Analytical characteristics of a multilayer dispersion element ($2d = 60$ Å) in the determination of fluorine in minerals by electron microprobe

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Abstract

The analytical characteristics of a W/Si multilayer dispersion element (MLDE) with a nominal $2d$ spacing of 60 Å are assessed and compared with those of a conventional thallium acid phthalate (TAP) crystal for the determination of fluorine in silicate and phosphate minerals by electron microprobe. Measured count rates for fluorine were found to be up to fourteen times higher using the MLDE compared with TAP giving improved detection limits of 0.02 to 0.08 wt.% F (six sigma, 100s count time) compared with equivalent data of 0.06 to 0.12 wt.% F by TAP. At equivalent spectrometer angles, peak widths by MLDE were broader by a factor of 2 to 3. However, an important advantage of MLDE was found to be the absence of multiple order diffractions higher than the second order. In consequence, the troublesome third order P-$K\alpha$ line interference on the F-$K\alpha$ line, normally encountered in the analysis of apatites, is absent in determinations made using the MLDE. Conversely small interferences on the F-$K\alpha$ line were detected from the first-order $L\alpha$ line of Fe and second-order $L\alpha$ line of Mg. X-ray data and spectra of selected minerals are presented to demonstrate these interferences. Detection limits for elements that can also be determined using the MLDE were 0.07 to 0.15 wt.% oxygen and 0.34 wt.% carbon.

KEYWORDS: electron microprobe analysis, fluorine, multilayer dispersion element.

Introduction

A RECENT innovation in X-ray spectrometry has been the introduction of the multilayer dispersion element (MLDE) (also known as the layered synthetic microstructure) for enhanced detection of low atomic number elements by X-ray fluorescence and electron microprobe analysis. These devices are designed as substitutes for the more conventional Langmuir-Blodgett 'pseudo crystals' (e.g. lead stearate) and thallium acid phthalate (TAP) in the determination of low atomic number elements using a wavelength dispersive spectrometer. The MLDE are fabricated by vacuum coating a suitable substrate (silicon) with alternate layers of high and low atomic number elements. The high atomic number layers (e.g. tungsten, hafnium, molybdenum, nickel) serve to reflect incident X-rays. The low atomic number layers (silicon, carbon) behave as low absorption 'spacers' so giving the device a pseudo-crystalline lattice suitable for diffracting long wavelength X-ray spectra. A typical MLDE consists of 200 layers, deposited to give the device a specified $2d$ spacing in the range 40 to 140 °.

In the field of X-ray fluorescence analysis, the general analytical characteristics of MLDE have been described, for example by Nicolosi *et al.*, 1986, 1987, and Gilfrich, 1986. There has also been considerable interest in demonstrating potential XRF applications of such devices, for example in the analysis of carbon in steels (Anzelmo and Boyer, 1987; Arai, 1987), fluorine in limestone (van Eenbergen and Volbert, 1987), boron in borosilicate glass and in the analysis of coal (Nicolosi *et al.*, 1987). Little work has yet been reported in the application of MLDE in the determination of low atomic number elements by electron microprobe, although some data on Be, B, C and O has been presented by Barbee *et al.* (1987). Furthermore, Bastin and Heijligers (1987) compared the measurement of nitrogen in binary nitrides using MLDE ($2d = 59.8$ Å) and lead

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TABLE 1. Theta angles of lines diffracted from a multilayer dispersion element having a theoretical 2d spacing of 60 Å.

element	line	λ (Å)	θ I	θ II	θ III	θ IV
C	Kα	44.7	**48.16**			
N	Kα	31.6	*31.78*			
O	Kα	23.62	**23.18**	**51.94**		
F	Kα	18.32	**17.78**	**37.64**	*66.35*	
Ne	Kα	14.61	*14.09*	*29.14*	*46.93*	
Na	K$\alpha_{1,2}$	11.91		**23.39**	*36.55*	*52.56*
Mg	K$\alpha_{1,2}$	9.89		**19.25**	*29.64*	*41.25*
Al	K$\alpha_{1,2}$	8.34		**16.14**	*24.65*	*33.78*
Si	K$\alpha_{1,2}$	7.126		*13.74*	*20.87*	*28.36*
	Kβ	6.778			*19.81*	*26.86*
P	K$\alpha_{1,2}$	6.158			*17.93*	*24.24*
	Kβ	5.804			*16.87*	*22.76*
S	K$\alpha_{1,2}$	5.373			*15.58*	*20.99*
	Kβ	5.032			*14.57*	*19.60*
Cl	K$\alpha_{1,2}$	4.729				*18.38*
	Kβ	4.403				*17.07*
Ar	K$\alpha_{1,2}$	4.193				*16.23*
	Kβ	3.886				*15.01*

