Dilute solutions of certain dyes are also unusually stable. Solutions of brucine sulfate with a concentration less than 0.00125 gram mol per liter do not affect the velocity of crystallization. These solutions, however, are much more stable toward spontaneous crystallization than pure water at the same temperature.

MADISON, WISCONSIN.

DIFFERENTIAL IODIMETRY.

1—DETERMINATION OF PERIODATES, IODATES, BROMATES AND CHLORATES IN THE PRESENCE OE EACH OTHER.*

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Considerable work has been done by various investigators[1-25] who have studied the rates of reaction between oxidizing agents of the type of the oxidized halogen compounds and potassium iodide. The larger portion of the previous work has been from a physico-chemical viewpoint, performed in an endeavor to establish the order of these reactions. This study has for its purpose the investigation of such reactions to ascertain the conditions under which they are applicable to analytical chemistry.

When potassium iodide is added to oxidizing agents in acid solution, free iodine is liberated more or less completely, the quantity of oxidizing agent transposed depending upon the concentrations of the substances involved, the temperature, and to a certain extent the pressure. The greater the concentration of iodide the more rapid the reaction. The greater the dissociation of the acid as well as the larger the amount of acid involved the faster the liberation of iodine occurs. This principle has been utilized for the purpose of determining the strength of acids[26-36], a mixture of iodide and iodate having been utilized for the purpose.

The utilization of such reactions for direct quantitative purposes has been studied to a comparatively limited extent. Certain reactions, like those between cupric salts, ferric salts, permanganate, dichromate, and the halogenates and an iodide, have been shown to be quantitative for the individual reactions, and they form the basis of laboratory determinations in common use. Moser[44] converted iron into a complex by the use of pyrophosphoric acid and titrated copper in the presence of iron. Edgar[45] reduced chromic and vanadic acids with hydrobromic acid, distilling into potassium iodide, then reduced the vanadium and iron with hydriodic acid, again distilling. In each case the iodine was titrated with thiosulfate. An arsenite method was used for the determination of chromic acid. By combining the schemes, chromic acid, vanadic acid and ferric iron were determined. However, no systematic study has

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been made in which it was attempted to titrate various oxidizing substances in the presence of each other, utilizing varying concentrations of acid and iodide to liberate iodine in a differential manner, subsequently titrating the iodine with a reducing agent such as thiosulfate. This paper considers the determination of periodates, iodates, bromates and chlorates in the presence of each other and also in the presence of perchlorates.

The halogenate solutions used in this investigation were tenth normal. The sodium thiosulfate and sodium arsenite solutions were approximately tenth normal and were accurately standardized when used. The potassium iodide solution was normal and contained no liberated iodine.

Determination of Periodate in the Presence of Iodate, Bromate and Chlorate.

Müller and Friedberger[46] state that periodate can be titrated in the presence of iodate, using an acidity of acetic acid between the concentrations of 0.02 *N* and 0.1 *N* with thirty per cent. sodium acetate. No results are recorded. However, they further state that an arsenite method, which is described, surpasses the thiosulfate method in exactness.

Periodates in neutral solution react with potassum iodide, yielding iodate and free iodine. The free iodine can be accurately titrated in the presence of an excess of sodium bicarbonate with a standard arsenite solution prepared in the usual manner. This confirms the work of Müller and Friedberger.

If an attempt is made to titrate the free iodine with thiosulfate, erratic results are obtained. If a weak acid is added to remove the alkali formed, conditions are improved somewhat; however, great care must be exercised in the choice of the acid and the concentration of the same. The acid must be very weak, otherwise it will cause interaction of iodide and iodate. The use of acetic acid and sodium acetate mentioned by Müller and Friedberger was found to be unsatisfactory. Stearic acid and sodium stearate, palmitic acid and sodium palmitate, carbonic acid and sodium bicarbonate were tried, but satisfactory results were not obtained.

When boric acid and an iodide are added to a solution containing a periodate, the latter is converted to iodate and the liberated iodine can be titrated with thiosulfate. However, the iodate is affected slightly. This slight effect can be removed by the addition of borax (normal sodium borate also has the same effect) which diminishes the acidity of the boric acid to a sufficient extent to practically prevent the iodate reaction. (Table I.)

