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POTENTIOMETRIC TITRATION OF ALUMINUM IN SILICATE ROCKS BY MEANS OF FLUORIDE

RIASSUNTO. — È stato sperimentato un nuovo metodo per determinare Al_2O_3 nelle rocce silicatiche mediante titolazione potenziometrica di Al con NaF. Le determinazioni sono state eseguite su alcune rocce e minerali standard. Sono discusse accuratezza e precisione del metodo.

ABSTRACT. — A new method to determine Al_2O_3 in silicate rocks has been applied to standard rocks and minerals by means of Al potentiometric titration with Na-fluoride. Accuracy and precision are discussed here.

Introduction

The present paper describes a method for the determination of Al-ion in the silicate rocks; the Orion fluoride electrode, model 94-09, has been used to perform the titration of Al ion with a sodium fluoride titrant.

Electrode potentials corresponding to additions of titrant are plotted directly on 10 % volume corrected Gran's Plot Paper.

The Al concentration in the solution should range between 0 and 2×10^{-4} M.

Concentrations of Al_2O_3 were determined in some international and special standards of silicate rocks and minerals:

G2	granite	U.S.G.S.
BR	basalt	A.N.R.T.
DRN	diorite	A.N.R.T.
JG1	biotitic granodiorite	G.S.J.
398	gabbro	(Internal Standard of this Institute)
M1	muscovite	(Penn State Standard)

Experimental

Equipment

A specific ion meter, model 407, was used with an Orion model 94-09 solid state fluoride electrode referred to an Orion model 90-01 single junction reference electrode.

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A 10 ml buret was used for titration with NaF.

All mv-readings were plotted on a Gran's Plot Paper. This paper is an available special volume-corrected graph paper for obtaining linear plots. The paper allows electrode potentials to be plotted directly without prior calculations. The property of this paper (semi-antilog) is extremely useful because it allows us to make linear titration plots which can be extrapolated to the equivalence point. The Gran's Plot Paper 10 % volume corrected is based on addition of up to 10 ml to 100 ml sample.

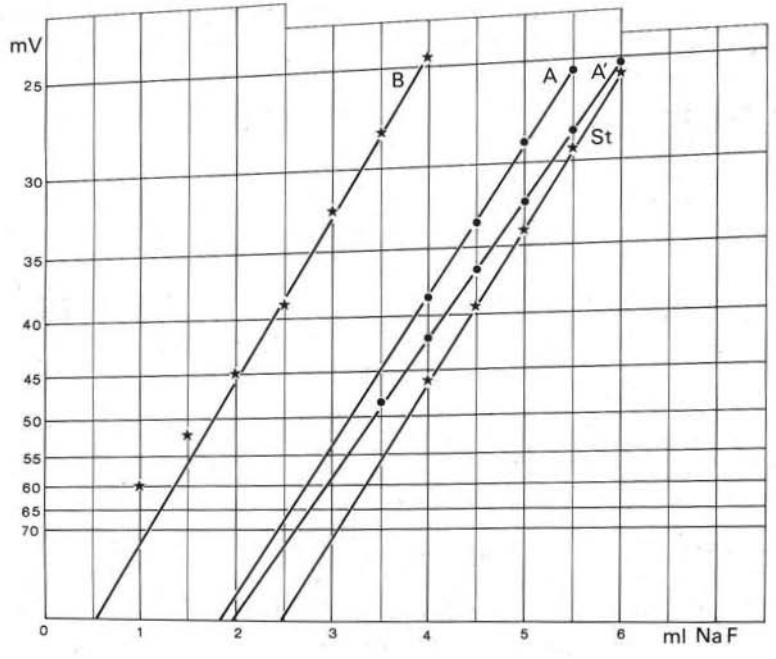

Fig. 1. — Gran's Plot titration for aluminum. Curve B: blank. Curve St: 0.96×10^{-4} M Al^{3+}. Curves A, A': a sample.

Reagents

Standard 0.1 M NaF solution, prepared with NaF, diluted 1+9 to obtain 0.01 M fluoride titrant.

