

МЕТОДЫ ИЗУЧЕНИЯ ХИМИЧЕСКОГО СОСТАВА МИНЕРАЛОВ/
METHODS OF STUDYING THE CHEMICAL COMPOSITION OF MINERALS

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Electron microanalysis of minerals: the advantages and pitfalls of wavelength-dispersive spectroscopy for mineral characterization

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Abstract. Accurate determination of mineral chemical composition is essential for various aspects of geoscience, including economic geology, geochemistry, thermodynamic modelling, mineralogy, etc. With the increasing complexity of the rules for mineral definitions, accurate chemical analysis has become crucial for proper mineral classification. Electron microanalysis is the most widely used technique, employing energy-dispersive (EDS) and wavelength-dispersive (WDS) spectroscopies. While EDS enables rapid, simultaneous acquisition of X-ray spectra, its analytical performance is limited by relatively poor spectral resolution and higher detection limits, which often lead to significant peak overlaps and uncertainties in compositionally complex phases. WDS offers significantly better spectral resolution, improved peak-to-background ratios, and lower detection limits, enabling precise quantification even in compositionally complex minerals. These advantages minimize spectral interferences and allow precise determination of elements from major to trace concentrations, down to tens of $\mu\text{g/g}$. Modern WDS devices support advanced applications such as light element analysis (Be–O) and quantitative determination of Fe oxidation states. Despite longer analysis times and a more demanding analytical setup, WDS is therefore the preferred method for high-precision mineral analysis and is considered the standard approach in advanced mineralogical research and new mineral characterization. EDS is an invaluable tool for simpler geochemical systems and for providing initial, first-order characterization of compositionally complex minerals, and together with WDS they form a highly complementary and powerful analytical approach.

Keywords: mineral microanalysis, energy-dispersive spectroscopy, wavelength-dispersive spectroscopy, X-ray spectra.

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Электронный микроанализ минералов: преимущества и ошибки волновой спектроскопии для характеристики минералов

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Аннотация. Точное определение химического состава минералов является важным для различных геологических наук, включая экономическую геологию, геохимию, термодинамическое моделирование, минералогию и т. д. С увеличением сложности правил определения минералов точный химический анализ стал критически важным для правильной классификации минералов. Электронный микроанализ применяется наиболее широко и включает энерго-дисперсионную (ЭДС) и волно-дисперсионную (ВДС) спектроскопию. Хотя ЭДС позволяет быстро и одновременно получать рентгеновские спектры, ее аналитические возможности ограничены относительно низким спектральным разрешением и более высокими пределами обнаружения, что часто приводит к значительному перекрытию аналитических пиков элементов и неопределенностям для фаз сложного состава. ВДС обеспечивает более значительное спектральное разрешение, улучшенное отношение пика к фону и более низкие пределы обнаружения, что позволяет проводить точные количественные определения даже для минералов со

сложным составом. Эти преимущества минимизируют спектральные помехи и позволяют определять элементы как в основных, так и в следовых концентрациях, вплоть до десятков микрограммов на грамм. Современные приборы с ВДС также обеспечивают количественное определение легких элементов (Be–O) и степеней окисления Fe. Несмотря на более длительное время анализа и более сложную процедуру анализа, ВДС является предпочтительным методом высокоточного анализа минералов и считается стандартным в передовых минералогических исследованиях и характеристике новых минералов. ЭДС является бесценным инструментом для анализа более простых в химическом отношении систем и для первичной характеристики минералов сложного состава, составляя вместе с ВДС взаимодополняющий мощный аналитический подход.

Ключевые слова: микроанализ минералов, энергодисперсионная спектроскопия, волнодисперсионная спектроскопия, рентгеновские спектры.

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INTRODUCTION

Each mineral species is defined by its crystal structure, i. e. the arrangement of atoms in space, and by its chemical composition. The interplay of these two factors governs all other mineral properties, including the types of chemical bonds, density, hardness, color, luster, refractive indices, electrical and thermal conductivity, radioactivity, stability within the p–T field, among other properties (Klein, Dutrow, 2007; Nesse, 2021).

For this reason, a detailed characterization of mineral phases is a key prerequisite for the understanding and accurate identification of mineral species. Furthermore, variations in chemical composition may reveal substitution mechanisms within solid-solution series between two or more endmembers and can also provide information on minor and trace elements reflecting the geochemical characteristics of the environment in which the minerals formed.