The titrations were performed at room temperature. The results show that addition of solid boric acid in excess and two grams of borax to the iodate solution gives such a very slight reaction between 0.1 *N* iodide and a 0.1 g. of iodate in a volume of 100 cc., and that the iodate influence may be considered negligible during the titration of the iodine resulting from the periodate decomposition.

TABLE I.—INFLUENCE OF BORIC ACID AND BORAX UPON THE REACTION BETWEEN IODATE AND IODIDE.

Volume 100 cc.

Expt. No.	Boric acid. G.	Borax. G.	Time. Hours.	KIO_3 present. G.	KIO_4 indicated. G.	Oxygen. indicated. G.
1	2	0.1	24	0.0892	0.0138	0.00096
2	2	0.2	24	0.0892	0.0048	0.00034
3	2	0.5	24	0.0892	0.00071	0.00005
4	2	1.0	24	0.0892	0.00021	0.00002
5	2	2.0	24	0.0892	...	...
6	2	4.0	24	0.0892	...	...
7	2	6.0	24	0.0892	...	...
8	4	...	24	0.0357	0.0437	0.00304
9	2	...	24	0.0892	0.0564	0.00355
10	solid in excess	2	24	0.0892	0.0003	0.00002

Allowing thiosulfate in excess to remain a short time in the presence of iodate does not cause reduction of iodate. However, periodate does react with thiosulfate, hence the periodate should be allowed to react completely with iodide before titration is commenced, otherwise, results may be vitiated to a greater or less extent. Three minutes is sufficient time to allow for the completion of the periodate reaction.

TABLE II.—DETERMINATION OF PERIODATE BY REACTION WITH IODIDE IN SOLUTIONS CONTAINING BORIC ACID AND BORAX.

Experiment No.	Added.		KIO_4.	
	Substance.	Gram.	Present. G.	Found. G.
1	...	..	0.2835	0.2839
2	...	..	0.2835	0.2836
3	...	..	0.1134	0.1135
4	...	..	0.0567	0.0568
5	...	..	0.5670	0.5669
6	KIO_3	0.0892	0.0567	0.0568
7	KIO_3	0.0892	0.1134	0.1137
8	KIO_3	0.0892	0.2835	0.2836
9	$KBrO_3$	0.1	0.1134	0.1135
10	$KClO_3$	0.1	0.1134	0.1132
11	$KClO_4$	0.1	0.1134	0.1136

A series of periodate titration results is given in Table II. In each experiment 2 g. of borax were added to the solution (about 90 cc.) containing the periodate in an Erlenmeyer flask, followed by an excess of solid boric acid and 10 cc. of normal potassium iodide. The total volume was 100 cc. in each instance. Three minutes' time was allowed for interaction of iodide and periodate, after which the resulting iodine was titrated with standard thiosulfate to the disappearance of the iodine color. The column "g. KIO_4 present" contains the amounts of periodate computed on the basis of the sodium arsenite titration in bicarbonate solution. The results of the two methods are thus seen to be in close agreement. Bromate, chlorate, perchlorate, as well as iodate, do not interfere.

Determination of Iodate in Presence of Bromate and Chlorate.

For the liberation of iodine from an iodide by iodate only a slight acidity of a mineral acid is required; however, bromate also reacts with iodide in only slightly acid solutions when mineral acids are used. With acetic acid there is a marked difference between iodate and bromate within certain limits of acidity (see Fig. 1). At room temperature (25°) it was found that 0.125 *N* acetic acid in presence of 0.1 *N* iodide would cause liberation of iodine corresponding to the entire oxidizing value of 0.1 g. of iodate in a volume of 100 cc. within three minutes. On the other hand 0.1 g. of bromate under the same conditions liberated a slight amount of iodine, sufficient to require 0.30 cc. of 0.1 *N* thiosulfate when the reaction had proceeded for three minutes. This bromate reaction can be retarded by the addition of sodium acetate, but when a sufficient amount is added to accomplish the purpose the speed of the iodate reaction is also lessened, requiring a much longer time for its reaction with the iodide and the lengthened time introduces the bromate influence again. The extent of the action of the bromate is appreciably lessened by lowering the temperature, the iodate being much less affected thereby. A very effective method found to be applicable was to chill to 3° or 4° the solu-

