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Micro Determination of Iodine by a Catalytic Method.

By

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The first suggestion that iodine can be determined by measuring its accelerating effect on the interaction of two substances which otherwise are more or less inert toward each other, appears to have been made by *R. Lang*, who at the end of a paper on the titration of trivalent arsenic with potassium permanganate in the presence of iodate or iodide as catalyst makes the statement, „Zum Schluß sei noch auf die Möglichkeit hingewiesen, Spuren von Jodverbindungen, die mit sonstigen analytischen Methoden nicht erfaßbar sind, durch Zuhilfenahme der Jodkatalyse der Reaktion Mn^{III}-salz—arsenige Säure nicht nur qualitativ nachweisen, sondern auch, da ja im allgemeinen meist einfache Proportionalität zwischen Geschwindigkeitskonstante und Katalysatorkonzentration besteht, quantitativ bestimmen zu können."[1] A number of years ago *H. Baines*[2] described a chronometric method for the determination of iodine as iodide, "depending on the pseudocatalysis by iodide of the oxidation of thiosulphate by nitrous acid". The procedure given was suitable for the determination of amounts of iodine corresponding to 5—50 mg. of potassium iodide.

In a preliminary note[3] it was shown that it is possible to estimate small amounts of iodine (as iodide) by measuring its catalytic effect on the reaction between quadrivalent cerium and trivalent arsenic in sulfuric acid solution. Even at the boiling point in dilute sulfuric acid medium, the reaction between ceric cerium and excess arsenious oxide is incomplete[4] in the absence of a catalyst, and at room temperature the velocity is ex-

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[1] *R. Lang*: Ztschr. anorgan. allg. Chem. **152**, 206 (1926).

[2] *H. Baines*: Journ. Soc. chem. Ind. **49**, 481 T (1930).

[3] *E. B. Sandell* and *I. M. Kolthoff*: Journ. Amer. chem. Soc. **56**, 1426 (1934).

[4] *P. E. Browning* and *W. D. Cutler*: Ztschr. anorgan. allg. Chem. **22**, 303 (1900).

tremely small, as was observed by *H. H. Willard* and *P. Young*,[1] who proposed the use of iodine (as iodide) or iodine monochloride as catalysts for the reaction in hydrochloric acid solution for volumetric purposes.

The results reported here were obtained in a brief study of the possibilities of determining very small amounts of iodide by measuring its accelerating effect on the ceric-arsenite reaction, especially in the presence of the other halides. It is emphasized that this investigation was of a general nature, and the application of the method to specific cases was not considered. If the general method is found to be of value, it is left to others to modify the procedure to suit their needs and possibly to improve its accuracy.

General.

The reaction $2\,Ce^{IV} + As^{III} \rightarrow 2\,Ce^{III} + As^{V}$ proceeds with extreme slowness in dilute sulfuric acid medium at room temperature in the absence of a catalyst. A mixture of 1 ml. of 0,1 *N* ceric ammonium sulfate solution, 2 ml. of 0,1 *N* arsenious oxide solution and 2 ml. of 1 : 10 sulfuric acid retains its yellow color for two to four days at room temperature. The addition of a microgram or two of an iodide causes the decolorization of the solution within a few minutes. In addition to iodine, osmium catalyzes the reaction strongly as found by *K. Gleu*,[2] the effect of the latter element being much greater than that of the former, weight for weight. Presumably, ruthenium will behave in the same manner as osmium. With the exception of these, no elements have been found that markedly catalyze the reaction. Chloride and bromide are weak catalysts, the latter being more effective than the former. The following elements were tested for catalytic activity, and found to be inert: antimony, bismuth, chromium, cobalt, copper, gold, iron, lead, manganese, mercury, molybdenum, palladium, silver, thallium, tin, titanium, tungsten, uranium, and vanadium. Columbium, iridium, rhodium, ruthenium, selenium, tantalum, and tellurium were not tested. Platinum, tested in the form of potassium chloroplatinate, showed weak catalytic activity, about 0,0005 as strong as iodine, which may have been due to the presence of traces of osmium as an impurity. Bromide in the presence of manganous salt markedly catalyzes the reaction.[3]

The catalytic effect of chloride on the ceric-arsenite reaction is approximately 2×10^{-7} as great as an equal weight of iodide, and the corresponding value for bromide is about 3×10^{-6}. These figures are to be looked upon as expressing merely the order of magnitude of catalytic activities of chloride and bromide compared to iodide, because the ratios are not constants, but change considerably with the concentration of chloride and bromide present in the reaction mixture.

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[1] *H. H. Willard* and *P. Young*: Journ. Amer. chem. Soc. **50**, 1372 (1933).

[2] *K. Gleu*: Ztschr. analyt. Chem. **95**, 305 (1933).

[3] cf. *R. Lang* and *J. Zwerina*: Ztschr. analyt. Chem. **91**, 5 (1933).

There are a number of substances which strongly inhibit the iodine-catalyzed reaction between ceric and arsenious oxide. Among these are fluoride, mercury salts, cyanide and silver. Fluoride forms a stable complex with ceric ions and mercuric ions form complexes with iodide, whereas cyanide gives rise to the quantitative transformation of iodide into iodine cyanide (JCN). Apparently, iodine in the latter form does not catalyze the ceric-arsenious oxide reaction. The presence of traces of silver interferes seriously on account of the very small solubility of silver iodide. In this connection it may be mentioned that the addition of a milligram or two of mercuric nitrate to a mixture of supposedly iodine-free arsenious oxide and ceric ammonium sulfate solutions (prepared as described later) decreased the already slow speed of reduction of cerium, indicating that a trace of iodine was present in the reagents. The catalytic effect of osmium is not destroyed by mercuric salts, so that by the use of the latter it is possible to distinguish between osmium and iodine. Naturally, reducing substances, such as nitrite, thiocyanate, ferrous iron, etc. which are oxidized by ceric sulfate must be made harmless before the procedure is applied. Substances which oxidize trivalent arsenic, such as bromate and permanganate, when present in more than traces, should be reduced in an appropriate way.

