Discussion

An inspection of the tables shows that in most cases the coprecipitation is small and one precipitation may yield satisfactory results. If the coprecipitation cannot be neglected, a reprecipitation by dissolving the precipitate in hydrochloric acid and repeating the procedure will give a virtually complete separation.

Quite generally the coprecipitation increases with increasing amounts of benzoate and time of boiling. This may partly explain why the coprecipitation with chromium alone is more serious than with aluminum and iron. Fortunately, those cases in which chromium alone has to be separated from the divalent cations rarely occur. Addition of aluminum or ferric iron reduces the coprecipitation with chromium markedly. None of the trivalent metals volatilize on ignition of the benzoate precipitate. However, phosphate, if present in the original solution, is partly coprecipitated with the trivalent metals and will be present in the ignited residue. In the quantitative analysis of the benzoate precipitate it is preferable to follow a procedure similar to that described in the qualitative part[9] of this paper.

After oxidizing in alkaline medium with hydrogen peroxide and removing the excess of the latter by boiling, the iron is filtered off and determined volumetrically. The filtrate is acidified and the aluminum precipitated according to the benzoate method. The chromate in the filtrate is determined volumetrically. The aluminum in the precipitate is determined by precipitation from ammoniacal tartrate solution with 8-hydroxyquinoline.

Summary

The benzoate method gives a simple and rapid procedure for the separation of iron, aluminum and chromium from other cations of the third and fourth groups. In all cases the coprecipitation is much less than that which occurs in the ammonia method, and one precipitation will often suffice in ordinary separations. In more precise analyses a reprecipitation is made. Phosphate is partly precipitated with the trivalent metals.

[9] See also Hillebrand and Lundell, Ref. 3, p. 85.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Volumetric Determination of Tin; Use of Potassium Iodate

BY J. B. RAMSEY AND J. G. BLANN

Iodine in potassium iodide solution is most generally used in the volumetric determination of stannous tin. Since the iodine–stannous reaction induces the oxygen–stannous reaction, according to Kolthoff,[1] the possible existence of less "inducing" oxidants suitable for determining tin in the presence of oxygen was considered. That iodate might be such an oxidant is indicated from the results obtained by its use in the determination of sulfite,[2,3] if the lower results found with other oxidants are considered as due principally to the induced sulfite–oxygen reaction. Under the experimental conditions of Bonner and Yost,[3] the relative number of equivalents of iodate reduced to iodide by sulfite is slightly but definitely greater than that of triiodide.

The reduction of iodate to iodine monochloride via iodine, according to the method of Andrews,[4] has been applied by Jamieson[5] to the determination of tin. A high concentration of hydrochloric acid (above 4 *N*) must be maintained in this method. A study of the reduction of iodate to iodide by stannous tin in acid solution has to our knowledge not been reported. The effects of variation in acid concentration, stannous concentration, and order of mixing have been studied.

Reagents

Sodium oxalate, obtained from the United States Bureau of Standards, was the weight basis of the standard solutions (approximately 0.1 *N*) used. The methods of preparation and standardization were as follows: potassium permanganate according to the method of McBride;[6] sodium thiosulfate (containing 0.2 g. of sodium carbonate per liter) by the Volhard method, under the conditions recommended by Bray and Miller;[7] potassium iodate

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[1] Kolthoff and Furman, "Volumetric Analysis," 1929. Vol. II, p. 412.

[2] Hendrixson, THIS JOURNAL, **47**, 1319 (1925).

[3] Bonner and Yost, *Ind. Eng. Chem.*, **18**, 56 (1926).

[4] Andrews, THIS JOURNAL, **25**, 756 (1903).

[5] Jamieson, *J. Ind. Eng. Chem.*, **8**, 500 (1916).

[6] McBride, THIS JOURNAL, **34**, 393 (1912).

[7] Bray and Miller, *ibid.*, **46**, 2209 (1924).

with standard sodium thiosulfate solution, employing the same procedure as used in obtaining the ratio $Na_2S_2O_3/KMnO_4$ in standardizing sodium thiosulfate solution with potassium permanganate solution; potassium triiodide by titration with standard sodium thiosulfate solution, after acidifying 25-cc. aliquots of potassium triiodide solution with 1 to 5 cc. of 3 *N* sulfuric acid (since the sodium thiosulfate solution is alkaline): potassium dichromate with the standard sodium thiosulfate solution, under the conditions recommended by Bray and Miller.[7]

The potassium permanganate solution used remained constant in titer during the investigation. The other solutions were restandardized at frequent intervals. No change in titer of the iodate solution was found.

