

Spectrophotometric Determination of Chlorine and Fluorine in the Standard Silicate Rocks

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Abstract

The chlorine and fluorine contents in eight standard silicate samples have been determined by spectrophotometric method.

The sample was fused with sodium carbonate and zinc oxide, and the melt was dissolved in hot water, and after filtration the solution was neutralized with nitric acid. Then chlorine and fluorine were determined by the absorption measurement utilizing the stable colored iron (III) thiocyanate and zirconium-eriochrome cyanine R complex.

This method gives higher sensitivity, simpler chemical treatment, and the relative standard deviation in the determination of 60–300 ppm chlorine was 5–16%, and that of 300–4,000 ppm fluorine 2–5%.

1. Introduction

Although a lot of data have been reported on the contents of chlorine and fluorine in standard silicate rock samples (ANDO et al., 1971; FLANAGAN, 1969; HUANG et al., 1967), the agreement is very poor for several samples (Table 1). Consequently, a higher degree of accuracy should be required to determine the standard values for chlorine and fluorine in the samples.

Recently, HUANG and JOHNS (1967) described a method for determining chlorine and fluorine in silicate rocks, and the method has been applied to the determination of fluorine in phosphates, micas, and stony meteorites by Sen GUPTA (1968). AKAIWA and AIZAWA (1973) modified this method and used it for fluorine determination of sedimentary rocks. The features of the method are that the determination can be higher sensitivity, the simpler chemical treatment, and that chlorine and fluorine can be determined from the single sample dissolution.

In this study, chlorine and fluorine in standard rocks were determined after a modification of

Table 1 Published data for chlorine and fluorine in some standard silicate rocks.

Samples	Cl, ppm				F, ppm			Ref.
JG-1 (Granodiorite)	57*	200			500	510	800	1)
JB-1 (Basalt)	190*				360			1)
G-2 (Granite)	{ 53* 192	100	150	300	{ 500 1205	1300	2000	2) 3)
GSP-1 (Granodiorite)	{ 200 342	311*	400	600	{ 1900 1940	3700	4000	2) 3)
AGV-1 (Andesite)	{ 115* 319	150	200	400	{ 400 435	500		2) 3)
BCR-1 (Basalt)	{ 58* 62	100	600		{ 500 485	500		2) 3)

Ref: 1) Ando et al., (1971). 2) Flanagan (1969). 3) Huang and Johns (1967).

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the method of HUANG and JOHNS (1967), and Sen GUPTA (1968).

2. Analytical Method

2.1 Apparatus and reagents

A HIRAMA Rika Type-6 spectrophotometer with flow type 1.0 cm glass cell was used for measuring the absorbance of complex solution.

Witt's filtering bottle and Sibata 1G-4 glass filter were used for filtration.

Ferric ammonium sulfate solution (reagent A for Cl). Dissolve 48.2 g of $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 400 ml of 9 M nitric acid.

Mercury (II) thiocyanate solution (reagent B for Cl). Dissolve 1.0 g of $\text{Hg}(\text{SCN})_2$ in 400 ml of methanol.

Eriochrome cyanine R solution (reagent A for F). Dissolve 1.80 g in 1,000 ml of water.

Zirconyl chloride solution (reagent B for F). Dissolve 0.265 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in about 10 ml of water and dilute with concentrated hydrochloric acid to 1,000 ml.

Aluminum solution (1 mg Al/ml). Dissolve 6.95 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 500 ml of water.

Standard chlorine solution (20 μg Cl/ml). Dry reagent NaCl for 2 h at 110°C and cool in a desiccator. Dissolve 0.8242 g in 500 ml of water, take a 10 ml aliquot and dilute to 500 ml.

Standard fluorine solution (10 μg F/ml). Dry reagent NaF for 2 h at 110°C and cool in a desiccator. Dissolve 0.5525 g in 1,000 ml of water, take a 10 ml aliquot and dilute to 250 ml.