element	line	λ (Å)	θ I	line	λ (Å)	θ I
Ca	L$\alpha_{1,2}$	36.33	*37.26*	Lβ_1	35.94	*36.80*
Sc	L$\alpha_{1,2}$	31.35	*31.50*	Lβ_1	31.02	*31.13*
Ti	L$\alpha_{1,2}$	27.42	*27.19*	Lβ_1	27.05	*26.80*
V	L$\alpha_{1,2}$	24.25	*23.84*	Lβ_1	23.88	*23.45*
Cr	L$\alpha_{1,2}$	21.64	*21.14*	Lβ_1	21.27	*20.76*
Mn	L$\alpha_{1,2}$	19.45	*18.92*	Lβ_1	19.11	*18.57*
Fe	L$\alpha_{1,2}$	17.59	**17.05**	Lβ_1	17.26	**16.72**
Co	L$\alpha_{1,2}$	15.972	*15.44*	Lβ_1	15.666	*15.14*

λ = wavelength of X-ray line (Angstrom units).

θ = spectrometer angle (degrees).

I, II, III, IV = order of diffracted line.

Wavelength data abstracted from White and Johnson (1970).

Bold data represent spectral lines identified in the course of this work.

stearate. The purpose of this application note is to present some analytical characteristics of MLDE devices particularly relevant to the determination of fluorine in silicate and phosphate minerals. Sufficient practical detail is included to permit a scheme of analysis to be set up and to compare the analytical performance of a MLDE with that of a more conventional TAP crystal.

Instrumentation

Measurements were made on a Cambridge Instruments M9 electron microprobe operated at 20 kV, 30 nA (Potts *et al.*, 1983). The multilayer dispersion element (reference OVML060-001) consisted of alternate layers of tungsten and silicon mounted on a curved Cambridge Instruments diffracting crystal mount as supplied by Ovonic Synthetic Materials (Troy, Michigan). The nominal 2*d* spacing was 60 Å, the calibrated value (supplied by the manufacturer) being 58.4 Å. Anzelmo and Boyer (1987) have shown that this diffraction spacing is optimum for the determination of fluorine. The MLDE was installed on a wavelength dispersive spectrometer fitted with a gas-flow proportional counter filled with argon-10% methane gas (P10). The counter window consisted of an ultra thin formvar membrane (approximately 20 nm thick) supported on a nickel grid. All measurements were made with the slits out.

Spectral interferences

Before making detailed count measurements, an investigation was carried out to identify spec-

