

[CONTRIBUTION FROM THE HYGIENIC LABORATORY OF THE U. S. PUBLIC HEALTH SERVICE AND THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

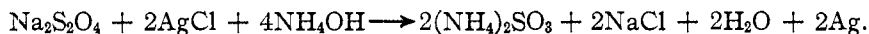
THE ESTIMATION OF SODIUM HYPOSULFITE.¹

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The usual methods of determining the degree of purity of sodium hyposulfite are unsatisfactory for ordinary laboratory work because they require either extreme care to exclude air or the use of uncommon reagents. Direct titrations with ferric³ or cupric⁴ salts were very inaccurate when performed without keeping the air away from the easily oxidized hyposulfite solution. The use of an excess of standard dye solution to oxidize the hyposulfite, the excess of dye being titrated with titanium trichloride,⁵ requires reagents that are uncommon. In the average laboratory a dye of standard purity is difficult to obtain. Hence a method was looked for which requires no extraordinary pains in the exclusion of air, uses only common reagents and which is fairly rapid.

Seyewetz and Bloch⁶ oxidized the hyposulfite with ammoniacal silver chloride, reducing the silver salt to metallic silver as follows.



The silver was collected and weighed in a Gooch crucible. In principle this method is superior to the direct titration methods in that the easily oxidized solution of the hyposulfite is eliminated. The solid hyposulfite is flooded with the oxidizing solution, thus excluding the effect of the air. Another advantage recommends this method, *viz.*, that the impurities sulfite and thiosulfate, do not affect the silver salt as they do such reagents as iodine, permanganate and ferric alum. The method, however, has two drawbacks: First, the gravimetric procedure is slow; second, it is inaccurate because of the insoluble impurities in the hyposulfite which are caught in the Gooch crucible and weighed. For these reasons we sought a method which would use the above principle but eliminate its disadvantages.

Both faults can be remedied by solution of the silver on the Gooch crucible in nitric acid and titration of the silver nitrate by the Volhard method. A minor modification was made in the use of silver nitrate instead of the

¹ Sodium hyposulfite is more commonly, but incorrectly, known as sodium hydrosulfite.

² This work was carried out by me as chemist in the employ of the U. S. Public Health Service, under the direction of J. Stieglitz in his capacity of adviser to the Hygienic Laboratory of the U. S. P. H. S. The work was done at the University of Chicago and is published with the consent of the Surgeon General.

³ Ekker, *Rec. trav. chim.*, **13**, 37-45 (1894); and R. Formhals, *Chem.-Ztg.*, **44**, 869 (1920).

⁴ Fradiss, *J. Chem. Soc. Abs.*, [II] **78**, 44 (1900).

⁵ Knecht and Hibbert, *Ber.*, **40**, 3819 (1907).

⁶ Seyewetz and Bloch, *Bull. soc. chim.*, [III] **35**, 293 (1906).

silver chloride of the original method. By these modifications, then, the method becomes both rapid and accurate.

Analytical Procedure.

About 0.4 g. of the solid sodium hyposulfite is weighed into a dry beaker. A 100% excess of ammoniacal silver nitrate is poured over the solid hyposulfite. As the hyposulfite dissolves, it is oxidized immediately by the silver nitrate, and metallic silver is precipitated. At this point the solution must not be warmed, or inaccurate results will be obtained. The precipitate is filtered on a Gooch crucible, and washed free from silver salts with an ammoniacal solution of ammonium nitrate. The purpose of the ammonium nitrate is to keep the finely divided silver from being washed through the Gooch crucible. When pure water is used, there is often cloudiness in the filtrate. The crucible is then placed in the same beaker, and the silver dissolved in nitric acid. The solution is boiled to insure complete solution of the silver, and also to remove nitrous acid which would interfere with the Volhard titration. The crucible is now removed, the solution diluted, and titrated with 0.1 *N* potassium thiocyanate solution, ferric alum being used as the indicator. The asbestos need not be removed.

The calculation is based on the relation that one mol of sodium hyposulfite is equivalent to 2 mols of potassium thiocyanate.

It was thought that a known volume of standard silver nitrate could be used to oxidize the hyposulfite, the silver removed and the excess silver nitrate titrated. This variation does not seem to be as rapid as the one given above; moreover, when the filtrate containing the excess silver nitrate is acidified with nitric acid it turns to a brownish color, which greatly interferes with the sharpness of the end-point.

Experimental Part.

The following results were obtained on hyposulfite of English manufacture.

Sample, g.....	0.1371	0.1454	0.5423	0.6059
Volume of 0.1001 <i>N</i> KCNS, cc.....	12.89	13.81	51.48	57.26
Na ₂ S ₂ O ₄ %.....	81.99	82.78	82.76	82.39

It is impossible to obtain a uniform sample, as there are coarse impurities in the material, such as bits of wood and paper.

Summary.

1. A review of the usual methods of analysis of sodium hyposulfite is given. These require unusual reagents and elaborate precautions.
2. The method of Seyewetz and Bloch is modified to substitute volumetric for gravimetric procedure. The sodium hyposulfite precipitates metallic silver, which is estimated by the Volhard method.
3. A series of typical analyses is given.