evident that the characteristics of yttrium show that this element does not conform to the general behavior of the members of the rare earth group. It is possible that these peculiarities on the part of yttrium are due to the combined effect of the difference in atomic weight and similarity in atomic structure.

Summary

1. The basicity of illinium when measured by the intensive sodium nitrite precipitation has been found to be slightly greater than that of yttrium, these two elements being less basic than neodymium but more basic than samarium.

2. The order of decreasing basicity for the entire group has been shown to agree with the increasing order of atomic numbers, with the single exception of yttrium.

3. The quantitative determination of illinium was made by the magneto-optic method, while yttrium was determined spectroscopically.

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The Volumetric Determination of Arsenic. Potentiometric Titrations of Reduced Arsenic Solutions with Potassium Iodate in Sulfuric and Hydrochloric Acid Solutions

BY IRL C. SCHOONOVER AND N. HOWELL FURMAN

The more commonly used volumetric methods for the determination of arsenic are those in which the arsenic in the trivalent form is oxidized with iodine or iodate. The first of these methods has been studied carefully from a theoretical standpoint by E. W. Washburn[1] and experimentally by Thiel and Myer[2] and later by I. M. Kolthoff.[3]

The second method, that of the oxidation with iodate, was developed by G. S. Jamieson,[4] who extended L. W. Andrews'[5] work on iodate oxidations in strong hydrochloric acid to the determination of arsenic. This method depends upon the oxidation of the iodine first formed to iodine monochloride and the disappearance of the iodine color from an inert solvent such as carbon tetrachloride.

In this investigation, the oxidation of arsenious oxide with iodate in hydrochloric and sulfuric acid solutions has been studied; the potentiometric method was employed. Oxidations of arsenious oxide in hydrochloric acid to which mercuric salt was added were also studied.

(1) Washburn, THIS JOURNAL, **30**, 31 (1908); **35**, 681 (1913).
(2) Thiel and Myer, *Z. anal. Chem.*, **55**, 177 (1916).
(3) Kolthoff, *ibid.*, **60**, 393 (1921).
(4) Jamieson, *J. Ind. Eng. Chem.*, **10**, 290 (1918).
(5) Andrews, THIS JOURNAL, **25**, 756 (1903).

The concentration of the acid was found to be an important factor in oxidations in hydrochloric acid. Two end-points in the same titration were possible; both were accurate. The first end-point corresponded to the reduction of the iodate to iodine in solutions 0.10 to 2.0 normal in hydrochloric acid, $5H_3AsO_3 + 2KIO_3 + 2HCl \longrightarrow I_2 + 5H_3AsO_4 + 2KCl + 2H_2O$. The second end-point was obtained in a solution more concentrated in hydrochloric acid, by adding enough concentrated hydrochloric acid at the first end-point to make the solution 4 to 6 normal in acid. Further addition of the iodate oxidized the iodine formed at the lower hydrogen-ion concentration to iodine monochloride according to the equation $2I_2 + KIO_3 + 6HCl \longrightarrow 5ICl + KCl + 3H_2O$.

It was noticed in the above titrations in which the hydrogen-ion concentration was between 0.1 and 2.0 normal in hydrochloric acid (conditions which are suitable for formation of iodine) that iodine did not appear immediately upon addition of the iodate. In some cases as much as 5 or 6 cc. of iodate could be added before any permanent color due to iodine was formed. This was thought to be due to the formation of an iodide as an intermediate step in the reaction. G. F. Smith[6] noticed that in certain reactions with iodate in which iodide was formed as an intermediate product, the presence of mercuric ion entirely inhibited the reaction. The iodide forms a stable complex with the mercury and prevents further reaction.

Titrations of arsenic in dilute hydrochloric acid 0.5–2.0 normal, to which mercuric mercury was added, gave a correct determination of the arsenic and reduction of the iodate to iodide, which formed a complex with the mercury present. The concentration of the acid was found to be an important factor as the complex was stable only over a very short range of acidity. In solutions 2 normal and above the complex decomposed and the liberated iodide immediately reacted further with any excess iodate added. The instability of the complex mercuric iodide at higher hydrogen-ion concentrations was made the basis of a second end-point in the same titration. Concentrated hydrochloric acid was added at the first end-point until the solution was 4 to 6 normal in acid and the liberated iodide was oxidized with iodate to iodine monochloride.