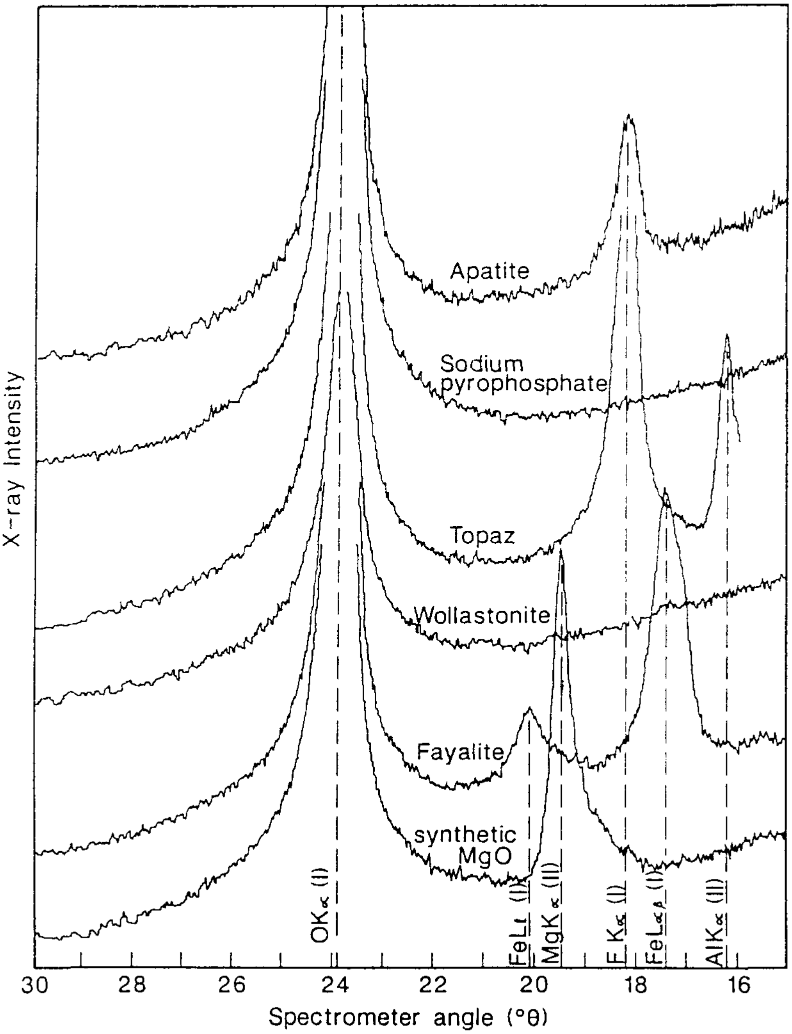

FIG. 1. Spectral scans of selected samples in the region of the F-*Kα* line using a multilayer dispersion element ($2d = 60$Å) used to identify potential interferences (see text for details).

tral interferences that would affect the determination of fluorine in silicate and phosphate minerals. Spectral scans were carried out on representative minerals, selected results being plotted in Fig. 1. The X-ray lines appearing in these scans have been correlated with calculated spectrometer angles for specified X-ray lines, listed in Table 1. To make these latter data generally applicable, spectrometer angles have been calculated for a MLDE having a nominal $2d$ spacing of 60 Å. However, due allowance must be made for the 58.4 Å spacing of the MLDE used in this work which shifts the angles as follows: C-*Kα*: 48.16° to 49.94° θ, N-*Kα*: 31.78° to 32.75° θ, O-*Kα*: 23.18° to 23.86° θ and F-*Kα*: 17.78° to 18.28° θ.

Careful examination of the spectral scan data shows that although the first order lines of C-*Kα* to F-*Kα* and second-order lines of O-*Kα* to Al-*Kα* can be identified within the range of the spectrometer (15 to 66° θ), higher order lines are absent. This is demonstrated by the absence of the third-order P-*Kα* line at 18.40° θ in the spectrum of synthetic sodium pyrophosphate and of the third-order Si-*Kα* line at 21.50° θ in the spectrum of wollastonite ($CaSiO_3$) plotted in Fig. 1. These results (the absence of third and higher order

TABLE 2. Example of interference correction in the determination of fluorine using multilayer and TAP diffracting media.

Interference	Apparent F content of mineral	Interference correction factor
Multilayer		
Mg K II on F K I	0.52 % F in magnesium oxide (60.31% Mg)	0.009% F per % Mg
Fe L I on F K I	0.21% F in fayalite (52.28% Fe)	0.004 % F per % Fe
TAP		
P Kα III on F K I	1.06% F in sodium pyrophosphate (23.29% P)	0.045% F per % P

Calibration of fluorine count rate to concentration has been carried out relative to the response from topaz ignoring ZAF attenuation factors. Precise interference effect depends on resolution characteristics of spectrometer used for measurements.

lines) confirm the observations of other workers (for example Nicolosi *et al.*, 1987) in X-ray fluorescence applications. One important consequence for mineralogists is that the troublesome third-order P-$K\alpha$ interference on F-$K\alpha$ in the analysis of fluorine in apatites will not be encountered in measurements made on a MLDE. The relatively large overlap interference correction that must be applied if a TAP crystal is used to make this measurement is listed in Table 2.

Two relatively small interferences may be identified in the spectral scans shown in Fig. 1. These are the overlap of Mg-$K\alpha$ (second order) and of Fe-$L\alpha$ (first order) on F-$K\alpha$ (see scans of synthetic MgO and fayalite in Fig. 1). The magnitude of corrections for these interferences are also listed in Table 2 but are not expected to bias significantly the determination of fluorine in apatites or other common fluorine-bearing minerals.

Spectral performance of MLDE compared with TAP

In comparing data, account must be taken of the different 2*d* spacings of these two dispersion devices (MLDE = 58.4 Å, TAP = 25.75 Å). Not only are X-ray lines diffracted at different angles, but also due to the finite travel of the spectrometers, a different range of elements can be detected. Within these constraints, selected parameters for the MLDE in the detection of the F, O and C $K\alpha$-lines are compared with equivalent data for F, Na, Mg, Al and Si measured on a TAP crystal. The relevant features of these data are as follows:

Resolution. The full width half maximum (FWHM) of a measured X-ray line is a function of spectrometer angle as well as the characteristics of the dispersion device. Data in Table 3 show that when comparing resolution on the basis of *equivalent spectrometer angle*, the FWHM of the F-$K\alpha$ line on a MLDE is between 2 and 3 times greater than that of the Si-$K\alpha$/Al-$K\alpha$ lines scanned on a TAP crystal. However, it is interesting to note that the FWHM of the F-$K\alpha$ line at 17.78° θ on the MLDE is equivalent to that of the same line measured at 45.33° θ on a TAP crystal.

