A STUDY OF THE USE OF BARIUM THIOSULPHATE AS A PRIMARY STANDARD FOR IODINE SOLUTION

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THESIS

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INTRODUCTION

In analytical work the determination of iodine is generally carried out by titrating it with sodium thiosulphate. As this salt is not very stable, efflorescent in warm, dry air, and somewhat deliquescent in moist air, it requires great care to keep it from being effected, even at ordinary room temperature. This is also true of the sodium thiosulphate solution. The sodium thiosulphate solution, even when made up of the recrystallized salt must be standardized because of the efflorescent property of the salt. The salt is so efflorescent that it cannot be weighed accurately when exposed to the air.

The use of barium thiosulphate in standardizng the iodine solution was first investigated by Plimpton and Chorley (Jour. Chem. Soc. 67, 314 (1895)). Although this method was recommended by J. C. Olson in his "Quantitative Chemical Analysis" for more than twenty years, its use in the quantitative laboratory is not common. Barium thiosulphate, as it was stated by the original investigators and confirmed by our experiments, is considerably more stable than sodium thiosulphate, can be easily prepared with a high degree of purity and requires no particular precausion in storing as it does not effloresce nor deliquesce. The reason that it is not in general application in the quantitative laboratory may be well attributed to the slight solubility of the barium thiosulphate in water. Titrating the barium thiosulphate, using water as a solvent, while the undissolved salt still remains, is a very slow process. This disadvantage, however, can be avoided by the choice of a suitable solvent. The object of this investigation was the selection of a proper solvent. Several inorganic salts were tried. It was found that the halides of the alkali metals, such as KBr, NaBr, KCl and NaCl are all suitable. But for practical work sodium chloride is most economical. In the preliminary work Baker's analyzed product was used, but it was not quite pure, and the solution was always turbid. The turbidity settled down in several hours. The amount was so minute that an analysis was impracticable. Undoubtedly it was a trace of barium sulphate held in colloidal suspension. The preparation of pure thiosulphate was then started and a brief study of its important properties was made.

PREPARATION OF MATERIALS

Preparation of distilled water:- The laboratory distilled water was redistilled in tin lined copper still with about one gram of KOH and about one gram of $KMnO_4$. The first liter of the distilled water was discarded.

Barium chloride:- The highest purity $BaCl_2$ was recrystallized twice. About 450 grams of barium chloride were dissolved in 700cc. of the distilled and evaporated down to about 500 cc. The salt was then crystallized with shaking under cold running water. In the second crystallization less water was used and recrystallization allowed to take place by itself on cooling.

Sodium thiosulphate:- The Baker's analyzed sodium thiosulphate was recrystallized twice. 600 grams of the thiosulphate were dissolved in 400 cc. of the distilled water. It was slowly evaporated down to almost the crystallizing point. The solution was allowed to cool and was crystallized by introducing a few crystals of sodium thiosulphate. In the second recrystallization a saturated solution of the crystallized thiosulphate was made at 35°C and recrystallization was allowed to take place by itself.

Preparation of barium thiosulphate:- About 300 grams of the recrystallized $BaCl_2$ were dissolved in about one liter of the distilled water, and about 300 grams of the recrystallized sodium thiosulphate were dissolved in the same amount of distilled water.

The solutions were slowly mixed with constant stirring. The molecular weight of sodium thiosulphate is only about four more than that of barium chloride. The excess of the sodium thiosulphate used was to insure the complete removal of the barium chloride which is the least soluble of the four possible salts in the mixture. Since sodium thiosulphate is the most soluble, it can be readily washed off. The barium thiosulphate precipitated out in snow-white, tiny, silky leaflets. After the solutions were mixed, the stirring was continued for about a quarter of an hour. Then the whole precipitate was divided into two parts, and each washed four times with 600 cc. of distilled water by decantation. After that it was filtered with suction, using a platinum cone as filter. When all the water was sucked out, the precipitate was taken out of the funnel and washed again with about one liter of distilled water by decantation. This was repeated several times until the filtrate was free from chloride. Since some of the thiosulphate was dissolved in the filtrate, the ordinary method of testing free chloride was inapplicable, because silver nitrate gives white precipitates of silver thiosulphate, which turns reddish brown and finally into black silver sulphide. So the following method was employed: 10 cc. of the filtrate were taken into a small beaker. After 1 cc. of sulphuric acid was added to it, the solution was heated to boiling for a quarter of an hour or longer until the complete decomposition of the thiosulphate.