Solutions of known tin content (about 0.05 formal) were prepared by dissolving weighed quantities of mossy tin of the highest C. P. grade in constant-boiling hydrochloric acid, known to be about 6.1 *N*. Five grams of this tin, analyzed by the methods given by Murray,[8] were found to contain less than 0.03% of lead and no measurable quantities of other possible impurities.

Platinized platinum foil was used to hasten solution, and loss of spray prevented by tilting the flask. The resulting solution was then made up to the desired volume at 20.0° with the above hydrochloric acid (6.1 *N*), and maintained at this temperature during use.

Analytical Procedure

Among the methods of reducing stannic tin to the stannous state, the use of tin, plated out by a more electropositive metal, has the distinct disadvantage of requiring much time to redissolve the tin, even in hot moderately concentrated solutions of hydrochloric acid (5 to 6 *N*). Platinum foil in this case is not satisfactory due to the difficulty of maintaining contact with the plated-out tin. A metal plated out by, and adhering to, the tin, which would act like platinum foil would be ideal. We have found nickel and cobalt to have these properties. Upon addition of small quantities of nickel or cobalt chloride, the nickel or cobalt which is plated out immediately in these hot moderately concentrated acid solutions decreases the time for solution of about 0.1 g. of tin remarkably—from over forty-five minutes to less than five minutes. It is of interest to note that under these conditions the reduction potential of Sn^0–Sn^{+2} is greater than that of Ni^0–Ni^{+2}.

The procedure adopted is as follows: 1.5 to 2.0 g. of C. P. granular zinc (20 mesh) is added to a 25-cc. aliquot of known tin solution, previously diluted with an equal volume of water, in a 500-cc. Erlenmeyer flask. The flask is then covered with a porcelain crucible lid and inclined during evolution of hydrogen. After action has ceased the lid and walls are washed down with 10 to 15 cc. of water. The flask is then fitted with a two-holed stopper carrying inlet and outlet tubes for carbon dioxide (from liquid carbon dioxide). With the flask inclined the solution is gently boiled in a stream of carbon dioxide for ten minutes. That this time assures complete reduction of any stannic tin was found by boiling known tin solutions initially in the stannic state for periods of time varying from five to thirty minutes in contact with plated-out tin. Boiling is then stopped momentarily while 7 to 8 cc. of 12 *N* hydrochloric acid, containing about 0.1 g. of nickel chloride or cobalt chloride is added. Additional boiling for three to five minutes is sufficient to dissolve the metals present. While the solution is cooled to room temperature in a water-bath, a sufficient stream of carbon dioxide is maintained (as shown by a bubble tube attached to the outlet) to prevent any sucking back of air. It is then diluted with 100 cc. of 0.2 *N* sodium bicarbonate solution previously freed from air by boiling and cooling in a stream of carbon dioxide. This volume was found well over the minimum required to eliminate any error due to the induced oxygen–stannous reaction. Use of sodium bicarbonate renders surer protection to the stannous solution against oxidation by air during dilution owing to the formation of carbon dioxide. The resulting solution is approximately 1 *N* in acid. With carbon dioxide flowing through the flask, the potassium iodate solution is added from the buret until a faint yellow color of iodine persists. The equivalent point is seldom exceeded by more than two drops (0.08 cc.). The sides of the flask are immediately washed down and 5 cc. of 0.2% starch (soluble) solution added. The iodine formed is determined by back-titration with 0.025 *N* sodium thiosulfate.

The total time required for a single determination is between thirty and forty minutes. Variation in the rate of addition of the oxidant produced no measurable effect in the results.

Bureau of Standards calibrated burets and calibrated Normax pipets and flasks were used in this work.

Results

Results obtained by the above procedure with both potassium iodate and potassium triiodide are given in Table I. Each result for tin "found" is the average of at least four determinations with a maximum deviation of not over 0.2%—and in most cases less than 0.1%.

The only oxygen entering the stannous solution, by this method, is that present in the solution of oxidant.

Table I

Direct Titration in Absence of Air

Series	Tin present, g./liter	Found with KIO_3, g./liter	Error, %	Found with KI_3, g./liter	Error, %
A	6.5012	6.5007	−0.01	6.4791	−0.34
B	6.5012	6.4687	− .50	6.4483	− .81
C	5.5013	5.5036	+ .04	5.5029	+ .03
D	5.5013	5.4708	− .55		

A, according to Procedure; B and D, without dilution with 100 cc. of air-free 0.2 *N* sodium bicarbonate; C, dilution with 100 cc. of air-free 1 *N* sodium bicarbonate.