E. Müller and D. Junck[7] have found that in reduction of iodate with an iodide a sulfuric acid solution is preferable to hydrochloric. The potential readings were more easily obtained, the reaction was less sensitive to hydrogen-ion concentration, and the possibility of reduction products other than iodine was prevented.

Titrations of arsenic with iodate in sulfuric acid solution confirm the findings of these authors. A correct potentiometric titration of arsenic with iodate was obtained at any hydrogen-ion concentration between 0.5 and 8.0 normal in sulfuric acid, provided chlorides in any appreciable

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(6) Smith. THIS JOURNAL, **45**, 1417 (1923).

(7) Müller and Junck, *Z. Elektrochem.*, **31**, 200 (1925).

quantities were absent. The iodate was reduced to iodine. In the presence of chlorides concordant results were not possible, probably due to formation of some iodine monochloride. However, in all titrations below one normal in acid, it was necessary to add a small amount of hydrochloric acid; otherwise the oxidation did not occur even with excess iodate present except on long standing. Reaction was instantaneous in solutions 0.0002 normal in hydrochloric acid and 0.5 to 1.0 normal in sulfuric acid. Above 1.0 normal in sulfuric acid the reaction was instantaneous without chloride present.

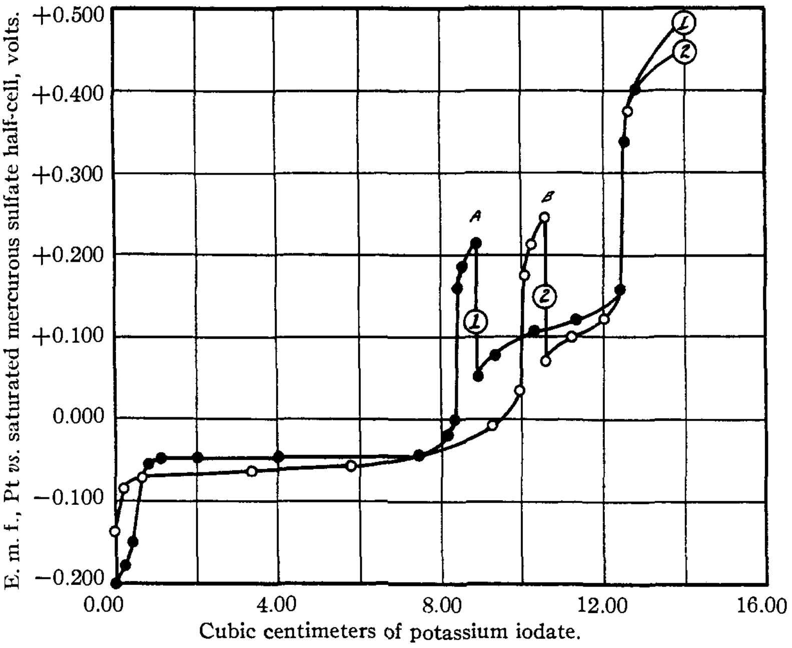

Fig. 1.—Curve I. Titration in the presence of mercuric mercury. The first point of inflection represents complete oxidation of the arsenic and reduction of the iodate to iodide; the second, to the oxidation of the iodide to iodine monochloride. Curve II. Titration in dilute hydrochloric acid. The first point of inflection represents complete oxidation of the arsenic and reduction of the iodate to iodine; the second, to the oxidation of the iodine to iodine monochloride. The abrupt drops in potential at points (A) and (B) are due to the addition of concentrated hydrochloric acid.

Apparatus and Materials

A Leeds and Northrup students' type potentiometer, a portable galvanometer (Type 2320d), and a Weston saturated standard cell were used. A bright platinum wire was used as an indicator electrode and a saturated $K_2SO_4/HgSO_4/Hg$ reference electrode connected to the titration cell with a saturated potassium sulfate salt bridge.

The calibration of the volumetric glassware was carefully checked and the necessary corrections were applied.

Three standard arsenate solutions were prepared from carefully dried and weighed U. S. Bureau of Standards As_2O_5 which was dissolved in dilute sodium hydroxide and then neutralized with dilute hydrochloric or sulfuric acid. The normalities of these were determined both from the direct weight of the sample taken and by standardization against a standard iodate solution following Jamieson's procedure.

