Determination of micro-amounts of silver in rocks by atomic absorption spectrometry with a carbon tube atomizer

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Abstract

A method is proposed for the determination of a ppb level of silver in silicate rocks by atomic absorption spectrometry using a carbon tube atomizer. The sample is decomposed with $HClO_4$ and HF, and the silver diethyldithiocarbamate is extracted by benzene. The interferences from matrix elements are eliminated by adding of citric acid and EDTA before extraction. The sensitivity is 0.0002 $\mu g/ml/1$ % abs., and the limit of detection 0.01 ppm in rock samples. The relative standard deviation in the determination of 0.05 to 0.25 μg of silver is 6–11 %. The method is satisfactorily applied to the variety of standard silicate samples, as seen in Table 5.

1. Introduction

Few papers have described atomic absorption analyses with a air-acetylene flame for silver. RUBESKA et al. (1967), PURUSHOTTAM et al. (1972) and NG (1973) applied it for sulphide ores, and CHAO et al. (1971) analyzed silver in soils, sediments and rock samples for geochemical exploration. However, content of silver in general silicate rocks is less than 0.2 ppm and direct application of the atomic absorption analyses with a air-acetylene flame is difficult.

The recent development of higher sensitivity carbon tube or furnace atomization method enables us to apply the atomic absorption method to various trace metal analyses (WEST et al., 1969; AMOS et al., 1971). BRATZEL et al. (1972) demonstrated the advantages of the carbon tube atomization method for the determination of silver in parts-per-billion or lower levels in geological and metallurgical samples. The rock sample was digested with aqua regia and then the silver was extracted as an ammonium pyrrolidine dithiocarbamate or a triisooctyl phosphorothioate complex into methyl isobutyl ketone.

In this study, ppb levels of silver in silicate rocks are determined after a modification of BRATZEL et al. (1972). The modification was made on decomposition of samples, extraction of silver, and preparation of calibration curves.

2. Analytical method

2.1 Apparatus and reagents

A NIPPON JARRLEL ASH AA-780 atomic absorption spectrophotometer with a carbon tube atomizer unit FLA-10 was used for measuring the silver absorbance. Argon was employed as sheath gas. Optimum operating conditions are shown in Table 1. Sampling of solution was accomplished with a hypodermic microliter syringe (P-200,

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Table 1 Experimental conditions for the determination of silver.

Wavelength (Å)	3281 (3383)
Slit width (mm)	0.075
Lamp current (mA)	8
Argon flow (1/min)	2.0
Dry {Org.	30 A–10 sec.
{Aqu.	30 A–20 sec.
Ash {Org.	50 A–15 sec.
{Aqu.	50 A–30 sec.
Atomize	140 A– 5 sec.

Org.: Organic solution   Aqu.: Aqueous solution

RAININ Instrument Co. Boston).

Standard silver solution (Ag 100 μg/ml): Dissolve 0.1580 g of anhydrous silver nitrate in 1000 ml of 0.1 M HNO_3.

Citric acid solution (40 W/V %): Dissolve 200 g of citric acid in 500 ml of water.

EDTA solution (20 W/V %): Dissolve 200 g of ethylenediamine-tetraacetic acid in 1000 ml of 1.5 M NH_4OH.

DDC solution (0.2 W/V %): Dissolve 0.4 g of sodium diethyl-dithiocarbamate in about 100 ml of water. After filting, dilute to 200 ml with water.

Magnesium solution (Mg 25 mg/ml): Dissolve 8.3 g of magnesium oxide in 50 ml of $HClO_4$ and dilute to 200 ml with water.