Then 100 cc. of the distilled water were added to the solution and the sulphate was filtered off. A few cc. of the filtrate were taken into a test tube and tested with $AgNO_3$ solution after acidifying with HNO_3 acid. If the chloride is present, AgCl will be precipitated. If the thiosulphate is not completely decomposed, it will be detected when the filtrate is acidifed. When the thiosulphate was free from chloride, it was taken out and put on a large filter paper and dried in the air. It was put in a partially opened balance case and covered with another sheet of filter paper. The balance case was located in a cool place, free from dust and sunlight. When the thiosulphate was partially dry, it was taken out into a large beaker and loosened with a porcelain spatula. Then it was put back on the filter paper. Drying was hastened by spreading the salt in thin layer and frequently running the spatula over it lengthwise and crosswise. This kept the crystals from adhering and permitted better circulation of the air. Care was taken not to rub nor to scratch the filter paper. In about two weeks the barium thiosulphate was thoroughly dried. Then it was analyzed, both volumetrically and gravimetrically.

Preparation of iodine solution:- The iodine solution, prepared from resublimed iodine, was approximately 0.1 N and contained 22 grams KI in one liter. The solid iodine and potassium iodide were ground together and triturated with small portions of water until all were dissolved and finally diluted with distilled water. It was kept in a brown bottle in a dark place. After three days the solution was standardized against pure arsenious oxide according to directions given in Talbot's "Quantitative Chemical Analysis", except flasks were used instead of beakers. Calibrated volume burettes were used. The burettes were calibrated at every 5 cc. and filled with distilled water when it was not in use. The water was run out several minutes before using the burette, and then rinsed out with 15 cc. of iodine solution. The starch solution was always prepared fresh.

EXPERIMENTAL PART

Procedure of gravimetric analysis:- Portions of 1 gram of barium thiosulphate were gently heated in porcelain crucibles. At first the flame was very small. Sulphur was evolved which redened and soon caught fire. The flame was then removed. When sulphur had stopped burning the flame was applied again. After the sulphur had all burnt out, the flame was raised and heating continued for several minutes. The change during the heating is as follows:

$$6BaS_2O_3 = 3BaSO_4 + 2BaSO_3 + BaS + 6S$$

In order to convert the sulphite and sulphide into sulphate, the contents of the crucibles were allowed to cool and then thoroughly moisten with dilute H_2SO_4. Then they were heated on sand bath until all the white fumes were given off. They were removed from the sand bath and cooled. Then treated again with strong H_2SO_4 and heated on sand bath. After all the fumes were given off they were directly heated with a strong flame for five minutes. They were cooled in dessicator and weighed. The process was repeated many times until the weights were constant. The objection to use strong acid in the first treatment is that the ignited mass is rather loose. If concentrated acid is used the SO_3 evolved is too dense and might carry some of the particles away.

The following table gives the weights of the precipitate obtained by converting one gram of $BaS_2O_3H_2O$ to $BaSO_4$:

Samples -	Wt. of $BaSO_4$
(1)	.8723 grams
(2)	.8723 "
(3)	.8723 "
(4)	.8721 "
Mean	.8722
Theoretical amount	.8726

Procedure of volumetric analysis:- Portions of 1.07 grams of barium thiosulphate were weighed out into 400 cc. beakers. The weight taken was the calculated amount for 40 cc. of .1 N iodine solution, .02675 being the mili-equivalent weight for that normalty. To each beaker were added 150 cc. saturated potassium chloride solution (15 grams of NaCl in 150 cc. of water will be able to dissolve 1 gram of barium thiosulphate with ease). The mixtures were stirred until the thiosulphate completely dissolved and then each solution was diluted with 100 cc. of water. They were titrated with iodine solution, using as the indicator freshly prepared starch solution which was added toward the end of each titration. The iodine solution was run at first fairly rapidly until the end point was almost reached. Then drop by drop and finally fractions of drops were added by touching the burette tip with stirring rod. Using fresh starch solution, the end-point first reached was always bluish pink. The following results were obtained on the same day when the iodine solution was standardized. The three titrations of arsenious oxide with iodine solution gave the mean normalty of .10433 N of the solution.

