DETERMINATION OF POTASSIUM, SODIUM AND CALCIUM IN FELDSPARS

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ABSTRACT

A combined flame photometric method is described for the determination of potassium, sodium and calcium in feldspars. Magnesium is used to minimize variations in the depressant effect of aluminum on calcium emission resulting from deviations from stoichiometry. Standard solutions, approximating the compositions of the sample solutions, are prepared from pure reagents. An analysis can be done on as little as 10 milligrams of sample.

INTRODUCTION

In the course of continuing studies on feldspars, a need arose for a simple, rapid method for determining potash feldspar, albite and anorthite in many pure mineral samples.

Considering each sample as a mixture of the three molecules, $K_2O.Al_2O_3.6SiO_2$, $Na_2O.Al_2O_3.6SiO_2$ and $CaO.Al_2O_3.2SiO_2$, such mixtures have the following properties:

(a) Determinations of potassium, sodium and calcium are sufficient to establish feldspar composition.

(b) Alumina and silica concentrations are dependent variables, governed by the relative proportions of the three "diagnostic" elements (potassium, sodium and calcium).

Aluminum content is significant because that element depresses the flame emission of calcium. Silica is of no importance, because it is volatilized (along with any quartz impurity present) on decomposing the sample with hydrofluoric acid.

Flame photometry was favored over other techniques because it is applicable to all three elements, with a minimum of chemical pretreatment. In this technique, interelement effects are generally unpredictable. Such effects can be largely overcome by using a reference standard whose composition is close to that of the unknown. The literature contains many contradictions regarding the effects of other elements on alkali element emission, but such effects tend to be small. Chemical separations or the addition of a "radiation buffer" (a large excess of the extraneous elements) may be used to bring the compositions of sample and standard closer together.

The literature of calcium flame photometry is virtually unanimous in reporting that aluminum depresses calcium emission. "Releasing agents," such as polyhydric alcohols (Rains *et al.*, 1963), magnesium or other cations (Dinnin, 1960), have been used to restore calcium emission to the level it would attain in the absence of the depressant ion. However, studies on releasing agents have paid little attention to possible effects of other constituents of the sample solution. An attempt was made to eliminate the depressant effect of aluminum by adding that element to the standard solutions, in amounts deduced from the proportions of the three diagnostic elements in the samples, as determined in a rough preliminary analysis. Satisfactory results were obtained for the alkali metals, but calcium results were low. Analysis revealed that the samples actually contained more alumina than expected, resulting in a greater depression of calcium emission in the samples than in the standards.

It was then decided to try magnesium as a releasing agent. This additive was not intended to overcome the influence of aluminum entirely, but merely to "smooth out" the effects of small deviations from stoichiometry. The major portion of the aluminum depression of calcium is cancelled out by using standards whose compositions approximate those of the samples. Most of the published work on releasing agents deals with relatively low concentrations of calcium. It was therefore decided to take flame photometric readings at relatively high dilution (10 mg. of sample per 50 ml. of solution). High dilution also permits the analysis of small samples. A recording spectrophotometer was used to minimize uncertainties resulting from background radiation surrounding the calcium peak at 554 millimicrons.

RECOMMENDED PROCEDURE

Reagents

1. *Standard K-feldspar concentrate.* Using oven-dried potassium chloride and" as received" aluminum nitrate, prepare 500 ml. of a solution containing the equivalent of 168.5 p.p.m. K_2O and 181 p.p.m. Al_2O_3. Expel nitrate and chloride by fuming to dryness with perchloric acid, and add 15 ml. of concentrated HCl before final dilution to volume. The final concentrations of potassium and aluminum are equal to what would be obtained on decomposing 0.5 g. of pure $K_2O.Al_2O_3.6SiO_2$ by the analytical procedure below, and diluting to 500 ml. Store this solution in polyethylene.

2. *Standard albite concentrate.* Using oven-dried sodium chloride, proceed as above, but make the final concentrations equivalent to 118.5 p.p.m. Na_2O and 193 p.p.m. Al_2O_3.