The standard iodate solutions were prepared from Merck Reagent quality potassium iodate and were standardized against weighed samples of U. S. Bureau of Standards arsenious oxide following Jamieson's procedure.

Determination of Arsenic with Iodate in Hydrochloric Acid Solutions.—Measured portions of the standard arsenite solution were diluted to various volumes and acid concentrations with dilute hydrochloric acid (Table I). Standard potassium iodate was added from a buret and the progress of the oxidation followed with the potentiometer. The platinum indicator electrode was negative to the reference electrode at the start of the titration. The first few drops of iodate caused a rapid rise in potential, the indicator electrode becoming more positive. Although conditions were favorable for the formation of the iodine end-point, permanent appearance of the iodine did not occur in certain cases until after 5 or 6 cc. of the iodate had been added. After the first rapid

TABLE I

TITRATION OF ARSENIC WITH IODATE IN HYDROCHLORIC ACID SOLUTION IN WHICH THE IODINE AND THE IODINE MONOCHLORIDE END-POINTS WERE OBTAINED

Expt.	As_2O_3 soln., cc.	KIO_3 req. for I_2 end-pt., cc.	As present, g.	As found, g.	Error, mg.	KIO_3 req. for ICl end-pt., cc.	As found, g.	Error, mg.	Concn. of HCl at start, *N*	at end, *N*
3	10.0	10.03	0.03749	0.03754	±0.04				0.3	
4	10.0	10.00	.03749	.03743	− .06				.6	
5	10.0	10.01	.03749	.03747	− .02				1.2	
6	10.0	10.03	.03749	.03754	+ .04				2.4	
7	10.0	9.95	.03749	.03725	− .24	12.37	0.03703	−0.46	2.4	2.3
8	10.0	9.93	.03749	.03717	− .32				2.6	2.5
9	10.0	10.02	.03749	.03751	+ .02	12.51	.03745	− .04	0.5	3.4
10	10.0		.03749			12.52	.03748	− .01		
11	24.75	24.80	.09278	.09283	+ .05	30.90	.09251	− .27	0.4	3.4
13	24.75	24.79	.09278	.09279	+ .01	30.98	.09275	− .03	.4	4.5
14	49.50	49.28	.18560	.1845	−1.10	61.49	.1841	−1.5	2.4	4.0
16	49.50	49.50	.18560	.1853	−0.3				0.5	
17	49.50	49.58	.18560	.1856	± .00				.2	
19	49.50	49.58	.18560	.1856	± .00				.3	
20	49.50	49.60	.18560	.1857	+ .10	61.98	.1856	±0.00	.3	4.4
21	49.50	49.58	.18560	.1856	± .00	62.03	.1857	+ .1	.15	4.0
22	49.50	49.60	.18560	.1857	+ .10				.08	
24	49.50	49.56	.18560	.1855	− .10				.5	
26	10.00	10.00	.03749	.03743	− .06	12.53	.03758	+ .09	.3	6.0
27	10.00	10.02	.03749	.03751	+ .02	12.52	.03748	− .01	.2	4.0
45	24.75	24.78	.09278	.09276	− .02	31.00	.09281	+ .03	.3	4.6
46	24.75		.09278			30.95	.09287	+ .09		4.8

In determinations 3 to 7 no carbon tetrachloride was added. In the remaining instances from 6 to 25 ml. of carbon tetrachloride was present in each case. The total initial volume ranged from 70 to 300 ml.

The iodate solution was 0.0999 *N* for the iodine end-point and 0.0799 normal for the iodine monochloride end-point.

rise in potential the e. m. f. readings became fairly constant, gradually rising with each addition of iodate until at a point just before the end-point the indicator electrode became positive to the reference electrode. The change in potential at the first end-point indicating complete oxidation of the arsenic and reduction of the iodate to iodine amounted to 0.035 to 0.070 volt per 0.05 cc. of iodate added. It was found that this potential change could be increased three-fold in most cases by addition of an inert solvent for removing iodine. Carbon tetrachloride was used. Accurate results for this end-point are possible only when the concentration of hydrochloric acid is between 0.10 and 2.0 normal. The conditions which were found to be most favorable for maximum potential changes of 0.070 to 0.130 volt per 0.05 cc. of iodate were those in which the hydrochloric acid concentration was from 0.5 to 1.0 normal and 15 to 25 cc. of an inert solvent was present.

