Summary.

(1) A new double pipet for liquid reagents in gas analysis is described.

(2) The use of sodium pyrogallate as a reagent for the determination of oxygen in gases is proposed. Complete absorption in four minutes was secured from a number of solutions containing pyrogallol, sodium hydroxide and water in varying proportions. No carbon monoxide was detected in using the proposed reagent under varying conditions and the specific absorption of the best practicable solution was found to be five times that of the corresponding best solution for potassium pyrogallate.

(3) The total volume of oxygen absorbed was found to be in excess of the proportion of 3 atoms of oxygen for each molecule of pyrogallol.

(4) Ammonium and barium pyrogallate were found to be impracticable for general use in gas analysis.

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[CONTRIBUTION FROM THE KENTUCKY AGRICULTURAL EXPERIMENT STATION.]

THE ESTIMATION OF THIOSULFATE SULFUR IN LIME-SULFUR SOLUTIONS BY IODINE TITRATION.

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The question of the accuracy of the so-called "Iodine Methods" for the estimation of thiosulfates and polysulfids in commercial lime-sulfur solutions has vexed agricultural chemists for some years past. Recently one of us[1] published a paper in which he proved that the substance titrated with iodine after removing polysulfids, actually was thiosulfate, by means of a process in which tetrathionate was reconverted to thiosulfate and estimated.

Roark[2] stated that in the iodine titration there is reason to believe that iodine may cause an increased formation of sulfate, thus introducing an error.

We have undertaken to test the accuracy of the iodine method for thiosulfate in another fashion, namely, by converting the tetrathionate formed to sulfate and comparing this value with the titration figure.

Experimental.

The following experiments were conducted with two objects in mind: to ascertain whether the oxidation of thiosulfate or tetrathionate to sulfate occurs sufficiently rapidly and in such quantity, particularly under poor working conditions, as to cause serious analytical errors; and to learn as much as possible about the chemistry of the lime-sulfur titration after the removal of polysulfid sulfur.

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[1] S. D. Averitt, *J. Ind. Eng. Chem.*, **8**, 623 (1916).

[2] *J. Assoc. Off. Agr. Chem.*, **1**, 65.

Three portions of 0.05 *N* (factor 0.9948 0.05 *N*) thiosulfate were titrated exactly with approximately 0.1 *N* (factor 0.995 0.1 *N*) iodine solution to form tetrathionate, and a definite excess of iodine was added to each. The solutions were well stoppered and allowed to stand in the dark for two weeks. $BaCl_2$ was then added and the $BaSO_4$ weighed. Where the ratio of iodine to thiosulfate in two experiments was approximately 2 : 1, about 18% of the sulfur present was found as sulfate; with the ratio $3^1/_3$ to 1 in another experiment about 36% of the sulfur was found as sulfate. In each case, the blank for sulfate originally present in the thiosulfate was deducted. Evidently a considerable oxidation of *tetrathionate* occurred under the conditions of the experiment.

It is, therefore, conceivable that in a titration, if the iodine were to be run into a thiosulfate solution rapidly, without constant shaking, the formation of regional excesses of iodine might cause a slight oxidation of some of the tetrathionate first formed, to sulfate. In most cases this error would be small, since in a titration there is usually only a very short time in which iodine is in excess, and the action upon tetrathionate is by no means rapid.

To get an idea of the possible extent of this action, under working conditions, a series of experiments was conducted as follows:

Ten portions of 20 cc. each of a thiosulfate solution (0.1 *N*) were treated as follows: 1 and 2 had 2 cc. 10% $BaCl_2$ added and were then allowed to stand overnight, to permit the sulfates present to separate out. This served as a control on the sulfate content of the thiosulfate solution. 3 and 4 were carefully titrated with iodine solution, with constant shaking, so as to avoid regional excesses of iodine, and afterward the same amount of $BaCl_2$ was added. 5 and 6 were rapidly titrated, permitting regional excesses of iodine to form, shaking only toward the end of the titration so as to simulate careless work; after completion, $BaCl_2$ was added. 7 and 8 were similar to 3 and 4, except that $BaCl_2$ was added before titrating to remove $\overset{--}{SO_4}$ ions as rapidly as formed. 9 and 10 also had $BaCl_2$ added first and were otherwise identical with Nos. 5 and 6. To all except Nos. 1 and 2 a little 0.1 *N* HCl was added after the titration to prevent BaS_4O_6 formed from decomposing, experience having shown that HCl stabilizes the barium salt. The average weight of $BaSO_4$ obtained in each pair was as follows: 0.55, 0.90, 0.95, 1.25 and 1.25 mg., respectively. The quantity of sulfate produced in the last four sets (3–10 inclusive) by the action of iodine upon tetrathionate was, therefore, 0.35, 0.4, 0.7 and 0.7 mg., respectively. A slight difference in the iodine titration values could be noticed. The averages of the titrations were 19.82 cc., 19.85 cc., 19.84 cc. and 19.86 cc., respectively, the maximum difference being 0.04 cc. in Nos. 9 and 10 as compared to Nos. 3 and 4. The difference in weight of $BaSO_4$ between the averages of the same two sets is 0.35 mg. It would require 0.048 cc. of 0.1 *N* I to produce this amount of $BaSO_4$ according to the equation $Na_2S_4O_6 + 7I_2 + 10H_2O = 2NaHSO_4 + 2H_2SO_4 + 14HI$, a good agreement considering the difficulty of estimating such small quantities. However, even if iodine does oxidize thiosulfate or tetrathionate all the way to sulfate, the quantity so produced in a lime-sulfur analysis would be almost negligible (less than 0.01% S), since the quantity of thiosulfate here employed is four to eight times as great as one encounters in actual analysis, according to the official procedure. It seems probable that in every titration a small quantity of iodine is used to produce sulfates by direct oxidation; we know of no method to prove this directly, since the error of weighing thiosulfate as $BaSO_4$ is fully as great as the titration error, and there is no other method[1] known to us of standardizing a thiosulfate solution except by iodine titration of one kind or another.