3. *Standard anorthite concentrate.* Using oven-dried calcium carbonate (dissolved in nitric acid), proceed as above, but make the final concentrations equivalent to 201.5 p.p.m. CaO and 367 p.p.m. Al_2O_3.

4. *Magnesium solution* (10,000 p.p.m. Mg). Dissolve 2g pure magnesium in 35 ml HCl (1:1) and dilute to 200 ml.

Apparatus

Beckman Model DU Spectrophotometer
A.C. Power Supply
Flame Photometry Attachment (Oxy-acetylene burner)
Spectral Energy Recording Adaptor
Varian G-10 Recorder.

Calibration

Prepare two series of calibration standards, a K-Na series and a Na-Ca series. Into 50 ml. volumetric flasks, pipette the indicated volumes of the standard feldspar concentrates ("SFC" in Tables 1 and 2). (The "p.p.m." columns indicate final concentrations.) To each, add 5 ml magnesium solution, make up to volume, and store in polyethylene.

TABLE 1. CALIBRATION STANDARDS—K-Na SERIES

Feldspar Composition		ml SFC		p.p.m./solution		Equiv. pct./sample	
Or	Ab	K	Na	K_2O	Na_2O	K_2O	Na_2O
100	0	10	0	33.7	0.0	16.85	0.00
80	20	8	2	27.0	4.7	13.50	2.35
60	40	6	4	20.2	9.5	10.10	4.75
40	60	4	6	13.5	14.2	6.75	7.10
20	80	2	8	6.7	19.0	3.35	9.50
0	100	0	10	0.0	23.7	0.00	11.85

To calibrate for potassium, aspirate standard Or 100, and adjust instrument (see Table 3) to read about 95 (after background correction). Without altering any settings, take readings on all of the Or standards in descending order, repeat in ascending order, and again in both descending and ascending order. Calculate the mean of the four readings for each standard, and multiply each mean by $100/M$, where M

TABLE 2. CALIBRATION STANDARDS—Na-Ca SERIES

Feldspar Composition		ml SFC		p.p.m./solution		Equiv. pct./sample	
Ab	An	Na	Ca	Na_2O	CaO	Na_2O	CaO
100	0	10	0	23.7	0.0	11.85	0.00
80	20	8	2	19.0	8.1	9.50	4.05
60	40	6	4	14.2	16.1	7.10	8.05
40	60	4	6	9.5	24.2	4.75	12.10
20	80	2	8	4.7	32.2	2.35	16.10
0	100	0	10	0.0	40.3	0.00	20.15

TABLE 3. FLAME PHOTOMETER SETTINGS

	K	Na	Ca
Photomultiplier Sensitivity	(Red Tube)	5	7
Load Resistor, megohms	10,000	22	22
Slit, mm.	0.045	0.015	0.050
Scan time (down scale)	10	30	10
Begin scan at (millimicrons)	775	592	562
Peak (millimicrons)	766	589	554
Oxygen pressure, p.s.i.	13	13	13
Acetylene pressure, p.s.i.	4	4	4

Note: "Sensitivity" and "scan time" are in arbitrary units, characteristic of the instrument actually used.

is the mean reading for standard Or 100. Plot adjusted means *vs* p.p.m. K_2O.

Similarly, calibrate for sodium in both K-Na and Na-Ca series (plotting separate curves) and for Ca in the Na-Ca series.

Analysis of samples

Accurately weigh 100 mg. of sample (or less—see below) into a 100 ml. platinum dish. Decompose by digestion with 5 ml. of nitric, 5 ml. of hydrofluoric and 1 ml. of perchloric acids. Evaporate twice to perchloric fumes on a sand bath, rinsing down walls with water between fumings. Finally evaporate until all fumes are expelled. Redissolve in 20-30 ml. of water and 3 ml. of HCl. Dilute to volume in a 100 ml. volumetric flask and transfer to polyethylene. Pipette 10 ml. into a 50 ml. volumetric flask. Add 5 ml. of magnesium solution, dilute to volume, and transfer to polyethylene. This solution is used for flame photometry.

If the supply of sample is limited, the weight used may be reduced and all operations scaled down proportionally, provided the final 50 ml. solution contains 10 mg. of sample and 5 ml. of magnesium solution.

