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Quantitative determination of analcime in pumice samples by X-ray diffraction

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SUMMARY. A quantitative X-ray diffraction method has been successfully applied to the determination of analcime in pumice rock samples. A calibration line was constructed from spiked pumice standards (range: 0 to 42 %) and the mean relative error of the standards on the calibration line was < 0·6 %. The major-element compositions of the samples and standards were available, and this allowed the total mass absorption coefficients to be calculated. The latter were then used to correct the sample and standard intensities for absorption effects resulting from compositional variations. When compositional data already exist, the calculation of the total absorption coefficient provides a rapid and accurate alternative to direct measurement, or to the use of an internal standard.

VARIOUS techniques for quantitative X-ray diffractometric (XRD) determination of mineral concentrations have been discussed by Klug and Alexander (1973). If an internal standard is not used then a knowledge of the mass absorption coefficients of the samples and standards is required. These coefficients may be determined directly on the powders (Leroux *et al.*, 1953; Williams, 1959; Norrish and Taylor, 1962; Niskanen, 1964). As an alternative to direct measurement, the absorption coefficients may be calculated, provided that major-element concentration data is available for the powders. While Klug and Alexander (1973) discuss in detail a large number of quantitative XRD techniques, they do not include the method of calculating the absorption correction, and the purpose of this paper is to draw attention to the potential of this technique in quantitative XRD.

The present work is concerned with the quantitative determination of analcime in certain pumice samples recovered from the Vulsini volcano in central Italy. The volcanic rocks from this area are noted for their high potassium values and the presence of leucite. Leucite readily alters to analcime even at relatively low surface (25 °C) temperatures (Gupta and Fyfe, 1975). The author is engaged in a geochemical study on these Vulsini pumice samples and in order to correct the determined whole-pumice geochemistry for the leucite → analcime alteration, the concentration of analcime in the samples was required. Apart from variable amounts of analcime, the pumice samples are composed essentially of a volcanic glass matrix and minor amounts of feldspar and pyroxene phenocrysts. The friable nature of the analcime in these samples results in a significant loss of analcime on thin-sectioning the sample. This precluded the use of quantitative point-counting methods using optical microscopy.

Table I lists three leucite and three analcime analyses. The analcime samples were purified using a combination of hand picking, sieving through −400 mesh (the analcime was very friable and could be gently brushed through the mesh, leaving the other mineral components behind) and electromagnetic separation. Leucite samples were purified by hand picking and electromagnetic separation. XRD scans were used to check the purity of the mineral separations.

The XRD determinations were based on a calibration line constructed from seven standards prepared by spiking a pumice sample with varying weight fractions of purified analcime. The required range of the calibration line was 0 to 40 % analcime. The XRD intensities from the standards were adjusted for absorption effects due to the change in the total mass absorption coefficient resulting from the addition of the spiked analcime. The major element compositions of the standard powders were used to calculate total mass absorption coefficients using the formula:

$$\mu_t = \sum_i \mu_i W_i$$

where μ_t = total mass absorption coefficient for the standard at a given wavelength, μ_i = mass absorption coefficient for pure element i in the standard at the given wavelength, and W_i = weight fraction of element i in the standard. The μ_i were calculated for Cu-K_α from an algorithm supplied by K. Norrish to M. T. Frost (pers. comm.). Alternative sources for these coefficients abound (Heinrich, 1966). The weight fraction of oxygen in the powder was

TABLE I. *Leucite and analcime analyses*—all data on moisture (H_2O-)free basis*

	Leucite				Analcime			
Sample	2503	4601	4701	Ave.	2502	2802	6506	Ave.
SiO_2	55·24	55·41	55·41	55·35	54·78	55·05	55·05	54·96
TiO_2	0·05	0·05	0·05	0·05	0·06	0·05	0·06	0·06
Al_2O_3	22·49	22·28	22·55	22·44	21·85	21·90	22·11	21·95
Fe_2O_3†	0·41	0·42	0·45	0·43	0·50	0·43	0·48	0·47
MgO	0·44	0·28	0·38	0·37	0·25	0·21	0·18	0·21
CaO	0·05	0·06	0·06	0·06	0·25	0·50	0·48	0·41
Na_2O	0·28	0·36	0·31	0·32	11·92	12·19	11·97	12·03
K_2O	20·17	20·32	20·49	20·33	0·97	0·27	0·71	0·65
Rb_2O	0·23	0·15	0·16	0·18	0·31	0·20	0·29	0·27
Ign.‡	1·60	1·02	0·62	1·08	9·32	9·20	9·54	9·35
Total	100·96	100·35	100·48	100·61	100·21	100·00	100·87	100·36

* Samples analysed using XRF techniques described in Norrish and Hutton (1969), Parker and Willis (1977), and Parker (1978).

† Total iron.

‡ Loss on ignition, 850 C for 30 minutes, calculated as H_2O.

