Art. XXV.—*A Method for the Determination of Iodine in Haloid Salts;* by F. A. Gooch and P. E. Browning.

(Contributions from the Kent Chemical Laboratory of Yale College.—I.)

Few problems of analysis have been more discussed than the estimation of iodine accompanying chlorine and bromine in haloid salts; and yet the constant succession of new processes is sufficiently indicative that the solution of the question is not generally regarded as satisfactorily settled. The method of Fresenius, according to which iodine is liberated by nitrous acid, collected in carbon disulphide and titrated by sodium thiosulphate, finds ready acceptance for the determination of small amounts of iodine; but when the quantity of iodine to be estimated is considerable, the method is unwieldy. Probably the process most generally in use is that based upon the liberation of iodine by means of a ferric salt, and the titration of the distillate by one or other of the well-known iodometric methods. The latter method is fairly accurate, but the requirement of special apparatus for properly condensing the distillate is detrimental to rapidity and ease of execution. In this process the amount of iodine set free should be measured exactly by the reduction of the ferric salt, and were the ferrous salt produced in the course of the action sufficiently stable, the determination of its amount might be substituted for the titration of the iodine, and so the collection and further treatment of the distillate might be dispensed with; but ferrous salts are too sensitive to atmospheric influence to preserve under the conditions of this process their own degree of oxidation, and the amount of iron found in the ferrous condition cannot be made to serve as a trustworthy indication of the reducing action which actually takes place in the separation of the iodine. The advantage of replacing the collection and ex-

* Ann. chim. et phys. III, vol. vii, p. 489, 1843; Manuel de Minéralogie, vol. ii, p. 119, 1874.

† Traité, 2d ed., vol. ii, p. 37, 1822.

amination of the distillate by treatment of the residue is, however, so great as to constrain us to search for some substitute for the ferric salt, which, by virtue of easy reducibility may act as a liberator of iodine from hydriodic acid, and, at the same time, by reason of stability after reduction, shall register accurately the quantity of iodine set free in the reducing process. The results of our experience are contained in the following account.

Strong sulphuric acid, as is well known, acts upon an iodide in a way to liberate iodine at the cost of its own loss of oxygen, though by simple dilution of the mixture thus formed the action is reversed, the iodine going back into the form of hydriodic acid, and the products of the reduction of sulphuric acid again taking back their oxygen and re-forming the acid. In the presence of any substance easily reducible by the deoxidation products of sulphuric acid the liberation of iodine, by the action of that acid upon iodides, should take place without interference, and even more easily and completely than in the absence of such a substance, while the sulphuric acid should remain at the end of the process in its original form. If the products of reduction which appear in such a case in the place of those of the sulphuric acid should be neither readily oxidizable nor easily volatilizable, it ought to be possible to remove by heat the iodine set free in the action without disturbing the record kept of its amount by the reduced substance remaining in the residue.

The qualities of arsenic acid suggest it as a substance likely to possess just these qualities; for, though arsenious acid is converted into arsenic acid by the action of iodine in alkaline solution, in acid solution the reverse is true to at least a limited extent, and arsenic acid liberates iodine according to the equation,

$$H_3AsO_4 + 2HI = H_3AsO_3 + H_2O + I\text{-}I.$$

In company with sulphuric acid of such strength as to liberate the iodine from hydriodic acid, the reduction should fall in the end upon the arsenic, and the arsenious oxide produced should, under proper conditions, preserve the record of the iodine liberated and removed by volatilization. We therefore undertook experimentation upon this line, and the accompanying table shows the results of a preliminary investigation of the mode of action of a mixture of sulphuric and arsenic acids upon an alkaline iodide. In making these tests a standard solution of potassium iodide was put into a test-tube, a solution of potassium arseniate was added, sulphuric acid mixed with its own volume of water was introduced, the volume of the liquid was adjusted, a film of kerosene 3 mm. thick was placed upon the surface of the liquid, and the whole was heated gently and agitated. Kerosene was chosen in preference to other solvents of iodine on account of its lightness, which makes it float upon the mixture, and its high boiling-point, which permits the application of heat to hasten and complete the reaction. Its disadvantage is the persistency with which it adheres to the walls of the test-tube, so that washing with alcohol (or other solvent) after the completion of each test is necessary to prevent the transfer of the iodine of one test to the test next succeeding. The data of these experiments are indicated in the headings.

