Bulletin of the Geological Survey of Japan, vol. 33 (12), p. 619–625, 1982 543.062 : 543.25

Determination of Bismuth in Geological Materials by Anodic Stripping Voltammetry

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KANAI, Yutaka (1982) Determination of bismuth in geological materials by anodic stripping voltammetry. *Bull. Geol. Surv. Japan*, vol. 33 (12), p. 619–625.

Abstract: Anodic stripping voltammetry is a sensitive electrochemical method and the technique for the determination of bismuth in geological materials was investigated. The geological materials contain relatively much amount of iron which interferes. The reduction of iron by ascorbic acid made the measurement possible. The peak potential changed with changing hydrochloric acid concentration and 0.3 N was used for the measurement of bismuth to avoid positive interference. The contents of bismuth were determined and they were in good accordance with the reference values.

1. Introduction

Recently much study have been achieved about the trace elements in the environmental samples from several viewpoints. In these studies, emission spectroscopic method or atomic absorption spectroscopic method has been used by reason of their high sensitivities. Anodic stripping voltammetry (ASV), one of the electrochemical methods, can also be used for this purpose, because ASV is more sensitive than the conventional polarography and less mercury is needed (MIWA and MIZUIKE, 1975; LUND and SAGBERG, 1980).

High content of bismuth in the ores is generally determined by gravimetry or titrimetry. However the abundance of bismuth in the earth crust is reported to be 0.17 ppm (TAYLOR, 1964). As the content of bismuth in rocks and sediments is very low, the analysis of bismuth has been complex and time consuming. For this reason, bismuth content in geological materials is poorly reported.

The application of ASV to the determination of lead and tin in geological materials is reported (BOND *et al.*, 1970; KHASGIWALE *et al.*, 1972), however the application to the determination of bismuth has been scarecely reported.

In this study ASV technique for the determination of bismuth in low concentration level in geological materials is discussed.

2. Experimental

2.1 Apparatus

Yanagimoto Voltammetric Analyser (P-1000) and Anodic Stripping Timer (AST-100) were used for measurement. A hanging mercury drop electrode (HMDE) was used as a working electrode, a platinum electrode as auxiliary, and a saturated caromel electrode (SCE) as reference. The voltammograms were recorded by Watanabe Sokki X-Y Recorder.

2.2 Reagents

The standard solutions of 10,100 and 1,000 ppb bismuth were prepared by diluting 1,000 ppm bismuth solution obtained from Nakarai Chemicals, Ltd.. They were acidified to 0.3 N by adding hydrochloric acid to avoid hydrolysis or adsorption. Hydrochloric acid, nitric

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acid, perchloric acid, hydrofluoric acid, and other reagents were all reagent grade purity. Five percent solution of ascorbic acid was reserved in a refrigerator to avoid decomposition.

3. Determination of Analytical Conditions

3.1 Influence of electrolyte

It is difficult to separate the peak of bismuth from that of copper in the nitric acid solution because the stripping potential of bismuth is the same as that of copper. However each peak could be separated in the hydrochloric acid solution which was used for the electrolyte in this study.

On the peak of bismuth in the hydrochloric acid solution, no interference by one tenth amount of nitric acid, perchloric acid, and sulfuric acid, which are often used for the acid digestion of geological materials, was observed.

3.2 Effect of pulse amplitude

It has been reported that in a differential pulse anodic stripping voltammetry the peak height is generally proportional to the pulse amplitude (Kawai *et al.*, 1980). The proportional relation of the peak height of bismuth to the pulse amplitude was observed in a range of 0 to 25 mV, however the peak height decreased with increasing the amplitude more than 25 mV as seen in Fig. 1. On the other hand, the width of half-height of the peak increased with increasing the pulse amplitude, and the ratio of the peak height to the width of half-height was maximum at 25 mV. Therefore the pulse amplitude was determined to be 25 mV.