In studying the determination of iodine by its effet on the ceric-arsenite reaction, a simple chronometric technique can be used, viz., the ceric solution is added to an excess of the arsenite solution containing the iodide, and the time required for the solution to become colorless, indicating complete reduction of the ceric salt, is noted. Since ceric ions possess a strong yellow color, the end point of the reaction can be determined fairly satisfactorily by the disappearance of the yellow color. The precision with which the end point can be determined is increased somewhat by using o-phenanthroline ferrous sulfate[1] as indicator. The o-phenanthroline iron complex possesses a strong red color in the presence of a reducing agent, such as arsenious oxide, whereas it is pale blue in the presence of a strong oxidizing agent. Accordingly the color change exhibited by a mixture of arsenite (in excess) and ceric sulfate reacting with one another in the presence of a catalyst and indicator is from yellow through colorless or very pale blue to pink or red. The first appearance of a pink tinge in the solution can be detected with considerable precision.

The effect of the following factors on the velocity of the iodine catalyzed ceric sulfate-arsenite reaction was studied: the iodide concentration, the temperature, and the presence of foreign substances. The experimental conditions were usually the following. The potassium iodide solution of known concentration was measured from a microburet into a 2 × 7 cm.

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[1] *G. H. Walden, L. P. Hammett* and *R. P. Chapman*: Journ. Amer. chem. Soc. **55**, 2649 (1933).

vial, followed by 2,00 ml. of 0,100 *N* sodium arsenite solution (prepared as described subsequently), 1,00 ml. of 6 *N* sulfuric acid, 0,10 ml. of 0,001 *M* o-phenanthroline ferrous sulfate, and finally sufficient water to make the total volume 4,00 ml. This mixture was poured at one stroke into another vial containing 1,00 ml. of 0,100 *N* ceric ammonium sulfate solution which was 1,5 *N* in sulfuric acid. A stop watch was started at the instant of mixing. The mixed solution was then quickly transferred back to the original vessel, which was immersed in a water bath and gently shaken during the course of the reaction, especially near the end point. The color change marking the complete reduction of ceric ions was observed over a white background in good light. The first appearance of a pink tinge in the solution was taken as marking the completion of the reaction, the stop watch being stopped at this instant.

Table I. Relation between Reaction Time and Iodide Concentration.

Iodide Concentration γ of J per ml.	Reaction Time (25° C)		
	A[1]	*B*[2]	*C*[3]
	Minutes		
0,02	110	—	—
0,04	32	—	—
0,05	20,4	—	9,2
—	18,5	—	—
0,10	9,1	9,3	4,5
—	8,8	—	—
0,20	4,50	5,03	2,1
—	4,57	—	—
0,40	2,47	—	—
0,50	1,90	2,22	0,78
—	1,85	2,17	0,83
0,80	1,17	1,45	—
1,00	1,01	1,18	0,42
—	1,00	1,23	—

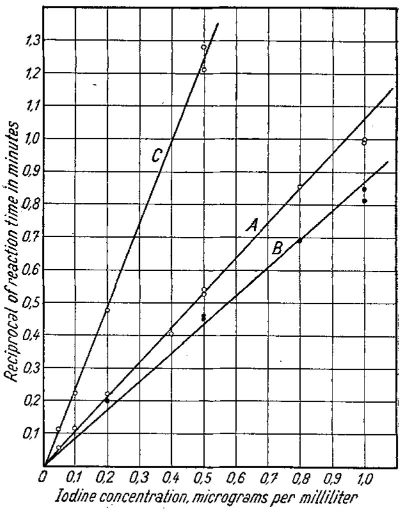

Figure 1.

The relation between reaction time and iodide concentration is shown in Table I and Figure 1. In the figure the reciprocal of the reaction time has been plotted against the iodine concentration of the mixed solution. Line *A* represents the data obtained under the conditions described in the last paragraph, whereas *B* represents those found under conditions the same except that 0,100 gram of pure sodium chloride was present in each

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[1] 2 ml. arsenite and 1 ml. ceric solution, 1 ml. 6 *N* sulfuric acid; total volume = 5 ml.

[2] Conditions as in *A* except 0,100 g. sodium chloride present.

[3] Conditions as in *A* except 0,2 ml. ceric solution used.

experiment. Finally, line *C* is the plot of values obtained under the same conditions as *A* except that 0,20 ml. of ceric solution was used instead of 1 ml. as in *A*. These experiments were all run at 25°. It will be seen from the results that within the limits of experimental error the time required for a given amount of ceric salt to react with an excess of arsenious oxide at constant temperature is inversely proportional to the concentration of iodide in the reaction mixture, in the range 1 : 1000000 to 1 : 20000000. In solutions more dilute than 1 : 20000000 the linear relation fails, the catalytic activity of the iodine becoming relatively smaller; the deviation of the values for the concentration 1 : 1000000 appears to exceed slightly the experimental error. The presence of relatively much chloride (more than present in series *B*) and much bromide may be expected to destroy the linear relationship, because these ions, as already mentioned, act as catalysts for the reaction when present in high concentrations. The difference in slope of lines *A* and *B* results from a salt effect, of which more will be said later.

Table II. Relation between Reaction Time and Temperature (5,0 γ iodine present).

