

TABLE I. SENSITIVITY OF TESTS

Material Tested	Weight of Sample Mg.	Metal Detected
$\text{Cb}_2\text{O}_3 + \text{Ta}_2\text{O}_5$ mixture	50	Cb
Columbite (40% $\text{Cb}_2\text{O}_3$ )	150	Cb
Columbite	100	Cb
$\text{WO}_3$	25	W
Ferberite (6.26% $\text{WO}_3$ )	100	W
Ferberite (26.8% $\text{WO}_3$ )	30	W
$\text{Na}_2\text{WO}_4$	3 ( $\text{WO}_3$ )	W
Scheelite	120	W
Wolframite	100	W
Häbnerite	100	W
$\text{TiO}_2$	10	Ti
Brookite	100	Ti
Perovskite	120	Ti
Ilmenite	100	Ti
$\text{Co}(\text{NO}_3)_2$	2	Co
Smaltite	100	Co
$\text{V}_2\text{O}_5$	10	V
$\text{NH}_4\text{VO}_3$	2	V
Carnotite (1.28% $\text{V}_2\text{O}_5$ )	200	V
Roscoelite (5.04% $\text{V}_2\text{O}_5$ )	50	V
Uranyl acetate	4	U
Carnotite (0.28% $\text{U}_3\text{O}_8$ )	200	U
$\text{Cr}(\text{NO}_3)_3$	18	Cr
Chromite	100	Cr
$\text{MoO}_3$	4	Mo
Molybdenite (4.07% Mo)	150	Mo
Wulfenite	100	Mo
$\text{MnSO}_4$	0.05 (Mn)	Mn
Pyrolusite	50	Mn
$\text{TeO}_2$	10	Te
Sylvanite	100	Te

tinctly basic, followed by the addition of hydrogen peroxide, gives a yellow-orange colored solution if uranium is present. It is better to filter off any solid matter in order to observe the color of the filtrate. Neither vanadium nor chromium gives a yellow-orange color in basic solution. If the green color of the melt is due to chromium, no change in color takes place when hydrogen peroxide is added.

**MOLYBDENUM.** All molybdenum minerals give a reddish-brown melt, except molybdenite, which is not completely decomposed by the fusion. Therefore, in testing for molybdenum, the melt is treated with concentrated nitric acid, the acid is boiled off, and the mixture is heated to fusion again. The resulting melt is green or blue-green, which changes to yellow upon addition of water.

**MANGANESE.** Manganese minerals give a clear melt. When concentrated nitric acid is added and the excess acid

boiled off, the melt takes on the well-known color of permanganate. Nitric acid does not usually oxidize manganese to permanganate, but in the presence of the melt it does this readily. None of the metals in the usual scheme of analysis interferes with this test for manganese.

**TELLURIUM.** Tellurium minerals are reduced to metallic tellurium by the fusion and small globules of the metal may be seen floating on the surface of the melt. Strong heating for 2 or 3 minutes causes a deep wine color to appear around each globule of molten tellurium. Addition of water to the warm melt causes the wine color to turn black.

**COLUMBIUM.** Columbium minerals impart no color to the melt but fine black particles are observed throughout the melt. When concentrated hydrochloric acid is added, the mixture heated to boiling, and a small piece of mossy tin added, an intense blue color develops in a few seconds if columbium is present. Since columbium and tantalum are nearly always associated together in minerals, this test can be used for the detection of both metals.

### Sensitivity of Tests

Table I shows that these tests are applicable to different minerals containing the elements for which the tests have been devised, and are sufficiently sensitive to detect appreciable quantities of the metals in question.

It is not claimed that by this method any one of these metals can be detected in the presence of any or all of the others, but it is possible to detect any one metal in any of the naturally occurring minerals thus far tested. Tungsten, for example, can be detected in any one of the tungsten minerals which the authors have been able to obtain. Manganese was detected in a mixture containing 0.5 mg. each of silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, cobalt, nickel, chromium, aluminum, zinc, and manganese. During the fusion iron and copper are reduced to colorless compounds which in no way interfere with the tests. If a mineral gives no color, all the metals included in these tests are absent, except columbium and manganese.

### Literature Cited

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## Use of Bromate in Volumetric Analysis

### Determination of Arsenic and Antimony Using Internal Indicators at Ordinary Temperatures

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**GYÖRY'S** method (1) for the determination of arsenic and of antimony by titration of strong hydrochloric acid solutions of the trivalent elements, using potassium bromate with methyl orange or indigo sulfonate as internal indicators, requires that the reaction be carried out at 80° to 90° C. The same determination can be carried out at lower hydrochloric acid concentration and at room temperature if the reaction is followed potentiometrically, as shown by Zintl and Wattenberg (5). More recently benzopurpurin B was proposed by Raikhinshtein (2) for the determination of antimony using bromate, and Utzel (4) sug-

gested a colloidal suspension of alpha-naphtholflavone as a reversible indicator for bromate titrations.