2.2 Preparation of sample and blank solution

Weigh out the powdered 0.500 g of sample into a 30 ml platinum crucible, add 3.5 g of Na_2CO_3 (Merck) and 0.6 g of ZnO (Wako) and mix thoroughly with a glass rod. Cover the crucible with the lid and fuse in an electric furnace at 950°C for 10 min. Raise the temperature to 1000°C and heat for an additional 20 min.

Cool the crucible to room temperature in a desiccator, and add 10 ml of water and 4-5 drops of 95% ethanol. Place the crucible on a hot plate, boil for 3-4 min, and transfer the contents into a 100 ml polyethylene beaker. Cover the beaker and place for 0.5-1.0 h on a hot water bath, and crush the contents until the solid lump was completely broken with a flat-ended glass rod and stir the solution.

Filter the hot solution through a glass filter into a 100 ml polyethylene beaker by means of vacuum filtrator. Wash the filter and residue with hot water (total volume should not exceed 40 ml). Cover the beaker, add cautiously 4.2 ml of concentrated nitric acid and stir the solution to expel most of the CO_2 . Wash the cover glass and the inside of the beaker with water, and transfer the solution into a 50 ml flask and make up to the volume (sample solution).

Prepare a blank solution by taking 3.5 g of Na_2CO_3 and 0.6 g of ZnO, and treating as described above. But final volume of the blank solution is made up exactly to 25 ml.

2.3 Chlorine determination

After stirring, pipette a 20 ml of sample solution into a 25 ml flask. Add 2.0 ml each of reagents A and B for Cl. Mix the solution, dilute to volume with water and mix again. Allow the color to develop for 30 min, and measure the absorbance of the sample against water at 460 nm.

Prepare a series of standard solutions by taking 0, 20, 50, 100, 150 and 200 μg Cl in 25 ml flasks. To each standard solutions add 10 ml of the blank solution. Add the reagents, color development and absorbance measurement are as outlined above.

2.4 Fluorine determination

Pipette 5.0 ml each of reagents A and B for F into a 50 ml flask, add 25–30 ml water and mix well.

After stirring, pipette an aliquot of the sample solution containing less than 70 μg F, and make up to volume with water and mix again.

Prepare a series of standard solutions by taking 5.0 ml each of reagents A and B for F, 1 ml of aluminum solution and 2.5 ml of the blank solution in six 50 ml flasks, and dilute to 30–35 ml with water. After adding 0, 20, 40, 60, 70 and 100 μg F, make up the standard solutions to the volume with water and mix.

Allow the solution to stand for 2.5–3.0 h for elimination of aluminum interference (Sen GUPTA, 1968). Set zero absorbance at 532 nm, using the standard containing 100 μg F, and measure the absorbance of each sample and other standard solutions. It is necessary that the standard curve is checked by 0, 40, and 100 μg F for each batch of fluorine determinations.

3. Results and Discussion

The standard curves for chlorine and fluorine which were obtained by the way described above are shown in Figs. 1 and 2. These standard curves were affected by concentration of all reagents.

The analytical results of chlorine and fluorine in eight standard silicate samples are given in Table 2. Each figure shows the five measurements, averages, standard deviations and relative standard deviations. The relative standard deviations in the determination of 60–300 ppm chlorine are 5–16%. The main cause for the error in the determination of chlorine is contamination from

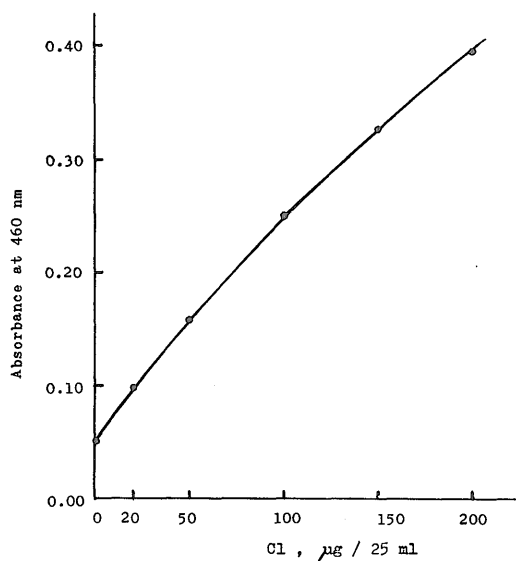


Figure. 1 Standard curve for chlorine.