The second end-point in the hydrochloric acid solutions was obtained by adding enough concentrated hydrochloric acid at the first end-point to make the solution 4 to 6 normal in acid. An abrupt drop in potential occurred following the addition of the acid and further addition of the iodate produced a gradual rise in potential e. m. f. values, finally ending in a break of potential of 0.100 to 0.186 volt per 0.05 cc. of iodate at the iodine monochloride end-point, which corresponds to the complete oxidation of all iodine formed at the lower hydrogen-ion concentration. Tabulated results may be found in Table I.

Oxidation of Arsenic with Iodate in Hydrochloric Acid Solution when Mercuric Mercury is Present ($HgSO_4$).—Ten to twenty-five cc. portions of a saturated mercuric sulfate solution one normal in hydrochloric acid were added to measured samples of arsenite, and the resulting solution was diluted to various volumes with 6 *N* hydrochloric acid and distilled water. Standard iodate was added from a buret at room temperature and the progress of the reaction was followed with a potentiometer; the potential of the platinum indicator electrode was negative to that of the reference electrode at the start (satd. $K_2SO_4/Hg_2SO_4/Hg$) and became positive to the potential of the reference electrode at the end-point of the titration. The change in potential at the end-point corresponding to the oxidation of the arsenic and reduction of the iodate to iodide (the iodide being present as a complex mercuric iodide) was from 0.080 to 0.220 volt for 0.05 cc. of iodate added.

Addition of concentrated hydrochloric acid at this end-point to make the solution 4 to 6 normal caused an abrupt drop in potential and liberation of the iodide from the complex mercuric iodide. The second end-point in this titration, corresponding to the oxidation of the liberated iodide to iodine monochloride, was obtained by further addition of iodate. The potential change at this end-point was from 0.100 to 0.180 volt for 0.05 cc. of iodate added. Results of these experiments will be found in Table II.

Oxidation of Arsenic with Iodate in Sulfuric Acid Solution.—A procedure similar to those already described was used. Measured portions of arsenite were diluted with dilute sulfuric acid and distilled water. Iodate was added from a buret and the end-point obtained potentiometrically. In some cases 10–25 cc. portions of benzene or other inert solvents were present.

The presence of chlorides was found to be an important factor. Concordant results were impossible when appreciable amounts of chlorides were present in all solutions above one normal in sulfuric acid, while in those solutions one normal or less a small amount of chloride was necessary, otherwise oxidation was too slow to be measured. The addition of enough hydrochloric acid to make the solution 0.0002 normal in this acid caused instantaneous oxidation of the arsenate by the iodate in solutions below one normal in sulfuric acid. The potential of the platinum indicator electrode was positive to that of the reference electrode at the start and rapidly became negative to it on addition of the first few drops of iodate. Further additions of iodate caused the potential to

TABLE II

POTENTIOMETRIC TITRATION OF ARSENIC WITH IODATE IN THE PRESENCE OF MERCURIC MERCURY ($HgSO_4$) IN HYDROCHLORIC ACID SOLUTION

Expt.	As_2O_3 soln., cc.	KIO_3 req. I^- end-pt., cc.	As present, g.	As found, g.	Error, mg.	KIO_3 req. for ICl end-pt., cc.	As found, mg.	Concn. HCl at start, *N*	Error in mg. at end-pt.	Concn. HCl at end, *N*
30	10.0		0.03749			12.52	0.03748	0.3	−0.01	2.5
32	10.0		.03749			12.52	.03748	2.0	− .01	4.0
34	10.0	8.32	.03749	0.03738	−0.11			0.9		
38	10.0	8.32	.03749	.03738	− .11			1.5		
39	10.0	8.32	.03749	.03738	− .11			0.7		
40	10.0	8.35	.03749	.03751	+ .02	12.53	.03751	1.7	+ .02	4.0
41	10.0	8.33	.03749	.03743	− .06			1.5		
42	10.0	8.33	.03749	.03743	− .06	12.52	.03748	1.5	− .01	4.6
43	24.75	20.64	.09278	.09273	− .05	30.95	.09277	1.5	− .01	5.0
44	24.75	20.65	.09278	.09274	− .04	31.01	.09282	1.3	+ .04	6.0
3	24.75	20.75	.09316	.09330	+ .14			1.0		
4	24.75	20.74	.09316	.09325	+ .09			0.5		
5	49.50	41.45	.18632	.18640	+ .20			.6		
6	24.75	20.75	.09316	.09330	+ .14			2.0		
7	24.75	20.72	.09316	.09316	± .00			1.2		
8	24.75	20.76	.09316	.09333	+ .17			1.0		