3.3 Effect of rest time

The effect of the rest time on the peak height is shown in Fig. 2. The peak height slightly increased with increasing the rest time because during the rest time the pre-electrolysis potential was kept constant till stripping began. This

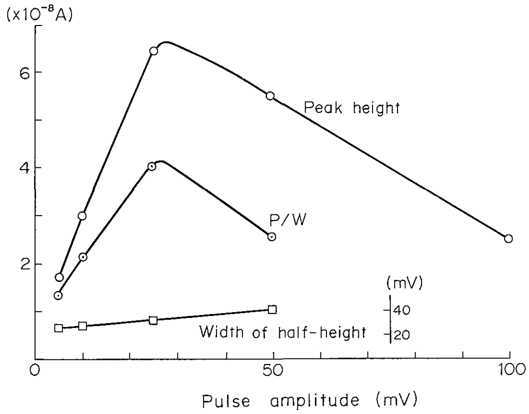

Fig. 1 Effect of pulse amplitude on peak height of bismuth (Bi 20 ppb).

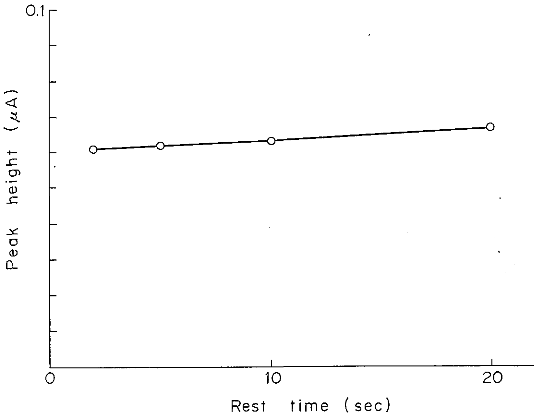

Fig. 2 Effect of rest time on peak height of bismuth (Bi 20 ppb).

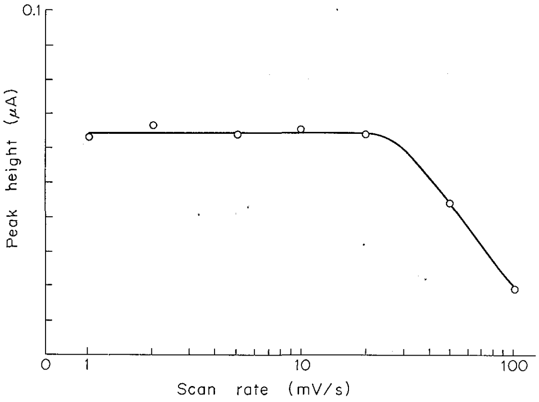

Fig. 3 Effect of scan rate on peak height of bismuth (Bi 20 ppb).

increase, however, does not interfere with the measurement if the analytical conditions are the same for all the sample solutions. Ten seconds was satisfactory for the sample solution to be quiet after stopping stirring, so the rest time was determined to be ten seconds.

3.4 Effect of scan rate

The scan rate was varied from 1 to 100 mV/s. As is shown in Fig. 3, the peak height unchanged until the scan rate was 20 mV/s, but sharply decreased when it was over 20 mV/s. This is probably because the electrode reaction cannot follow the change of potential applied. Therefore the scan rate was determined to be 5 mV/s.

3.5 Relationship between electrode surface area and peak height

The surface area of HMDE can be changed by turning the micrometer screw. The relationship between the surface area and the peak height is shown in Fig. 4. The line is slightly curved though the peak height is reported to be proportional to the surface area of the electrode (Kawai *et al.*, 1980). The true area of the surface might be a little smaller than the calcurated area.

Because too big hanging mercury drop was apt to fall down, a drop with 1.82 mm^2 surface area was used for HMDE.