Temperature °C	Time Minutes
2,5	3,8
3,0	3,85
3,5	3,4
12,5	2,1
21,5	1,2
22	1,15
25	0,90
29	0,77
39,5	0,42
40,5	0,38
54,5	0,23

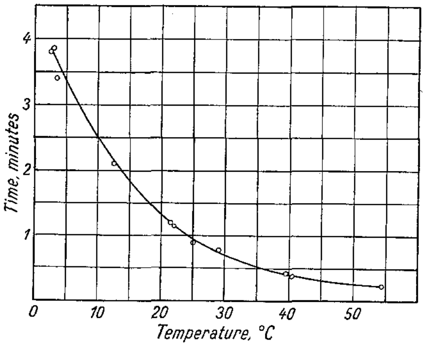

Figure 2.

The variation in reaction time with temperature is recorded in Table II and plotted in Figure 2. In each experiment 5,0 γ iodine as iodide were present, thus making the iodide concentration one part per million. The reaction velocity has a large temperature coefficient. In the neighbourhood of 25° C a change in temperature of one degree alters the reaction time approximately 5 per cent under the conditions described.

The effect of a number of neutral salts on the reaction time in the presence of a constant quantity of iodide is shown in Table III and Figure 3. The amount of iodine present in each experiment was 2,5 γ, corresponding to a concentration of one part in two million of reaction mixture. It will be seen that the presence of salts leads to a considerable change in reaction velocity. With chloride, and especially with bromide, there is first produced a decrease in reaction time as the halide concentration is increased and then an increase.[1] In the case of bromide the reaction time becomes constant or falls off slightly as the concentration is further increased. Potassium nitrate and potassium sulfate increase the time over the whole range of concentrations, the effect being especially marked in the case of the latter. Magnesium sulfate (for which numerical data have been omitted in the table and in the graph) gives a curve lying between those of potassium sulfate and potassium nitrate. Doubtless the reduction in reaction velocity generally produced by salts is to be attributed to the decrease in activity of the components of the system.

Table III. Effect of Salts on Reaction Time in Presence of Iodide (2,5 γ iodine in each experiment).

Weight of Salt Gram	NaCl	KBr	KNO_3	K_2SO_4
	Minutes			
0,000	1,85	1,85	1,85	1,85
0,005	1,78	1,60	—	—
0,01	1,83	1,47	—	1,92
0,025	1,82	1,50	1,95	—
0,05	1,98	1,72	2,00	2,37
0,10	2,13	2,00	2,40	2,75
0,20	2,6	3,7	3,0	4,37
0,35	3,5	4,35	3,9	7,55
0,50	4,6	4,2	4,8	10,75

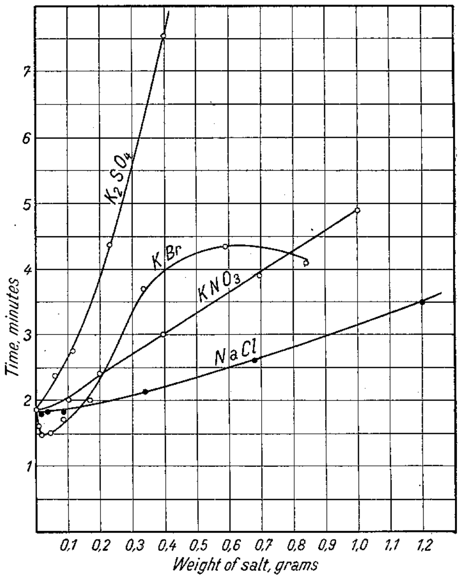

Figure 3.

At this point it may be mentioned that an increase in the sulfuric acid concentration of the reaction mixture from 1,5 N (that ordinarily used) to 3 N caused a slight increase in the reaction velocity. It is necessary to have the reaction mixture fairly acid to prevent the precipitation of ceric arsenate.

Proposed Method.

In the determination of iodine in the general case, there will be present in the sample greater or less amounts of foreign substances which will affect the rate of the catalyzed reaction between quadrivalent cerium and trivalent arsenic, so that iodine in an unknown solution can hardly

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[1] With an iodine concentration of 1 in 5000000, the effect of sodium chloride was qualitatively the same as in the 1 : 2000000 concentration, but the minimum was more pronounced in the former case.

be determined by comparing the effect of such a solution on the reaction rate with that produced by a known iodide solution in pure water. The difficulty can be overcome with fair success by adding a suitable known amount of iodide to the unknown solution and comparing the catalytic activity of the solution so obtained with the activity exhibited by the original solution, there being present the same initial amounts of ceric cerium and arsenite in both cases. That is, after the reaction time has been noted with the unknown amount of iodine and the given amounts of cerium and arsenite, let there be added the known amount of iodine and sufficient ceric salt and arsenite to replace that destroyed in the reaction, and let the time required for the completion of the reaction the second time be noted. Then it is a simple matter, at least in principle, to find the unknown amount of iodine by proceeding as follows.

Let x = quantity of iodine (as iodide) in the sample
a = known quantity of iodine added
v_1 = original volume of reaction mixture containing the sample
v_2 = volume of reaction mixture after the known quantity of iodine (iodide) solution, and sufficient ceric and arsenite solutions to restore these to their original amounts have been added.
t_1 = reaction time with the quantity x of iodine in the volume v_1
t_2 = reaction time with the quantity $a + x$ of iodine in the volume v_2.