Since the determination of arsenic and antimony using the Györy (1) method is still preferred by industrial analytical laboratories and has not been discarded in favor of the Zintl and Wattenberg (5) or other procedures, suitable modification of the Györy methods, by means of which the reaction is carried out at ordinary temperatures, has been suggested to the authors. This article describes the use of three internal oxidation indicators of the irreversible type in the Györy procedure, by means of which the oxidation of arsenic and of

TABLE I. DETERMINATION OF BROMATE REQUIRED FOR OXIDATION OF 1 ML. OF INTERNAL INDICATOR IN AQUEOUS HYDROCHLORIC ACID SOLUTION

B. C. I. No.	Indicator Concentration %	Indicator	0.1 N Bromate Required Ml.
88	0.1	Bordeaux	0.08
185	0.2	Brilliant Ponceaux 5R	0.05
246	0.1	Naphthol blue-black	0.03

TABLE II. TITRATION OF TRIVALENT ANTIMONY BY BROMATE AT VARIOUS HYDROCHLORIC ACID CONCENTRATIONS

(Bordeaux used as indicator)				
Volume of Concd. HCl %	No. of Determinations	Antimony Calcd. Gram	Antimony Found Gram	Error Mg.
35	3	0.1523	0.1523	0.0
25	3	0.1523	0.1522	-0.1
20	3	0.1523	0.1523	0.0
15	3	0.1523	0.1522	-0.1
10	3	0.1523	0.1521	-0.2
5	3	0.1523	0.1523	0.0

antimony by bromate can be carried out at ordinary temperatures and over a wide range, from low to high hydrochloric acid concentrations. The previous papers in the series (3) should be consulted for further bromate analytical procedures.

### Disadvantage of Irreversible Internal Oxidation Indicators

The organic dyes, Brilliant Ponceaux 5R, B. C. I. No. 185 (0.2 per cent aqueous solution), Bordeaux, B. C. I. No. 88, and naphthol blue-black, B. C. I. No. 246 (0.1 per cent aqueous solution), are irreversible oxidation indicators. Their intense color permits the use of 0.1 to 0.2 ml. of a 0.1 per cent solution for titration, and the potentials at which they are oxidized and the color destroyed, using hydrochloric acid solutions with bromate as oxidant, are above the equivalence point potential for the oxidation of trivalent to pentavalent arsenic or antimony. Their destruction results from the liberation of bromine from the action of the first minute excess of bromate in the presence of hydrochloric acid. The mechanism of the reaction for the destruction of methyl orange or indigosulfonate in the Györy method is the same, except that the reaction mixture must be hot. With all these irreversible oxidation indicators the destruction of the indicator is often premature to a slight extent and the color of the solution fades before the equivalence point of the reaction is reached. While this is troublesome, the required use of additional indicator incurs no appreciable indicator blank in the present case, as shown by Table I. The indicator blank is negligible in all cases. Additional indicator to counteract "fading" can be used without appreciable blank determination.

### Reagents Employed

Tenth normal solutions of potassium dichromate, potassium bromate, iodine, and potassium antimonyl tartrate as well as 0.2 N sodium thiosulfate solution were made up in accordance with accepted procedures.

The iodine solution was standardized using Bureau of Standards arsenic trioxide (standard of reference No. 83), the sodium thiosulfate was then standardized by liberation of iodine from measured portions of the bromate in 1 N hydrochloric acid solu-

tion by addition of excess potassium iodide, and the liberated iodine was titrated using the standard thiosulfate with starch as indicator. The antimony solution was standardized using the iodine solution in the presence of excess sodium bicarbonate with starch as indicator in the accepted manner. In all cases calibrated pipets, burets, and flasks were employed and the determinations were made with sufficient duplications to ensure an accuracy of one or two parts per thousand.

### Effect of Variation in Hydrochloric Acid Concentration at Ordinary Temperatures

In the titration of the antimony solution with the bromate, the acid concentration was varied over a wide range to study the applicability of the indicator. The volume at the beginning of the titration was 100 ml. in all cases. One or two drops of the indicator solution were used, and by the time the end point was reached most of the indicator had been oxidized by the local excesses of the bromate during its addition. As the indicator fades another drop can be added without causing any error. At the end point the indicator is irreversibly destroyed and the solution becomes colorless. If the fading of the indicator is confused with the end point, another drop of the indicator may be added. If the indicator has faded, the additional drop will color the solution. If the end point has been reached, the additional drop of indicator will be destroyed by the excess bromate in the last drop added.

The results of the titrations of the antimony solution using Bordeaux as the indicator are found in Table II.

The results of the titrations of the antimonyl solution using naphthol blue-black and Brilliant Ponceaux 5R are given in Table III, which also includes the titration of samples of Bureau of Standards arsenic trioxide using Bordeaux.

Bordeaux, Brilliant Ponceaux 5R, and naphthol blue-black are satisfactory indicators for the titration of trivalent antimony at acidities varying from 5 to 35 per cent of concentrated hydrochloric acid, using bromate as oxidant and with titration at ordinary temperatures. The same indicators were used in the oxidation of trivalent arsenic, using 20 per cent by volume of concentrated hydrochloric acid, the other conditions being the same. The influence of the fading of

TABLE III. TITRATION OF ANTIMONYL SOLUTION AND ARSENIC TRIOXIDE

Volume of Concd. HCl %	No. of Determinations	Indicator Used	Antimony		Arsenic		Error Mg.
			Taken Gram	Found Gram	Taken Gram	Found Gram	
10, 15, 20, 25, and 35	5	Naphthol blue-black	0.1523	0.1523	...	...	0.0
10, 20, 25, and 35	4	Brilliant Ponceaux 5R	0.1523	0.15225	...	...	-0.05
20	5	Bordeaux	...	...	0.09361	0.09362	+0.05

these irreversible internal oxidation indicators upon the procedures in question has been discussed and the absence of an appreciable titration error shown. The procedures described are superior to the older method of Györy without requiring titration either in the hot or at higher hydrochloric acid concentrations. At the same time the necessity of a potentiometric titration to gain these advantages as in the Zintl and Wattenberg procedure is avoided.

### Literature Cited

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- (5) Zintl and Wattenberg, *Ber.*, **56**, 472 (1922).