3.6 Influence of coexisting elements

Iron, aluminium, magnesium, calcium, sodium, and potassium are considered to be the major elements of geological materials. In these, the most undesirable element for the measurement by HMDE is iron, because in ferric solution the surface of mercury was darkened and then the drop fell down during the pre-electrolysis. It was observed, however, that in ferrous solution the surface of mercury unchanged and iron (II) no longer interfered. For the reduction of iron, hydroxylamine or ascorbic acid is often used (Kimura *et al.*, 1979; Ishii *et al.*. 1977). Because the rate of reduction with the former was slower than that with the latter, ascorbic acid was used for the reduction of iron in geological materials. For the reduction of 1,000 ppm iron, 0.5% of ascorbic acid in final solution was sufficient.

The influence of other major elements is shown in Table 1. The concentration of each element in Table 1 is considered to be the maximum concentration in the solution of geological materials. The influence of these elements will be negligible. The reproducibility is also shown in the Table, proving to be less than 10%.

The effects of several minor elements on the peak height of bismuth in 3 N hydrochloric acid solution are shown in Fig. 5. Lead, tin, nickel, and vanadium up to 5 ppm had no interference. Copper interfered slightly. On the contrary, antimony had a strong positive

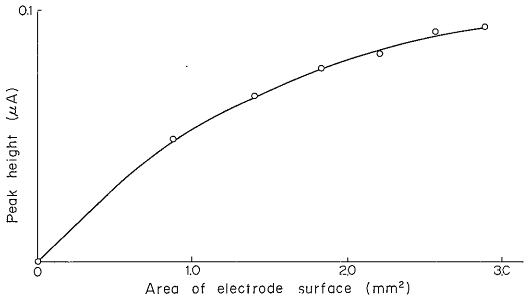

Fig. 4 Relationship between area of electrode surface and peak height of bismuth (Bi 20 ppb).

Table 1 Effect of coexisting elements on peak height of bismuth (Bi 20 ppb).

Element	Conc. (ppm)	$\overline{X}$*	σ	CV (%)	Relative height
	0	64.5	2.8	4.4	100
Fe (III)	1,000	—	—	—	—
Al (III)	1,000	65.4	1.8	2.7	101
Ca (II)	1,000	66.5	5.1	7.6	103
Mg (II)	500	63.6	4.3	6.7	99
Na (I)	500	67.0	3.5	5.2	104
K (I)	500	65.7	1.1	1.6	102
Ti (IV)	150	65.4	2.8	4.3	101
Mn (II)	20	64.4	5.0	7.8	100
P (V)	20	64.3	4.0	6.2	100

* average (n=5)

interference. This is because the peak potential of antimony is near that of bismuth. Accordingly, it is difficult to determine bismuth in the presence of antimony in this condition. This problem was solved by varying the concentration of hydrochloric acid.

3.7 Effect of hydrochloric acid concentration

Fig. 6 shows the peak potentials of several elements in the various hydrochloric acid concentrations. The changes of peak potentials of the elements except antimony and tellurium are almost parallel with one another. For antimony and tellurium, it is considered that secondary reactions might be occurring on the electrode and further investigation will be necessary.

For the determination of bismuth, the peak potential should be away from that of other elements. In the 3 N hydrochloric acid solution, the peak potential of bismuth is away from that of copper (−0.25 V and −0.37 V vs. SCE respectively), but near that of antimony (−0.27 V vs. SCE). The separation of bismuth from antimony will be achieved in the lower acid concentration, but bismuth will be easily hydrolyzed in this condition. Accordingly, 0.3 N hydrochloric acid concentration was used for the determination of bismuth. In this condition, the peak of bismuth (−0.10 V vs. SCE) was no longer interfered positively by the other elements (copper −0.22 V, antimony −0.20 V vs. SCE), and the determination was carried out by means of standard addition method.