Assuming reaction time to be inversely proportional to the iodine (iodide) concentration under the conditions described, the following expressions should hold:

$$t_1 = \frac{k\, v_1}{x},$$

$$t_2 = \frac{k\, v_2}{a + x},$$

$$\text{and } \frac{t_1}{t_2} = \frac{v_1}{v_2} \cdot \frac{(a + x)}{x},$$

$$\text{whence: } \quad x = \frac{a\, v_1\, t_2}{v_2\, t_1 - v_1\, t_2}.$$

The correctness of this formula rests on the assumption that the observed catalytic activity of the iodine is directly proportional to its concentration in the mixture. This condition cannot be strictly fulfilled under the experimental conditions, since the solutions added in bringing the volume to v_2 necessarily alter the concentrations of the foreign salts present, and therewith the effect of the latter on the catalyzed reaction between ceric cerium and arsenite as illustrated in Figure 3. The error thus introduced by dilution in the presence of sodium chloride, potassium bromide, potassium nitrate, or potassium sulfate when the iodine concentration is one in 2000000 may be roughly derived from Figure 3. Even in the absence of foreign salts, the procedure described is subject to an error, since the activities of the reacting components change slightly when the volume is altered from v_1 to v_2.

In practice it is convenient to arrange matters so that after the first reaction time, t_1, has been measured, only ceric solution, in addition to the known amount of iodide solution, need be added to obtain t_2. In the directions given below, the original amounts of ceric ammonium sulfate and sodium arsenite solutions are respectively 1,00 and 2,00 ml., each 0,100 *N*. After the reaction has run to completion there will remain 1,00 ml. of arsenite solution. By adding 0,50 ml. of ceric solution, the ceric-arsenite ratio will be the same as before, and if there were no volume change, the reaction time would remain very nearly the same; this was proven experimentally. Therefore, the formula given above may be applied under these conditions.

If sufficient sample is available, the difficulty due to volume change can be overcome by taking two equal portions of unknown, adding to one a known quantity of iodide, making the volumes of both portions the same, and then measuring the reaction with the same amounts of ceric and arsenite solutions in the two cases. Then the formula for calculating the unknown amount of iodine becomes $x = \frac{a\,t_2}{t_1 - t_2}$. It is assumed that the catalytic activity of the iodine present is directly proportional to its concentration.

Since the relative error of determining the time of reaction remains approximately the same over a wide range of iodide concentrations, the known amount of iodine a to be added should in general be large compared with x in order that the experimental error associated with the term $v_2 t_1 - v_1 t_2$ may be as small as possible. The average error in time measurement is estimated to lie between 2 and 3 per cent. Thus if $t_2 = \frac{t_1}{2}$ and v_1 and v_2 are nearly the same, the error of the difference may amount to 5 per cent; the smaller t_2 is made (within limits), the smaller will be the error. However, if t_1 is comparatively small it is impossible to reduce t_2 to a very small value in order to make $t_1 - t_2$ as great as possible, because the measurement of very small reaction times cannot be made accurately. The case mentioned is of small practical importance because the method is not likely to be applied to the determination of relatively large quantities of iodine. It may not always be desirable to arrange matters so that t_2 will be small compared to t_1. If there is present a large amount of a substance, such as bromide, which exercises a weak catalytic effect on the reaction, it may be advisable not to make the discrepancy in value of t_1 and t_2 too great. In such a case an appreciable compensation of errors may be expected if a is chosen of such magnitude that the values of t_1 and t_2 are not too disproportionate, while still sufficiently different to avoid the introduction of a large percentage error in the time difference. If in any case the catalytic activity of the iodine should not be strictly proportional to its concentration, better results will be obtained when t_1 and t_2 are not too greatly different.

The results obtained in the application of the proposed method are given in Table IV. The determinations were made according to the directions given in the procedure below, with the exception of Nos. 4, 6, 7, 26 and 45 in which 0,20 ml. of ceric ammonium sulfate solution was used instead of 1,00 ml. as in the other experiments. The volumes v_1 and v_2 usually fell between 5–6 ml.; the temperature was 25–30^0. Some of the results recorded in the table were not obtained under the best conditions from the analytical point of view, because a was varied considerably with the intention of seeing whether the formula given above would hold satisfactorily.

In the following paragraphs conclusions regarding the accuracy of the method, especially in the presence of foreign substances, are summarized.

In the absence of chloride, the values for iodine are seriously low when the amount present is less than 0,25–0,5 γ, in consequence of the failure of the linear relationship between catalytic activity and iodine concentration at very low concentrations. If a small amount of chloride is added, the linear relation is fulfilled at concentrations of iodide as low as 1 : 100000000. Therefore if chloride is not present in the sample, it is necessary to add it in small amount (ca. 10 mg. of sodium chloride) when quantities of iodine of the order of a few tenths of a microgram are to be determined. The concentration of iodine in the reaction mixture should generally be less than 1 : 2000000, for otherwise the second reaction time, t_2, becomes so small that it cannot be measured precisely. With amounts of sodium chloride of the order of 10 mg., positive and negative errors appear to be nearly equally prone to occur. For amounts of iodine (as iodide) ranging from 0,05 to 1 γ in the presence of 5 to 15 mg. of sodium chloride, the largest error was 20 per cent, and the average error was approximately 10 per cent. Considering the small absolute amount of iodine and the rather large ratio of chloride to iodide (as great as 100000 to 1), the accuracy may be regarded as satisfactory. The values in the table appear to justify the conclusion that amounts of iodine of the order of 0,001 per cent in sodium chloride can be determined with an accuracy of 10 to 20 per cent by using a sample as small as 10 mg. When the quantity of sodium chloride present is in the neighborhood of 100 mg., the average error in estimating amounts of iodine ranging from 0,1 to 3 γ is about 15 per cent; the results tend to be high. Amounts of

Table IV. Determination of Iodine.

