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A new X-ray method for the estimation of fluorine content in montebrasites

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Abstract

A method has been developed for indirect fluorine determination of montebrasites, by using a group of X-ray powder reflections lying between 46° and 54° 2θ CuK. The method is based on angular separation of reflections 012, $1\bar{2}2$, $14\bar{1}$, and 131, and no internal standard is needed. The 90 percent tolerance limit of the difference between the estimated and chemically-determined fluorine content is 0.7 weight percent when the content lies between 1 and 8 weight percent.

Studies on the relationship between fluorine content and X-ray powder patterns of montebrasites and amblygonites, $LiAlPO_4(F,OH)$, have been published by Moss *et al.* (1969), Dubois *et al.* (1972), and Černá *et al.* (1973). For indirect determination of fluorine content, Moss *et al.* (1969) suggested a method based on the changes in the 2θ angle of the 131 reflection. They also presented a qualitative method for grouping montebrasites and amblygonites into five pattern types correlated with the fluorine content. The qualitative method is based on the differences between six diffraction lines lying between 26° and 29° 2θ (Cu$K\alpha$). Dubois *et al.* and Černá *et al.* improved this six-peak method by giving quantitative graphical solutions. At the same time they improved the $2\theta(131)$ method and presented new regression equations. Dubois *et al.* established that the dependence between $2\theta(131)$ and the fluorine content is more interesting than the relationship between the six peaks and fluorine content. Independently, Černá and her coworkers, studying determination techniques based on different physical properties, were led to confirm (Černá *et al.*, 1973, p. 299):

> "X-ray powder diffraction is evidently the best method available at present. The 2θ values of the 131 reflection, calibrated against quartz peaks, seem to be the most accurate. The "six-peak method" shows lower correlation coefficients but is faster in investigations where many dozens of samples are to be examined. Accurate unit cell dimensions should also yield quite reliable estimates, at least in the montebrasite half of the series, but the data collecting and computing process is time-consuming."

Previous investigations have shown that a and γ decrease while all other cell dimensions increase as a function of increasing fluorine content. Thus the angular separation of selected pairs of reflections must also decrease or increase when the fluorine content increases. For twenty-nine montebrasites and amblygonites we calculated or measured the following quantities, in degrees 2θ Cu$K\alpha_1$: A = $(131–14\bar{1})$, B = $(1\bar{2}2–021)$, C = $(131–1\bar{2}2)$, and D = $(14\bar{1}–012)$. The fluorine content of the specimens in question ranges between 0.39 and 11.8 weight percent. The quantities were calculated for the four specimens published by Moss *et al.* (Table II, 1969) and the four primary specimens of Dubois *et al.* (Table V, 1972), and were measured from fifteen original diffractograms used earlier in the work of Černá *et al.* (1973) and six diffractograms of Finnish specimens (Tables 1 and 2). These data have been used to calculate the linear regression lines presented in Table 3. The actual regression lines may follow very flat arcs, but curved regression lines showing better agreement than the linear ones were not found.

In this paper, indirect determination of fluorine content by the use of regression lines A, B, C, and D is called the four-peak method. Because both the regression and correlation coefficients of these four regression lines are equal in magnitude to those for regression line $2\theta(131)$, the maximum errors in read-

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Table 1. List of chemically-analyzed Finnish specimens

1	Marginal part of a montebrasite crystal, Hunnakko, Alavus.
2	Central part of the same crystal.
4	Montebrasite II/RA, Surmasuo, Tohmajärvi.
8	Analysed montebrasite/RA, Surmasuo, Tohmajärvi.
10	Haapala's (1966) montebrasite. Fluorine content reanalysed from the original chemically analysed sample.
14	Pale yellow amblygonite/SL, Viitaniemi, Orivesi (Eräjärvi).

ing of fluorine contents must also be equal. This equality is consistent with the calculated tolerance limits. With 90 percent confidence the 90 percent tolerance limit of the difference between the four-peak estimate and the chemically-analyzed fluorine content is 0.7 weight percent, and between the chemical analysis and the $2\theta(131)$ estimate 0.8 weight percent. The corresponding tolerance limit of the difference between the fluorine contents, determined by Dubois *et al.* (Table 6, 1972) with neutron activation and ion-sensitive electrode, is 0.8 weight percent. The greatest differences were 0.7, 0.8, and 0.7 weight percent, respectively, which shows that the errors in estimating fluorine content by different X-ray methods is similar in size to the error encountered in chemical determinations.

To test the four-peak method against the $2\theta(131)$ method, X-ray diffractograms were run for fourteen nonanalyzed montebrasite and amblygonite specimens. Fluorine contents determined by the four-peak method ranged from 0.40 to 7.39 weight percent and those determined by the aid of reflection 131 from 0.22 to 7.92 weight percent. The difference between the results of the two methods, on the average 0.12 weight percent, is statistically insignificant; the standard deviation of this difference is 0.39 weight percent, the Student t-test value is 0.34 and the probability of $|t| > 0.34$ with 13 degrees of freedom is 0.74. The greatest difference in this test was 0.53 weight percent.