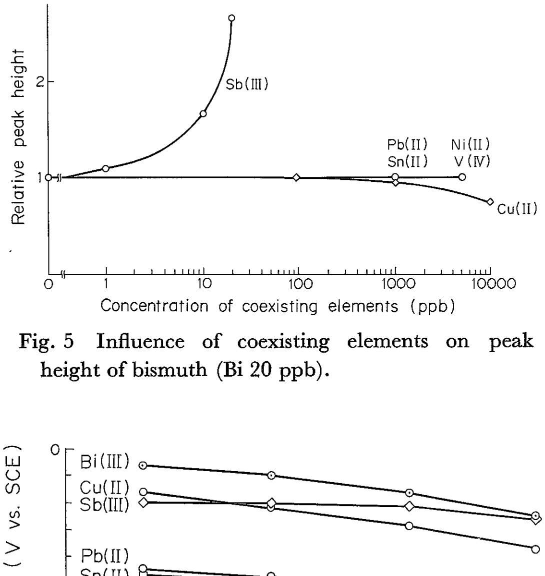

Fig. 5 Influence of coexisting elements on peak height of bismuth (Bi 20 ppb).

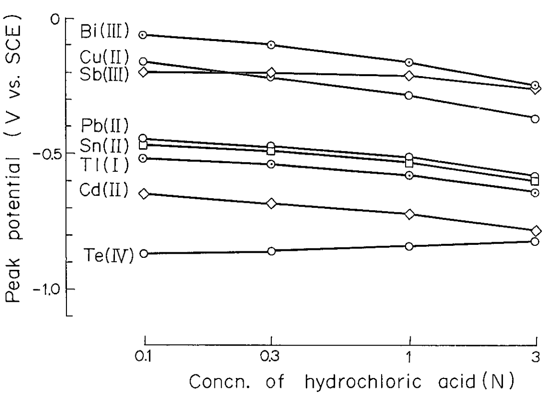

Fig. 6 Dependence of peak potential of some elements on concentration of hydrochloric acid.

3.8 Measurement of peak height

The peak of bismuth appears between the peaks of copper and hydrogen. In the case of measuring the height of peaks, the shape of baseline is important because the peak cannot be detected when it is small. In the preliminary study, about 1 ppb bismuth in the solution could not appear as a peak when the straight baseline was used (straight line in Fig. 7). Therefore much attention was delivered to determine a trace amount of bismuth. The curve recorded in settling the pre-electrolysis time to 0 second was regarded as a baseline (curved dotted line in Fig. 7). In this method a little uncertainty remains, but the error is considered to be less than 0.5 ppb.

4. Determination of Bismuth in Some Geological Samples

4.1 Analytical procedure

Transfer 0.1–0.5 g of the geological sample to a platinum crucible and add 5 ml of nitric acid. Evaporate to dryness on a sand bath. Then add 2.5 ml of hydrochloric acid (1+1) and heat gently to dissolve the salts. Dilute with distilled and deionized water to 25 ml in a volumetric flask. Transfer 5 ml of the stock solution to a volumetric flask, add 1 ml of ascorbic acid solution (5%), and dilute to 10 ml to adjust to 0.3 N hydrochloric acid concentration in final solution. In the case of standard addition method, add appropriate amount of bismuth standard solution before diluting to 10 ml. Transfer this solution to the cell and deoxygenate for 5 minutes by passing high-purity nitrogen through the solution with stirring. Continue to pass the nitrogen through the solution during the electrolysis and stripping. Electrolyze at −0.20 V vs. SCE for 1–60 minutes with stirring (250 rpm). Then stop the stirrer and after the rest time (10 seconds) begin the stripping with increasing the potential from −0.20 to 0 V vs. SCE, using a scan rate of 5 mV/s.

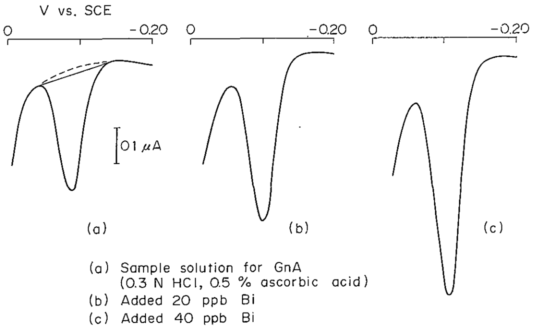

Fig. 7 Typical voltammogram of ASV.