2 M acetate buffer to hold the sample at about pH 4.

0.01 M aluminum standardizing solution diluted to make 10^{-4} M aluminum solution.

5 M sodium perchlorate ionic strength adjustor.

Orion's total ionic strength adjustment buffer TISAB, containing CDTA.

0.1 % KCN solution.

Interferences

Fluoride ion was complexed by Si^{4+}, Fe^{3+}, Al^{3+}, H^+.

The silica was removed by treating the rock powders with H_2SO_4 and HF. The obtained solution was dried in order to remove the fluoride ion, then it was put to a fixed volume with distilled water.

The pH buffer was added to the sample to obtain about pH 4, because the stoichiometry varies as a function of pH (JASELSKIS B., BANDEMER M.K., 1969).

Ferric ion at a level equal to that of the aluminum ion interferes, so 0.1 % KCN solution was added to complex the ferric ion in the sample.

Procedure

The sample solution was diluted until an Al concentration of about 2×10^{-4} M was obtained. In such a solution, the concentration of residual fluorides was determined according to the direct procedure for fluoride determination; then the readings in ppm of fluorides were changed in milliliters of 0.01 M NaF, which were considered as already added before titration.

100 ml of sample solution were taken. Then aliquots of 2 or 3 ml of buffer solution to make about pH 4, and 2 ml of ionic strength adjustor were added. If ferric ion level was equal to that of the supposed aluminum ion, 1 ml of KCN was added.

A 10^{-4} M aluminum solution and a blank solution were made.

Stirring bars were used to mix the sample. The stirred solutions were titrated potentiometrically with 0.01 M NaF in 0.5 ml increments.

Each addition of NaF caused decreases of potential.

Instable readings for the initial points were disregarded; the following additional increments of titolant readings, that were obtained, were plotted on the Gran's Plot Paper.

The Gran's Plot Paper was calibrated with the potential values of the blank. The best straight line for standard solution and unknown solutions was drawn.

The unknown level of aluminum, x, was calculated from the ratio:

$$\frac{x}{10^{-4}} = \frac{\text{(unknown intercept)} - \text{(blank intercept)}}{\text{(standard intercept)} - \text{(blank intercept)}}$$

Accuracy and discussion

Table 1 gives some statistic parameters and comparison with the averages of international standards according to Flanagan (1973) and other Authors.

The values of standard deviation include the error of analytical factor, because the data are usually expressed in percentage of alumina.

We can observe from the examination of accuracy that in the range of Al_2O_3 concentration (12-19 %) in the more common igneous rocks of continental litosphere, the relative deviation falls to the lowest values.

The concentration value of BR is higher than the Flanagan average, this is probably due to the high concentration of Fe_2O_3 (12.97 %); iron, as well as aluminum, in fact, forms very stable complexes (FeF_3).

The concentration value of M1 is lower than the international average; this fact is probably due to a high percentage of alumina (35.77 %). In this case, the sample solution has to be more diluted in order to remain within the instrument's range of detection.

TABLE 1

Data of accuracy for Al_2O_3 determination

Sample material	Reference n.	$\bar{x}$	s	C	Limits of acceptability	Authors averages
Basalt	BR	10.87	0.47	5.70	10.40 - 11.34	10.25
Granite	G2	15.71	0.57	1.97	15.14 - 16.28	15.40
Diorite	DRN	17.07	0.23	2.87	16.84 - 17.30	17.56
Biotitic granodiorite	JG1	14.22	0.41	0.07	13.81 - 14.63	14.21
Gabbro	398	17.62	0.50	0.62	17.12 - 18.12	17.51
Muscovite	M1	33.34	0.36	7.28	32.98 - 33.70	35.77

$\bar{x}$, arithmetic mean

s, standard deviation

C, relative deviation or coefficient of variation = $\frac{s}{\bar{x}} \cdot 100$

In comparison with the BAUMANN procedure (1970), this method enables one to work on high concentrations and to eliminate the main interferences without further chemical handlings.

In conclusion, with this method several determinations can be made in a short time, because about 15 minutes are needed for each analysis.

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