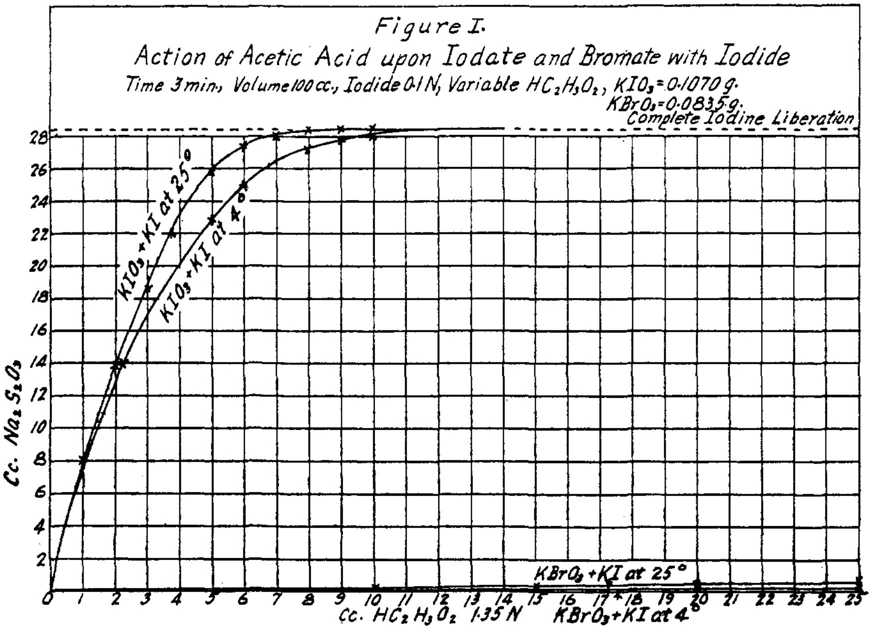

Figure I.

Action of Acetic Acid upon Iodate and Bromate with Iodide

Time 3 min., Volume 100 cc., Iodide 0·1 N, Variable $HC_2H_3O_2$, KIO_3=0·1070 g. $KBrO_3$=0·0835 g.

tion containing 0.25 *N* acetic acid and 0.1 *N* iodide, under which conditions 0.1 g. of potassium bromate in 100 cc. required 0.15 cc. of 0.1 *N* thiosulfate for titration of the iodine liberated at the end of three minutes. For smaller amounts of bromate a correspondingly smaller quantity of thiosulfate is required (see Table III).

Table III.—Determination of Iodate in Presence of Bromate.

Experiment No.	$KBrO_3$ present. G.	$Na_2S_2O_3$.			KIO_3	
		Total cc.	Blank cc.	Corrected cc.	present. G.	found. G.
1	0.0835	9.48	0.08	9.40	0.0357	0.0357
2	0.0557	9.44	0.04	9.40	0.0357	0.0357
3	0.0413	18.84	0.00	18.84	0.0714	0.0715
4	0.0278	28.24	0.02	28.22	0.1070	0.1070
5	0.0835	4.74	0.06	4.68	0.0178	0.0177
6	0.0835	1.04	0.10	0.94	0.0036	0.0036
7	0.0974	28.40	0.14	28.26	0.1070	0.1071
8	0.1531	28.48	0.18	28.30	0.1070	0.1073
9	0.1531	1.12	0.18	0.94	0.0036	0.0036

The procedure adopted for the determination of iodate in presence of bromate is as follows: A 0.1 g. sample* (or corresponding aliquot portion if in solution) is dissolved in about seventy cc. of water in an Erlenmeyer flask and the solution chilled in ice water for some time. To the cooled solution is added about 10 cc. of normal potassium iodide, followed by about 20 cc. of 1.25 *N* acetic acid also chilled in ice water. The time is noted and the solution allowed to stand a minute or more; then the titration with standard thiosulfate is completed at the end of a certain definite time—let us say three minutes (not less). The titration is conducted with the solution immersed in a dish of water containing an excess of ice. After the titration has been completed and the reading noted the solution is allowed to stand in ice water an equal length of time and more thiosulfate is again added to bleach any iodine which may have been produced by action of bromate. The second titration is the amount of thiosulfate which must be subtracted from the first titration, inasmuch as it represents the amount of bromate decomposed during the titration of the iodate. On the basis of the corrected volume of thiosulfate the iodate is computed. The results of Table III show that excellent results can be obtained in the presence of relatively small and large amounts of bromate, the only effect of the varying quantities of bromate being to vary the amount of the "blank" to be subtracted from the total volume of thiosulfate required in the first titration. Naturally, any periodate present with the iodate would be titrated by this procedure, thus giving a means of determining their total oxidizing value, and by application of the pre-

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* In some experiments of Table III larger amounts of bromate are used than corresponds to this weight of sample, the purpose being to show in more marked manner the effect of the bromate.

ceding titration of periodate in the presence of iodate the two can be determined in the presence of each other.