No.	Addition	Iodine Taken γ	Iodine Found γ	Error γ	a γ	t_1 Min.	t_2 Min.
1	—	0,10	0,045	−0,055	1,00	78	3,8
2	—	0,20	0,12	−0,08	1,00	37	4,7
3	—	0,20	0,13	−0,07	1,00	33	4,3
4[1]	—	0,15	0,16	+0,01	0,25	11,3	5,1
5	—	0,15	0,135	−0,015	0,20	27	12,2
6[1]	—	0,25	0,24	−0,01	0,50	6,8	2,6
7[1]	—	0,50	0,53	+0,03	0,25	2,1	1,63
8	—	0,50	0,48	−0,02	1,00	7,9	2,9
9	—	1,00	1,02	+0,02	1,50	4,1	1,93
10	—	3,00	2,65	−0,35	5,00	1,27	0,57
11	NaCl, 5 mg.	0,20	0,22	+0,02	1,00	19	3,9
12	,, , 5 ,,	0,25	0,22	−0,03	1,50	17,3	2,6
13	,, , 10 mg.	0,045	0,048	+0,003	1,50	90	3,0
14	,, , 10 ,,	0,10	0,095	−0,005	0,15	35,5	16
15	,, , 10 ,,	0,10	0,093	−0,007	1,00	46	3,1
16	,, , 10 ,,	0,15	0,14	−0,01	0,35	22	7,0
17	,, , 12 ,,	0,10	0,115	+0,015	0,50	34,5	7,25
18	,, , 15 ,,	0,10	0,12	+0,02	0,15	37	18,5
19	,, , 10 ,,	1,00	1,00	0,0	1,50	4,05	1,87
20	,, , 10 ,,	1,00	1,20	+0,20	1,25	3,8	2,15
21	,, , 10 ,,	3,00	2,67	−0,33	5,00	1,27	0,58
22	,, , 50 ,,	1,40	1,42	+0,02	1,50	3,1	1,75
23	,, , 100 mg.	0,10	0,12	+0,02	1,00	31	3,85
24	,, , 100 ,,	0,10	0,125	+0,025	0,16	37,5	18
25	,, , 100 ,,	0,11	0,11	0,00	0,15	33	16
26[1]	,, , 100 ,,	0,10	0,13	+0,03	0,15	18,5	9,25
27	,, , 100 ,,	0,19	0,20	+0,01	0,15	8,0	5,25
28	,, , 100 ,,	0,50	0,55	+0,05	1,00	8,0	3,25
29	,, , 100 ,,	0,65	0,70	+0,05	0,80	6,25	3,3
30	,, , 100 ,,	1,00	1,20	+0,20	1,50	3,4	1,75
31	,, , 100 ,,	1,00	1,25	+0,25	1,50	3,8	2,0
32	,, , 100 ,,	1,00	1,12	+0,12	1,00	3,9	2,35
33	,, , 100 ,,	1,00	1,18	+0,18	1,00	3,9	2,4
34	,, , 100 ,,	1,00	0,95	−0,05	0,75	4,4	2,8
35	,, , 100 ,,	3,00	2,98	−0,02	5,00	1,37	0,67
36	,, , 150 ,,	0,50	0,55	+0,05	0,50	8,2	4,8
37	,, , 150 ,,	2,30	2,2	−0,1	1,4	2,4	2,7
38	,, , 200 ,,	0,10	0,13	+0,03	1,0	29	4,0
39	,, , 250 ,,	0,02	0,03	+0,01	0,05	85	35
40	KBr, 2 mg.	0,10	0,08	−0,02	0,15	31	12
41	,, , 10 mg.	0,05	0,06	+0,01	0,19	19	4,7
42	,, , 10 ,,	0,50	0,36	−0,14	0,70	6,3	2,4
43	,, , 10 ,,	1,00	0,84	−0,16	1,00	2,6	1,35
44	,, , 10 ,,	1,00	0,90	−0,10	1,00	2,6	1,4
45[1]	,, , 20 ,,	0,10	0,14	+0,04	0,25	6,8	2,9

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[1] 0,2 ml. of 0,1 N Ce^{IV} used.

Continuation of Table IV.

