

The spectrochemical determination of feldspars within the field microcline-albite-labradorite

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Summary. Two spectrochemical methods of feldspar determination are described: one based on the flame spectrophotometer; the other on the quartz spectrograph. For the first method, unknown feldspars are dissolved in a mixture of hydrofluoric and perchloric acids and diluted to 1:10⁴. Percentages of Or and An are determined by comparison with dissolved feldspar standards at the same dilution; percentages of Ab are estimated by difference. For the second method, unknown feldspars are burned, unadulterated, in the cathode of the spectrograph arc and a visual estimation is made of the intensities of the following lines: Na5688, Na5683, Ca4455, Ca4435, Ca4425, K4047, K4044, Ca3644, K3447, Na3303, Na3302, and Ca3159. The estimated intensities are then substituted in two empirically determined functions:

$$(I_{Ca4455} + I_{Ca4435} + I_{Ca4425} + I_{Ca3644} + I_{Ca3159}) - \frac{4}{3}(I_{Na5688} + I_{Na5683} + I_{Na3303} + I_{Na3302})$$

and $(3I_{Na5688} + 3I_{Na5683} + 2I_{Na3303} + I_{Na3302}) - \frac{4}{3}(4I_{K4047} + 3I_{K4044} + 2I_{K3447})$.

From the algebraic values of these two functions, the compositions of the unknown feldspars, expressed as percentages of Or, Ab, and An, are read directly from a chart based on results obtained from feldspar standards of known chemical composition.

IN connexion with a departmental study of mineral transformations, two spectrochemical methods of feldspar determination have been developed: an accurate method based on the flame spectrophotometer, and a rapid method based on the quartz spectrograph.

Method based on flame spectrophotometer

The flame spectrophotometer is not sufficiently sensitive to aluminium and silicon to permit complete analysis of feldspar. It has frequently been used to estimate potassium and sodium in feldspar solutions from which aluminium has been removed. It has not previously been used to determine calcium in feldspar solutions, for the other ions have a strong repressive effect on the intensity of the flame emission spectrum of calcium. Investigation has shown, however, that, if solutions of unknown feldspars are compared with dissolved feldspar standards at the same dilution, the factors of mutual interference are balanced out.

By eliminating the need for precipitating or adsorbing aluminium, this procedure saves time.

The feldspars meantime used as standards are: microcline (amazonstone), Pike's Peak; albite, Amelia Co.; and labradorite, St. Paul Island. Each of these was analysed twice by the methods of Groves.¹ Table I shows the mean of the two analyses for each feldspar, the maximum deviation of the analyses from this mean, and the composition expressed as percentages of Or, Ab, and An.

TABLE I. Compositions of feldspar standards

	Microcline, Pike's Peak	Albite, Amelia Co.	Labradorite, St. Paul Island
SiO ₂	65.06 ± 0.20	67.79 ± 0.25	54.63 ± 0.20
Al ₂ O ₃	19.79 ± 0.10	19.89 ± 0.17	28.73 ± 0.13
CaO	0.14 ± 0.01	0.52 ± 0.03	11.72 ± 0.07
Na ₂ O	1.94 ± 0.05	11.52 ± 0.08	4.92 ± 0.04
K ₂ O	13.53 ± 0.07	0.30 ± 0.00	0.45 ± 0.01
Total	100.46	100.02	100.45

Composition: Or_{82.4}Ab_{16.7}An_{0.9} Or_{1.7}Ab_{98.5}An_{2.5} Or_{2.7}Ab_{40.6}An_{56.7}

To prepare stock solutions of standard or unknown feldspars, 0.5 gm of feldspar is dissolved in a 3:1 mixture of hydrofluoric and perchloric acids² and diluted to 500 ml with deionized water (the use of either hydrochloric or sulphuric acid instead of perchloric is liable to cause precipitation of a small proportion of the lime as CaF₂). To prepare solutions for spraying into the flame photometer, stock solutions are further diluted to a tenth of their former strength, so the final dilution of the feldspar is 1:10⁴. To prepare comparison standards, various proportions of diluted feldspar standards are mixed so as to produce a series of compositions, at intervals of between 3 % and 5 % Or, Ab, or An, between microcline and albite, albite and labradorite, and labradorite and microcline. Three-constituent comparison standards have been found to be unnecessary.