Determination of Bromate in Presence of Chlorate.

Bromate will liberate iodine from an iodide with much lower acidity than will chlorate; however, weak acids will not cause iodide to completely transpose the bromate within a reasonable period of time. A preliminary study of the effect of various acids and potassium iodide upon chlorate and bromate indicated dilute hydrochloric acid to be very well adapted for the determination of the bromate without chlorate interference (Fig. 2).

Table IV contains the results of determinations of bromate under various conditions. In all cases the temperature was that of the room (24°) except in Expt. 14, in which case the solutions were chilled in ice water to about 4°. The solutions were prepared by adding the acid after all the other reagents. Expts. 6–12 show a wide latitude in the amount of acid which may be added without introducing an appreciable error due to chlorate. Expts. 1–5 and 15–17 show that 0.1 g. of potassium bromate may be accurately titrated in 100 cc. of a solution which contains 0.05 *N* iodide and 0.2 *N* hydrochloric acid within a reasonable time after adding the various reagents.

TABLE IV.—DETERMINATION OF BROMATE IN THE PRESENCE OF CHLORATE.
Total volume in each experiment = 100 cc.

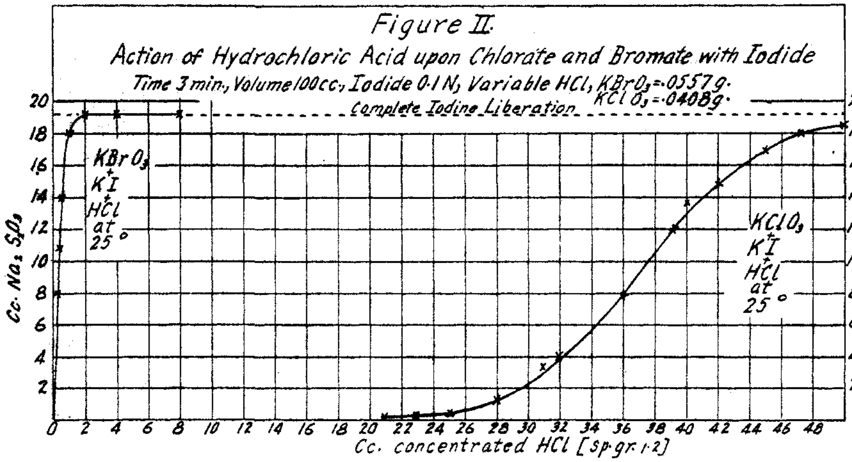
Experiment No.	KI. Normality.	HCl sp. gr. 1.1. cc.	Time. Min.	$KClO_3$ present. G.	$KBrO_3$ present. G.	$KBrO_3$ found. G.
1	0.05	2	1	..	0.0557	0.0474
	..	..	2	..	..	0.0505
	..	..	3	..	..	0.0513
2	0.05	3	1	..	0.0557	0.0550
	..	..	2	..	..	0.0559
3	0.05	5	Immediate	..	0.0557	0.0557
4	0.05	5	Immediate	..	0.1114	0.1114
5	0.05	5	Immediate	..	0.1392	0.1393
6	0.05	5	3	0.1021	..	0.0001*
7	0.05	10	3	0.1021	..	0.0001*
8	0.05	10	32	0.1021	..	0.0002*
9	0.05	20	3	0.1021	..	0.0002*
10	0.05	20	26	0.1021	..	0.0008*
11	0.05	25	3	0.1021	..	0.0002*
12	0.05	30	3	0.1021	..	0.0003*
13	0.05	45	3	0.1021	..	0.0029*
14	0.05	45	3	0.1021	(at 4°)	0.0001*
15	0.05	5	Immediate	0.1021	0.0557	0.0556*
16	0.05	5	Immediate	0.1021	0.1392	0.1393*
17	0.05	5	Immediate	0.1021	0.1114	0.1114*

* A slight trace of bromate was present in the chlorate used, which accounts for the slight liberation of iodine immediately and no more liberation for a considerable period of time in experiments 6–9, 11 and 12.