In each instance from 10 to 20 cc. of saturated mercuric sulfate solution was present. The total volumes at the start of the titrations ranged from 50 to 225 cc.

The iodate was 0.0799 normal for the iodine monochloride end-point and 0.1199 normal for the iodide end-point.

The arsenite solution used for experiments 30 through 44 was 0.1000 *N*.

The arsenite solution used for experiments 3 through 8 was 0.1005 *N*.

increase until finally the potential of the indicator electrode was again positive to that of the reference electrode. The change in the potential at the end-point which represents complete oxidation of the arsenic and reduction of the iodate to iodine was from 0.085 to 0.245 volt per 0.05 cc. of iodate added. Here again as in the case of the oxidation in hydrochloric acid the potential change at the end-point was increased by having present an inert solvent for iodine.

In conjunction with this work on sulfuric acid solutions, a study of the various inert solvents which have been employed in iodimetric work was made in order to determine their value as methods of increasing the potential changes at iodine end-points.

F. L. Hahn and H. Wolf[8] have used ethyl acetate for removing the color due to iodine in permanganate titrations. Tamaki Nakazno[9] recommends the use of benzene in preference to carbon tetrachloride, chloroform, or carbon disulfide in iodimetric titrations. All of these were tried in oxidations of arsenic in which the iodine end-point was desired. It was found that each of the above gave the same effect, that of increasing the potential break, but in the case of benzene the e. m. f. values were easier to obtain and its use is recommended in preference to the others.

Theoretical Considerations

W. S. Hendrixson[10] in his paper on the action of some oxidizing agents on sulfite bases his explanation of the dissimilar nature of iodate from other

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(8) Hahn and Wolf, *Chem.-Ztg.*, **50**, 674 (1926).

(9) Nakazno, *Sci. Repts. Tôhoku Imp. Univ.*, **14**, 101 (1925).

(10) Hendrixson, THIS JOURNAL, **47**, 1319 (1925).

TABLE III

POTENTIOMETRIC TITRATION OF ARSENIC WITH IODATE IN SULFURIC ACID SOLUTION

Expt.	As_2O_3 soln., cc.	KIO_3 req. for I_2 end-pt., cc.	As present, g.	As found, g.	Error, mg.	Concn. of H_2SO_4, N	Concn. of HCl, N	Total vol., cc.	Inert solvent added, cc.	E. m. f. change, volts
2	10.0	9.96	0.03749	0.03732	−0.17	0.6	Present	140	15 CCl_4	0.153
3	10.0	9.85	.03749	.03691	− .58	1.0	Present	155	15 CCl_4	.181
4	10.0	9.87	.03749	.03698	− .51	1.0	Present	150	25 EtOAc	.095
6	10.0	9.86	.03749	.03695	− .54	1.0	Present	150	25 C_6H_6	.085
7	10.0	9.90	.03749	.03710	− .39	1.0	Present	175	25 C_6H_6	.153
9	24.75	24.63	.09278	.09229	− .49	1.0	0.072	150	25 C_6H_6	.120
11	10.0	10.00	.03749	.03747	− .02	1.0	.0002	150	25 C_6H_6	.125
12	24.75	24.73	.09278	.09266	− .12	1.0	.0002	150	25 C_6H_6	.120
13	10.0	10.00	.03749	.03747	− .02	2.6	None	135	25 C_6H_6	.161
14	10.0	10.01	.03749	.03749	± .00	6.8	None	100	25 C_6H_6	.220
15	24.75	24.74	.09278	.09270	− .08	6.9	None	110	25 C_6H_6	.227
16	49.50	49.50	.1856	.1855	− .10	6.0	None	90	25 C_6H_6	.230
17	24.75	24.60	.09278	.09217	− .61	6.5	Present	110	25 C_6H_6	.245
18	10.0	9.99	.03749	.03743	− .06	7.4	0.002	97	25 C_6H_6	.225
21	24.75	24.88	.09316	.09332	+ .16	1.0	0.0002	100	25 C_6H_6	.174
22	24.75	24.87	.09316	.09330	+ .15	1.2	None	75	25 C_6H_6	.145
23	24.75	24.85	.09316	.09311	− .05	0.5	0.0002	55	25 C_6H_6	.122
25	49.50	49.70	.18632	.1862	− .12	3.6	None	130	25 C_6H_6	.158
26	49.50	49.75	.18632	.18640	+ .08	1.2	None	140	25 C_6H_6	.166
27	24.75	24.84	.09316	.09307	− .09	3.0	None	100	25 C_6H_6	.155

