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Risk and benefit of diffraction in Energy Dispersive X-ray fluorescence mapping

Wilhelm Nikonow *, Dieter Rammlmair

Federal Institute for Geosciences and Natural Resources (BGR), Stilleweg 2, 30655 Hannover, Germany

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ABSTRACT

Energy dispersive X-ray fluorescence mapping (μ-EDXRF) is a fast and non-destructive method for chemical quantification and therefore used in many scientific fields. The combination of spatial and chemical information is highly valuable for understanding geological processes. Problems occur with crystalline samples due to diffraction, which appears according to Bragg's law, depending on the energy of the X-ray beam, the incident angle and the crystal parameters. In the spectra these peaks can overlap with element peaks suggesting higher element concentrations. The aim of this study is to investigate the effect of diffraction, the possibility of diffraction removal and potential geoscientific applications for X-ray mapping. In this work the μ-EDXRF M4 Tornado from Bruker was operated with a Rh-tube and polychromatic beam with two SDD detectors mounted each at ±90° to the tube. Due to the polychromatic beam the Bragg condition fits for several mineral lattice planes. Since diffraction depends on the angle, it is shown that a novel correction approach can be applied by measuring from two different angles and calculating the minimum spectrum of both detectors gaining a better limit of quantification for this method. Furthermore, it is possible to use the diffraction information for separation of differently oriented crystallites within a monomineralic aggregate and obtain parameters like particle size distribution for the sample, as it is done by thin section image analysis in cross-polarized light. Only with μ-EDXRF this can be made on larger samples without preparation of thin sections.

1. Introduction

X-ray fluorescence mapping is a technology gaining more and more importance in a wide area of applications [1]. It is used in electronics [2], art and cultural objects [3], medicine [4], pharmaceutics [5], forensics [6] and also with an increasing extent for geoscientific samples. There are several good reasons for using such devices in a geological context. Most importantly, chemical and textural information can be available within a short time. Sample preparation is very fast, since the only requirement is a sample with a flat surface parallel to the measuring level. It is easy to operate in a laboratory and it is a non-destructive method that allows almost every kind of further analysis with the mapped sample. The combination of spatial and spectral information gives a quick chemical and textural overview with spatially resolved trace element information, but also very detailed information with increasing measurement time invested. Therefore, large and heterogeneous samples of various rock types and mineralogies can be measured and analyzed for selection of areas for follow-up investigations like thin section microscopy or sampling for other chemical analyses.

Nevertheless, there are boundaries to the method which have to be pushed. The resolution of the mapping depends on the X-ray beam size which is in most cases several micrometers to several hundreds of micrometers resulting in a mixed analysis of e.g. several fine grained particles. Due to the high energy incident X-ray beam there is information from below the sample surface e.g. Si from the glass plate of a thin section. The quantification of the spectra using a fundamental parameter (FP) approach developed by Sherman [7] and refined by Shiraiwa & Fujino [8] correlates well with other chemical methods (for metal alloys [9], alloys and thin films/coatings [10], metal layers on glass [11] and particulate matter filters [12–14]). However, there had been difficulties to be solved especially at the lower ppm-scale because of several factors: It is well known that matrix effects play an important role in quantification [15–17]. Sample thickness has to be considered [18] as well as shape and surface, since geological samples are often heterogeneous in all directions. There are artifacts like pile-up or coincidence peaks [19] that can overlap with other element peaks.

This article deals with the effect of diffraction that appears with crystalline samples and creates non-element peaks that have to be considered to improve quantification accuracy X-ray diffraction on polycrystalline samples is a known phenomenon of XRF in the analysis of crystalline samples [20,21]. According to Bragg's law ($n\lambda = 2d^*\sin(\theta)$) [22], diffraction occurs for a certain wavelength (λ), angle (θ) and crystal lattice parameters (n, d) creating signals in the spectrum which might lead to misinterpretation and affect the chemical analysis as well as the element distribution map. In this work, the μ-EDXRF

* Corresponding author.
E-mail address: wilhelm.nikonow@t-online.de (W. Nikonow).

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spectrometer M4 Tornado from Bruker [23] works with a polychromatic beam, therefore the Bragg condition may be satisfied for different wavelengths creating diffraction peaks which might overlap element peaks. Quantification and classification of spectra containing diffraction is problematic, since diffraction peaks increase intensities of underlying elemental peaks.

Single detector mapping and bulk data evaluation might be problematic and lead to an overrepresentation of elements overlapping with diffraction peaks, since influence of diffraction might be not recognized without the time consuming process of manual verification. If an element is present, all measurable peaks (Kα, Kβ, Lα etc.) should be present and, considering peak ratios, errors could be recognized. In the provided case, e.g. quartz can be easily recognized and elevated signals of other elements can be falsified with the relevant mineralogical information. Problems arise, when the elevated element concentrations could fit well into the geological or mineralogical expectations. Without comparing the mapping with the spectral information it might be very difficult to recognize false information. In X-ray diffraction monochromators are used to obtain a brilliant X-ray beam and sharp diffraction peaks while the angle of the sample changes during measurement. Within the M4 Tornado though, the angles are fixed, but due to the polychromatic beam many diffraction peaks at different energies are possible. This makes a manual but time consuming verification of each element peak necessary, if a certain level of confidence is required.