No.	Addition	Iodine Taken γ	Iodine Found γ	Error γ	*a* γ	t_1 Min.	t_2 Min.
46	KBr, 25 mg.	0,05	0,06	+0,01	0,25	36	7,9
47	„ , 15 „	0,105	0,155	+0,05	0,25	9,8	4,2
48	„ , 15 „	0,095	0,105	+0,01	0,25	16,7	5,5
49	„ , 15 „	0,21	0,20	−0,01	0,40	9,9	3,7
50	„ , 15 „	0,25	0,24	−0,01	0,50	7,4	2,7
51	„ , 15 „	1,20	0,9	−0,3	1,7	2,7	1,1
52	„ , 15 „	0,20	0,19	−0,01	0,30	12,8	5,4
53	„ , 30 „	0,055	0,057	0,00	0,10	35	14
54	„ , 35 „	0,50	0,44	−0,06	0,75	5,0	2,1
55	„ , 50 „	0,10	0,12	+0,02	0,25	18,4	6,7
56	„ , 50 „	0,10	0,13	+0,03	1,0	22,0	2,86
57	„ , 50 „	0,10	0,07	−0,03	0,15	31	11
58	„ , 50 „	1,00	0,82	−0,18	1,00	2,85	1,47
59	„ , 65 „	0,10	0,107	+0,007	0,15	20	8,0
60	„ , 65 „	0,50	0,56	+0,06	1,00	4,9	2,0
61	„ , 75 „	1,00	0,80	−0,20	1,50	3,7	1,5
62	„ , 100 mg.	0,10	0,10	0,00	0,15	25	11
63	„ , 100 „	0,25	0,36	+0,11	1,00	9,1	2,77
64	„ , 100 „	0,50	0,55	+0,05	1,00	5,8	2,36
65	„ , 100 „	0,50	0,56	+0,06	0,50	5,6	3,3
66	$KClO_3$, 10 mg.	1,00	0,92	−0,08	1,00	4,4	2,40
67	$KBrO_3$, 0,3 mg.	1,00	0,94	−0,06	1,50	3,37	1,50
68	NaCl, 50 mg + KBr, 10 mg. + $KClO_3$, 10 mg.	1,00	0,80	−0,20	1,00	3,25	1,65
69	NaCl, 10 mg. + ferric alum, 20 mg.	0,50	0,49	−0,01	0,50	7,4	4,1
70	NaCl, 10 mg. + $MgSO_4 \cdot 7\,H_2O$, 50 mg.	0,50	0,50	0,00	0,60	7,7	3,9
71	NaCl, 10 mg. + KH_2PO_4, 10 mg.	0,50	0,46	−0,04	0,55	7,7	3,9
72	NaCl, 10 mg. + $MnCl_2 \cdot 4\,H_2O$, 0,4 mg.	0,50	0,53	+0,03	0,75	7,0	3,3
73	NaCl, 10 mg. + $MnCl_2 \cdot 4\,H_2O$, 2 mg.	0,50	0,57	+0,07	0,75	5,5	2,7
74	KBr, 30 mg. + $MnCl_2 \cdot 4\,H_2O$, 3,5 mg.	0,25	1,25	+1,0	0,75	3,8	2,7
75	KNO_3, 100 mg.	1,00	0,84	−0,16	2,00	4,67	1,63
76	„ , 100 „	1,00	0,99	−0,01	2,00	4,67	1,54
77	K_2SO_4, 100 mg.	1,00	0,72	−0,28	2,00	6,2	1,93
78	„ , 100 „	1,00	0,87	−0,13	2,00	6,2	1,80
79	$AlCl_3 \cdot 6\,H_2O$, 100 mg.	0,50	0,50	0,0	0,75	5,5	2,5
80	$CuCl_2$, 2 mg.	0,50	0,555	+0,055	0,50	7,8	4,6
81	$CoCl_2$, 2 „	0,50	0,575	+0,075	0,50	7,5	4,5
82	$CrCl_3$, 2 „	0,50	0,60	+0,1	0,50	7,5	4,8
83	$Pb(NO_3)_2$, 0,5 mg.	0,50	0,41	−0,09	0,45	8,6	4,6
84	$ZnCl_2$, 2 mg.	0,50	0,47	−0,03	0,70	6,6	3,0
85	$Hg(NO_3)_2$, 0,5 mg.	0,50	?	?	—	?	—

Continuation of Table IV.

No.	Addition	Iodine Tacken γ	Iodine Found γ	Error γ	a γ	t_1 Min.	t_2 Min.
86	$CdCl_2$, 2 mg.	0,50	0,46	−0,04	0,60	7,6	3,7
87	$(NH_4)_2MoO_4$, 2,5 mg.	0,50	0,37	−0,13	0,50	16	7,5
88	NH_4VO_3, 1 mg.	0,50	0,47	−0,03	0,50	8,7	4,7
89	$UO_2(C_2H_3O_2)_2 \cdot 2\,H_2O$, 0,3 mg.	0,50	0,46	−0,04	0,50	7,7	4,1
90	NH_4F, 8 mg. + $AlCl_3 \cdot 6\,H_2O$, 75 mg.	0,50	0,43	−0,07	0,45	10,0	5,7
91	$NaNO_2$, 0,5 mg. + NaCl, 50 mg.[1]	0,50	0,40	−0,10	0,50	8,7	4,3

sodium chloride larger than 100 mg. are not conveniently worked with, without change of procedure, when the amount of iodine present is very small, because on long standing a precipitate gradually appears in the reaction mixture. High concentrations of other salts also lead to the formation of a precipitate. It appears to be possible to determine one part of iodine in the presence of a million parts of sodium chloride with an accuracy of 20 per cent. The relative error is nearly independent of the quantity of iodine in the range 0,1 to 3 γ.

The average error in the determination of 0,05 to 1,2 γ of iodine in the presence of 2 to 15 mg. of potassium bromide by the recommended procedure was found to be approximately 16 per cent; the results apparently tend to be low rather than high. In the range 25 to 100 mg. of potassium bromide the results of the determination of 0,1-1 γ iodine showed an average error slightly greater than 15 per cent; it is noteworthy that the values do not tend to be seriously high, in spite of the unfavorable ratio of bromide to iodide. The method therefore is suitable for determining very small amounts of iodides in the presence of comparatively much bromide.

Chlorate does not interfere in the procedure, nor do small amounts (a few tenths of a milligram) of bromate, but larger amounts of the latter oxidize the arsenite and render the determination impossible. Ferric iron, aluminum, magnesium, and small amounts of copper, cadmium, zinc, cobalt, and chromium are without effect, although when colored ions are present the detection of the end point becomes less accurate. Mercury and silver make the determination impossible, as already mentioned. Phosphate is not harmful, at least when present in small amounts. The interference of fluoride can be prevented by the addition of aluminum chloride to form fluoaluminate; aluminum is more suitable for binding the fluoride than is boric acid. Small amounts of nitrites can be oxidized

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[1] Nitrite first oxidized with ceric ammonium sulfate.

in acid solution by the careful addition of ceric ammonium sulfate solution to the first permanent yellow tinge. Lead and calcium, in small amounts, do not interfere but large amounts are undesirable because of the precipitates they yield. Manganese (Mn^{II}) in small amounts does not interfere in the presence of chloride but does do so when appreciable amounts of bromide are present, because in combination with the latter it acts as a positive catalyst for the ceric-arsenite reaction.

Iodine to be determined by the method must be in the form of iodide; if the element is present as iodate, it exerts a much weaker catalytic effect. It seems possible that iodate can be satisfactorily reduced to iodide by allowing the sample to stand for some time after the addition of sulfuric acid and arsenite solution, although the matter has not been carefully tested; in one experiment in which 1,14 γ of iodine as iodate was allowed to stand with the acidified arsenite solution for 20 minutes before the addition of the ceric solution, 0,96 γ of iodine was found.