Should periodate or iodate be present they will give up their available oxygen to potassium iodide for iodine liberation and hence be titrated also. By use of the previously outlined methods the periodate, iodate and bromate may be determined in presence of each other.

Determination of Chlorate in the Presence of Perchlorate.

Perchlorate[47] will not readily liberate iodine from potassium iodide in acid solution at ordinary temperatures. Although chlorate has an inappreciable rate of reaction with iodide in dilute acid solution, when the acid concentration becomes considerably stronger the rate increases with increasing acidity very markedly, until the chlorate can be completely transposed with an equivalent liberation of iodine (Fig. 2).



As is well known, considerable care must be exercised when high concentrations of acid and iodide are involved to prevent the air from causing high results. The oxygen of the air, either directly or through the intermediate formation of ozone, liberates iodine quite readily from such solutions. If the temperature is increased the rate is much accelerated. Moreover iodine cannot be accurately titrated with thiosulfate in strong acid solutions, inasmuch as the latter decomposes the thiosulfate during titration. Hence the air in the flask must be replaced by an inert atmosphere, such as carbon dioxide, before starting the experiment. Likewise, the large excess of acid must be removed by neutralization or dilution before titration.

Various so-called "Inducing Agents"[37-43] were tried to increase the rate of reaction of chlorate and iodide at a low acid concentration, but they were not found to be as serviceable as was anticipated. Arsenious acid, cuprous chloride, manganous chloride, cerous chloride and thallous chloride produced practically no effect. Vanadyl salts and ferrous salts accelerated the reaction, but not to a sufficient extent to warrant their use for this purpose. The application of vanadium would introduce a colored solution which would also be a disadvantage. While the vanadium and iron salts increased the rate, it was difficult to make the last trace of chlorate react by the use of low acid concentration with these "inducers" present.

A method of treating the chlorate to form an equivalent amount of iodate and then titrating the iodate gives excellent results. This conversion is accomplished by liberating iodine by the reaction of the chlorate with iodide in strong acid solution and then dissolving the iodine by addition of alkali. After cooling the solution, it is made faintly acid with hydrochloric acid which causes reaction between iodate and iodide, and the iodine is then titrated with thiosulfate.

TABLE V.—DETERMINATION OF CHLORATE IN PRESENCE OF PERCHLORATE.

Experiment No.	HCl normality.	KI normality.	Total volume. cc.	Time. Min.	$KClO_4$ present. G.	$KClO_3$ present. G.	$KClO_3$ found. G.
1	2.7	0.10	100	3	..	0.0408	0.0008
2	2.7	0.10	100	6	..	0.0408	0.0015
3	2.7	0.10	100	15	..	0.0408	0.0032
4	4.1	0.10	100	3	..	0.0408	0.0039
5	4.1	0.10	100	6	..	0.0408	0.0076
6	5.4	0.10	100	3	..	0.0408	0.0340
7	5.4	0.10	100	6	..	0.0408	0.0373
8	5.4	0.10	100	15	..	0.0408	0.0404
9	5.4	0.20	100	3	..	0.0408	0.0347
10	5.4	0.20	100	6	..	0.0408	0.0378
11	5.4	0.20	100	15	..	0.0408	0.0408
12	6.7	0.20	100	3	..	0.0408	0.0402
13	6.7	0.20	100	6	..	0.0408	0.0405
14	6.7	0.20	100	15	..	0.0408	0.0408
15	6.7	0.20	100	5	..	0.0612	0.0609
16	6.7	0.20	100	15	..	0.0612	0.0611
17	5.6	0.16	120	5	..	0.1021	0.0980
18	5.6	0.16	120	10	..	0.1021	0.1011
19	5.6	0.16	120	12	..	0.1021	0.1022
20	5.6	0.16	120	15	..	0.1021	0.1021
21	5.6	0.16	120	21	..	0.1021	0.1021
22	6.0	0.20	100	15	0.1000	0.1021	0.1023
23	6.0	0.20	100	15	0.2000	0.1021	0.1022
24	6.0	0.20	100	15	0.5000	0.1021	0.1024
25	6.0	0.20	100	15	0.5000	..	0.0001