It will be noted that in Series A, in which the absolute amount of iodine employed, its proportion to the entire volume, and the amount of the arsenic salt remained the same, the proportion of sulphuric acid being the variable element, it is shown that the proportion of sulphuric acid should reach at least twelve parts by volume in one hundred of the solution in order that the maximum distinctness of the test may be developed. An excess of sulphuric acid beyond this proportion is not disadvantageous.

In Series B the proportion and absolute amount of iodine vary as well as the proportion of acid, while the quantity of arsenic remains invariable. The results of this series confirm those of the previous series as to the proper proportion of sulphuric acid to be used, and the sensitiveness of the test is shown to reach (in round numbers) one part by weight of iodine in six hundred thousand parts of the solution.

The tests of Series C indicate plainly that it is the sulphuric acid which is the potent agent in liberating the iodine, the experiment in which acetic acid was substituted for sulphuric acid being particularly noteworthy in this connection. The presence of arsenic acid increases the sensitiveness of the reaction, but its addition beyond a very moderate amount does not appear to be necessary or advantageous. The presence of a chloride or bromide does not impair the delicacy of the test.

The quantities of iodine taken in the experiments just described were necessarily small, and the question arises naturally as to whether the course of action would be similar in the presence of larger amounts of that substance and the correspondingly greater amount of arsenious oxide which is produced with its tendency to reverse the reaction according to which the elimination of iodine proceeds. The solution of this question was reached in the following experiments:

To 50 cm^3 of liquid containing 10 cm^3 of sulphuric acid [1 : 1], and 1 cm^3 of a decinormal solution of iodine in potassium iodide (0·001265 grm. of the former in 0·0018 grm. of the latter) was added 1 cm^3 of a decinormal solution of arsenious oxide (0·00495 grm.), an amount ten times as much as would be necessary to convert the iodine into hydriodic acid were the solution alkaline. The color of the iodine vanished gradually under the action of the arsenious acid, but was restored by the addition of 1 grm. of hydrogen potassium arseniate, and again dispelled by another portion of arsenious acid equal in amount to that introduced at first. Heat was applied at this

SERIES A.

KI.	Grms. of Iodine to cm³ of solution.	H_2KAsO_4	H_2SO_4. [1 : 1]	H_2SO_4 (strong) in 100 parts by volume.	NaCl.	KBr.	Total vol.	Reaction for Iodine.
grm.		grm.	cm³		grm.	grm.	cm³	
0·0001	1 : 132000	1	2	10 : 100	----	----	10	Faint.
0·0001	1 : 132000	1	2	10 : 100	----	----	10	Faint.
0·0001	1 : 132000	1	2·5	12·5 : 100	----	----	10	Faint.
0·0001	1 : 132000	1	2·5	12·5 : 100	----	----	10	Distinct.
0·0001	1 : 132000	1	3	15 : 100	----	----	10	Distinct.
0·0001	1 : 132000	1	4	20 : 100	----	----	10	Distinct.
0·0001	1 : 132000	1	4·5	22·5 : 100	----	----	10	Distinct.
0·0001	1 : 132000	1	5	25 : 100	----	1	10	Distinct.

SERIES B.

0·0005	1 : 26400	1	2·5	12·5 : 100	----	----	10	Distinct.
0·000133	1 : 99000	1	2·5	12·5 : 100	----	----	10	Distinct.
0·0001	1 : 198000	1	3	10 : 100	0·007	----	15	Faint.
0·000067	1 : 198000	1	2·5	12·5 : 100	----	----	10	Faint.
0·000067	1 : 198000	1	2·5	12·5 : 100	----	1	10	Faint.
0·0001	1 : 198000	1	5	16·6 : 100	0·005	----	15	Distinct.
0·0001	1 : 198000	1	5	16·6 : 100	0·005	----	15	Distinct.
0·0001	1 : 264000	1	2 5	6·25 : 100	----	----	20	Invisible.
0·0001	1 : 264000	1	2·5	6·25 : 100	----	----	20	Faint.
0·0001	1 : 264000	1	5	12·5 : 100	----	----	20	Faint.
0·000033	1 : 396000	1	2·5	12·5 : 100	----	----	10	Faint.
0·000033	1 : 396000	1	2·5	12·5 : 100	----	----	10	Faint.
0·000033	1 : 594000	1	5	16·6 : 100	0 005	----	15	Faint.

