2.   A circuit is described for starting the lamps by sparking.

3.   The distribution of energy in capillary arcs of bismuth, cadmium, lead, mercury, thallium and zinc has been determined.

4.   A photographic method is described for recording the thermopile-galvanometer deflections.

5.   Intense sources of light, comparable with those of the constricted mercury arc, can be obtained for several additional wave lengths.

6.   When an external resistance is used the potential drop across the lamp should be at least half the line voltage.   When this condition cannot be met a shunt is used, and a method for adjusting to maximum constancy is described.

MADISON, WISCONSIN

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. X.   THE DETERMINATION OF ANTIMONY AND ARSENIC[1,2]

BY N. HOWELL FURMAN

Introduction.—Conflicting evidence has been reported by Rathsburg[3] and by Willard and Young,[4] respectively, regarding the oxidation of tri-valent antimony by ceric sulfate.   In some preliminary work[5] our own conclusions differed somewhat from those of Willard and Young,[4] who stated that the oxidation was too slow to be practical at room temperature without the addition of a catalyst.   The further work presented in this paper supports the conclusion of Rathsburg[3] that the reaction is sufficiently rapid at room temperature in solutions containing *high concentrations of hydrochloric acid* (one-sixth to one-third by volume of acid of sp. gr. 1.19). Rathsburg stated that antimony could be titrated in the presence of arsenic under these conditions.   The author has found that the results for antimony tend to become erratic when the concentration of arsenious acid is roughly equivalent to that of the antimony.   If the initial volume per cent. of hydrochloric acid is below 40, simultaneous oxidation of arsenic is apt to occur.   When the amount of antimony exceeds that of the arsenic the results here presented show that it is possible to determine both antimony and arsenic in a single potentiometric titration with ceric sulfate. After the end-point of the oxidation of the antimony, iodine monochloride

[1] Presented at the Eighty-third meeting of the American Chemical Society, New Orleans, La., 1932.

[2] For previous papers of this series, see THIS JOURNAL, **50**, (a) 755, (b) 1675 (1928); **51**, (c) 1128, (d) 1449 (1929); **52**, (e) 1443, (f) 2347 (1930); **53**, (g) 1283, (h) 2561 (1931).

[3] Rathsburg, *Ber.*, **61**, 1664 (1928).

[4] Willard and Young, THIS JOURNAL, **50**, 1376 (1928).

[5] Furman and Wallace, unpublished, 1928.

is added as a catalyst and the arsenic is then determined as was suggested by Willard and Young.[4]

Experimental

Apparatus and Materials.—The potentiometric titrations were in part made with the apparatus used in previous studies of this series, and in part with the continuous reading device described by Furman and Wilson.[6] The preparation and standardization of ceric sulfate solutions has also been described.[2c] Antimony solutions were prepared by dissolving weighed quantities of the metal in concentrated sulfuric acid, and adding hydrochloric acid to prevent hydrolysis (250 cc. of hydrochloric acid of sp. gr. 1.19 per liter). Pure sublimed arsenious oxide was dissolved in alkali, and the solution neutralized with hydrochloric acid. Both materials were from a supply used in previous investigations. Portions of the solutions were titrated with potassium bromate which had been standardized against Bureau of Standards arsenious oxide. The content of the antimony solutions (per 25 cc.) found in this manner was on the average 1 part in 1250 lower than the quantity calculated from the weight of metal taken. The arsenic found agreed with the amount calculated from material weighed.

Iodine monochloride (0.005 M) dissolved in 1:1 hydrochloric acid was prepared as described by Willard and Young.[7]

Methyl orange was found to be a satisfactory indicator for the end of the oxidation of the antimony. Two drops (0.1 cc.) of a 0.1% aqueous solution were used. Methyl red was stated by Rathsburg[3] to be satisfactory, but our experience showed that it was less satisfactory than methyl orange because of its greater ease of oxidation by ceric sulfate.

Determination of Antimony.—Some results which indicate the accuracy and limitations of the method are given in Table I.

These results, and a number of others not presented here, indicate that the method is best applied to cases in which the quantity of arsenic is much exceeded by that of the antimony. The experiments indicated that the simultaneous oxidation of arsenic could be prevented by diminishing its absolute concentration by diluting the solution with hydrochloric acid (40% hydrochloric acid of sp. gr. 1.19 by volume). In one case, for example, a satisfactory determination of antimony was made in the presence of 1.8 times as much arsenic. If the concentration of hydrochloric acid is decreased (Expt. 9, Table I) the arsenic begins to be oxidized before the completion of the oxidation of the antimony, and very erratic results are obtained.

Successive Determination of Antimony and Arsenic.—Measured volumes of arsenic and antimony solutions were mixed and enough hydro-

[6] Furman and Wilson, This Journal, **50,** 277 (1928).

[7] Willard and Young, *ibid.*, **50,** 1322 (1928).