Table V contains a series of titration results with and without perchlorate present. In these experiments a 500 cc. glass-stoppered flask or bottle was used. Carbon dioxide was passed into the bottle or flask to remove the air, then the solutions were introduced in the amounts enumerated in the table. The flask or bottle was kept stoppered during the decomposition period. After lapse of the time specified the stopper, was removed, a watch glass or inverted crystallizing dish substituted and a slight excess of sodium hydroxide was added all at once and the solution shaken immediately, meantime cooling it in running water. 100 cc. of water were then added to wash down the sides of the vessel and to dilute the solution. The amount of sodium hydroxide was regulated by using a solution of such strength that each cubic centimeter neutralized one cubic centimeter of acid originally added. The use of a calculated amount makes it possible to add a slight excess of alkali at once, without danger of adding an insufficient amount, in which latter case iodine would be volatilized by the heat of reaction between the strong acid and alkali. The solution was cooled to room temperature, then hydrochloric acid (6 *N*) was added slowly with agitation of the solution until free iodine was liberated in quantity, followed by about 3 cc. more. The iodine was then titrated with thiosulfate.

The results given in Table V show that chlorate can be titrated iodimetrically without distillation. By the use of a pressure bottle and heating the solution the time of reaction and also the concentration of reagents could undoubtedly be reduced, but such a procedure would greatly increase the tendency for any slight amount of oxygen present in the bottle to react with the hydriodic acid, inasmuch as hot hydriodic acid readily reacts with the oxygen of the air. Experiments 9–21 show that 6 *N* hydrochloric acid and 0.2 *N* potassium iodide in a volume of 100 cc. will cause complete transposition of 0.1 g. of chlorate within a period of fifteen minutes at room temperature (21°). Experiments 6–11 indicate only a slight advantage of 0.2 *N* over 0.1 *N* iodide. Experiments 21–25 show that chlorate can be accurately titrated in the presence of perchlorate under the conditions outlined.

Periodate, iodate and bromate are also transposed by iodide in strong acid solutions, hence they would be titrated with chlorate in such solutions. In such cases the periodate, iodate and bromate should be titrated separately and the amount of chlorate ascertained by difference.

Analysis of Mixtures containing Periodate, Iodate, Bromate, Chlorate and Perchlorate.

Separate 0.1 g. samples are taken for each titration, for all except the periodate, in which case 0.2–0.3 g. samples are used, or a 2 g. sample is dissolved and diluted to a liter and 50-cc. portions (100 cc. in case of periodate) of the larger sample are used for the individual titrations.

Periodate.—The 0.2 g. sample in 100 cc. volume is treated in a suitable Erlenmeyer flask with 2 g. of borax, an excess of solid boric acid and 20 cc. of normal potassium iodide added, and the solution allowed to stand three minutes. The iodine is then titrated with standard sodium thiosulfate (about 0.1 *N*). Or, to the sample may be added sodium bicarbonate in excess, followed by 10 cc. of normal potassium iodide and titration of the iodine with standard arsenite solution.

Periodate and Iodate.—A 0.1 g. sample in 70 cc. of solution is chilled in ice water to about 3° or 4° and to the chilled solution is added 10 cc. of normal potassium iodide and 20 cc. of one-fourth normal acetic acid, also chilled in ice water. After standing a minute or two the thiosulfate titration is started and completed within a definite time from the moment of addition of acid and iodide (let us say three minutes, not less). The solution is then allowed to stand an equal time longer and any iodine which appears again titrated with thiosulfate. This second reading is subtracted from the first to give the corrected volume of thiosulfate equivalent to periodate and iodate.

Periodate, Iodate and Bromate.—To a 0.1 g. sample in a volume of about 90 cc. is added 10 cc. of normal potassium iodide and 5 cc. of six normal hydrochloric acid and the free iodine titrated with thiosulfate.

Periodate, Iodate, Bromate and Chlorate.—A 0.1 g. sample is dissolved in 50 cc. of water contained in a 500 cc. glass-stoppered bottle or flask and carbon dioxide passed into the vessel to effect as complete elimination of air as possible. 10–20 cc. of normal potassium iodide and 50 cc. of hydrochloric acid (sp. gr. 1.2) are added and the solution is allowed to stand 20 minutes. The stopper is then replaced by a watch glass or inverted small crystallizing dish, and while the solution is being cooled in running water, 50 cc. of sodium hydroxide solution (550 g. of 95% NaOH per liter of solution) are added *all at once* and the solution is twirled immediately.* After cooling the solution to room temperature 100 cc. of water are added to wash down the sides of the bottle or flask and for dilution. Six normal hydrochloric acid is then added slowly until iodine is liberated in quantity, followed by 3–5 cc. more of the acid. The free iodine is then titrated with the thiosulfate.