Results:

Samples	Iodine Solution used		Values of Iodine solution
(1)	38.34 cc.		.10432 N
(2)	38.33 "		.10433 "
(3)	38.34 "		.10432 "
(4)	38.35 "		.10430 "
		Mean	.10432 "

Effect of air:- Barium thiosulphate is quite stable in the air. One weight portion of Baker's product was left on an analytical balance for more than two weeks. The weight did not change. Two weighed portions of the pure laboratory prepared salt were put into two beakers and covered with watch glasses. After two weeks the samples were titrated with iodine solution. The results showed that they had not changed. Two other portions were also put in two beakers covered with watch glasses, but exposed to sunlight. After three days they were titrated, but no change was found.

Effect of temperature upon water content:- In regard to the temperature at which the water of crystallization of barium thiosulphate is expelled, literature varies more or less. Thorpe in his "Dictionary of Applied Chemistry" records that the barium thiosulphate loses its water of crystallization at 215° and the anhydrous salt gives off sulphur when heated to redness. Letts (Jour. Chem. Soc. 23, 424 (1870)) found that the salt lost all its water of crystallization at 100°C. Plimpton and Chorley found that the salt was obtained anhydrous at 120°. In heating two portions of one gram of barium thiosulphate in electric oven at a temperature 100°C - 105°C, we found that the two samples lost .0625 gram and .0621 gram respectively after one day. After twenty-four days one lost .0653 gram and the other .0655. One week after, both samples did not lose any more. One of the samples was dissolved in the chloride solution. The mixture was somewhat turbid, and small particles settled down after several hours. Since the thiosulphate was entirely air-dried and had already been analyzed, surely none of the water of crystallization had been lost previously. In another case a few grams of barium thiosulphate was put in a small beaker and heated in an electric oven where the temperature was regulated to 115°C. After three days the salt was found decomposed. When less than one gram was dissolved in the chloride, the solution was very turbid and considerable amount of particles settled down after a few hours. The writer is led to believe that the temperature at which this salt is dehydrated and decomposes will vary according to the manner of heating and the duration of heating, and that both Plimpton and

Letts' conclusion drawn from their experiments are correct. He is also inclined to think that decomposition of this salt will take place at the same temperature shortly after dehydration, if heating is continued and that in long, slow drying, decomposition may even take place before complete dehydration,as our experiments showed. To quote Letts' own words, "It has been found impossible to fix definitely the decomposing point of many hyposulphites. - - - - - Take for example the sodium salt, - this salt, if rapidly heated, will bear a temperature of 233oC without apparent decomposition, but if heat be applied more gradually the salt actually decomposes at 100oC. Attention is called, however, to the fact that barium thiosulphate will not stand the temperature of 215o,and that it begins to lose its water of crystallization at comparably low temperature. The following results will give an idea of how the salt loses its water. Two 1-gram samples heated in a steam clost with the following results:-

Sample 1					Sample 2				
Lost	.0018 g.	after	2	days	Lost	.0018 g.	after	2	days
"	.0018 "	"	4	"	"	.0018 "	"	4	"
"	.0105 "	"	7	"	"	.0106 "	"	7	"

Two 1-gram samples heated in an electric oven at 100oC - 105oC with the following results:

Sample 1	Sample 2
Lost .0625 g. after 1 day	Lost .0631 g. after 1 day
" .0630 " " 2 "	" .0629 " " 2 "
" .0635 " " 3 "	" .0634 " " 3 "
" .0638 " " 6 & 7 "	" .0638 " " 6 & 7 days
" .0641 " " 10 "	" .0640 " " 10 "
" .0644 " " 11 & 13 days	" .0644 " " 11 & 13 "
" .0653 " " 17 "	" .0653 " " 17 "
" .0653 " " 20 "	" .0655 " " 20 "
" .0653 " " 24 "	" .0655 " " 24 "

The calculated amount .0673

SUMMARY

The method of standardizing iodine solution with barium thiosulphate has been improved. The accuracy and convenience with which the titration can be done have been pointed out. The many advantages which this salt has over sodium thiosulphate may be well utilized in the standardization of iodine solution. With careful work the anhydrous salt may be obtained. But it does not seem advisable to use the anhydrous salt in standardizing iodine, since the crystallized salt can be well kept in ordinary temperature and as the anhydrous salt is not as readily soluble as the crystallized. Although this last mentioned fact has not been determined, the difficulty with which the partially dehydrated salt dissolves in the chloride solution as observed, gives support to the statement.