Accurate determination of chemical composition is therefore essential for mineral classification and for the description of new mineral species. As the total number of atoms in the crystallochemical formula increases, the demands on analytical precision become correspondingly higher. Typical examples include minerals of the arrojadite group, with general formula $A_2E_2CaNa_{2+x}M_{13}R(PO_3OH)_{1-x}(PO_4)_{11}W_2$ (Camara et al., 2006), in which inaccurate determination of the dominant cations in high-multiplicity crystallographic sites can strongly affect the calculated occupancies of cations in sites of low multiplicity when deriving the empirical formula. In the arrojadite group, an incorrect determination of P or M-site cations may propagate into significant errors in the derived occupancies of the A and B sites, amplified by a factor greater than five.

ELECTRON MICROANALYSIS

At present, the electron microanalysis is the most accessible and also most widely used laboratory method of chemical analysis of minerals in geoscience. This method associated with electron microscope or electron microprobe and is based on the detection of characteristic X-ray radiation generated from the excitation volume of the sample after bombardment with accelerated electrons. Depending on the analyzed material, the accelerating voltage is usually chosen between 15 and 25 kV. In some cases, for example in the analysis of light elements (N, C, B, Be), a lower accelerating voltage is used, for example 5–10 kV (Bastin, Heijligers 1991; Raudsepp, 1995). Two types of methods are used for the detection of X-rays: energy-dispersive spectroscopy (EDS, also abbreviated EDX) and wavelength-dispersive spectroscopy (WDS, also abbreviated WDX), where the “X” emphasizes X-rays. A great advantage of the electron microanalysis is its lateral and axial resolution. For common minerals at condition 15–25 kV, the analytical volume, the space from which the X-rays are generated, does not exceed 1–3 μm in diameter. Thus, any larger solid particle can be reliably analyzed.

Energy-dispersive spectroscopy

Energy-dispersive spectroscopy (EDS) utilizes an energy-dispersive X-ray spectrometer based on a semiconductor detector that measures the energy of individual X-ray photons. This detector requires to be cooled during operation. Older types are cooled using liquid nitrogen, whereas modern types are cooled by a series of thermoelectric (Peltier) elements. The EDS detector is commonly mounted on electron microscopes as a standard analytical tool together with secondary