SERIES C.

0·0020	1 : 8000	1	None. Acetic acid 1·5 grm. (absolute).	----	----	----	12	Invisible.
0·0010	1 : 13200	----	5 cm³	25 : 100	----	----	10	Distinct.
0·0002	1 : 66000	----	5·	25 : 100	----	----	10	Faint.
0·0010	1 : 13200	0·2	5	25 : 100	----	----	10	Marked.
0·0001	1 : 132000	0·2	5	25 : 100	----	----	10	Distinct.
0·000033	1 : 198000	0·5	1 25	12·5 : 100	----	----	5	Faint.
0·000033	1 : 198000	0·5	1·25	12 5 : 100	----	----	5	Faint.
0·0001	1 : 264000	2 0	4	10 : 100	----	----	20	Faint.
0·0001	1 : 264000	2·0	6	15 : 100	----	----	20	Faint.

point with the result that the color of iodine showed again faintly, and upon boiling the liquid until its volume decreased to 25 cm³ it became colorless and yielded no iodine when agitated with nitrous acid and chloroform.

An experiment differing from the last in that thirty times as much arsenious oxide and iodine were taken, gave similar results.

It is plain, therefore, that the arsenious acid and arsenic acid exert opposite effects under the conditions of these experiments, and that one or the other prevails according to the proportionate composition of the solution, the degree of dilution, and the temperature.

The experiments detailed in the following statement were intended to determine the conditions best adapted to eliminate the iodine from such quantities of potassium iodide as would ordinarily be dealt with in the course of analysis.

A solution of potassium iodide was placed in an Erlenmeyer beaker of 300 cm^3 capacity, followed by a solution of potassium arseniate and by dilute sulphuric acid [1 : 1], and the volume of the liquid was diluted to about 100 cm^3. A mark was put upon the beaker to indicate the level to which the liquid was to be reduced, a spiral of platinum wire was placed in the solution to prevent explosive ebullition, and the contents of the flask were boiled until the desired degree of condensation was reached. Colorlessness of the liquid at this point, though a fair indication of the absence of free iodine, is no indication that the hydriodic acid has been completely decomposed, and so, in the event of finding the liquid colorless, it was first cooled and shaken with chloroform to prove or disprove the absence of free iodine, and then tested for the presence of hydriodic acid by shaking with nitrous acid and chloroform.

An inspection of these results shows at once that when the larger amounts of iodine are to be eliminated the proportion of sulphuric acid to the final volume after boiling needs to be increased somewhat beyond that which is necessary to set free very small portions such as were dealt with in the experiments of the earlier series.

In Series D it appears that the proportion of sulphuric acid increases from 8·3 per cent to 25 per cent of the whole volume before the liquid is found to be free from iodine as such, and even then there sometimes remain minute, though probably insignificant traces of hydriodic acid.

In the experiment of Series E the liquid was diluted after concentration and the boiling repeated, and the volatilization of the iodine was thus more nearly perfected than in the corresponding experiments of the previous series—a proportion amounting to 16·6 per cent apparently accomplishing the work done by 25 per cent of the same acid in a single concentration. The results of Series F, G, and H, are closely comparable with those of the corresponding experiments of Series D. Throughout these experiments it is again made evident that it is the proportion, and not the absolute amount, of sulphuric acid which is the great factor in the liberation of the iodine. So far as concerns the purposes of good analysis these results indicate the elimina-

Series D.

KI.	H_2SO_4 [1:1].	Per cent of strong H_2SO_4 by volume.	H_2KAsO_4.	Final volume.	Free Iodine.	Combined Iodine.
0·5 grm.	10 cm^3	8·3	1 grm.	60 cm^3	Present	Abundant.
0·5	10	10	1	50	Present	Abundant.
0·5	10	12·5	2	40	Present	Distinct.
0·5	10	12·5	2	40	Trace	Distinct.
0·5	10	12·5	4	40	Trace	Distinct.
0·5	10	16·6	1	30	Trace	--------
0·5	10	16·6	2	30	Trace	--------
0·5	10	16·6	2	30	Trace	--------
0·5	10	16·6	4	30	None	Distinct.
0·5	10	16·6	5	30	Trace	Distinct.
0·5	10	25	1	20	None	Faintest trace.
0·5	10	25	2	20	None	Faintest trace.
0·5	10	25	2	20	None	Faintest trace.
0·5	10	25	2	20	None	Faintest trace.
0·5	10	25	2	20	None	Faintest trace.