In this work we investigate the influence of diffraction on μ-EDXRF measurements and the possibility to remove it by comparing data measured from different angles. Moreover, we examine an application for diffraction data for polycrystalline sample from μ-EDXRF for image analysis and grain size estimation.

2. Methods

2.1. Instrumentation

For data acquisition, the μ-EDXRF spectrometer M4 Tornado from Bruker was used [23]. It is operated with a Rhodium tube with a maximum excitation of 50 kV, 600 μA and 30 W. The polychromatic beam (0–50 keV) is focused by a polycapillary lens to a spot size of 17 μm at Mo Kα (17.48 keV). Due to the polycapillary optics the spot size increases at smaller energies resulting in a spot size of 32 μm for Mo Lα (2.29 keV). The incident beam and take-off angles are 51°. In this work the M4 Tornado is equipped with two silicon drift detectors (SDD XFlash 430 - PA Bruker nano GmbH) with a 30 mm^2 sensitive area and an energy resolution of <145 eV for Mn Kα. The detectors are facing each other at a 180° angle and 90° to the tube in respect to the sample surface. The sample chamber can be evacuated to 20 mbar and, therefore, light elements such as sodium can be measured. The maximum sample size is given as 200 × 160 mm with a maximum weight of 5 kg. In mapping mode, a minimum distance between measuring points is 4 μm, the maximum resolution is limited to about 5000 × 5000 points, depending on the dwell time per pixel due to hardware specifications.

The sample preparation for M4 measurements is fast and easy. Samples with an irregular shape are cut with a rock saw in order to create a plane surface, since the fluorescence signal is sensitive to the topography and distance to the detector. These samples are mounted with modeling clay and pressed parallel to the stage table. Samples with an even and flat surface like thin sections can be put directly on the stage table without coating. At constant exciting energies of 50 kV and 600 μA, the measurement conditions were adapted for sample types: The dwell time per pixel and the pixel resolution depend on the sample size and the required accuracy. A dwell time of only 0.5 ms can give a quick overview within half an hour. The measurement conditions are given in Table 1. The detailed measurement may take up to 6 H for a 10 megapixel image with long dwell times.

Table 1
μ-EDXRF measurement conditions.

	IOCG ore hand specimen	Quartz thin section
Tube excitation	50 kV, 600 μA	50 kV, 600 μA
Pixel size	25 μm	12 μm
Dwell time per pixel	1 ms	5 ms
Resolution	3680 × 2600	1000 × 1012

The result of a M4 Tornado measurement is stored in a data cube with spatial information of the sample surface area in x and y direction and with a full spectrum for each measured pixel in z. Each spectrum and also the sum spectrum of a selected sample area can be displayed and quantified chemically (Fig. 3, Table 2) or presented as an element distribution map which shows intensities of selectable element peaks or regions of interest in grey scale or false colors.

The spectra import and processing, the calculation of the minimum-file and classification were first performed manually with the M4 Tornado software and ENVI 5.1 from ExelisVis Inc. [24] and later integrated in the automated data import tool of newly developed BGR-owned IDL-based software "Petrographic Analyst" [25]. The manual import comprises saving element distribution maps of desired energies as 16-bit grey scale tif images and combining them in ENVI as one file. The minimum calculation is done by the ENVI spectral math tool. Various morphological filters are part of the ENVI software package.

For thin section image acquisition the Nikon Super Coolscan 5000 was used. The manual grain size measurement of the thin section was done with image processing software Olympus AnalySIS 3.2.

2.2. Diffraction reduction

In the M4 Tornado there are two detectors mounted, facing each other at 180°. The tube is positioned at 90° to each detector with a take-off angle of 51°. Considering the dependency of diffraction on the angle θ, diffraction peaks will change for each detector. In order to minimize the influence of diffraction, the values of the two opposing detectors are compared and the minimum of each spectrum channel or a region of interest of each pixel is calculated. So that element peaks remain whereas diffraction peaks on one detector are corrected by the minimum value of the other one. Only for the rare case when one grain underlies another one with a small absorption, the Bragg-condition may fit for both detectors and diffraction will appear for the same spot at different depths for both detectors in the minimum-spectrum.

To ensure that the measurements with two detectors are similar, hand specimen and pressed powder samples of plutonic rocks were measured separately with both detectors. If the peak positions or intensities of the detectors are slightly different, calculation of the minimum

Table 2
Chemical analysis of region A (Fig. 3) using the Bruker quantification algorithm based on the single detector measurements and a pixel-based minimum spectrum of detector 1 and 2. The results are normalized to 100%.

in wt.-%	Detector 1	Detector 2	Minimum
SiO_2	95.69	96.41	96.84
Al_2O_3	0.91	1.21	0.70
Fe_2O_3	0.13	0.11	0.12
MnO	0.06	<0.00	0.01
CaO	0.79	0.39	0.46
K_2O	0.08	0.08	0.06
SO_3	1.86	1.73	1.78
NiO	0.02	0.00	0.00
Cu	0.01	0.01	0.01
Sb	0.02	0.04	<0.00
Pt	0.13	0.01	0.01
Au	0.05	<0.00	0.01
Sm_2O_3	0.15	<0.00	<0.00
EuO	0.10	0.01	<0.00