Analytical conditions
Deoxygen: 5 min.
Pre-electrolysis potential: −0.20 V vs. SCE
Pre-electrolysis time: 120 sec.
Rest time: 10 sec.
Scan rate: 5 mV/s
Pulse amplitude: 25 mV
Pulse interval: 0.1 sec.

4.2 Ratio of recovery

Table 2 shows the recovery for the determination of bismuth. After the addition of constant amount of bismuth to JA-1 and JB-1, the standard rocks, they were digested, and bismuth was determined by ASV with this method. The content of bismuth in these rocks is less than the detection limit of this method (0.5 ppb) and the peak height of added sample was measured from the baseline of non-added sample. Added 0.25 μg bismuth corresponds to 0.50 ppm in the rock samples and to 5 ppb in the measured solution. The ratios of recovery for the determination of such trace amount are

Table 2 Recovery for determination of bismuth.

Samples	Taken (g)	Bi (μg) Added	Found*		Recovery (%)
JA–1	0.50	0.25	0.23	0.24	93
JB–1	0.50	0.25	0.23	0.29	103

* peak height was measured from the baseline of non-added solution

Table 3 Determination of bismuth in some geological materials.

Samples		Bi (ppm) This work*	Other values				References
GnA	Greisen	220	220				ABBEY (1980)
GXR–1	Jasperoid	1,500	1,000^a,	1,205^b,	1,478^c,	1,700^d	ALLCOTT and LAKIN (1974); VIETS (1978)
GXR–4	Porphyry copper ore	23	18^b,	22^d,	30^c,	50^a,	〃
GXR–5	Soil	0.43	0.35^d,	1^b,	15^c,	70^a	〃
JA–1	Andesite	<0.05					
JB–1	Basalt	<0.05	0.03,	2			HEINRICHS (1979)
JB–2	Basalt	<0.05					
JG–1	Granodiorite	0.42	0.41,	0.60,	0.62,	2	HEINRICHS (1979)

* Average (n=2–8) a: Colorimetry b: Emission spectrometry c: Flame atomic absorption spectrometry d: Flameless atomic absorption spectrometry

Issued organization of SRMs. GnA: Zentrales Geologisches Institut (DDR)
GXR: U.S. Geological Survey
JA–1・JB–1・JB–2・JG–1: Geol. Survey of Japan

satisfactory and bismuth can be determined in the matrix of andesite or basalt.

4.3 Determination of bismuth in samples

In the conditions mentioned above, bismuth in several reference samples was determined by ASV. Typical voltammogram is shown in Fig. 7. In Table 3, the values determined by ASV are tabulated with the reference values (ALLCOTT *et al.*, 1974; VIETS, 1978; ABBEY, 1980).

The reference values determined by colorimetry, emission spectrometry, flame and flameless atomic absorption spectrometry are so varied. The values by ASV are in good accordance with those by flameless atomic absorption spectrometry which is relatively sensitive.

With this method bismuth in geological materials can be determined by means of ASV without any complex separations.

5. Acknowledgement

The author wishes to thank Drs. S. TERASHIMA and T. FUJINUKI of the Geological Survey of Japan, for their helpful suggestions.

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アノーディック・ストリッピング・ボルタンメトリーによる地質試料中ビスマスの定量

金井　豊

要　旨

地質試料中に含まれるビスマスを，電気化学的分析法のひとつであるアノーディック・ストリッピング・ボルタンメトリーを用いて定量する方法を検討した．地質試料中に大量に含まれる鉄は，アスコルビン酸で還元することによりその妨害を除くことができた．また，塩酸濃度を変えることによりピーク電位を変えることができ，0.3Nの濃度がビスマスの測定に使用された．いくつかの地質試料中のビスマスを本法により定量を試みた結果，文献値と良い一致を示した．

（受付：1982年5月14日；受理：1982年8月2日）