[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

I. STANDARDIZATION OF SOLUTIONS USED IN IODIMETRY

BY STEPHEN POPOFF AND F. L. CHAMBERS

Received December 4, 1922

A survey of the literature on standardization of solutions used in iodimetry shows that potassium permanganate is not commonly used in standardizing sodium thiosulfate. Most workers use arsenious oxide as a standard for iodine solutions and iodine, copper and potassium dichromate as the standard for sodium thiosulfate solutions. A few texts state that potassium permanganate could be used but the method is not generally recommended so far as we have been able to determine.

Our first attempt in comparing the iodine method with the permanganate method for standardizing sodium thiosulfate failed to check any closer than 0.1%. In every case the former standard gave the higher results in spite of repeated sublimation and fusion of the iodine. Bray and McKay[1] show that the iodine method and the potassium permanganate method of standardizing sodium thiosulfate do not give concordant results. Peters[2] states that while various methods of standardization of sodium thiosulfate give close checks among themselves, they do not agree when compared with one another. Vosburgh's[3] excellent work on the standardization of sodium thiosulfate shows that potassium dichromate gives results 0.1% higher than those by the iodine method but he states that the deviation is well within the experimental error.

From theoretical considerations, the two methods should agree if they are carried out under identical conditions. It must be borne in mind, however, that actually one titration of iodine is carried on in neutral solution, the other in acid solution, and that it is necessary to have at least 4% of potassium iodide during all titrations involving iodine, according to Chapin,[4] whose conclusions we have corroborated. Vosburgh[3] states that 1 g. or 4 g. of potassium iodide gave erratic results while 2 to 3 g. gave good results.[5]

In acidified potassium iodide solution hydrogen iodide is readily oxidized by air. Stieglitz[6] shows that *M* hydriodic acid solution requires a concentration of iodine of 10^{22} in order to prevent the oxidation of hydrogen iodide by the air. Any iodate present or formed will liberate iodine.

[1] Bray and McKay, THIS JOURNAL, **32**, 1193 (1910).

[2] Peters, *ibid.*, **34**, 422 (1912).

[3] Vosburgh, *ibid.*, **44**, 2120 (1922).

[4] Chapin, *ibid.*, **41**, 357 (1919).

[5] Preliminary experiments performed indicate that the amount of iodide is more of a factor than Vosburgh and the others have considered.

[6] Stieglitz, "Qualitative Chemical Analysis," Century Co., **1913**, vol. 1, 306.

Washburn[7] finds that the upper limit of concentration of the hydroxyl ion is 10^{-5} so that if the solution is alkaline (beyond 10^{-5}) there will be a tendency for the iodine to form potassium hypo-iodite or similar compounds which will not react with the sodium thiosulfate. Since the iodine method is usually carried on in neutral solution and the potassium permanganate in acid solution, the two methods will not agree if the factors stated above are not considered. The following experiments show conclusively that the above factors must be considered in iodimetry. The results given are the averages obtained from at least three runs which did not differ by more than 0.05 to 0.06%.

Forty cc. of 0.1 *N* iodine solution, containing 4% of potassium iodide, was titrated with 0.1 *N* sodium thiosulfate solution, the iodine solution being added to the following before titration: (1) to 100 cc. of water; (2) to 100 cc. of 8% potassium iodide; (3) to 100 cc. of 8% potassium iodide and 15 cc. of 1 to 5 sulfuric acid; (4) the same as the third with only 8 cc. of the acid. The time for all titrations was 15 minutes.

	Vol. ratio of sodium thiosulfate to iodine
1. No KI, no H_2SO_4	1.1008
2. Maintaining at least 4% of KI; no acid	1.1016
3. Maintaining at least 4% of KI and 15 cc. of acid	1.1025
4. Maintaining at least 4% of KI and 8 cc. of acid	1.1025

Expt. 4 shows that by using 15 cc. of sulfuric acid in Expt. 3 the oxidation of hydrogen iodide by the air was not increased.

Standardization of Sodium Thiosulfate

Materials.—C.P. Sodium thiosulfate was dissolved in conductivity water and the solution was kept in a dark bottle provided with a soda-lime tube. The potassium iodide was free from iodate. The iodine[8] was resublimed once from potassium iodide and twice alone, and was kept in a greaseless desiccator which contained phosphorus pentoxide and which was sealed with paraffin. The iodine solution, containing 4% of potassium iodide, was prepared by dissolving the iodine in a concd. solution of potassium iodide and diluting. The potassium permanganate was prepared from recrystallized potassium permanganate dissolved in conductivity water, left to stand for several months, filtered and standardized against sodium oxalate (obtained from the Bureau of Standards), according to the method of McBride.[9]

Iodine Method.—The usual procedure[10] was followed in weighing iodine. The iodine solution, before titration with the thiosulfate, contained 140 cc. of water, 10 g. of potassium iodide and 15 cc. of 1 to 5 sulfuric acid. The time of titration was 15 minutes.

[7] Washburn, THIS JOURNAL, **31**, 31 (1909).

[8] The procedure is the same as that used by Foulk in Iodine 2 and found to be 100.02%. *Ibid.*, **44**, 221 (1922).

[9] McBride, *ibid.*, **34**, 393 (1912).

[10] Treadwell and Hall, "Treatise on Analytical Chemistry," John Wiley and Sons, **1913**, 3d. ed., vol. 2, p. 646.

Permanganate Method.—To 100 cc. of 10% potassium iodide solution, containing 15 cc. of 1 to 5 sulfuric acid, enough potassium permanganate was added to liberate about the same amount of iodine as was used in the iodine method. The liberated iodine was titrated with sodium thiosulfate solution; the time of titration was 15 minutes.

All titrations, except the standardization of potassium permanganate, were made electrometrically.[11] Calibrated burets were employed, the temperature of the room being kept at 20°. The curves for the various titrations of iodine with thiosulfate were almost identical whether the iodine came from an iodine solution or from the addition of potassium permanganate or potassium iodate to an acidified potassium iodide solution.

Results[12]

The normality of sodium thiosulfate by the iodine method was determined to be 0.10053, while by the permanganate method the value 0.10052 was found. The two methods of standardization of sodium thiosulfate give close checks only when carried out under identical conditions. The normality of the sodium thiosulfate is correct only if used under the conditions given above. Under any other conditions its normality may be determined by finding the volume ratio of an iodine solution to the sodium thiosulfate and comparing the result with the conditions used in the standardization.

Summary

The potassium permanganate method for the standardization of sodium thiosulfate gives results which agree very closely with those obtained by the iodine method but only when carried out under identical conditions.

IOWA CITY, IOWA

[11] The electrometric method complicates the titrations but when it is considered that most titrations, with only very few exceptions, do not differ by more than 0.05%, the complicated system may be an advantage.

[12] The results are the averages obtained from 4 or 5 runs which differed by not more than 0.05%. One result showed about 1% difference, indicating that a large error was made; this result was not included in the calculations.