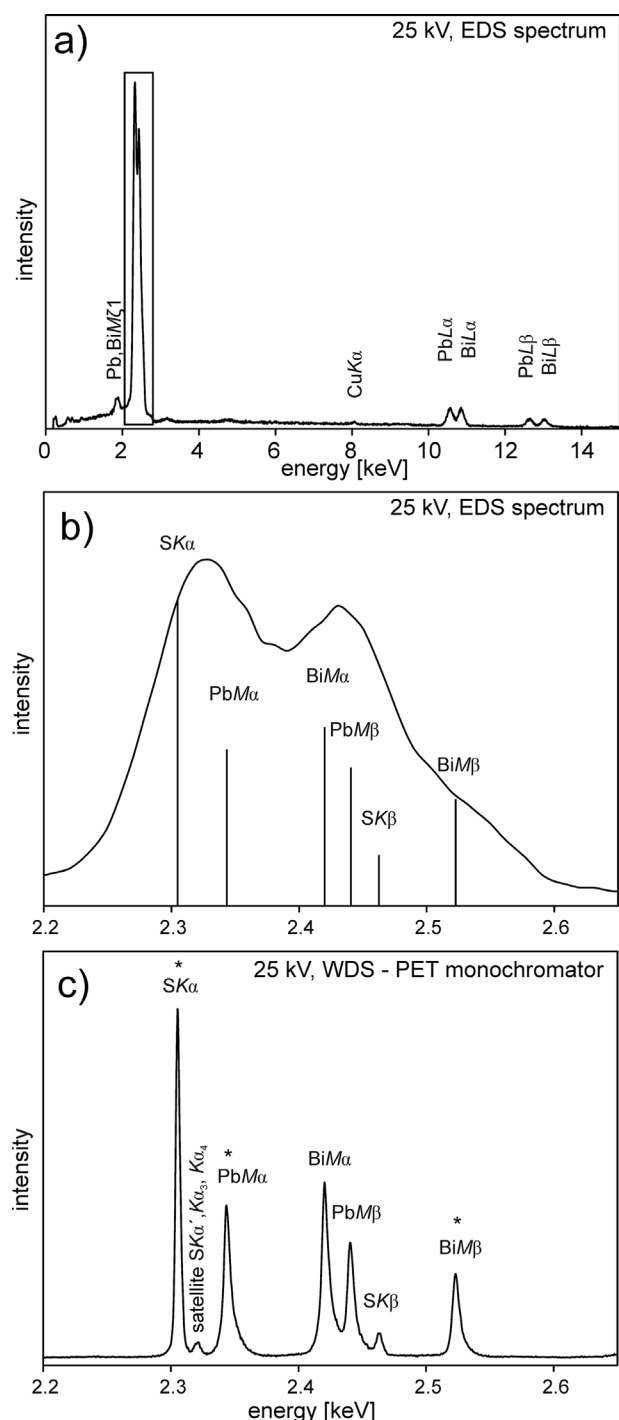


Fig. 1. Comparison of the energetic resolution of EDS and WDS spectra for the Bi–Pb–S mineral cosalite: a) EDS spectrum collected at 25 kV, 10 nA, 23 % dead time, 60 s, using a Thermo Scientific UltraDry silicon drift detector (SDD), 10 eV per channel, mounted on a Cameca SX100, signals < 0.2 keV were removed by software filtering; b) close-up view of the spectral window 2.20–2.65 keV from the EDS spectrum in Fig. 1a, showing overlapping S, Pb, and Bi X-ray lines; c) the same spectral window acquired in WDS mode at 25 kV, 10 nA, 0.2 s dwell time, 730 steps (0.5–0.7 eV step size), using a PET monochromator on a Cameca SX100.

electron (SE) and back-scattered electron (BSE) detectors. The main advantage of EDS is that the entire energy spectrum can be recorded simultaneously in a short time, typically within seconds; however, for high-quality analysis, X-ray counts are accumulated over tens of seconds. The recorded EDS spectrum, stored on a computer, can be processed offline. However, the main disadvantages include poor energy resolution, which ranges from 120–125 eV (Full Width at Half Maximum (FWHM) at Mn $K\alpha$) for modern silicon drift detectors (SDD), and 130–140 eV (FWHM at Mn $K\alpha$) for older Si(Li) detectors. Typical EDS spectrum is shown in Fig. 1a. The poor energy resolution, which may result in serious spectral interferences, together with relatively high detection limits (0.X wt. %), represents a major analytical limitation of the method.

Typical spectral interferences in energy-dispersive X-ray spectroscopy arise from overlaps between K -lines of light elements and L or M lines of heavier elements, as well as from extensive overlaps within the L -series of transition metals. Particularly problematic combinations include: Na $K\alpha$ (1.041 keV) – Zn $L\alpha$ (~1.012 keV); Mg $K\alpha$ (1.253 keV) – As $L\alpha$ (~1.282 keV); S $K\alpha$ (2.307 keV) – Pb $M\alpha$ (2.342 keV)/Bi $M\alpha$ (2.419 keV); S $K\alpha$ (2.308 keV) – Mo $L\alpha$ (2.293 keV); Sn $L\beta$ (~3.663 keV) – Ca $K\alpha$ (3.690 keV); Ca $K\beta$ (4.012 keV) – Sc $K\alpha$ (4.090 keV); V $K\alpha$ (4.952 keV) – Ti $K\beta$ (4.931 keV); Fe $L\alpha$ (~0.705 keV) – F $K\alpha$ (0.677 keV); U $M\beta$ (~3.342 keV) – K $K\alpha$ (3.312 keV).

Additional severe interferences occur among rare-earth elements and platinum-group elements due to strongly overlapping L - and M -series emissions. In such cases, quantification of EDS spectra requires spectral deconvolution of overlapping peaks, and the results are often associated with large uncertainties. Involving the analysis and subsequent processing of minerals with compositions similar to those of the unknowns, but well constrained by another analytical method (e. g., WDS), can partially improve the deconvolution procedure and help verify EDS results. Incorporating analyses of reference minerals with compositions similar to those of the unknowns, but well constrained by an independent analytical method (e.g., WDS), into the calibration and processing procedure can partially improve the deconvolution procedure and resulting quantification. The analysis of minerals containing light elements (F, N, C, B) is also problematic in EDS due to strong attenuation of low-energy X-rays in the detector window, which leads to reduced detection efficiency at low energies (Reed, 2005).