Under the conditions adopted the potassium iodate reduced is seen to be equivalent to the tin present, whereas the iodine reduced is 0.3 to 0.4% less (Series A). That the elimination of this error, in Series C, is not due solely to the greater decrease in hydrochloric acid concentration pro-

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[8] Murray, "Standards and Tests for Reagent and C. P. Chemicals," 2d ed., D. Van Nostrand Co., Inc., New York, 1927, p. 516.

duced with the 1 *N* sodium bicarbonate but to the simultaneous decrease in the stannous concentration as well is shown by the results given later (Table II). That dilution of the solution, 4 to 5 *N* in hydrochloric acid, is necessary is shown in Series B and Series D.

TABLE II

EFFECT OF HYDROCHLORIC ACID CONCENTRATION

Series	HCl, equiv./liter	Stannous present	KIO_3 reduced equiv./liter	Deviation, %	KI_3 reduced equiv./liter	Deviation, %
A	0.3	0.1043	0.1043		0.1037	−0.6
B	.6	.09829	.09829		.09792	− .4
C	.9	.1474	.1474		.1467	− .5
D	3.0	.09968	.09942	−0.3		
E	4.0	.09870	.09826	− .4		
F	6.1	.09892	.09827	− .7	.09812	− .8

The "stannous present" (column 3) in solutions 3 *N* or greater in hydrochloric acid was determined by titration with potassium iodate after decreasing the hydrochloric acid concentration to about 1 *N* with air-free 0.2 *N* sodium bicarbonate.

With potassium permanganate and potassium dichromate solutions, direct titrations under the conditions giving precise results with potassium iodate give less satisfactory results than does potassium triiodide. The error with potassium permanganate is on the average −0.7% and with potassium dichromate −1.3%.

In studying the effects of variation of conditions, and order of mixing, the desired stannous solutions were prepared from C. P. $SnCl_2 \cdot 2H_2O$ and constant-boiling hydrochloric acid. Atmospheric oxidation of these solutions was prevented by maintaining carbon dioxide above them while standing and during removal of aliquots.

Twenty-five cc. portions of air-free stock stannous chloride solution, 3.0 *N* in hydrochloric acid and approximately 0.1 *N* in stannous tin, were diluted with 25 to 200 cc. of air-free 0.2 *N* sodium bicarbonate. No appreciable variation (less than 0.2%) was found in the quantity of iodate reduced at the acid concentrations produced: 1.4, 0.87, 0.44, 0.26 and 0.16 *N*. In the undiluted 3.0 *N* hydrochloric acid solution the quantity of iodate reduced was on the average 0.25% less. A wide range of acid concentrations may therefore be used when directly titrating stannous solutions with iodate in the absence of air.

A five-fold variation of the stannous concentration alone (0.1 and 0.02 *N*) produced no measurable change in the quantity of potassium iodate reduced, in solutions having hydrochloric acid concentrations 0.3, 0.6 and 1.2 *N*. With potassium triiodide this five-fold dilution eliminated the oxygen error (about −0.4%) in solutions 0.3 and 0.6 *N* in hydrochloric acid. In solutions approximately 1 *N* in hydrochloric acid, this dilution does not eliminate the oxygen error, as shown by Series A of Table I.

Appreciable error might be expected if enough iodide were formed, or initially present, during titration with iodate. Apparently the iodide formed in the stannous solutions used is not sufficient to cause such error if the hydrochloric acid concentration is low enough. In solutions 0.6 *N* in hydrochloric acid and 0.05 *N* in stannous chloride, the initial iodide concentration was varied from 0.025 to 0.250 *N*. Variations in the quantity of iodate required from that obtained without iodide initially present were: at 0.025 *N*, 0.0%; at 0.050 *N*, −0.3% and at 0.125 and 0.250 *N*, −0.7%. It follows that in solutions of such low hydrochloric acid concentration stannous tin may be present at concentrations as great as 0.25 *N* without producing appreciable error on account of the iodide formed.

The effect of varying the acid concentration, without change in the stannous concentration, is shown by the results given in Table II. A series of solutions differing in hydrochloric acid concentration, approximately 0.1 *N* in stannous tin, were prepared.

From the results in Table II it is seen that with stannous tin near 0.1 *N*, precise results cannot be obtained with potassium triiodide at any acid concentration used, whereas with potassium iodate the oxygen error becomes appreciable (more than 0.2%) at acid concentrations 3 *N* or above. The method of Andrews,[4] as used by Jamieson,[5] cannot therefore yield precise results. In 6 *N* hydrochloric acid equal deviations are obtained with potassium iodate and potassium triiodide. This deviation agrees with that expected if all the oxygen present in the solution of oxidant is reduced by stannous tin.