Preliminary photometry

Prepare a blend of the feldspar concentrates with a composition in the range where the samples are expected to fall. For each element, adjust the instrument with the standard to give a reading close to that indicated by the calibration curve. Take readings for standard and samples, and correct the latter proportionally to the deviations of the former from the calibration curves. Using the corrected readings, determine the concentration of each element from its calibration curve. Choice of sodium curve will depend on whether the sample is high in potassium or in calcium.

Final photometry

Using the approximate values obtained in the preliminary photometry, prepare a new standard blend to match each sample. Adjust the instrument for each element as before, and take at least two readings for each element, each reading being preceded and followed by a reading on a closely matching standard. Apply corrections as before, based on the standard readings before and after each sample reading. Calculate a mean for each element reading, after rejecting aberrant values, and determine concentration from the calibration curve. A procedure for these corrections has been described elsewhere (Abbey & Maxwell, 1960).

RESULTS

Four analysed feldspars, of varying compositions, were analysed by the method herein described. Results are given in Table 4, as percentages of oxides, and as calculated feldspar components in Table 5. The largest discrepancy (CaO in 279-63) involves comparison with a result obtained by *x*-ray fluorescence. Mineralogical examination of the sample has revealed the presence of prehnite, which may account for anomalous "total feldspars".

TABLE 4. RESULTS BY PROPOSED METHOD—OXIDES

Sample No.	K_2O		Na_2O		CaO	
	Present	Found	Present	Found	Present	Found
D-409	0.32	0.25	4.84	4.59	11.40	11.52
NBS-99	0.41	0.30	10.73	10.75	0.36	0.28
NBS-70	12.58	12.61	2.38	2.41	0.07	0.18
279-63	0.70	0.94	1.2	1.22	17.0	17.80

Note: "Present" values on NBS-99 and NBS-70 are National Bureau of Standards certificate values. CaO "present" in D-409 by gravimetric oxalate method. K_2O "present" in D-409 and Na_2O in D-409 and 279-63 by established flame method. CaO and K_2O "present" in 279-63 by *x*-ray fluorescence.

TABLE 5. RESULTS CALCULATED AS FELDSPARS

Sample	Or		Ab		An		Total	
No.	Pres.	Fd.	Pres.	Fd.	Pres.	Fd.	Pres.	Fd.
D-409	2	1	41	39	52	52	94	92
NBS-99	2	2	90	91	2	1	94	94
NBS-70	75	75	20	20	0	1	95	96
279-63	4	6	10	10	84	88	98	104

DISCUSSION

Fraser & Downie (1964) have described two procedures for solving the same problem as that considered in this work, one involving flame photometry, the other spectrographic analysis. In both, they used analysed samples of microcline, albite and labradorite to prepare standards. They found that different flame conditions were required for sodium than for potassium and calcium, and therefore determined albite by difference. In their spectrographic method, Fraser & Downie made estimates on some 12 spectrum lines, and used a complicated "determinative chart". Both of these procedures evidently assume that Or + Ab + An = 100 on all samples. Their detailed studies on the effect of "various solutions" on emission of potassium and calcium are essentially confirmation of the fact that potassium flame emission is little affected, and calcium greatly affected, by variations in aluminum concentrations.

The following advantages are claimed for this method over that of Fraser & Downie:

(a) The use of synthetic standards makes the method applicable over a wider range of compositions than where analysed samples are used, aside from eliminating errors in the analysis of such samples.

(b) Independent determination of the three diagnostic elements and calculation of "total feldspars" serve as a rough check on accuracy and on sample purity.

(c) The proposed method is simpler, both in development and in application.

A possible disadvantage is the need to use a recording spectrophotometer. However, with some modification, the method should be applicable with any flame photometer.

The magnitude of the deviations in Table 4 suggests that the percentages of the oxides should be reported to only one decimal place. Rounding of Or, Ab and An contents to the nearest whole percentage in Table 5 is more realistic than reporting them to the nearest 0.1 per cent, as was done by Fraser & Downie.

Further work is planned to determine what modifications, if any, are necessary in order to apply this method to aluminosilicate rocks, and to minerals other than feldspars.

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