To determine the Or percentage in unknown feldspars, the instrument is set so as to burn with a 'hot' flame and the waveband K7665 is selected. The comparison standards microcline-albite and microcline-labradorite are run through to give the data for two virtually identical curves relating galvanometer deflection to Or percentage. Solutions of unknown feldspars are then run through three times each, after which a few standards are run through a second time to check that there has

¹ A. W. Groves, *Silicate analysis*, 1951, London.

² J. P. Riley, *Analytica chimica acta*, 1958, vol. 19, p. 413.

been no drift in the galvanometer zero. If drift has occurred, it is distributed evenly over all the readings in the run. The Or percentage in each unknown is found by comparing the mean of the three galvanometer deflections with the curves based on standard solutions.

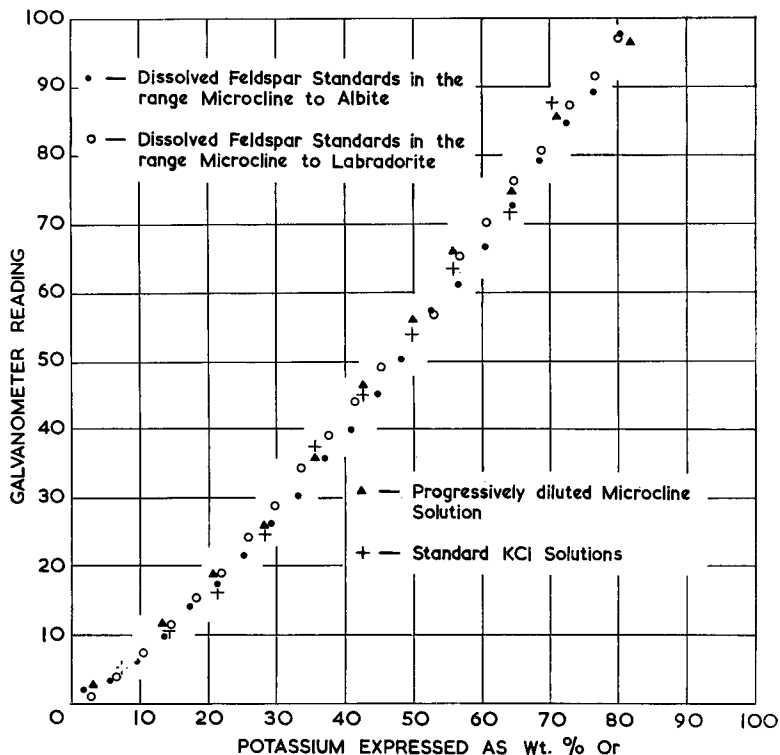


FIG. 1. Relationship between galvanometer deflection and K-concentration, expressed as wt. % Or, in various solutions.

Fig. 1 shows the relationship between galvanometer deflection and K-concentration, expressed as wt. % Or, in the following solutions: KCl; microcline-albite and microcline-labradorite standards; and progressively diluted microcline. Apart from a slight scatter, all the points plotted lie on a single curve. This suggests that, in the case of potassium, interference effects from other ions in feldspar solutions are negligible; thus, if Or were the only component to be determined, the use of feldspar standards would be unnecessary.

The An percentage is determined in a similar way, with no readjustment of the flame. The instrument is set on the broad band at Ca5580: this is more sensitive than Ca4227 for solutions, such as those of microcline, in which amounts of calcium are low relative to the concentration

