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ABSTRACT

Thallium(I), as well as iodide, can be quantitatively oxidized by bromine at pH 5 and is not reduced by formic acid in the Kainrath method for iodine determination. It subsequently liberates iodine, as does the iodate, by reaction with potassium iodide. A useful method for the determination of iodine in thallium(I) iodide precipitates, mounted for counting radioactivity, is based on this observation. Some aspects of the reaction of thallium(III) with iodide are noted.

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In certain radiochemistry studies, as in the production of iodine fission products by bombardment of uranium with protons, the recovery of carrier iodine must be determined in order for the total yield of radioactive iodine to be computed. Precipitation of the iodide with silver ion, which generally yields a product composed of uneven curds that do not form a uniform layer on the filter paper, is undesirable for counting the β activity. However, the use of thallium(I) to bring down the iodide produces a uniform layer of small particles which is quite acceptable for the purpose of counting, but is unlikely to be quantitative for iodine.

The small amounts of carrier iodine (5 to 12 mg.) recovered by means of thallium(I) precipitation and submitted to this laboratory for analysis had to be determined within one percent. These samples had been prepared by precipitation of the iodine from 20 ml. of approximately 0.1 M nitric acid solution by the addition of 3 drops of 1 M sodium sulfite and 10 drops of thallium(I) nitrate (50 mg./ml.), and washed with thallium(I) nitrate (2 mg./ml.), 1% acetic acid, and finally acetone. They had been filtered on 7/8-inch-diameter discs of Whatman No. 42 filter paper, mounted on aluminum plates by means of double-coated cellophane tape (Scotch Brand No. 666), and covered either with 2 drops of Zapon lacquer in ethyl acetate (1:20) or with a strip of Pliofilm (0.5 mg./cm.^{2}). The activity had been counted and the samples allowed to decay to a negligible level when received.

Several methods of analysis presented themselves for consideration. It was soon determined that recommended methods for oxidation of the iodide to iodine, followed by distillation or extraction, gave erratic low results. The method of Kainrath[3] for oxidation of iodide to iodate appeared to offer possibilities. It was known that thallium(I) could be oxidized to thallium(III)

by bromine in slightly acid solution and subsequently reduced by potassium iodide,[6] but the quantitative behavior of the thallium in the presence of the acetate buffer and formic acid, used to reduce excess bromine, was not known. Quantitative oxidation and reduction of thallium under the conditions used for iodide would yield eight equivalents of free iodine per iodide ion instead of the usual six equivalents, an added advantage when working with small iodide samples:

$$TlI + 4Br_2 + 3H_2O = Tl^{+3} + IO_3^- + 8Br^- + 6H^+,$$

$$Tl^{+3} + IO_3^- + 7I^- + 6H^+ = Tl^+ + 4I_2 + 3H_2O.$$

The work presented here was undertaken to test the method for combined thallium and iodine in the presence of the organic matter used to mount the precipitates.

EXPERIMENTAL

The solubility of thallium(I) iodide is appreciable[1] and the loss on this account would be relatively high for samples of the size used in this work. It was necessary to check the procedure with the precipitate actually on the filter paper and covered with either Zapon or Pliofilm, and, at the same time, to account for the material in the filtrate. The following procedure was used to take care of both of these factors. Essentially equivalent aliquots (250 to 600 λ) of standardized solutions of thallium(I) nitrate and potassium iodide were added to 5 ml. of water containing 0.2 ml. of glacial acetic acid. The precipitates were filtered on cones of Whatman No. 42 filter paper, washed with 1 ml. of 1% acetic acid and 1 ml. of acetone, and allowed to dry. Some of the samples were then treated with 2 drops of a solution of Zapon lacquer in ethyl acetate (1:20), and some simply had a strip of Pliofilm (0.5 mg./cm.^{2}) added to the filter cone. The samples, with all organic material used, were then added to their respective filtrates and washings (about 4 ml.) in 125-ml. glass-stoppered flasks in which all subsequent reactions took place.

Standard Thallium Solution. A 4.39-g. quantity of thallium(I) nitrate (Fisher Scientific Co.) was dissolved in water to give 100 ml. of solution.

The solution was standardized by precipitating and weighing the thallium in 1-ml. aliquots as thallium(I) chromate,[2] and found to contain 33.18 mg. of thallium per ml.

Standard Iodide Solution. Reagent grade potassium iodide (Baker and Adamson) was dried at 110° and 2.6974 g. was dissolved in water to give 100 ml. of solution. This was used without further standardization as containing 20.62 mg. of iodine per ml.

Sodium Thiosulfate Solution. A solution of approximately 0.02 M strength was prepared from reagent grade material (Baker and Adamson) and standardized before each run by the reaction of reagent grade potassium dichromate (Baker and Adamson) with excess potassium iodide.[4]

Thallium(I) Iodide. This material, used to check the procedure, was precipitated from a solution of thallium(I) nitrate with a solution of potassium iodide. The conditions for the precipitation, washing, and drying were those recommended for a gravimetric determination of thallium.[1]

Procedure. A synthetic sample, prepared as above, was treated with 10 ml. of pH 5 buffer solution (10% w/v sodium acetate in glacial acetic acid) and 10 drops of liquid bromine and allowed to stand at room temperature to complete oxidation. Sixteen hours were allowed for oxidation and solution of a sample which had been coated with Zapon and 3 hours for one covered with Pliofilm. Weighed amounts of thallium(I) iodide, without filter paper or covering, were also run as a check. These required only 1 hour for oxidation. To each flask was then added 10 ml. of water and 7 drops of 88% formic acid, and the solution was swirled to reduce excess bromine, giving a clear colorless solution. About 0.5 g. of potassium iodide and 5 ml. of 1 M sulfuric acid were added and the iodine was titrated with thiosulfate. When thallium iodide started to precipitate, an additional amount of thiosulfate, equal to one eighth of that already used, was added. Approximately 2 ml. of starch solution was added, giving a dirty green coloration, and the titration was completed to a solution containing the bright yellow precipitate of thallium iodide. The end-point was reached slowly and a short waiting period was needed to avoid over-running it. The solutions remained yellow for 15 seconds at the end-point.