Bray and Ramsey[9] have pointed out that less induction is to be expected when the reductant (R) is added to excess of oxidant (O_α) in those cases in which "much of the reaction between R and O_α takes place during the mixing." The stannous–iodate and stannous–triiodide reactions are very rapid in acid solution. The induced oxidation should therefore vary with the order of mixing.

(9) Bray and Ramsey, THIS JOURNAL, **55**, 2279 (1933).

The results given in Table III were obtained by adding air-free stannous chloride solution, at acid concentrations shown in column 2, to excess of the oxidant solution in the presence of air. The excess of oxidant was determined by directly titrating with 0.1 *N* sodium thiosulfate solution, after adding 1 or 2 g. of potassium iodide in the case of potassium iodate. The quantity of stannous tin present, given in column 3, was determined by direct titration with potassium iodate in the absence of air, with proper dilution when necessary.

TABLE III

EFFECT OF ADDING REDUCTANT TO EXCESS OXIDANT

Series	HCl equiv./liter	Stannous present equiv./liter	KIO_3 reduced equiv./liter	KI_3 reduced equiv./liter
A	0.3	0.1043	0.1045	0.1042
B	.6	.09745	.09742	.09748
C	.9	.1466	.1465	.1464
D	1.2	.1008	.1007	.1008
E	3.0	.09776	.09774	.09782
F	4.0	.1061	.1060	.1062
G	6.0	.1076	.1076	.1077

By this order of mixing, both potassium iodate and potassium triiodide give precise results with air-free stannous chloride solutions having hydrochloric acid concentrations even as great as 6 *N*.

Incidentally, some experiments have been carried out to determine the effect of the presence of a few basic constituents, commonly found with tin, on the quantity of iodate required when titrating in the absence of air. Solutions 0.1 *N* in stannous chloride and 1.2 *N* in hydrochloric acid were used. With trivalent antimony present high results were obtained, due presumably to its simultaneous oxidation by iodate. Trivalent arsenic was likewise found detrimental although apparently not as completely oxidized as antimony under these conditions. Copper, added as cupric sulfate, to the extent of 1.2% of the weight of the tin present, produces no error; with 5% copper the error becomes about −0.2%. With 5 % iron, introduced as ferrous ammonium sulfate (free from ferric iron), 0.4% less iodate was required.

Summary

1. Direct titration of air-free stannous solutions with potassium iodate in the absence of air gives precisely the quantity of tin present at acid concentrations as high as 1.5 to 2.0 *N*.

2. With potassium triiodide, appreciable error (about 0.5%) is found even at the lowest hydrochloric acid concentrations used (0.3 *N*). This error may be diminished by decreasing the stannous concentration.

3. When the air-free stannous chloride solution is added to an excess of the oxidant (potassium iodate or potassium triiodide), precise results are obtained at any concentration of hydrochloric acid up to 6.1 *N* without excluding air.

4. The addition of small quantities of nickel or cobalt chloride to the solution reduced by plated-out tin, hastens considerably the redissolving of this tin.

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The Chlorine-Sensitized Photochemical Oxidation of Chloroform in Carbon Tetrachloride Solution

BY ALAN T. CHAPMAN[1]

The effect of dissolved oxygen on a reaction in which chlorine normally adds to a double bond has been studied in the photo-oxidation of tetrachloroethylene.[2] The simplest example of a compound in which substitution by chlorine may take place is that of chloroform. The photochemical oxidation of this compound was undertaken to ascertain (1) whether or not dissolved oxygen inhibits the chlorination of chloroform,[3] (2) the products of the reaction, and (3) the kinetics of the photo-oxidation. This paper concerns itself with the process in the liquid phase alone. A study of the reaction in the gas phase is now being pursued.

Apparatus

(1) Reaction Vessels.—Figure 1 depicts one of two reaction vessels composed of an illumination vessel A, a 100-cc. bulb B, a well-ground glass joint C, and two sealed-off tips D and E. The flat-walled illumination vessels, each about 1 cm. in thickness, contained 3 and 8 cc., respectively. All portions of the apparatus except the

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[1] National Research Fellow in Chemistry.

[2] Dickinson and Leermakers, THIS JOURNAL, **54**, 3852 (1932).

[3] Schwab and Heyde, *Z. physik. Chem.*, **B8**, 147 (1930).