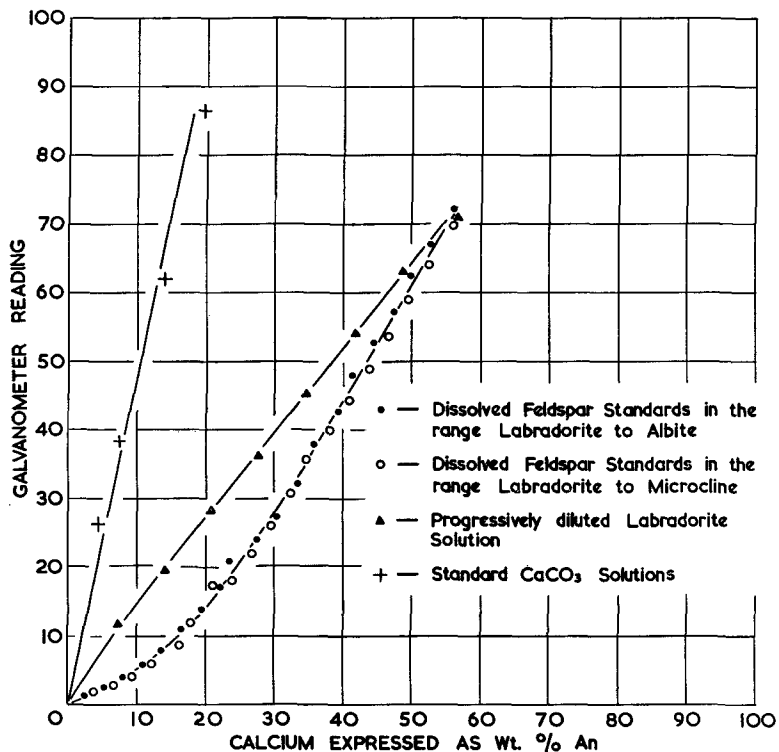


FIG. 2. Relationship between galvanometer deflection and Ca-concentration, expressed as wt. % An, in various solutions.

of the other ions. The standards used are labradorite-albite and labradorite-microcline.

Fig. 2 shows the relationship between galvanometer deflection and Ca-concentration, expressed as wt. % An, in the following solutions: CaCO₃; labradorite-albite and labradorite-microcline standards; and progressively diluted labradorite. The figure clearly demonstrates not only that feldspar standards are in this case essential but also that the dilution of feldspars, whether standard or unknown, must be kept constant. Since feldspar standards are necessary for An determinations

and perfectly suitable for Or determinations, it is obviously expedient to use them throughout.

The determination of Ab percentage by direct comparison necessitates the use of feldspar standards, for the other ions have been found to increase the sensitivity of the instrument to sodium. It also necessitates a 'cool' flame and therefore readjustment of the instrument. Since the accuracy ultimately achieved is distinctly less than in the case of Or and An, Ab percentages are estimated by difference.

TABLE II. Comparison of results of spectrophotometric and spectrographic determination of eight unknown feldspars

	Spectrophotometric method			Spectrographic method		
	Or	Ab	An	Or	Ab	An
1.	73.8	25.1	1.1	72.5	26.0	1.5
2.	68.5	30.4	1.1	70.0	28.5	1.5
3.	23.2	56.7	20.1	24.1	61.8	14.2
4.	27.7	57.8	14.4	24.9	62.0	13.1
5.	73.4	25.6	1.0	72.4	26.3	1.3
6.	68.3	30.8	0.9	68.0	31.0	1.0
7.	5.6	68.4	26.0	4.0	71.0	25.0
8.	2.8	86.3	10.9	2.0	88.5	9.5

The accuracy of the final results depends on that of the chemical analyses of feldspar standards and on that of the spectrophotometric technique; it cannot therefore be specified. In the case of the data presented in table II, however, it was found that, for seven separate determinations of the Or content of each of eight unknown feldspars, the standard deviation was 0.8 % Or and the maximum single deviation was 2.2 % Or; for five separate determinations of the An content of each of the same unknown feldspars, the corresponding standard and maximum deviations were 0.4 % An and 1.1 % An respectively. Under these circumstances, estimation of Ab by difference is considered justified.

Method based on quartz spectrograph

As in the previous method, spectrographic determinations of unknown feldspars are based on comparisons with feldspar standards that have been burned under strictly analogous conditions. The procedures involved are standard ones; the intensity functions recommended, on the other hand, have been evolved after a fairly comprehensive survey of the many possibilities offered by the feldspar spectrum.