2. 2 Analytical procedure

Weight out the powdered rock sample (0.1 to 0.5 g) into a 50 ml of Teflon beaker and moistene with water. Add 1 ml of $HClO_4$ and 5 ml of HF, and heat to dryness on the hot plate at 200 to 230°C. Repeat the evaporation with 1 ml of $HClO_4$ and 5 ml of water. Dissolve the residue by heating with 5 ml of 3 M HNO_3 and cool the solution to room temperature. Add 5 ml of 40 % citric acid, 5 ml of 7.5 M NH_4OH and 10 ml of 20% of EDTA, then adjust the pH to 8.0 to 8.5 by adding 7.5 M NH_4OH.

Transfer the solution into a 100 ml of separatory funnel and add 1.0 ml of 0.2% DDC solution. After diluting the solution to about 50 ml with water, extract silver for 5 min with 5 ml of benzene. Take out 5 to 20 μl of the benzene layer, and determine silver with the operating condition described in Table 1. The silver concentration was calculated directly from the calibration curve, which was obtained by a peak height method.

Prepare a calibration curve by taking 0, 0.01, 0.02, 0.05, 0.10, 0.15 and 0.20 μg of silver in Teflon beakers. Add 1 ml of magnesium solution (Mg 25 mg/ml) to each beaker and proceed as described above.

3. Results and Discussion

3.1 Interferences

No interference was caused by the 0.01 to 1.2 M of HNO_3 and 0.06 to 0.3 M of HCl. Higher concentration of both acids yield a shorter life of the carbon tube. Inter-

Table 2   Effect of diverse ions on the determination of silver in 0.3 M nitric acid.

Ions	Compound added	Interference (%)	
		10,000-fold	100,000-fold
Na^+	$NaNO_3$	0	-15
K^+	KNO_3	0	-10
Mg^{2+}	in HNO_3	0	-8
Ca^{2+}	in HNO_3	$+3$	-13
Fe^{3+}	in HNO_3	-3	-16
Al^{3+}	$Al(NO_3)_3$	0	-10
Cr^{3+}	K_2CrO_4	0	n.d.
Cu^{2+}	in HNO_3	-5	n.d.
Mn^{2+}	in HNO_3	0	n.d.
Zn^{2+}	in HNO_3	0	n.d.
Ni^{2+}	in $HCl+HNO_3$	-5	n.d.
Pb^{2+}	$Pb(CH_3COO)_2 . 3H_2O$	0	n.d.
V^{5+}	NH_4VO_3	-4	n.d.

Ag: 0.01 ppm   n.d.: Not determined

ferences from various elements were studied and the results are shown in Table 2. No interference was observed in the presence of 10,000-fold metals. But the 100,000-fold of sodium, potassium, magnesium, calcium, iron and aluminium was suppressed of the silver absorbance. In some cases, large amounts of salts gave enhancing effects on the silver absorbance. These effects were probably owing to the molecular absorption and light scattering of the salts.

The interferences were avoided by separating silver from matrices. The extracting separation of silver-DDC complex with benzene described by TAKAHISA et al. (1971) was adopted for the extraction of silver. They reported that more than 99% of silver was extracted at the pH 4 to 9, and the extraction time (1 to 10 min) was not critical. The obstructions of large amounts of iron, nickel, aluminium and copper can be eliminated by addition of citric acid and EDTA.

3.2   Preparation of sample and calibration curve

The decomposition method of samples with $HClO_4$ and HF was proposed by HAMAGUCHI and KURODA (1959). In this method, small amounts of undissolved residues were remained on dunite, peridotite and pyroxenite. The residues was fused in this study with potassium pyrosulfate and silver was determined. The amounts of silver retained were so small that this fusion is essentially unnecessary. Acids decomposition method gave rise to smaller contamination them platinum crucible-sodium carbonate fusion method. Generally, about 0.004 μg of silver contamination was detected from all of the procedure.