Series E.

0·5 grm.	10 cm^3	16·6	1 grm.	30 cm^3 / 30	None	Faintest trace.
0·5	10	16·6	1	30 / 30	None	Faintest trace.
0·5	10	16·6	1	30 / 30	None	Faintest trace.
0·5	10	16·6	1	30 / 30	None	Faintest trace.

Series F.

0·5 grm.	15 cm^3	25	2 grm.	30 cm^3	None	Faintest trace.
0·5	15	25	2	30	None	Faintest trace.
0·5	15	25	4	30	None	Faintest trace.

Series G.

0·5 grm.	20 cm^3	25	2 grm.	40 cm^3	None	Faintest trace.
0·5	20	25	2	40	None	Faintest trace.
0·5	20	25	2	40	None	None.
0·5	20	28·6	2	35	None	None.
0·5	20	28·6	2	35	None	None.
0·5	20	33·3	2	30	None	None.

Series H.

0·5 grm.	30 cm^3	25	2 grm.	60 cm^3	None	Faintest trace.
0·5	30	25	2	60	None	Faintest trace.

tion of iodine to a reasonable sufficiency when the reduction of bulk raises the percentage by volume of the strong sulphuric acid to twenty-five, and to perfection, as in the latter determinations of Series G, when the percentage reaches twenty-eight and a half. It remains to be seen whether the arsenious oxide reduced in the separation of the iodine will resist successfully, under the conditions of these experiments, the tendency to volatilize which the presence of chlorides and bromides, and the consequent liberation of hydrochloric and hydrobromic acids, might presumably induce.

The experiments of Series I were directed to the elucidation of this point.

Decinormal solutions of iodine and arsenious acid prepared, standardized, and tested against one another in the usual manner. Definite portions of the solution of arsenious acid were measured from a burette into Erlenmeyer beakers such as were used in the previous experiments, sulphuric acid [1 : 1], and sodium chloride were added, the volume of the liquid was adjusted to 100 cm^3, or a little more, and the process of concentration by boiling was carried to the point desired and indicated by a mark upon the flask. After cooling, the acid was neutralized and the titration effected in the usual manner in the presence of an excess of acid potassium carbonate and starch employed as the indicator. These experiments were arranged upon the presumption that the essential conditions determining the degree of volatility of the arsenic when the reduction is effected by hydriodic acid are imitated, though neither hydriodic acid, nor arsenic acid, nor free iodine is present.

SERIES I.

H_2SO_4 [1:1].	NaCl.	Final volume.	Per cent of strong H_2SO_4 by volume.	As_2O_3 taken.	As_2O_3 found.	Loss.
10 cm^3	1 grm.	20 cm^3	25	0·0495 gr.	0·0485 gr.	0·0010 gr.—
10	1	20	25	0·0495	0·0493	0 0002 —
10	1	20	25	0·0495	0·0488	0·0007 —
10	0·8	20	25	0·0495	0·0488	0·0007 —
10	0·5	20	25	0·0405	0·0495	0·0000
20	1	40	25	0 0495	0·0490	0·0005 —
20	1	40	25	0·0495	0·0490	0·0005 —
20	0·8	40	25	0 0495	0·0490	0·0005 —
20	0·5	40	25	0·0495	0·0490	0.0005 —
20	0·5	40	25	0·1385	0·1380	0·0005 —
20	1	30	33·3	0·0495	0·0476	0·0019 —
20	0·8	30	33·3	0·0495	0·0466	0·0029 —
20	0·5	30	33·3	0·0495	0·0481	0·0014 —
20	0·5	30	33·3	0·0495	0·0485	0 0010 —
20	0·5	30	33·3	0·0595	0·0490	0·0005 —
20	0·5	30	33·3	0 0495	0·0490	0·0005 —
20	0·5	30	33·3	0·0495	0·0490	0·0005 —
30	1	60	25	0·0495	0·0485	0·0010 —
30	0·8	60	25	0·0495	0·0490	0 0005 —
30	0·8	60	25	0·0495	0 0490	0·0005 —
30	0·5	60	25	0·0495	0·0490	0·0005 —

SUMMARY OF SERIES I.