Cathode excitation is used, and the apparatus is virtually identical with that described by Mitchell.¹ Instead of an optical collimator, however, two brass screens, 8 cm apart, are placed between the arc and the slit of the spectrograph: the screen nearer the arc has a circular aperture of 2 mm diameter; the screen nearer the slit of the spectrograph has a circular aperture of 9 mm diameter; the centres of both apertures are aligned with the centre of the slit and the external optical axis of the spectrograph. When burning is in progress, the small aperture of the first screen throws an inverted image of the arc on to the second: it is therefore easy to adjust the arc so that only cathode light reaches the spectrograph; it is also easy to maintain the arc gap at between 7 and 8 mm. The rotation step sector used has nine steps with a multiplication factor of 2; it is set slightly low so as to provide an additional, continuously illuminated, step on the photograph of the spectrum. In order to facilitate the counting of steps when intensities are estimated, steps 1 (continuously illuminated), 4, and 7 have been made distinctly higher than the others.

Unknown feldspars, ground to less than 100 mesh, are loaded, unadulterated, into a hollow cathode and compacted with an 0.7 mm diameter pin. The cathode is then mounted on the lower arm of the arc stand and an anode consisting of a flat-ended 5 mm diameter carbon rod is mounted on the upper arm. The instrument is set for the range 2970–6000 Å and Ilford R 40 plates are used. The width of the slit is set at 0.002 mm; the height at 11 mm.

The arc is struck in series with a resistance of 70 ohms and a voltage of 200 d.c.; exposure is continued for $2\frac{1}{4}$ minutes after the cathode has been aligned. During the first quarter minute, the resistance is dropped progressively to 30 ohms and the current rises to between 5 and 6 amps; this setting is maintained for the remainder of the burn.

Line intensities are estimated visually on a Judd Lewis comparator, the difficult part of this operation being to estimate the intensity of the last step visible on the photographic plate. Thus if, for example, there are six steps visible, the observer attempts to decide whether the intensity of the sixth step is $1/11$, $2/12$, $3/13$, ..., $10/20$ of the intensity of the fifth. This is done by a process of bracketing: an estimate of, say, 5.3 means that, in the observer's opinion, the intensity of the sixth step is between $2/12$ and $4/14$ of the intensity of the fifth. In practice, it has been found that the same observer may sometimes estimate high and sometimes

¹ R. L. Mitchell, *The spectrographic analysis of soils, plants and related materials*, 1948. Commonwealth Bureau Soil Science, Tech. Comm. No. 44, 183 pp.

low but that, provided he remains consistent for the short time required to scan one spectrum completely, the final result is not seriously affected.

Estimates of intensity are made for: Na5688, Na5683, Ca4455, Ca4435, Ca4425, K4047, K4044, Ca3644, K3447, Na3303, Na3302, and Ca3159. These estimates are then substituted in two functions:

$$(I_{Ca4455} + I_{Ca4435} + I_{Ca4425} + I_{Ca3644} + I_{Ca3159}) - \\ -\frac{4}{3}(I_{Na5688} + I_{Na5683} + I_{Na3303} + I_{Na3302}),$$

and

$$(3I_{Na5688} + 3I_{Na5683} + 2I_{Na3303} + I_{Na3302}) - \frac{4}{3}(4I_{K4047} + 3I_{K4044} + 2I_{K3447}).$$

The first of these is the best of nearly 500 functions of intensities that were used in attempts to differentiate 16 plagioclase powders in the range albite-labradorite; the second is the best of roughly 400 similar functions that were used on 16 alkali feldspar powders in the range microcline-albite.

None of the simple intensity ratios investigated was comparable in accuracy with the functions given above. The best of such ratios were found to be: $(I_{Ca3644} - I_{Na5688})$ and $(I_{Na5688} - I_{K4047})$. These are quoted as differences because the intensity estimates are already logarithmic. They are recommended for any method in which the use of an accurate measuring device is contemplated for the estimation of intensities.