Wavelength-dispersive spectroscopy

Detection of X-rays in wavelength-dispersive mode utilizes their wave nature and is based on diffraction of X-rays emitted from the interaction volume within the sample. The principle of a wavelength-dispersive spectrometer follows Bragg's Law:

$$n\lambda = 2d\sin\theta$$

where n is the order of diffraction ($n = 1, 2, \dots$), λ is the wavelength of the X-ray, d is the interplanar spacing of the monochromator crystal, and θ is the Bragg angle (i. e., the angle between the incident X-ray beam and the diffracting crystal planes). As monochromators, the most commonly used crystals include LiF (lithium fluoride, $d \approx 2.01$ Å), PET (pentaerythritol, $d \approx 4.37$ Å), and TAP (thallium acid phthalate, $d \approx 12.95$ Å). The combination of these crystals provides coverage for elements with atomic numbers $Z \geq 9$. Disregarding stearates due to their low efficiency, multilayered "pseudocrystals" have been developed for light elements, providing effective d -spacings in the range of approximately 22–100 Å. Those monochromators are suitable for analyzing elements from F down to Be. Due to the very low energies and long wavelengths, lighter elements (H, He, and Li) cannot be detected using conventional crystal-based diffraction methods.

A major advantage of WDS is its excellent spectral resolution (~ 10 eV FWHM at Mn $K\alpha$ using a LiF monochromator) and high peak-to-background ratio, which result in lower detection limits. Detection limits can reach tens of $\mu\text{g/g}$ under special conditions involving high beam current and long counting times, but typically range in the hundreds of $\mu\text{g/g}$. Comparison of the EDS and WDS spectral resolution is shown in the Fig. 1b, c. However, analyses are generally more time-consuming because a WDS spectrometer measures one wavelength (energy) at a time and must sequentially change the Bragg angle (θ) to detect another.

Spectral interferences for most elements are not critical in WDS, as the β lines can be selected for quantification. On the other hand, WDS may in some cases suffer from higher-order diffraction effects, which can negatively affect quantification if analytical conditions are not properly optimized. These effects can be largely minimized by appropriate instrumental settings, in particular using pulse height analysis (PHA), careful selection of analyzing crystals, and operating conditions.

The analysis of F in common rock-forming silicates is a relatively routine procedure under appropriately chosen analytical conditions and with a suitable standard, which is more critical for F measurements on TAP than on multilayer monochromators. The latter exhibit significantly higher reflectivity for F $K\alpha$ radiation. However, multilayer monochromators suffer from a higher level of spectral interferences due to their lower spectral resolution compared to crystal-based monochromators. For X-ray peaks of elements lighter than F (O–Be), peak shape and the position of the peak maximum are strongly influenced by the chemical bonding environment. From this perspective, integrated peak intensities are preferred over peak-top intensities for quantification (Bastin, Heijligers 1991; Raudsepp, 1995)

Due to the limited sensitivity to low-energy X-rays, for the same reasons as in EDS, alternative, more sensitive methods for the determination of elements with $Z < 8$, such as laser inductively coupled plasma mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (SIMS), laser-induced breakdown spectroscopy (LIBS), wet chemistry, or Carbon, Hydrogen, Nitrogen, Sulfur (CHNS) analysis, are more suitable.

Matrix correction

The raw X-ray intensities, collected by EDS or WDS must be corrected for composition-dependent matrix effects in order to obtain "true concentration". This procedure is conventionally termed as ZAF corrections, where it represents an acronym for correction procedure for atomic number (Z), X-ray absorption (A) and fluorescence yield (F). All these factors are dependent on chemical composition of the sample. Software of controlling the detector automatically computes the corrected elemental concentrations by iterative operations from the initial X-ray intensities. It is necessary to include all elements, including the (substantial) not-analyzed (O, N, C, B, Be, Li, H) into the matrix correction algorithm to obtain reliable results (e. g., Lane, Dalton, 1994) otherwise a disrupted stoichiometry can be expected.