H_2SO_4 [1:1].	Final volume.	Per cent of strong H_2SO_4 by volume.	NaCl.	Mean loss of As_2O_3.	Number of determination.
10 cm^3	20 cm^3	25	1 grm.	0·0006 gr—	3
20	40			0·0005 —	2
30	60			0·0010 —	1
10	20	25	0·5 and 0·8	0·0003 —	2
20	40			0·0005 —	3
30	60			0·0005 —	3
20	30	33·3	0·5	0 0008 —	5
			0·8	0·0019 —	1
			1·0	0·0029 —	1

It appears in these results that there is some loss of arsenic in nearly every case within the limits of our experimentation, the amount of volatilization increasing with the ratio of sulphuric acid to the entire volume when the quantity of chloride present is constant, and likewise with the amount of chloride when the ratio of the acid to the total liquid is constant.

The effect of increasing the amount of chloride is naturally accounted for by the "mass action" of the hydrochloric acid thus liberated upon the arsenious oxide in solution; that it is the proportion, and not the absolute amount, of sulphuric acid which determines the degree of volatility of the arsenic is explicable upon the assumption that the smallest quantity of sulphuric acid employed is sufficient to liberate all the hydrochloric acid (or, at least, nearly all), and that this, by its action on the arsenious oxide, forms the volatile chloride proportionately to the amount of water removed bodily by concentration or withheld from effective action by the attraction of the sulphuric acid.

In extending this line of experimentation to cases involving the action of hydrobromic acid upon arsenious oxide we found it sufficient for our purpose to employ only the highest degree of concentration recorded in the previous experiments and to use 1 grm. of potassium bromide—an amount corresponding, molecule for molecule, to about 0·5 grm. of sodium chloride. The results, given in Series J, indicate that under these circumstances the loss of arsenic is inappreciable.

SERIES J.

H_2SO_4 [1:1].	KBr.	Final volume.	Per cent of strong Hs_2SO_4 by volume.	As_2O_3 taken.	As_2O_3 found.	Loss.	Mean loss.
	grm.			grm.	grm.	grm.	grm.
20 cm^3	1	30 cm^3	33·3	0·0495	0·0490	0·0005	0·0001—
20	1	30	33·3	0·0495	0·0493	0·0002	
20	1	30	33·3	0·0495	0·0495	0·0000	
20	1	30	33·3	0·0495	0·0495	0·0000	
20	1	30	33·3	0 0495	0 0495	0·0000	

It appears, therefore, from the results of Series I, that, when the amount of sodium chloride present is restricted to 0·5 grm., the liquid may be boiled until the sulphuric acid amounts to 33·3 per cent of it, with a loss, on the average, of 0·0008 grm. of arsenious oxide, and to 25 per cent with a loss of 0·0004 grm. With either of these proportions the results are sufficiently favorable to warrant quantitative testing of a method for separating chlorine and iodine based upon the volatility of iodine and the non-volatility of arsenious oxide under the conditions. The case is even more favorable for the similar separation of bromine from iodine—the loss of arsenic amounting on the average to 0·0001 grm., under similar conditions. The experiments of Series D to H indicated that the degree of concentration at which all iodine vanishes from the liquid corresponds to the presence of 28·6 per cent of the acid—a point midway between the points of concentration indicated above. We fixed this proportion, therefore, for the following experiments, as being rather more favorable as regards the fixity of the arsenic and perfect as to the elimination of iodine. The smallest absolute amount of sulphuric acid which we have used—10 cm^3 of the [1 : 1] mixture—demands evaporation of the liquid to a bulk too small to be easily determined with certainty in flasks of the shape and dimensions which we found convenient for this work. The larger amounts of acid are uncomfortably large in the subsequent neutralization. We took, therefore, 20 cm^3 of the [1 : 1] mixture of sulphuric acid and water as the amount best adapted to our purpose and set the limit of concentration at 35 cm^3.