The iodate was 0.1000 *N* for iodine end-point.

Experiments 2 through 7 were made on 0.1000 *N* arsenate solutions in which dilute hydrochloric acid was used in preparation of the solution.

Experiments 8 through 18, including 17, were made on 0.1000 *N* arsenate solutions free from chlorides.

Experiments 21 through 27 were made on 0.1005 *N* arsenate solutions free from chlorides.

oxidizing agents such as potassium permanganate and dichromate on the work of Landolt[11] and of Skrabal[12] on the kinetics of the iodate-sulfite reaction. Landolt found that the kinetics of the oxidation could be explained by three reactions

$$IO_3^- + 3SO_3^= = I^- + 3SO_4^= \qquad (1)$$

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O \qquad (2)$$

$$3I_2 + 3SO_3^= + 3H_2O = 6H^+ + 6I^- + 3SO_4^= \qquad (3)$$

the first of which initiates the oxidation and is the predominating reaction at the start. The reaction expressed by equation two above is very slow at the start and becomes increasingly more rapid as the oxidation progresses until a point is reached where it exceeds the speed of the first. The second reaction is rapidly increased by increased hydrogen-ion concentration. The third reaction expressed by equation three above is instantaneous from the start.

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(11) Landolt, *Ber.*, **19**, 1317 (1886); **20**, 745 (1887).

(12) Skrabal, *Z. Elektrochem.*, **28**, 224 (1922); **30**, 109 (1924).

In this work we have definitely proved that an iodide is formed as the first product of the reduction and that as the oxidation progresses iodine appears and is the final reduction product of iodate in dilute hydrochloric and sulfuric acid solutions. The following equations probably offer an explanation of this.

$$3H_3AsO_3 + KIO_3 \longrightarrow 3H_3AsO_4 + KI \qquad (4)$$

$$5KI + KIO_3 + 6HCl \longrightarrow I_2 + 6HCl + 3H_2O \qquad (5)$$

The non-appearance of the iodine at the start of the titration with iodate is probably due to the slowness of reaction two above. As the oxidation progresses, reaction two becomes increasingly more rapid and iodine is formed as fast as iodate is added. That the speed of this second reaction is increased by increasing the hydrogen-ion concentration was proved by titrations made in solutions 4 to 6 normal in hydrochloric acid in which iodine was found upon the addition of the first drop of iodate to the arsenite solution. Thus a similar process to that found by Landolt in the sulfite iodate reaction seems to be taking place in the iodate arsenite reaction.

Substances which are readily oxidized by iodate, as for example trivalent antimony, stannous ion, etc., will be titrated simultaneously with trivalent arsenic.

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Summary

This investigation has proved that iodide, iodine or iodine monochloride are formed as the final reduction products of the iodate in the oxidation of arsenic depending upon the hydrogen-ion concentration.

New methods based on the reduction of iodate to any one of the above products have been developed for a correct volumetric determination of trivalent arsenic with iodate.

The end-points have been determined potentiometrically, which has the decided advantage over the older methods in that colored solutions do not interfere.

A further application of mercuric mercury as a method for the removal of iodides has been studied and a new volumetric method for the determination of arsenic developed from this study.

A method for the oxidation of arsenic with iodate in solutions lower in hydrogen-ion concentration than hitherto possible has been developed.

A correct volumetric method for the oxidation of arsenic with iodate in sulfuric acid solution has been developed and a study of the effect of various inert solvents for iodine on the potential changes at end-points in which iodine is formed as the final reduction product has been made.

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