	31·913
	100·000

To this mixed solution, a quantity of carbonate of cadmium was added, and the whole was digested for some time, with frequent agitation. The mixture of sulphide, and undecomposed carbonate of cadmium was then filtered off, and treated with acetic acid to remove the latter salt. The residue of CdS was then treated with nitric acid. Only a portion of the sulphur was oxidized: the residue was collected by filtration, dried and weighed, giving 0·3205 grm. of sulphur. From the nitric acid solution, the sulphuric acid was thrown down as sulphate of baryta, and the weight of the latter was 1·3782 grammes. This and the separated sulphur represent 1·0833 of NH_4S = 28·5004 per cent.

To the filtrate from the cadmium salts, nitrate of silver was added as long as a precipitate was produced. The mixture was heated nearly to ebullition, and kept for some time at that temperature. The silver precipitate was then collected, washed, and partially dried, then treated with concentrated nitric acid. The whole of the sulphide was oxidized, and the sulphuric acid formed, was precipitated as sulphate of baryta, giving 1·0732 grammes = 1·1423 NaO , S_2O_2 + 5 HO = 30·0526 per cent.

The sulphuric acid in the filtrate from the silver precipitate, was thrown down as sulphate of baryta, and yielded 3·7276 grammes. Subtracting from this 1·9889 = the quantity of NaO , SO_3 present, and 1·0732 = the NaO , S_2O_2 , 5 HO , found above, the residue represents the quantity of NaO , SO_2 .

Total weight of BaO , SO_3	3·7276
BaO , SO_3 = 1·213 NaO , SO_3	1·9889
	1·7387
,, = 1·1423 NaO , S_2O_2 + 5 HO	1·0732
= BaO , SO_3 NaO , SO_2 remaining	0·6655

This residue, $0\cdot6655$ BaO, SO_3 represents $0\cdot3598$ of NaO, $\text{SO}_2 = 9\cdot4659$ per cent.

There are found therefore :—

Sulphide of ammonium	28·5004
Sulphite of soda	9·4659
Hyposulphite of soda	30·0526
Sulphate of soda	31·9130
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	99·9319

I now append the numbers collaterally, to prove at a glance the accuracy of the methods employed :—

	Theory.	Analysis.
Sulphide of ammonium	28·687	28·5004
Sulphite of soda	9·250	9·4659
Hyposulphite of soda	30·150	30·0526
Sulphate of soda	31·913	31·9130
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	100·000	99·9319

This process answers equally well in presence of a large proportion of alkaline carbonate; but in this case, it is necessary to treat the silver precipitate with liquid ammonia to remove carbonate of silver, previous to the oxidation of the sulphide.