The potassium iodide which we used was prepared with great care, by acting with re-sublimed iodine upon iron wire, three-fourths of the iodine being added to an excess of iron covered with distilled water, decanting the solution from the excess of iron when the color of iodine had vanished, adding the remainder of the iodine, pouring the filtered solution slowly into boiling water, to which the exact amount of acid potassium carbonate necessary to combine with the iodine had been added, and filtering off the magnetic oxide of iron thus precipitated. The solution of potassium iodide thus made, very faintly alkaline and entirely free from chlorine and bromine, was made up to a suitable volume and standardized by precipitating the iodine of aliquot portions by weight as silver iodide, which was heated and weighed upon asbestos. Weighed portions of this solution, containing approximately 0·5 grm. of potassium iodide to 30 cm^3, were taken for the tests in which the larger quantities of iodine were introduced; measured portions of a solution made by diluting the former were employed in the tests involving the smaller amounts.

The sodium chloride and potassium bromide used were shown to be free from iodine, and the hydrogen potassium arseniate contained no arsenious acid.

The mode of proceeding was, in general, like that of the previous experiments. The solution of potassium iodide was put in an Erlenmeyer beaker of 300 cm^3 capacity, two grams of hydrogen potassium arseniate were added in solution and followed by 20 cm^3 of sulphuric acid [1 : 1], the liquid was diluted with water to a little more than 100 cm^3, a platinum spiral was placed in the flask to secure quiet ebullition, a trap made by cutting off a two-bulb drying tube about an inch from the inside bulb was hung, large end downward, in the mouth of the flask to prevent mechanical loss, and the liquid was boiled until the level reached the 35 cm^3 mark put upon the flask. At this point the flask was cooled, the acid nearly neutralized with sodium hydrate in solution, the neutralization completed by acid potassium carbonate, 20 cm^3 of the last being added in excess, a definite portion of starch indicator added, and the contents in arsenious acid determined by titration with a decinormal solution of iodine for the larger amounts, and a centinormal solution for the smaller. Due correction was made for the amount of iodine necessary to develop the test-color in a solution prepared and treated similarly in all respects to the experimental solutions excepting the introduction of the iodide—the correction amounting to a single drop more of the decinormal solution than was required to produce the end reaction in the same volume of pure water containing only the starch indicator.

The decinormal solution of iodine was made by dissolving 12·65 grms. of carefully resublimed iodine in potassium iodide (proved free from iodate) and diluting to a liter. The centinormal solution was made by diluting the stronger solution. The standardizing was effected by comparison with a solution of arsenious oxide containing 4·95 grm. to the liter. This mode of fixing the value of the solution should, and, as the sequel proved, did indicate the correct standard, but for the sake of confirmation the value of the arsenic solution was redetermined by titration against iodine specially purified by subliming off potassium iodide, re-subliming between watch-glasses, and exposing during forty-eight hours over sulphuric acid. Portions of the iodine thus prepared were weighed in a glass-stoppered weighing bottle, dissolved in the same without danger of volatilization by introducing pure solid potassium iodide and a little water, and diluted and treated with the solution of arsenious acid measured from a burette until the color of iodine vanished. The excess of arsenious oxide was determined by titrating against the standard solution of iodine whose value in terms of measured portions of the solution of arsenious oxide was perfectly known.

In Series K are detailed experiments which follow the line marked out for the separation of iodine from chlorine and bromine in the haloid salts, excepting that the iodide was entirely omitted for the purpose of discovering whether hydrochloric and hydrobromic acids possess reducing action upon arsenic acid under the conditions. The evidence is plain that no arsenious oxide is formed by the action of 0·5 grm. of sodium chloride upon 2 grm. of the arseniate under the circumstances as given.

Hydrobromic acid, on the contrary, is slightly decomposed with the evolution of bromine enough to give visible color to the concentrated liquid, but the amount of bromine lost, as indicated by the arsenious acid produced in its evolution, is only 0·0003 grm. for 0·5 grm. of potassium bromide, and 0·0001 grm. for 0·1 grm. of the bromide. Further experiments indicated, however, that concentration cannot go on to a volume less than 35 cm^3 without causing serious loss when the maximum amount of bromide is present.

SERIES K.

H_2SO_4 [1:1].	H_2KAsO_4.	NaCl.	KBr.	Final volume.	Iodine corresponding to As_2O_3 reduced.	Chlorine corresponding (average).	Bromine corresponding (average)
					grm.	grm.	grm.
20 cm^3	2 grm.	0·5 grm.	--	35 cm^3	0·0000		
20	2	0·5	--	35	0·0000	0·0000	----
20	2	0·5	--	35	0·0000		
20	2	--	0·1 grm.	35	0·0003		
20	2	--	0·1	35	0·0001	----	0·0001
20	2	--	0·1	35	0·0001		
20	2	--	0·5	35	0·0005		
20	2	--	0·5	35	0·0005	----	0·0003
20	2	--	0·5	35	0·0005		

In Series L are given the results of twenty-six determinations of iodine by the method outlined.

