Colorimetric Determinations of Traces of Bismuth in Rocks

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By F. N. WARD *and* H. E. CROWE

CONTRIBUTIONS TO GEOCHEMISTRY

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A rapid method of determination devised primarily for use in geochemical exploration



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By F. N. Ward and H. E. Crowe

ABSTRACT

A rapid method for determining traces of bismuth in rocks has been devised primarily for use in geochemical exploration. The method is based on the reaction of bismuth with carbamate in a cyanide medium and subsequent extraction of the yellow complex with chloroform. The proposed procedure is applicable to rocks containing from 10 to 300 parts per million (ppm) of bismuth, and only slight modifications are necessary to extend the range upward. For two different rocks the confidence limits at the 95-percent level calculated from the mean values of 13.8 and 107.0 ppm obtained by 5 repeat determinations are respectively ±1.4 and ±3.4 ppm.

INTRODUCTION

A rapid method for determining traces of bismuth in rocks was needed in the Geological Survey to analyze several hundred rock samples to establish possible geochemical dispersion patterns of bismuth, which in turn might be useful in the exploration for bismuth mineralization. To date practically all trace determinations of bismuth in soils and rocks have been made with spectrographic procedures (Ahrens, 1945). The spectrographic determination of bismuth is normally good, although the procedure requires a moderately expensive spectrograph and a trained technician; for a routine geochemical exploration laboratory, however, a chemical method requiring neither specialized equipment nor trained specialists seemed highly desirable.

Traces of bismuth in such metals as antimony, mercury, silver, iron, and copper are usually determined by its reaction with dithizone in an acid medium (Sandell, 1950; Snell and Snell, 1949). Traces of bismuth in lead are collected by a hydroxide precipitation and subsequently determined by the reaction with potassium iodide (Robinson, 1939). Traces of bismuth in biological materials have been determined by either the iodide or the dithizone reaction.

Small amounts of bismuth in dilute sulfuric acid react with an excess of iodide to form a yellow complex that can be extracted by higher alcohols and esters, but attempts to apply the iodide method to the determination of bismuth in rocks were unsuccessful. Platinum, palladium, antimony, and tin also react with iodide yielding yellow

or rose-colored products (Sandell, 1950). Moreover, oxidizing agents liberate iodine from the iodide and the color of a dilute aqueous solution of iodine resembles that of the bismuth complex. Reducing agents such as sulfite and ascorbic acid prevent the formation of iodine until they are exhausted, but in a system as complex as a rock-sample solution the maintenance of reducing conditions in air becomes impracticable.

Methods for determining bismuth based on dithizone reactions are not easily applied to rocks because of the difficulty of separating lead from bismuth. The dithizonates of both elements are extracted under similar conditions, and the separation is based on the comparative stability of the bismuth dithizonate at a pH of less than 3 or by successive extractions of the organic solvent containing the dithizonates with portions of a phthalate buffer. The phthalate buffer preferentially decomposes the lead complex, leaving most of the bismuth in the organic phase.

Tompsett (1938) observed that bismuth reacted with diethyldithiocarbamate to form a complex extractable by ether from a weak acid solution. Strafford, Wyatt, and Kershaw (1945) and LaCoste, Earing, and Wiberley (1951) observed that chloroform also extracted the complex. Later Sedivec and Vasak (1950) and Cheng and Bray (1953) reported that bismuth was the only element causing interference when carbamate and ethylenediamine-tetraacetic acid were used to determine copper colorimetrically, and that cyanide destroyed copper carbamate but did not affect bismuth.

These observations provide a basis for determining traces of bismuth in rocks after preparing a suitable sample solution. Briefly, a pyrosulfate fusion of the rock sample is treated with hot moderately concentrated nitric acid. After addition of solid disodium ethylenediaminetetraacetic acid (EDTA), ammonia is added until the pH is about 6. The insoluble residue after the sample attack is removed by filtration, and, in the presence of cyanide, the bismuth carbamate complex is formed. Extraction of the complex with a small volume of chloroform concentrates it so that the yellow color is easily observable.

Cheng, Bray, and Melsted (1955) developed a method for determination of bismuth based on its reaction with carbamate and used the method to determine the element in lead-base alloys. They dissolved EDTA in an aqueous solution of cyanide and used the mixture to complex iron, aluminum, and other interfering elements which precipitate when the acidic bismuth sample is made alkaline. The quantity of interfering elements present governed the amount of EDTA required, but an excess did not interfere.

EXPERIMENTAL WORK

The present authors considered that varying the amount of EDTA added with the quantities of interfering elements present—often unknown—was not feasible in routine work. They therefore selected a tactite containing 200 ppm of bismuth determined spectrographically, and relatively large amounts of iron, aluminum, and other metals to use in determining experimentally the quantities of EDTA necessary to react with the interfering elements. One-half gram portions of the tactite were fused with pyrosulfate and treated with dilute nitric acid. The duplicate results obtained by adding various amounts of EDTA to the dilute nitric acid solution of the sample are given as follows:

Effect of disodium ethylenediaminetetraacetic acid (EDTA) on determination of bismuth

EDTA added, grams	*Bismuth found, ppm*	
0.25	28	20
1.0	190	225
1.5	200	225
2.0	190	225

In all the work reported here, solid EDTA and an aqueous cyanide solution are added separately to the sample solution in place of the mixture recommended by Cheng, Bray, and Melsted (1955), because the mixture prepared by the authors turned brown and became ineffective in less than two hours. The reagents were effective if added separately.