Count data. One of the important advantages in the determination of fluorine using a MLDE is that the count rate is up to fourteen times higher than data recorded on a TAP crystal (Table 2). However, when performance is expressed in terms of peak to background ratio, MLDE data for fluorine (4.3 on apatite, for example) are inferior to that from the a TAP crystal (12 on apatite), indicating that background counts on a MLDE are increased at a significantly higher rate than peak count rates. In view of the high peak count rates, it is not surprising that sensitivity data for fluorine on the MLDE show a significant improvement over TAP. Data for these parameters are listed separately for measurements made on lithium fluoride (73.25 wt.% F), apatite (3.65 wt.% F) and topaz (15.98 wt.% F) and show the large varitions in individual values caused by the variation in attenuation of low-energy fluorine X-rays within the mineral matrix, an area of active interest in the development of accurate correction models for light elements such as fluorine (see for example, Scott and Love, 1987).

TABLE 3. Spectrometer response characteristics for multilayer and TAP diffraction media.

element /line	spectrometer angle •θ	FWHM •θ	mineral	%element	count rate (s^{-1})	P/B	sensitivity (c.p.s. per % element)	detection limit (wt. %)
Multilayer								
F Kα	17.78	.62	lithium fluoride	73.25 %F	38700	274	528	0.019
			apatite	3.65 %F	395	4.3	108	0.075
			topaz	15.98 %F	2570	19	161	0.061
O Kα	23.18	0.83	olivine	41.33 %O	4290	55	104	0.072
			apatite	39.22 %O	1390	35	35	0.15
			topaz	44.70 %O	3410	53	76	0.090
C Kα	48.16	3.2	aragonite	12.00 %C	151	6	13	0.34
TAP crystal								
Si Kα	16.06	0.25	olivine	18.33 %Si	8607	80	470	0.042
Al Kα	18.89	0.28	jadeite	13.28 %Al	5255	99	396	0.029
Mg Kα	22.58	0.30	olivine	25.52 %Mg	6250	208	245	0.035
Na Kα	27.54		jadeite	11.20 %Na	1410	94	126	0.041
F Kα	45.33	0.63	lithium fluoride	73.25 %F	2835	405	39	0.06
			apatite	3.65 %F	56	12	15.3	0.12
			topaz	15.98 %F	175	70	11	0.12

P/B = peak to background ratio of specified line.

sensitivity is a measure of the intensity of the diffracted beam.

detection limit is the six sigma detection limit (Potts, 1987) calculated from:

$$6\sqrt{2}\sqrt{\frac{R_B}{T}}\;\frac{C}{R_P}$$

where R_B and R_P are the background and peak count rate respectively, C the concentration of the element and T the count time per spectrometer setting taken here as 20s (Si), 30s (Al, Mg), 40s (Na) and 100s (F, O, C).

Precise values will vary with the nature of the diffracting medium and thickness of the counter window.

Detection limits. Given the very much higher peak count rates for fluorine on the MLDE, it is disappointing to see that the MLDE detection limit (six sigma) of 0.019 wt.% F (on LiF), 0.075 wt.% (on apatite) and 0.061 wt.% (on topaz) are only two to three times lower than those based on TAP measurements. This arises from the corresponding increase in background signal referred to above. Detection limit data were also listed for oxygen and carbon, elements that can also be measured sensitively on a MLDE with $2d = 60$ Å. These detection limit values were from 0.07 to 0.15 wt.% for oxygen and 0.34 wt.% for carbon. No data are reported here for nitrogen due to the lack of a suitable reference mineral. However it is anticipated that nitrogen X-rays ($K\alpha = 0.392$ keV may suffer enhanced attenuation in the carbon polymer of the proportional counter window (carbon absorption edge = 0.284 keV), reducing sensitivity for this element.

Conclusions

The multilayer dispersion element with a $2d$ spacing of 60 Å is likely to become the dispersion element of choice for the electron microprobe determination of fluorine due to the following factors:

(a) Up to 14 times the F-$K\alpha$ count rate compared with measurements on a conventional TAP crystal.

(b) Absence of multiple order interferences greater than the second order (for example the third-order P-$K\alpha$ interference that affects the determination of fluorine in apatites using a TAP crystal).

(c) Improved detection limits, as listed in Table 3.

Further considerations are as follows:

(d) The enhanced FWHM of peaks on a MLDE does not present a disadvantage in the determination of fluorine since although TAP gives 2 to 3 times better FWHM at equivalent spectrometer angles, the higher spectrometer angle at which fluorine must be measured by TAP negates this advantage.

(e) It may be necessary to take into account small spectrum overlap interferences in the determination of F in some minerals arising from Fe and Mg when measurements are made on a MLDE.

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