Upon inspection of these results it appears that the method is good and reliable under all the conditions tested.

When neither chloride nor bromide is present, the iodine is determinable with a mean error of 0·0002 grm.

When sodium chloride accompanies the iodide, the results show a loss of arsenious oxide and a consequent apparent deficiency of iodine—as we should expect in accordance with the indications of Series I. This deficiency proves to be proportional to the amount of iodide broken up, or the arsenious oxide thus produced. For 0·56 grm., approximately, of potassium iodide and 0·5 grm. of sodium chloride the deficiency measured in iodine amounted to 0·0011 grm. When the potassium iodide is decreased ten-fold (or more) the deficiency falls to

0·0002 grm. It should be recalled, too, in this connection that the results of Series J pointed to increasing volatility of the arsenic with the increase of the sodium chloride present.

SERIES L.

No.	H_2SO_4 [1:1].	H_2KAsO_4.	NaCl.	KBr.	Final vol.	KI taken.	Theory for Iodine.	Iodine found.	Error.	Average error.
		grm.				grm.	grm.	grm.	grm.	grm.
(1)	20 cm³	2	....	....	35 cm³	0·5616	0·4080	0·4079	0·0001−	
(2)	20	2	....	....	35	0·5630	0·4091	0·4086	0·0005−	
(3)	20	2	....	....	35	0·5622	0·4083	0·4086	0·0003+	
(4)	20	2	....	....	35	0·0506	0·0400	0·0396	0·0004−	
(5)	20	2	....	....	35	0·0506	0·0400	0·0391	0·0009−	0·0002−
(6)	20	2	....	....	35	0·0506	0·0400	0·0400	0·0000	
(7)	20	2	....	....	35	0·0506	0·0400	0·0401	0·0001+	
(8)	20	2	....	....	35	0·0051	0·0040	0·0037	0·0003−	
(9)	20	2	....	....	35	0·0051	0·0040	0·0038	0·0002−	
(10)	20	2	0·5	....	35	0·5611	0·4077	0·4066	0·0011−	
(11)	20	2	0·5	....	35	0·5619	0·4082	0·4073	0·0009−	0·0011−
(12)	20	2	0·5	....	35	0·5624	0·4086	0·4073	0·0013−	
(13)	20	2	0·5	....	35	0·0506	0·0400	0·0402	0·0002+	
(14)	20	2	0·5	....	35	0·0506	0·0400	0·0395	0·0005−	0·0002−
(15)	20	2	0·5	....	35	0·0051	0·0040	0·0037	0·0003−	
(16)	20	2	0·5	....	35	0·0051	0·0040	0·0037	0·0003−	
(17)	20	2	....	0·5	35	0·5619	0·4082	0·4092	0·0010+	
(18)	20	2	....	0·5	35	0·5697	0·4138	0·4136	0·0002−	0·0008+
(19)	20	2	....	0·5	35	0·5622	0·4083	0·4099	0·0016+	
(20)	20	2	....	0·5	35	0·0506	0·0400	0·0410	0·0010+	
(21)	20	2	....	0·5	35	0·0506	0·0400	0·0404	0·0004+	0·0008+
(22)	20	2	....	0·5	35	0·0051	0·0040	0·0048	0·0008+	
(23)	20	2	....	0·5	35	0·0051	0·0040	0·0049	0·0009+	
(24)	20	2	0·5	0·5	35	0·5626	0·4087	0·4083	0·0004−	
(25)	20	2	0·5	0·5	35	0·5660	0·4112	0·4111	0·0001−	0·0003−
(26)	20	2	0·5	0·5	35	0·5622	0·4083	0·4079	0·0004−	

The presence of potassium bromide results in the liberation of minute amounts of bromine and a consequent increase in the arsenious oxide and apparent excess of iodine. The mean error due to this cause is 0·0008 grm. for 0·5 grm. of the bromide, and the variation in the quantity of iodide present is without effect upon it.