The calibration curves for silver which were obtained by the way described above are shown in Figure 1. The sensitivity using 20 μl of sample solution and 3281 Å line was 0.0002 ppm/1% abs., and a fairly linear calibration curve was obtained in the range 0 to 0.005 ppm. The range 0.005 to 0.04 ppm of silver was determined using 5 μl of sample solution and 3383 Å line. Some absorption profiles of silver are shown in Figure 2.
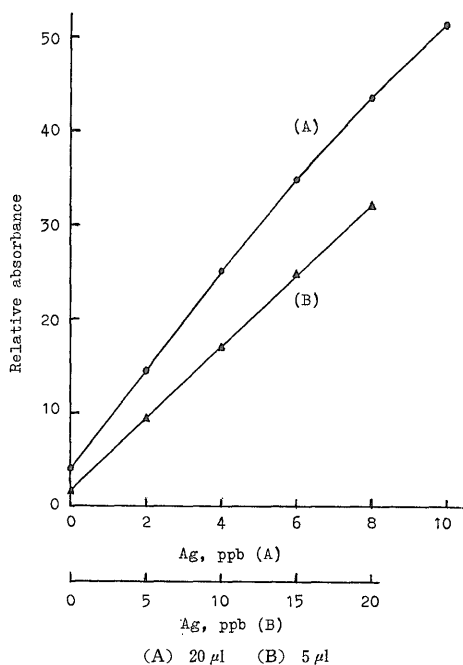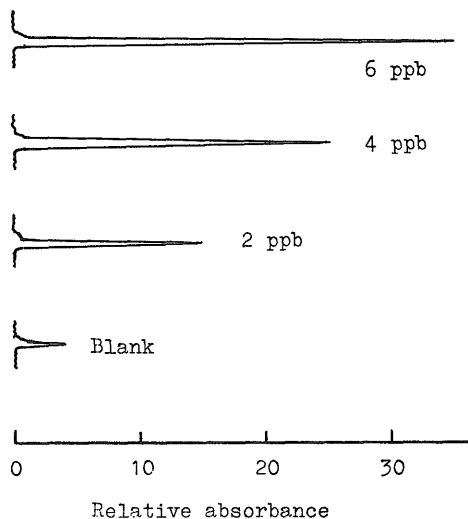
Fig. 1 Calibration curves for silver.

Fig. 2 The absorbance for silver.

3.3 Recovery of known silver

A set of experiments was made to test the recovery of silver from rocks. Known amounts of standard silver nitrate solution was added to 0.5 g of standard rock samples of JG-1 (Granodiorite) and JB-1 (Basalt). The samples were carried through the entire analytical procedure. The results are given in Table 3. The relative standard deviations are less than 14% and recovery is 96 to 102%. The time required for the determination of silver in ten samples is about 5 hours and limit of detection is 0.01 ppm.

Table 3 Precision and recovery.

| Samples | Taken (g) | Ag, μg | | R. S. D. (%) | Recovery (%) |
		Added	Found*		
JG–1	0.5	0.00	0.021	14	—
JG–1	0.5	0.05	0.072	11	102
JG–1	0.5	0.25	0.260	6	96
JB–1	0.5	0.00	0.026	12	—
JB–1	0.5	0.05	0.074	9	96
JB–1	0.5	0.25	0.279	8	101

* Average of five analyses, R.S.D.: Relative standard deviation

3.4 Comparison of results on standard silicates

The results of this study and recent summarized data are listed in Table 4 for comparison. The values by FLANAGAN (1973) are his recommended value, average and magnitude at 1972 compilation. The compiled data of ANDO et al. (1974) are those determined by the optical emission spectrometry and the atomic absorption spectrometry with a air-acethylene flame. Those of LANGMYHR et al. (1974) were obtained from

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Table 4　Silver content in ppm of selected silicate rock samples for comparison.