From the results of determinations Nos. 75 and 77 in Table IV it is seen that large amounts of potassium nitrate and potassium sulfate, respectively, lead to low results, especially the sulfate. If the determinations are made in such a manner that the total volume is the same when t_1 and t_2 are measured, then the values obtained are better as shown by Nos. 76 and 78.

When the amount of arsenite solution used is kept constant at 2,00 ml. but the volume of ceric solution is reduced from 1,00 ml. to 0,20 ml. with the purpose of diminishing the reaction time, thus increasing the convenience of the method for small amounts of iodine, the results obtained with pure solutions are good (Nos. 4, 6 and 7), but are less satisfactory usually in the presence of much chloride and are much too high in the presence of proportionately large amounts of bromide.[1] Consequently, it will usually be best to take amounts of arsenite and cerium solutions such that the former is not too greatly preponderant; it seems that a 2 : 1 ratio is practically a good one.

The method described is of value chiefly in those cases in which less than 1 γ of iodine must be determined. By the usual micromethods less than 0,2 or 0,3 γ of iodine can hardly be determined,[2] whereas the present method gives useful results with as little as 0,05–0,1 γ. It is to be expected that by reducing the volume, as little as 0,01 or 0,02 γ of the element can be determined, provided the amount of foreign salts is not too unfavorable. A more refined technique would doubtless increase the accuracy of the method.

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[1] To save space some of the substantiating data have been omitted from the table.

[2] *J. F. Reith*: Biochem. Ztschr. **216**, 266 (1929).

Procedure.

Special Solutions.

Sodium Arsenite, 0,1000 N. Dissolve 4,947 g. of pure dry arsenious oxide in 25–30 ml. of 1 *N* sodium hydroxide, warming to hasten solution: dilute to 200 or 300 ml. and add dilute sulfuric acid until the solution is neutral or slightly acid to litmus paper. Transfer the solution to a liter volumetric flask, make up to the mark, mix, and if the liquid is not entirely clear, filter it though a sintered glass or Gooch crucible.

Ceric Ammonium Sulfate, 0,10 N. Prepare an approximately 0,1 *N* solution by dissolving 63,3 g. of $Ce(SO_4)_2 \cdot 2\ (NH_4)_2SO_4 \cdot 2\ H_2O$ in 500 ml. of water to which has been added 45 ml. of concentrated sulfuric acid, and diluting to one liter. Filter the solution if it is turbid. Determine the normality of the solution as follows. Pipet 25 ml. of 0,1000 *N* arsenite solution into a small *Erlenmeyer* flask, add 15 or 20 ml. of 6 *N* sulfuric acid, 2 or 3 drops of 0,01 *M* osmium tetroxide solution[1] (0,25 g. OsO_4 in 100 ml. of 0,1 *N* sulfuric acid) and 0,5 ml. of 0,001 *M* o-phenanthroline ferrous sulfate indicator solution. Then titrate with the ceric solution until the color changes sharply to colorless or very pale blue. If the normality of the ceric ammonium sulfate solution is found to be within 1 per cent of 0,100, the solution may be used as it is, but if the difference is greater, either the ceric or arsenite solution must be diluted until the normality ratio is 1 : 1.

Standard Iodide Solution. Dissolve 0,01308 g. of pure dry potassium iodide in a liter of water (or if prefered, dilute a stronger solution to this strength). This solution contains 10,0 γ of iodine per milliliter. The solution should be preserved in a brown bottle; it may be kept for weeks.

o-Phenanthroline Ferrous Sulfate, 0,001 M.

The following directions hold for a sample which does not contain constituents reacting with either ceric cerium or arsenite in sulfuric acid solution at room temperature. Organic matter should be absent, as must such interfering substances as have been mentioned under "Proposed Method". Iodine should be present in the form of iodide. The sample may be neutral or slightly acid; if it is alkaline it should be neutralized with hydrochloric acid (iodine-free).

First of all, the reagents should be tested for the possible presence of traces of iodine. Mix 2 ml. of sodium arsenite, 1 ml. of ceric ammonium sulfate, 1 ml. of 6 *N* sulfuric acid, and 0,1 ml. of o-phenanthroline ferrous sulfate indicator, and allow the solution to stand at room temperature. The yellow color of the mixture should not be discharged within 24 hours.

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[1] If desired, iodine monochloride can be used as catalyst, in which case the directions given by *H. H. Willard* and *P. Young*: Journ. Amer. chem. Soc. **55**, 3267 (1933), are followed.

If the sample is a solid (soluble in aqueous solution) transfer a quantity sufficient to contain 0,05 to $3\,\gamma$ of iodine to a dry vial conveniently 2×7 cm. in size. The weight of sample should generally not exceed 0,1 g., because larger quantities may cause the formation of a precipitate in the reaction mixture when the reaction time is long. If the sample is in the form at a solution, transfer a known volume to the vial; the volume of liquid sample should be as small as possible, preferably not exceeding 1 ml., when very small amounts of iodine are to be determined, because the reaction time increases as the dilution of the reaction mixture is increased. Then add to the vial 2,00 ($\pm$ 0,01) ml. of sodium arsenite solution, and shake to dissolve the sample if solid; the volume change occuring with a solid sample may be neglected. At this point, if the sample does not contain chloride, and quantities of iodine less than $0{,}5\,\gamma$ are to be determined, add 10 mg. of pure sodium chloride.[1] Next add 1 ml. of $6\,N$ sulfuric acid (or more if the volume of sample is unavoidably large, so as to make the acidity 1,5 to $2\,N$) and 0,10 ml. of o-phenanthroline ferrous sulfate solution. In another vial, preferably 2×4 cm. in size and provided with a lip to facilitate pouring, measure out 1,00 ml. of ceric ammonium sulfate solution. Immerse both vials in a constant temperature water bath (room temperature), and keep therein until the contents have assumed the temperature of the bath.[2]