Because certain rock samples contained appreciable amounts of copper, experiments were made to determine how much copper could be tolerated in the proposed procedure. Various amounts of copper and 100 micrograms of bismuth were added to five 0.50 gram portions of a bismuth-free rock and the portions were taken through the entire procedure. The results are shown as follows:

Determination in micrograms, of added bismuth in presence of copper

Bismuth added	*Copper added*	*Bismuth found*
100	0	101
100	100	95
100	1000	95
100	5000	90
100	10000	88

The recoveries of the added bismuth show that up to 2 percent of copper in the original sample can be tolerated. Higher concentrations may cause erratic results simply because of the failure of the cyanide to break up the copper carbamate complex.

REAGENTS AND APPARATUS

[All chemicals are Reagent Grade]

Ammonium Hydroxide, sp. gr. 0.90.
Bismuth Standard A. Dissolve 0.5 gram bismuth metal in 500 ml concentrated nitric acid. Solution contains 1000 micrograms per ml.
Bismuth Standard B. Dilute 1 ml of standard A to 100 ml with water. Solution contains 10 micrograms per ml in 1:100 nitric acid (.16N).
Chloroform, C. P. boiling range Min. 95 percent between 59.5 and 61.5° C.
Disodium ethylenediaminetetraacetic acid (EDTA).
Nitric acid, 8 molar.
Potassium pyrosulfate.
Sodium cyanide, 5 percent aqueous.
Sodium diethyldithiocarbamate, 1 percent aqueous solution.
Bottle, dropping, 30 ml capacity.
Beakers, Pyrex, 60 ml capacity.
Cotton, absorbent.
Filter paper, 9 cm Whatman No. 1.
Funnels, filter, diam. 4.5 cm.
Funnels, separatory, 60 ml, Squibb type.
Pipette, graduated, 1 ml capacity.
Pipette, graduated, 5 ml capacity.
Pipette, volumetric, 1 ml capacity.
Photometer.
pH test paper, range 1–6.
Tubes, or cuvettes, for absorbance measurements.
Balance, sensitivity 2 mg or better.

PROCEDURE

Fuse 0.5 gram of finely powdered rock sample with 1.5 gram of potassium pyrosulfate in a 60 ml beaker. Cool and add 2 ml of 8 molar nitric acid. Boil for about 0.5 minute. Add 8 ml water and again heat until solution boils gently. Cool and add 2 grams solid EDTA. Stir for 10 to 15 seconds and add concentrated ammonium hydroxide drop by drop until pH is 5 to 6. Test externally with pH test paper. Add 5 ml sodium cyanide solution and filter, collecting filtrate in a 60 ml separatory funnel. To the filtrate add 1 ml concentrated ammonium hydroxide, 1 ml of carbamate reagent, and 5 ml of chloroform. Shake the funnel and contents 1 minute. Drain organic layer into a tube or cuvette through a piece of cotton inserted in the funnel stem and read absorbance at 400 millimicrons. From a previously established standard curve, read the number of micrograms of bismuth present. Double the results to convert to parts per million.

RESULTS

Although many methods useful in geochemical exploration do not require complete break-up of the rock sample, the easy solution of the major part of the constituent being determined is definitely advantageous. With the silicated limestones, which comprise most of the materials studied in this paper, the advantage is apparently realized, allowing good results to be obtained by the colorimetric method.

The good agreement between the spectrographic and the colorimetric method is indicative of the accuracy of the latter method when applied to the types of materials included in this paper.

Determination of bismuth in rocks by spectrographic and colorimetric methods

		Bismuth, ppm	
Laboratory No.	*Field No.*	*Spectrographic method*	*Colorimetric method*
54–3613	WH–3	50	68
3633	23	80	119
3635	25	10	17
3652	42	40	55
3657	47	50	40
3671	61	200	225
3711	101	100	115
3712	102	60	95

The recovery of added bismuth by the proposed method was tested by adding various amounts of soluble bismuth to 0.5 gram portions of 2 rock samples of known bismuth content and taking the portions through the entire procedure, starting with the pyrosulfate fusion. The results are tabulated below.

Recovery, in micrograms of added bismuth

Laboratory No.	*Field No.*	*Present*	*Added*	*Found*	*Recovered*
54–3796	WH–185	5	10	16	11
			20	26. 5	21. 5
			30	35	30
			40	45	40
			50	54	49
			80	85	80
			100	104	99
54–3795	WH–184	14	10	22. 5	8. 5
			20	31. 5	17. 5
			30	44	30
			40	52. 5	38. 5
			50	60	46
			80	87	73
			100	102. 5	88. 5

The amounts of bismuth found in the separate portions are shown in the 5th column, and the amounts recovered in the last column.

The accuracy of a useful method in geochemical exploration need not be great, but the precision or "repeatability" must be good. The repeatability of the proposed method was tested by making 5 separate determinations on 5 different samples. The results are shown below.

From the data shown in the table below the standard deviation and the confidence limits at the 95 percent level were calculated in the manner given by Youden (1951). The data show that, within the concentration range covered, the repeatability is good.

The proposed bismuth method is relatively simple, rapid, precise, and moderately accurate. A laboratory technician can determine traces of bismuth in more than 30 rock samples during an 8-hour day to provide data adequate for elimination of background materials and for the establishment of values useful in systematic investigation of the bismuth content of rocks relative to geochemical exploration.

Repeatability of bismuth determinations

[St. D.=Standard deviation]

Laboratory number	Field number	Bismuth, ppm, in run—					Mean	St. D.	95 percent level
		1	2	3	4	5			
54-3635	WH-25	15	13	13	13	15	13.8	1.095	±1.4
3652	42	42	42	38	44	42	41.6	2.19	±2.7
3613	3	87	82	85	85	85	84.8	1.79	±2.2
3633	23	105	105	110	110	105	107.0	2.74	±3.4
3711	101	125	121	125	125	125	124.2	1.79	±2.2

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