Perchlorate does not react readily with potassium iodide in acid solutions at ordinary temperatures and consequently cannot be determined in this manner.

The amount of thiosulfate required for each compound present is found by subtraction from each collective titration, the amount of thiosulfate, computed on the basis of equivalent samples, required for the next preceding groups titrated.

In the analysis of the mixtures given in Table VI the periodate, iodate, bromate, chlorate and perchlorate were weighed out accurately, transferred to a 250 cc. volumetric flask, dissolved in water and diluted to the mark. The potassium periodate contained iodate, hence the iodate con-

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* The solution at this point should be colorless, all the iodine being converted to iodate. If not colorless the heat of reaction will volatilize some iodine and cause low results, showing the addition of an insufficient amount of hydroxide.

tent of the periodate (as ascertained by previous analysis) weighed for each mixture, was added to the weight of iodate to get the actual iodate involved. Likewise the weight of periodate given is based upon the analysis. Aliquot portions were titrated by the method given previously and the weight of each compound of the mixture was computed. The perchlorate was calculated by difference.

TABLE VI.—ANALYSIS OF HALOGENATE MIXTURES.

	KIO_4		KIO_3		$KBrO_3$		$KClO_3$		$KClO_4$	
	present. G.	found. G.	present. G.	found. G.	present. G.	found. G.	present. G.	found. G.	present. G.	found. G.
Mixture I	0.2268	0.2268	0.2112	0.2110	0.0557	0.0562	0.0409	0.0410	0.1000	0.0998
Mixture II	0.1134	0.1136	0.3732	0.3728	0.0557	0.0561	0.0409	0.0406	0.1000	0.1001
Mixture III	0.0567	0.0565	0.0974	0.0974	0.2228	0.2231	0.0409	0.0405	0.1000	0.1003
Mixture IV	0.0567	0.0566	0.0974	0.0972	0.0557	0.0557	0.1636	0.1632	0.1000	0.1007
Mixture V	0.0567	0.568	0.0161	0.0162	0.2230	0.2230	0.0041	0.0040	0.1000	0.0997
Mixture VI	0.0057	0.0057	0.3576	0.3574	0.0056	0.0058	0.1636	0.1634	0.1000	0.1002

The results are thus seen to be good. The greatest error falls on the perchlorate, which has been determined entirely by difference. The perchlorate is introduced here mostly to show its negative effect on the other determinations, inasmuch as a method which relies entirely on calculation by difference is encumbered by many discrepancies and in general is not to be recommended. In a sense each titration, except the first one, involves a calculation by difference. However, the titration of the ingredient desired is a direct cumulative titration of the particular compound and on the basis of this increase its percentage or weight is computed. The result calculated from each titration is dependent only on that and the one next preceding. Periodates have a tendency to decompose with more or less ease, hence should be analyzed as soon as possible after weighing.

Summary.

1. Certain oxidizing agents can be determined in the presence of each other iodimetrically in a differential manner by regulation of the concentration of reagents, especially the acidity, the temperature and the time of reaction.

2. Periodate reacts completely with iodide in saturated boric acid solution, containing sufficient borax to diminish the acidity to a slight extent, forming iodate and free iodine.

3. Iodate is acted on by 0.1 N iodide in 0.25 N acetic acid solution and the free iodine can be titrated.

4. In 0.2 N hydrochloric acid solution containing 0.1 N iodide, bromate is completely decomposed, and the free iodine can be titrated.

5. 6 N hydrochloric acid acting in presence of 0.1–0.2 N iodide decomposes chlorate completely. After rendering the solution alkaline, and then acidifying the iodine can be titrated with thiosulfate.

6. By combination of 2, 3, 4 and 5, periodate, iodate, bromate and chlorate can be determined differentially in the presence of each other and in the presence of perchlorate.

The differential deportment of other oxidizing agents will also be studied.

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THE ELECTROMETRIC TITRATION OF VANADIUM.

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The titration of chromates with ferrous sulfate, using as an end point the change in potential of a platinum electrode immersed in the solution