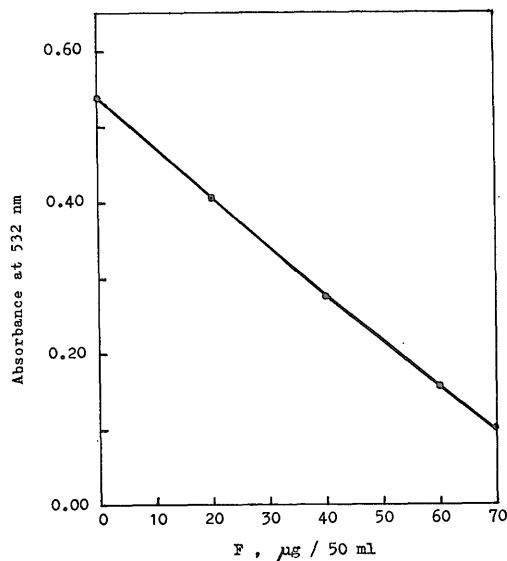


Figure. 2 Standard curve for fluorine.

Table 2 Determination of chlorine and fluorine in standard silicate rocks.

Samples	Found Cl, ppm						Found F, ppm					
				\bar{X}	S	C				\bar{X}	S	C
JG-1 (Granodiorite)	60	75	80	67	10.5	15.7	470	520	480	491	19.5	4.0
	63	55					485	500				
JB-1 (Basalt)	150	180	162	167	11.8	7.1	365	350	370	365	11.2	3.1
	175	170					360	380				
G-2 (Granite)	75	88	65	72	10.7	14.9	1320	1230	1210	1258	42.1	3.3
	70	60					1260	1270				
GSP-1 (Granodiorite)	300	325	343	318	16.8	5.3	3800	3750	3800	3790	74.2	2.0
	310	310					3900	3700				
AGV-1 (Andesite)	135	137	117	130	11.0	8.5	370	350	380	371	15.2	4.1
	142	120					365	390				
PCC-1 (Peridotite)	67	79	55	65	9.0	13.8	30	12	20	20	6.5	32.5
	60	66					20	18				
DTS-1 (Dunite)	13	17	11	15	6.1	40.7	20	24	18	18	5.2	28.9
	25	10					16	10				
BCR-1 (Basalt)	75	53	70	65	8.6	13.2	470	490	450	471	16.7	3.5
	65	60					485	460				

X: Average S: Standard deviation C: Relative standard deviation

the apparatus, experimentalist and laboratory. The contamination is decreased by washing the all apparatus with diluted nitric acid, and putting on gloves during the analytical procedure.

Among the methods for the determination of chlorine, the neutron activation analysis is better than other methods, because of little contamination and checking of the yield with chemical procedure. In this study, the results on chlorine in standard samples approximated to results from the neutron activation analysis (Table 1, Table 2).

The relative standard deviations of 300–4,000 ppm fluorine measurements are 2–5%. If precipitation appears in the sample solution, generally a portion of fluorine is co-precipitated. However, the precipitation is dissolved by transfer to acidic reagents solution.

The time required for the determination of chlorine and fluorine in ten samples is about 8 h.

Acknowledgement

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吸光光度法による標準岩石中の塩素およびふっ素の定量

寺 島 滋

要 旨

吸光光度法により、各種けい酸塩標準試料中の塩素およびふっ素を定量した。

試料を炭酸ナトリウムと酸化亜鉛で融解し、抽出、汙過したのち、塩素はチオシアン酸鉄塩、ふっ素はエリオクロムシアニンR-ジルコニウム塩溶液の吸光度を測定する方法で定量した。本法によれば、各種岩石中の 30 ppm 以上の塩素およびふっ素が簡単かつ迅速に定量でき、精度も良好である。