Table 2. Critical X-ray reflections and fluorine content of the chemically-analyzed Finnish specimens

Specimen	1	2	4	8	10	14
2θ CuKα_1						
012	46.21	46.28	46.28	46.41	46.47	46.66
$1\bar{2}2$	47.99	48.00	47.96	47.96	47.96	47.92
$14\bar{1}$	50.99	50.98	50.95	50.97	50.94	50.87
131	52.16	52.23	52.24	52.41	52.47	52.67
$F_{i.e.}$	0.39	1.20	1.77	3.62	4.24	7.24
F_{131}	0.63	1.59	1.73	4.06	4.88	7.62
Δ	-0.24	-0.39	+0.04	-0.44	-0.64	-0.38
$F_{f.p.}$	0.54	1.38	1.87	3.56	4.45	7.47
Δ	-0.15	-0.18	-0.10	+0.06	-0.21	-0.23

$F_{i.e.}$ fluorine content determined by Mrs Mervi Wiik with ion-sensitive electrode. F_{131} fluorine content determined by the $2\theta(131)$ method. $F_{f.p.}$ fluorine content determined by the four-peak method.

Table 3. Regression equations and correlation coefficients

F wt% = 13.708 x $^{o}2\theta$ CuKα_1(131) - 714.38	0.986
F wt% = 10.722 x A - 11.866	0.989
F wt% = -13.610 x B + 24.599	-0.977
F wt% = 12.096 x C - 49.907	0.989
F wt% = -12.084 x D + 58.329	-0.965

A=$^{o}2\theta$ CuKα_1(131-14$\bar{1}$), B=$^{o}2\theta$ CuKα_1($1\bar{2}2$-012),
C=$^{o}2\theta$ CuKα_1(131-$1\bar{2}2$), D=$^{o}2\theta$ CuKα_1(14$\bar{1}$-012).

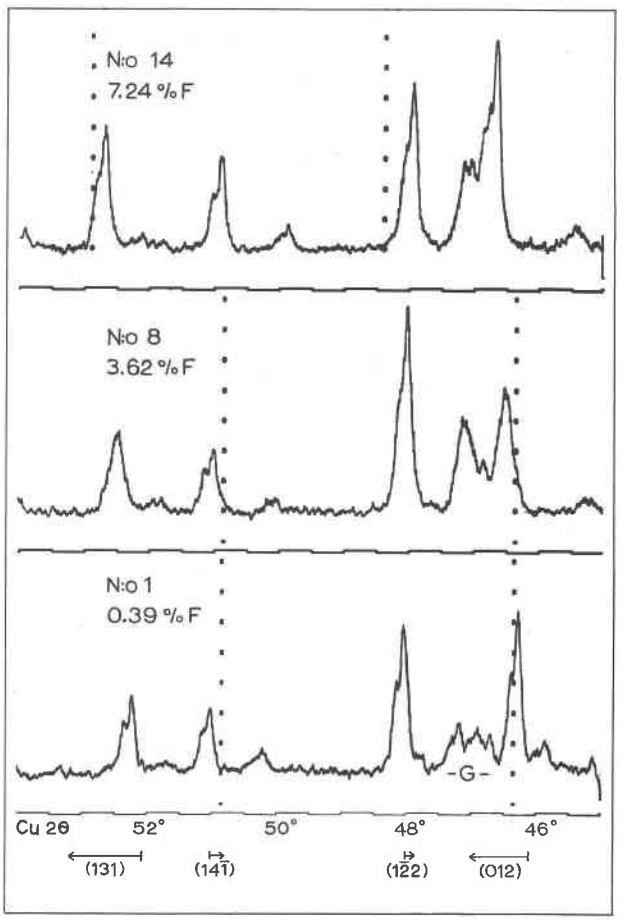

Fig. 1. Typical examples of the four reflections used for determination of fluorine content. ↦ indicates the movement of the peaks from the montebrasite pattern to the amblygonite pattern. G indicates the reflections $2\bar{1}1$, $0\bar{3}2$, $22\bar{2}$, and 230.

Conclusions

The four-peak method seems suitable for indirect determination of fluorine contents in montebrasites. The method is as accurate as the $2\theta(131)$ method but faster. In the amblygonite half of the series the group of reflections 230, $2\bar{1}1$, $0\bar{3}2$, and $22\bar{2}$ overlaps reflection 012 (Fig. 1), and only three peaks (131, $14\bar{1}$, and $1\bar{2}2$) are available for fluorine determination. In the data used to calculate the regression lines B and D, the range of fluorine content is 0.39–8.2 weight percent. To calculate the other lines, data of the amblygonite with fluorine content 11.8 weight percent were also included. The lines might in fact be very flat arcs, but the calculation of curved regression lines requires more data, especially for the amblygonite half of the series.

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