Samples	This study	FLANAGAN (1973)	Others		
			Data		Reference
JG–1	0.042	0.07	<0.05	(a)	
			<1	(b)	ANDO et al. (1974)
JB–1	0.051	—	<0.05	(a)	
			0.4	(b)	
GSP–1	0.089	0.10	0.12	(c)	LANGMYHR et al.
BCR–1	0.041	0.036	0.050	(c)	(1974)
DTS–1	0.009	0.008	0.03	(d)	BRATZEL et al. (1972)

(a): Emission spectrometry　(b): Atomic absorption spectrometry　(c): Atomic absorption spectrometry by atomizing solid sample in furnace　(d): Atomic absorption spectrometry by atomizing sample solution in tube.

solid sample in graphite furnace by atomic absorption spectrometry using a direct atomization method. In the method, the powdered samples were mixed with equal amounts of graphite, and the background absorption was corrected by a deuterium arc source corrector.

　　Analytical results for silver on a variety of standard samples supplied by the Geological Survey of Japan, the U.S. Geological Survey, the Canadian Standard Reference Materials Project and the National Institute for Metallurgy, South Africa are given in Table 5. The results on U.S. Geological Survey samples approximated to values compiled by FLANAGAN (1973). Silver column of the other standard samples is still vacant and the results of this study should be cross-checked by different analytical methods.

Table 5　Analytical results of silver in ppm of standard silicate and compiled data of FLANAGAN (1973).

	Samples	This study*	FLANAGAN(1973)
GSJ (Japan)	JG–1 (Granodiorite)	0.042±0.006	0.07
	JB–1 (Basalt)	0.051±0.006	—
USGS (U. S. A.)	G–2 (Granite)	0.043±0.005	0.049
	GSP–1 (Granodiorite)	0.089±0.007	0.10
	AGV–1 (Andesite)	0.096±0.009	0.11
	PCC–1 (Peridotite)	0.007±0.002	0.005
	DTS–1 (Dunite)	0.009±0.002	0.008
	BCR–1 (Basalt)	0.041±0.007	0.036
CSRM (Canada)	MRG–1 (Gabbro)	0.140±0.008	—
	SY–2 (Syenite)	0.022±0.006	—
	SY–3 (Syenite)	0.026±0.005	—
NIM (S. Africa)	NIM–D (Dunite)	0.017±0.006	<1
	NIM–G (Granite)	0.049±0.008	<1
	NIM–L (Lujavrite)	0.024±0.006	<1
	NIM–N (Norite)	0.035±0.005	<1
	NIM–P (Pyroxenite)	0.018±0.004	1
	NIM–S (Syenite)	0.050±0.008	<1

*: Average (n=5) ± Standard deviation

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炭素管アトマイザー原子吸光法による岩石中の微量の銀の定量

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　原子吸光法による岩石中の微量の銀の定量について測定条件，共存成分の影響，銀の分離などについて検討し，定量法を確立した．

　粉末試料 0.1-0.5 g をテフロンビーカーにとり，過塩素酸 1 ml とふっ化水素酸 5 ml を加え，蒸発乾固する．過塩素酸 1 ml と少量の水を加えて蒸発乾固を繰返したのち，硝酸 (3 M) 5 ml を加えて加温溶解する．クエン酸 (40%) 5 ml，アンモニア水 (7.5 M) 5 ml，EDTA (20%) 10 ml を加えたのち pH を 8-8.5 に合せる．分液漏斗に移し入れ，ジエチルジチオカルバミン酸ナトリウム溶液 (0.2%) 1 ml を加え，水で全量を約 50 ml にしたのちベンゼン 5 ml で 5 分間抽出する．ベンゼン層の一部 (5-20 μl) をとって Table 1 の条件で測定する．検量線は銀 0.0-0.2 μg をテフロンビーカーにとり，それぞれにマグネシウム溶液 (Mg 25 mg/ml) 1 ml を加えたのち試料と同様に操作して作製する．

　本法の感度は 0.0002 μg/ml/1% 吸収であり，0.05-0.25 μg の銀の定量における変動係数は 6-11% で，回収率は 96-102% であった．分析所要時間は 10 試料について約 5 時間であり，検出限界は岩石中約 0.01 ppm である．各種岩石標準試料中の銀を定量し，結果は Table 5 に示した．