The simultaneous action of the chloride and bromide tends, of course, to neutralize the error due to each. Thus, in the mixture weighing about 1·5 grm. and consisting of sodium chloride, potassium bromide, and potassium iodide in equal parts, the mean error amounts to 0·0003 grm. −. The largest error in the series is 0·0016 grm. +, when the bromide was at its maximum and no chloride was present; and the next largest was 0·0013 grm. − when the chloride was at its maximum and no bromide was present.

It is obvious that when the amounts of chloride and bromide present are known approximately it is possible to apply corrections which shall eliminate errors in the indicated amount of iodine due to the action of these substances. From the averages of Series L it is apparent that the amount to be added in each case may be obtained by multiplying the product of the weights in grms. of sodium chloride and potassium iodide by the constant 0·004; and the amount to be subtracted, by multiplying the weight in grms. of potassium bromide by 0·0016. Thus, for example, the correction in (24) will be 0·0011 grm.+ (=0·5 × 0·56 × 0·004) and 0·0008 grm. − (=0·5 × 0·0016). The individual results of Series L thus corrected will stand as follows;

No. of Exp.	Theory for Iodine.	Corrected amount of Iodine found.	Error.	Mean error.
(1)	0·4080 grm.	0·4079 grm.	0·0001 grm. −	0·0001 grm. −
(2)	0·4091	0·4086	0·0005 −	
(3)	0·4083	0·4086	0·0003 +	
(4)	0·0400	0·0396	0·0004 −	
(5)	0·0400	0·0391	0·0009 −	
(6)	0·0400	0·0400	0·0000	
(7)	0·0400	0·0401	0·0001 +	
(8)	0·0040	0·0037	0·0003 −	
(9)	0·0040	0·0038	0·0002 −	
(10)	0·4077	0·4077	0·0000	
(11)	0·4082	0·4084	0·0002 +	
(12)	0·4086	0·4084	0·0002 −	
(13)	0·0400	0·0403	0·0003 +	
(14)	0·0400	0·0396	0·0004 −	
(15)	0·0040	0·0037	0·0003 −	
(16)	0·0040	0·0037	0·0003 −	
(17)	0·4082	0·4084	0·0002 +	
(18)	0·4138	0·4128	0·0010 −	
(19)	0·4083	0·4191	0·0008 +	
(20)	0·0400	0·0402	0·0002 +	
(21)	0·0400	0·0396	0·0004 −	
(22)	0·0040	0·0040	0·0000	
(23)	0·0040	0·0041	0·0001 +	
(24)	0·4087	0·4086	0·0001 −	
(25)	0·4112	0·4114	0·0002 +	
(26)	0·4083	0·4082	0·0001 −	

The mode of proceeding in the analysis of a mixture of alkaline chlorides, bromides and iodides, according to this method may be briefly summarized as follows:

The substance (which should not contain of chloride more than an amount corresponding to 0·5 grm. of sodium chloride, nor of bromide more than corresponds to 0·5 grm. of potassium bromide, nor of iodide much more than the equivalent of 0·5 grm. of potassium iodide) is dissolved in water in an Erlenmeyer beaker of 300 cm^3 capacity, and to the solution are added 2 grms. of dihydrogen potassium arseniate dissolved in water, 20 cm^3 of a mixture of sulphuric acid and water in equal volumes, and enough water to increase the total volume to 100 cm^3, or a little more. A platinum spiral is introduced, a trap made of a straight two-bulb drying-tube cut off short is hung with the larger end downward in the neck of the flask, and the liquid is boiled until the level reaches the mark put upon the flask to indicate a volume of 35 cm^3. Great care should be taken not to press the concentration beyond this point on account of the double danger of losing arsenious chloride and setting up reduction of the arseniate by the bromide. On the other hand, though 35 cm^3 is the ideal volume to be attained, failure to concentrate below 40 cm^3 introduces no appreciable error. The liquid remaining is cooled and nearly neutralized by sodium hydrate (ammonia is not equally good), neutralization is completed by hydrogen potassium carbonate, an excess of 20 cm^3 of the saturated solution of the latter is added, and the arsenious oxide in solution is titrated by standard iodine in the presence of starch.

With ordinary care the method is rapid, reliable and easily executed, and the error is small. In analyses requiring extreme accuracy all but accidental errors may be eliminated from the results by applying the corrections indicated.