When samples were received mounted on aluminum plates with Pliofilm, the coverings were carefully cut around the filter discs and the tapes were moistened with acetone. Those coated with Zapon required no cutting but the tapes were moistened with acetone to loosen them. This allowed the filters and samples, with pliofilm or Zapon coverings, to be lifted off. They were then put into 125-ml. glass-stoppered flasks and treated as in the procedure described. Pliofilm covers came loose readily when the solutions were swirled so that the precipitates were easily exposed, but Zapon formed an adherent coating on both filter and precipitate.

DISCUSSION

The results are given in Table I, II, and III; they show no significant differences for the three sets of conditions except in time required for oxidation. These are not necessarily the minimum times required, but are those which insure complete oxidation for the most stubborn samples in each category. The 16-hour period was used for the samples coated with Zapon because they were not completely oxidized in the course of an ordinary working day and it was convenient to let them oxidize overnight. The many low and erratic results found for significantly shorter periods are not given here. Some attempts were made to increase the rate of oxidation by heating the samples on a steam bath, but the results were seldom correct within one percent.

Table I

Thallium Iodide Only — 1 Hour Oxidation			
mg. TlI weighed	mg. I taken	mg. I found	Error %
13.17	5.05	5.03	0.0
14.82	5.68	5.72	+0.4
14.92	5.72	5.75	+0.2
14.98	5.74	5.79	+0.5
20.89	8.00	8.00	-0.2
23.24	8.90	8.95	+0.2
29.55	11.32	11.36	+0.2

Table II

Thallium Iodide with Filter Paper and Pliofilm — 3 Hours Oxidation
Samples 1,2, and 3 — 250λ KI solution and 250λ $TlNO_3$ solution
Samples 4,5, and 6 — 600λ KI solution and 600λ $TlNO_3$ solution

Sample	mmoles $S_2O_3^=$ to titrate		Error
	Calculated	Used	%
1	0.3235	0.3240	+0.1
2	0.3235	0.3242	+0.2
3	0.3235	0.3255	+0.6
4	0.7801	0.7801	0.0
5	0.7801	0.7818	+0.2
6	0.7801	0.7800	-0.1

Table III

Thallium Iodide with Filter Paper and Zapon — 16 Hours Oxidation
Samples 1,2, and 3 — 250λ KI solution and 250λ $TlNO_3$ solution
Samples 4,5, and 6 — 600λ KI solution and 250λ $TlNO_3$ solution

Sample	mmoles $S_2O_3^=$ to titrate		Error
	Calculated	Used	%
1	0.3296	0.3300	+0.1
2	0.3296	0.3305	+0.3
3	0.3296	0.3303	+0.2
4	0.7906	0.7944	+0.5
5	0.7906	0.7926	+0.3
6	0.7906	0.7949	+0.5

The calculated amounts of thiosulfate are based on the formation of eight atoms of free iodine for each molecule of thallium iodide. The agreement with the amounts used shows that the oxidation and reduction of the thallium, as well as of the iodine, are quantitative. Essentially all the results are slightly

high and are probably due to some adsorption of iodine by thallous iodide, thus requiring about one drop excess of thiosulfate to complete the reaction. It is unlikely that the results are due to too much light,[8] as all titrations were carried out under diffuse artificial light.

The behavior of the thallium during the course of the titration is very interesting. No precipitate of thallium iodide appears until very close to three-fourths of the thiosulfate needed to reach the end-point has been added. Thallium iodide then continues to precipitate during the titration. It is not clear whether the thallium(III) is reduced immediately to form soluble thallium(I) triiodide or whether there is no substantial reduction until nearly all the iodine from the reaction with iodate has been titrated. In either case the precipitation of thallium(I) iodide would be delayed until six of the eight total iodine atoms were titrated. The oxidation potentials[5] indicate that thallium(III) should be reduced even in the presence of free iodine; but the presence of bromide and iodide, both of which complex thallium(III), may change the potentials considerably. If there is immediate reduction of most of the thallium(III) with formation of soluble thallium(I) triiodide, then the latter must be but slightly ionized; otherwise thallium(I) iodide would precipitate. After the iodine liberated by the iodate had been titrated the thiosulfate would reduce thallium(I) triiodide, forming insoluble iodide:

$$Tl^{+3} + 3I^- = TlI \cdot I_2,$$

$$TlI \cdot I_2 + 2S_2O_3^{--} = TlI + 2I^- + S_4O_6^{--}.$$

Equilibrium between the tautomeric forms, thallium(III) iodide and thallium(I) triiodide, has been considered likely in solution, even though the solid crystals obtained from the reaction of potassium iodide with thallium(III) appear to be thallium(I) triiodide.[7]

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