The ionic ratios per six oxygens are: leucite Si 2·014, Ti 0·001, Al 0·963, Fe 0·012, Mg 0·020, Ca 0·002, Na 0·023, K 0·944, Rb 0·004, ‡H_2O 0·131, Si+Al+Fe = 2·99, K+Na+2Ca+2Mg+Rb = 1·02; analcime Si 2·032, Ti 0·002, Al 0·957, Fe 0·013, Mg 0·012, Ca 0·016, Na 0·862, K 0·031, Rb 0·006, ‡H_2O 1·155, Si+Al+Fe = 3·00, K+Na+2Ca+2Mg+Rb = 0·95.

determined by difference and the absorption due to this element was included in the calculation of μ_t.

The correction for the variation of μ_t in the standards was as follows. The observed XRD intensity ($I_{\text{obs.}}$) for a given weight fraction of mineral x in a standard of coefficient μ_{t_1} is given by Klug and Alexander (1973): $I_{\text{obs.}} = W_x.K/\rho_x\mu_{t_1}$ where K = instrumental constant, W_x = weight fraction of mineral x, and ρ_x = density of mineral x. Now if we postulate a second, hypothetical standard containing the *same* weight fraction of mineral x, but having a different total mass absorption coefficient μ_{t_2} then the theoretical intensity ($I_{\text{theor.}}$) that would be observed in this standard will be $I_{\text{theor.}} = W_xK/\rho_x\mu_{t_2}$ and hence $I_{\text{theor.}} = I_{\text{obs.}}\mu_{t_1}/\mu_{t_2}$. Thus standards of dissimilar μ_t may be compared by normalizing the observed intensities of the standards with respect to a selected μ_t. These normalized intensities will then produce a linear relationship when compared to the weight fractions of mineral x in the standards. Note that the μ_t normalization may be carried out with respect to the μ_t of any one of the standards. The unknown samples may then be compared against the normalized calibration, provided the sample μ_t has been calculated and used to normalize the sample intensity with respect to the calibration line μ_t. For large batches of samples a suitable computer program will expedite the calculation of the sample μ_t from the major element composition of each sample.

Experimental. A Philips X-ray diffractometer was used with a nickel-filtered Cu tube operating at 40 kv and 20 ma. The divergence and scatter slits were 1° and the receiving slit was 0·2 mm. The X-ray intensities were measured on a scintillation counter having a linear response over the observed intensity range (max. observed intensity < 700 c.p.s.).

All the standard and sample powders (0·5 g aliquots) were hand ground in an agate mortar to pass a −400 mesh nylon sieve. A test powder, ground to −400 mesh, was found to give the strongest diffraction intensity for analcime when compared with coarser grindings (−300 and −170 mesh). The standards were homogenized using a high-speed shaker. By far the greatest variation in the diffracted intensity in repeated analyses of the same powder was found to be associated with the loading of the powder in the diffractometer cavity-mount. In order to assist the production of reproducible loadings, the cavity-mount was clamped upside down on a glass plate using a small metal clamp attached to a wooden base. The powder was then pressed into the cavity from the back and a small glass slide applied as a backing. The glass slide was held in place on the back of the cavity-mount by 'sticky' tape. The reproducibility of this method of loading will be further discussed in the results section below.

XRD scans (7 Å–1·5 Å) on the pumice powders produced sharp analytical peaks and a generally low and flat background reflecting the dominantly glassy matrix. Intensity measurements were made on the analcime 5·60 Å line. The leucite lines 5·54 Å and 5·39 Å are possible sources of interference, but careful scanning in this region did not detect the presence of these lines in any of the pumice powders. Initially integrated intensities were measured by counting the diffracted X-rays while scanning over the peak. It was found, however, that by carefully setting the goniometer on the 5·70 Å line and counting for a fixed time, good calibration data were produced. All the powders were counted in this manner for two consecutive periods of 40 sec and the results averaged. The background intensities were measured for 40 sec either side of the 5·60 Å line (normally ±0·5 2θ), and the averaged results subtracted from the peak intensities. Each standard powder was loaded and counted as above at least in duplicate. The net peak intensities from the loadings of a given standard were finally averaged.

A reference sample was permanently mounted in a separate cavity-mount and this sample was diffracted at $\sim$ 2 hour intervals to provide data to correct the peak-minus-background measurements for any machine drift. The stability of the X-ray generator and counting circuits were such that negligible drift occurred within this period.

Results and discussion. The XRD calibration data for the seven standards are presented in Table II. In order to evaluate the reproducibility of the sample loading technique, the standard deviation for the loadings of each analcime standard were computed and are listed in Table II with the corresponding relative standard deviation (as a percentage of mean counts). These data were not computed for standard 7 because it was only loaded twice. With regard to the other standards, the number of loadings for each standard are not enough to allow completely reliable relative standard deviation (RSD) data to be computed for each individual set of standard loadings. However, the narrow range of the computed RSD's, and the absence of large changes in RSD with concentration, indicates that the mean RSD should be significant. This mean value (2·07 %) is similar to the best mean RSD of 2·0 % reported by Niskanen (1964) for pure milled quartz loaded ten times in a rotating sample holder.