At one stroke pour the mixture of sample and arsenite (vial 1) into the ceric solution (vial 2), starting a stop watch at the instant of mixing. Quickly pour the mixed solution into vial 1, and drain out the second vial as completely as possible into the first. Return the vial containing the reaction mixture to the water bath, and shake gently at intervals, or continuously if the yellow color of the solution fades rapidly, taking care not to heat the contents inadvertently with the hand. When the yellow color has become very pale, hold the vial over a white background in good light in order that the end point may be observed under the best conditions. Obtain the time of the appearance of the first pink tinge in the solution. It is important to shake the solution near the end point. The color change is from yellow through colorless or very pale blue to red. If the reaction velocity is great, the colorless stage may not be observed. When the color change is slow (very small amounts of iodine present) it may be advantageous to use a comparison solution containing the same amount of indicator as the reaction mixture, which has been converted into the pale blue oxidized form by a *trace* of ceric solution.

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[1] Run a blank on the sodium chloride used to be sure that it does not contain appreciable amounts of iodine.

[2] If the room temperature is reasonably constant and the amount of iodine to be determined is not too small, so that the reaction time will not be too long, use of the water bath can often be omitted.

When the reaction has been completed, add to the solution by means of a microburet sufficient standard iodide solution to furnish an amount of iodine which is estimated to be two or three times as great as that present if the latter is in the approximate range 0,5 to 2,5 γ.[1] For quantities of iodine below 0,5 γ add 1 to 2 γ of the element. Allow the mixture to stand for a minute or two after the addition to insure the complete reduction of the cerium. Then measure out into a clean vial 0,50 ml. (measured with an accuracy of ± 0,005 ml.) of ceric ammonium sulfate solution, and add to the latter, all at once as before, the reacted arsenite-iodide solution, and determine the second reaction time. Calculate the quantity of iodine in the sample by making use of the formula

$$x = \frac{a\, v_1\, t_2}{v_2\, t_1 - v_1\, t_2},$$

where the symbols have the meaning given on page 15.

The procedure just described is to be used when the amount of sample, very low in iodine, is limited. When sufficient sample is available,[2] it is usually better to take two equal portions of sample and arrange matters so that the final reaction volumes, v_1 and v_2, are the same. This can be done by adding to the first portion, containing the quantity of iodine x, sufficient water to exceed slightly the maximum volume of iodide solution, which it is necessary to add to the second portion to furnish the amount a. Then after t_1 has been determined on the first portion of sample, there is added to the second portion, a suitable volume of iodide solution together with enough water to make the total volume the same as that of the other portion. For each portion of sample 2 ml. of arsenite and 1 ml. of ceric ammonium sulfate solution are used in obtaining the reaction times. Under these conditions $x = \frac{a\, t_2}{t_1 - t_2}$. This technique eliminates any error due to change of salt concentration, and is to be preferred to that described in the preceding paragraphs.

Summary.

A procedure is described for the determination of quantities of iodide of the order of 0,05 to 3 γ in 1 ml. solution or in a suitable amount of solid sample (sodium chloride). The method is based upon the strong catalytic

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[1] The quantity of iodine added should be so chosen that the second reaction time, t_2, is not less than 20 or 30 seconds, for otherwise the error in time measurement is likely to be unduly large. It will be seen that for the best accuracy the original iodine content should not be greater than approximately 3 γ, unless salts are present that appreciably decrease the reaction velocity.

[2] Or even if the absolute amount of iodine is very small it may be advisable in certain cases (as when relatively much sulfate is present) to divide the sample into two parts and proceed as described in the paragraph above.

effect of iodide upon the reaction between ceric sulfate and an excess of arsenious acid in dilute sulfuric acid (1,5–2 N). The effect of temperature and foreign substances has been investigated and procedures have been given which are applicable in the presence of salts affecting the rate of the catalyzed reaction. By refinement of the experimental technique it should be possible to determine quantities of iodine much smaller than 0,05 γ.

Zusammenfassung.

Es wird ein Verfahren für die quantitative Bestimmung von Jodid in Mengen von 0,05—3 γ in einer Lösung von 1 ccm oder in einer entsprechenden Menge fester Substanz (NaCl) beschrieben. Die Methode beruht auf einem stark katalysierenden Einfluß des Jod-Ions auf die Reaktion zwischen Cerisulfat und überschüssiger arseniger Säure in verd. Schwefelsäure. Der Einfluß von Temperatur und Fremdsubstanzen ist untersucht und Verfahren sind ausgearbeitet worden, die bei Anwesenheit von Salzen, die den Ablauf der katalysierten Reaktion beeinträchtigen, anwendbar sind. Durch Verbesserung der experimentellen Technik sollte es möglich sein, Mengen von Jod, die viel kleiner als 0,05 γ sind, nachzuweisen.

Résumé.

Un procédé est décrit concernant la détermination des quantités de iodure de l'ordre 0,05 à 3 γ dans une solution de 1 ml ou dans une quantité appropriée d'un corps solide (chlorure de sodium). Cette méthode se base sur l'effet puissant catalytique du iodure sur la réaction entre le cérisulfate et un excès d'acide arsénieux dans l'acide sulfurique dilué (1,5—2 n). L'effet de la température et des substances hétérogènes est recherché, et on indique des procédés lesquels peuvent être appliqués s'il y a des sels exerçant une influence sur le dosage de la réaction catalysée. Grâce à l'amélioration de la technique expérimentale, il sera possible de déterminer des quantités de iodure même plus petites que 0,05 γ.