In order to throw further light upon this sulfate-forming reaction and also upon the iodine titration methods as applied to lime-sulfur solutions, some experiments were carried out upon three lime-sulfur solutions which had already been analyzed by one of us (Averitt) during the progress of the work. Nos. 1 and 3 were commercial concentrates, No. 2 was made in the laboratory from pure chemicals and had a high thiosulfate content.

Three aliquots of Sample No. 1 were titrated with HCl to incipient acidity to methyl orange, the hydrogen sulfid was boiled out and $BaCl_2$ added. The precipitated sulfur (and barium sulfate, if present) was filtered on fine-mat Gooch crucibles, dried, ignited and weighed. No barium sulfate was found, indicating absence of sulfate in the sample and reagents and that no sulfate was formed during the removal of H_2S. Similar results were obtained upon samples Nos. 2 and 3.

A second set of three aliquots each of Nos. 1 and 2 was treated as before with HCl and boiled and, after $BaCl_2$ and starch had been added, the solution (containing precipitated sulfur) was titrated with approximately 0.1 *N* iodine solution. The iodine consumed represents thiosulfates and sulfites, if the latter are present—a disputed point. After standing overnight, a small amount of $BaSO_4$ was found which, on each series of aliquots, averaged 0.7 mg. and 1.2 mg. of $BaSO_4$, respectively. This sulfate must have resulted either from the oxidation of sulfite or from the interaction of thiosulfate or tetrathionate with iodine.

Ashless paper filters were substituted for the Gooch crucibles after this, as it was found difficult to retain very small quantities of sulfate on asbestos.

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[1] We have since heard of another method of standardization and hope to test it at a later period.

Next, three portions, each containing 1 gram of concentrate (No. 3) were treated as follows: One portion, after being titrated with HCl, having $BaCl_2$ added and H_2S boiled out, was titrated with iodine and allowed to stand several hours. The $BaSO_4$ weighed 1.0 mg. The filtrate was then oxidized with bromine and the barium sulfate weighed. Calculated from this figure, the thiosulfate sulfur was 0.51%, which was exactly the same as the iodine titration value.

The other two portions were titrated with HCl as before and the H_2S was boiled out. After filtering out the precipitated sulfur, barium chlorid was added and the solution allowed to stand overnight. No precipitate was found, which proved the absence of sulfate in the original sample and also that none was formed during the removal of H_2S by boiling from a barely acid solution. The samples were then titrated with iodine and allowed to stand overnight before filtering. The barium sulfate found weighed 1.2 and 1.1 mg., respectively. This sulfate came either from the presence of a small amount of sulfite or from the action of iodine on the tetrathionate or thiosulfate. The barium sulfate weighed from the oxidation of tetrathionate by bromine showed 0.51 and 0.54% sulfur as compared to 0.52 and 0.54% by the iodine titration.

Conclusions.

The following points are considered as being established:

1. An excess of iodine does react with tetrathionate in neutral or faintly acid solutions, upon standing.
2. In every iodine titration on a lime-sulfur solution a small quantity of sulfate is formed; in some lime-sulfur solutions this is the only sulfate found.
3. The quantity of iodine used to form sulfate in an ordinary titration does not cause an appreciable error in the determination of thiosulfate.
4. The iodine values obtained after decomposing polysulfids by HCl titration actually represent thiosulfate, since the barium sulfate obtained from such solutions after oxidation agrees very closely with the titration values. The presence of sulfites, which would also be titrated at this point, would tend to cause high results for thiosulfate as calculated from the iodine value. If anything, the gravimetric results for thiosulfate are a trifle higher than the titration values, which points to an absence of sulfites, although this in itself is not absolute proof of the fact.

The authors are now investigating the velocity of the reaction between iodine and sodium tetrathionate in neutral and acid solution, and will present these results shortly. They desire to extend their sincere thanks to Dr. A. M. Peter, of this laboratory, for kind and helpful suggestions, during the progress of this work.

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