TABLE I

USE OF CERIC SULFATE IN DETERMINING ANTIMONY

A. No arsenic present

No	Antimony present, g.	Ceric sulfate, cc.	Antimony found, g.	Error, mg.	Indicator	HCl (sp. gr. 1.19); per cent. by vol. Init.	Final
1	0.0503	8.80	0.0506	+0.3	M. orange	33	28.5
2	.0503	8.72	.0503	± .0	M. orange	71	57
3	.1256	21.77	.1257	+ .1	F. and W.	50	35
4	.1256	21.76	.1256	± .0	F. and W.	50	35
5	.1261	18.93	.1264	+ .3	F. and W.	50	36
6	.1261	18.90	.1262	+ .1	F. and W.	44	31
7	.1261	18.90	.1262	+ .1	F. and W.	37	25
8	.1261	18.89	.1261	± .0	F. and W.	28.6	18

B. Arsenic present

No	Antimony present, g.	Ceric sulfate, cc.	Antimony found, g.	Error, mg.	Indicator	HCl (sp. gr. 1.19) Init.	Final	As present, g.
9	0.1256	No end-point				33		0.0937
10	.1256	21.78	0.1257	+0.1	F. and W.	41	30	.0375
11	.1256	21.78	.1257	+ .1	M. orange	41	30	.0375
12	.1256	21.83	.1260	+ .4	M. orange	53	40	.0375
13	.1256	21.80	.1258	+ .2	M. orange	46	34	.0375

F. and W. refers to the galvanometric method of Furman and Wilson. The ceric solutions were: 0.0948 N, Expts. 1–4 and 9–13; 0.1097 N, Expts. 5–8. In Expt. 8 the reaction was very sluggish near the end-point due to the relatively low concentration of hydrochloric acid.

chloric acid, sp. gr. 1.19, was added to make up at least 40% of the total initial volume, which ranged from 40–70 cc. The completion of the oxidation of antimony was determined potentiometrically. Then 10 cc. of 0.005 M iodine monochloride was added, and the titration was continued to a second potentiometric end-point, which corresponded to the completion of the oxidation of the arsenic. If necessary the solution was adjusted to

TABLE II

USE OF CERIC SULFATE IN DETERMINING BOTH ARSENIC AND ANTIMONY

No.	Antimony present, g.	Ceric sulfate, cc.	Antimony found, g.	Error, mg.	Arsenic present, g.	Ceric sulfate, cc.	Arsenic found, g.	Error mg.
1	0.1256	21.82	0.1259	+0.3	0.0375	10.54	0.0374	−0.1
2	.0503	8.74	.0504	+ .1	.0937	26.53	.0943	+ .4
3	.0503	7.47	.0504	+ .1	.0375	9.17	.0379	+ .4
4	.0503	7.49	.0505	+ .2	.0375	9.13	.0378	+ .3
5	.1256	18.68	.1260	+ .4	.0375	9.15	.0378	+ .3
6	.1261	18.94	.1265	+ .4	.0374	9.09	.0374	± .0
7	.1261	18.95	.1265	+ .4	.0374	9.13	.0375	+ .1

NOTES: Ceric solutions: Expts. 1–2, 0.0948; Expts. 3–5, 0.1107 N; Expts. 6–7, 0.1097 N. Initial concentration of hydrochloric acid (sp. gr. 1.19), 40–50% by volume. Final concentration, 32–43%. The Furman and Wilson[6] galvanometric method was used in Expts. 1–2, 6–7; the classical potentiometric method with a Pt–normal calomel electrode system was used in Expts. 3–5.

the acid normality suggested by Swift and Gregory.[8]   Figure 1 presents a graph of the data in a typical instance.   Some representative results are given in Table II.
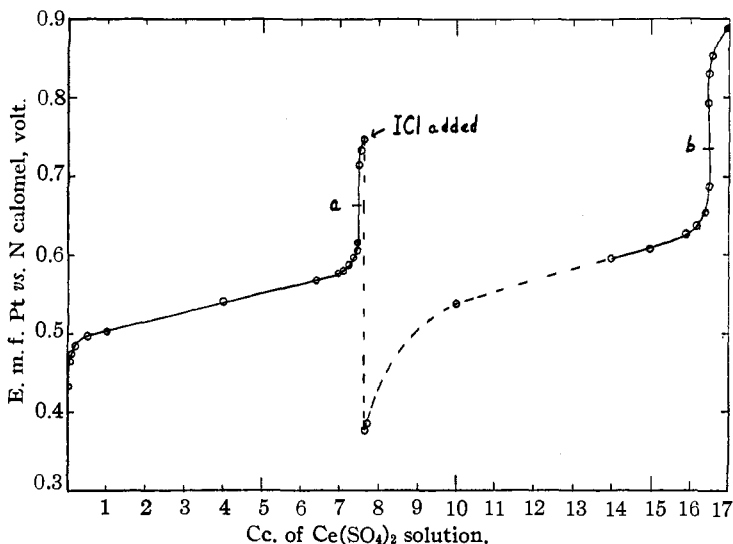

Fig. 1.—Graph of titration data for a mixture of 0.0503 g. of antimony and 0.0375 g. of arsenic in a solution containing 43% hydrochloric acid (sp. gr. 1.19) by volume.   Point a is the end-point of the oxidation of the antimony (0.104 volt change per 0.03 cc. reagent), and b that for the end of the oxidation of the arsenic (0.093 volt per 0.04 cc. of reagent).   The ceric sulfate was 0.1107 N.   Data of Expt. 4, Table II.

Summary

Antimony may be determined by titration with standard ceric sulfate at room temperature without addition of a catalyst if 30–50% by volume of hydrochloric acid (sp. gr. 1.19) is initially present.

The method may be applied to the determination of antimony in the presence of a minor amount of arsenic.   Simultaneous oxidation of arsenic may occur if the acid concentration is much below 40% by volume, or if the absolute concentration of the arsenic is relatively high.

After the end-point of the oxidation of antimony has been found, iodine monochloride catalyst may be added and the titration with ceric sulfate continued to a second end-point, which corresponds to the completion of the oxidation of the arsenic.

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[8] Swift and Gregory, THIS JOURNAL, 52, 901 (1930).