The factors that affect the variability of quantitative XRD data have been discussed by Klug and Alexander (1973), and the reproducibility of the standard loadings indicated in Table II is considered to reflect three factors: fine grain size achieved by hand grinding all powders to pass −400 mesh; the very poor cleavage exhibited by analcime meant that preferred orientation effects resulting from loading were negligible or absent; the ease of producing uniform loadings using the mounting clamp described above. It may be noted that the reproducibility of the loadings would have been further improved by the use of a rotating sample holder and a larger primary beam (2–4°). Furthermore, any preferred orientation effect (often present with other minerals) could have been mitigated by using a 'rough' pressing surface (ground glass or filter paper, see Norrish and Taylor, 1962, p. 107).

Table II lists the calculated total mass absorption coefficient and the absorption correction factor (ACF) for each standard. This last factor is simply the μ_t of the individual standard ratioed against the μ_t for the first standard. The ACF's were

TABLE II. *Calibration data*

Std.	Loadings	Mean P-B C/40 S	S.D. C/40 S	R.S.D. %	μ_t	A.C.F.	Corr. P-B C/40 S	% Spike	Total analcime	Calc. analcime	Abs. error	Rel. error %*
1	4	2458	47·0	1·91	57·77	1·000	2458	0·00	5·67	5·62	0·05	0·88
2	4	4762	137·2	2·88	56·53	0·979	4662	5·00	10·67	10·66	0·01	0·09
3	6	7241	85·9	1·19	55·36	0·958	6937	10·00	15·67	15·87	0·20	1·28
4	6	9626	193·8	2·01	54·04	0·935	9000	15·00	20·67	20·59	0·08	0·39
5	4	13 563	296·2	2·18	52·10	0·902	12 234	22·50	28·17	27·98	0·19	0·67
6	7	17 992	402·9	2·24	50·25	0·870	15 653	30·00	35·67	35·80	0·13	0·36
7	2	21 887	—	—	48·63	0·842	18 429	36·50	42·17	42·15	0·02	0·05

S.D. = Standard deviation. P-B = Peak minus background. R.S.D. % = Relative standard deviation as a percentage of mean loading intensity; mean for 1 to 6, 2·07 %. C/40 S = Counts per 40 seconds. A.C.F. = Absorption correction factor. * Mean for 1 to 7, 0·53 %.

used to compute a least-squares regression line tensities for the variations in μ_t.

The corrected intensities, together with the percentage spiked analcime in each standard, were then used to compute a least-squares regression line through the data. The slope (337·2 counts per 1 % analcime) and intercept (2478 counts) of this regression allowed the analcime concentration in the unspiked standard to be calculated (i.e. 5·67 % analcime). From this the total analcime concentrations in the spiked standards were calculated and the results are listed in Table II. Fig. 1 shows the standard concentrations plotted against intensities.

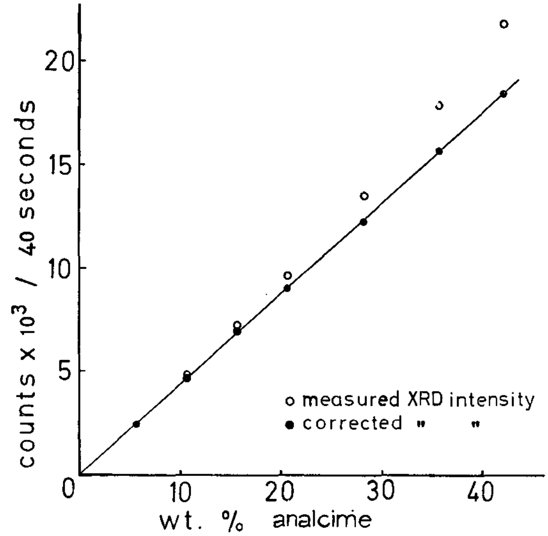

FIG. 1. Analcime XRD calibration line.

The slope of the calibration line and the corrected XRD intensities were then used to back-calculate the analcime concentrations in the standards. This allowed the calculation of the individual standard absolute errors, and hence the standard relative errors. Finally, the mean relative error (0·53 %) was calculated. In order to check the above calibration technique, a new pumice sample ($\mu_t = 53{\cdot}5$) was spiked to produce four standards (4·77, 9·77, 14·77, and 19·77 wt% analcime). These standards were mounted only in duplicate and the resulting calibration data computed as above. This produced a mean relative error of 0·52 %, with a relative error range of 0·10 % to 0·92 %, for the four standards.

The mean relative errors (0·53 % and 0·52 %) for these calibration lines indicate that with adequate care, the accuracy of this technique of mineral analysis can be brought within the 1 % relative-error band.

The advent of rapid and accurate whole rock major element analysis by X-ray fluorescence spectrometry combined with flux-fusion sample preparation (e.g. the Norrish method: Norrish and Hutton, 1969; Harvey *et al.*, 1973; Parker and Willis, 1977; Parker, 1978), has greatly facilitated the acquisition of major-element geochemical data. In petrological studies involving major-element analyses as well as the quantitative determination of sample mineral concentrations, the application of calculated mass absorption corrections to quantitative XRD intensities is recommended. This approach provides an accurate and rapid alternative to direct measurement of the mass absorption correction, or to the use of internal standard techniques.

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