From the algebraic values of the above functions, the compositions of unknown feldspars, expressed as percentages of Or, Ab, and An, are read directly from a determinative chart (fig. 3) based on results obtained by burning feldspar powders of known composition. The accurate construction of such a chart takes considerable time and requires many feldspar standards. When standards are too few, two binary charts can be used, the first relating the first function to An/Ab, the other relating the second function to Ab/Or. From these, the An/Ab and Ab/Or ratios for unknown feldspars can be read directly; their compositions can then be determined by a simple calculation. This method has proved effective in the range labradorite-bytownite for plagioclases containing up to 10% Or.

The accuracy of the final results depends on that of the chemical analyses of feldspar standards, on that of the determinative charts, and on that of the spectrographic technique; the accuracy of the last varies, but is greatest for compositions near the Ab corner of the system. As in the case of the spectrophotometric method, the overall accuracy cannot be specified. A comparison between fairly typical spectrographic and spectrophotometric results is, however, provided by table II. In

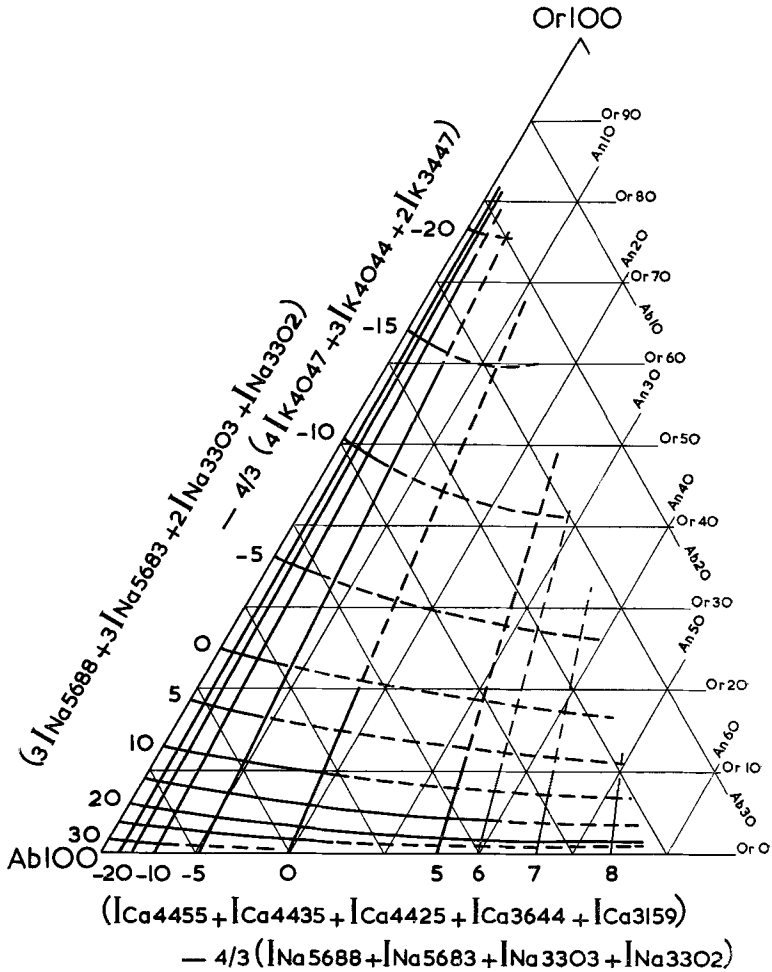


FIG. 3. Spectrographic determinative chart for the field microcline-albite-labradorite.

this table, the spectrographic results for the last two feldspars are based on triplicate burns; the results for the remainder are based on duplicate burns. Each of the spectrophotometric Or percentages on the other hand is based on seven separate determinations, and each of the An percentages on five. The only significant discrepancies between the two sets of results occur in the case of feldspars 3 and 4, whose compositions lie on

a portion of the ternary determinative chart for which adequate data are not yet available. Such feldspars are, in any case, automatically relegated to the less rapid spectrophotometric method.

In general, it is suggested that, if unknown feldspars are burned in triplicate and if the determinative charts are well established, the rapid spectrographic method is probably accurate to within 3 % Or, or Ab, or An when these components are present in large amounts; for small quantities of Or in plagioclase or of An in alkali feldspar, the method is probably accurate to within $\frac{1}{2}$ % Or or An.

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