Analysis of volatile elements and time-dependent signal variations

Migration of ions under bombardment by a beam of accelerated electrons may occur. A typical example is a decrease in the alkali (Na, K, and also Li,

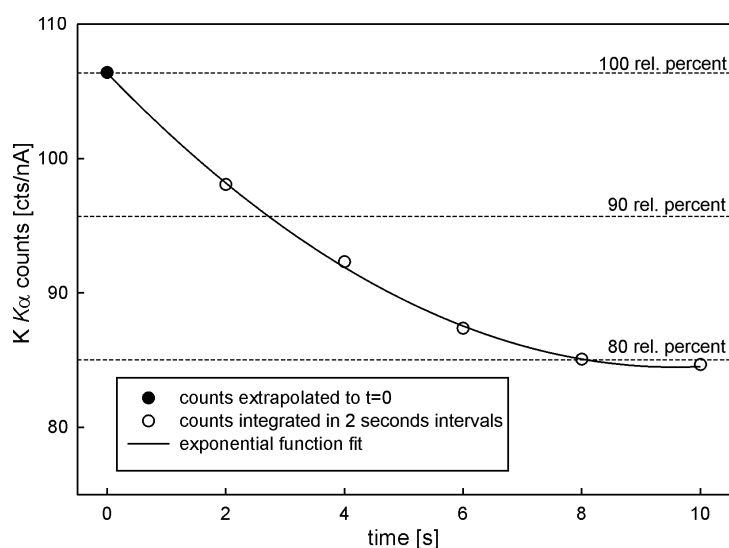


Fig. 2. Plot shows the K loss during the electron microprobe analysis of the electron-beam sensitive mineral mathesiusite, $K_5(UO_2)_4(SO_4)_4(VO_5) \cdot 4H_2O$. The K $K\alpha$ peak counting time (10 s) was divided into five two-second intervals. The number of counts from each interval is plotted (an average of five analyses). The initial K content was estimated from the K $K\alpha$ X-ray count rate obtained by extrapolation count rate by extrapolating an exponential fit of the time-dependent signal to $t = 0$. Note the K content decreases to 80 rel. % after eight seconds. Analytical conditions: Cameca SX100, (WDS mode, 15 kV, 4 nA, 15 μm beam diameter, and PET monochromator). Data were taken from Plášil et al. (2014).

even if not analyzed) contents in minerals and glasses or, for example, Cu in secondary U minerals (Plášil et al., 2009) during the analysis. Under certain conditions, the X-ray count rate of alkalis may initially increase with time and then decrease again (Reed, 2005). This behavior can be substantially reduced by lowering the beam current and defocusing the beam over a larger area. It is more critical in WDS analysis, as it typically operates at higher beam currents than EDS. In the case of beam-sensitive phases, the counting time for the affected element is divided into several time segments, and the X-ray count rates of each time segment is recorded separately. Extrapolation of the count rates from the individual time segments back to time “zero” can then be used to estimate the true concentration of the escaping element (Fig. 2).

The crystal-chemical bonding of F in apatite (incorporated into the structural channels), may influence its stability under the electron beam and its mobility during analysis. This mobility can be manifested by changes (increase/decrease) in the F $K\alpha$ count rate during analysis, which often leads to overestimation of F concentrations in apatite. These effects are strongly influenced by crystal orientation relative to the electron beam and by the duration of beam exposure. These phenomena can be minimized under optimized analytical conditions (defocused beam, low beam current, short counting intervals, extrapolation

to $t = 0$). Similar behavior is also observed for Cl; however, the temporal changes are generally less rapid (Stormer et al., 1993; Goldoff et al., 2012). Similar, less pronounced beam-induced effects on F have also been reported in triplite group minerals (Fialin, Chopin, 2006).

Quantitative determination of Fe oxidation state

Differences in the shape, position, and intensity ratio of Fe $L\alpha$ and $L\beta$ peaks, dependent on the oxidation state of Fe, can be used for quantification of Fe^{3+} / Fe_{tot} in minerals by WDS. This method, based on X-ray intensities recorded using a TAP monochromator, employs either a simple approach (e. g., Fialin et al., 2001, 2004) or a combined approach, the so-called flank method (Höfer, Brey, 2007), and has been so far applied to the quantitative determination of Fe^{3+} / Fe_{tot} in e.g. garnets, micas, glasses, amphiboles, tourmalines, and other minerals (Fialin et al., 2004; Höfer, Brey 2007; Mrkusová et al., 2025). The advantage of this method lies in its small spatial resolution (beam defocused to 2–30 μm) and high analytical speed, allowing several samples to be measured within one day. Its disadvantages include methodologically demanding preparation, the requirement for suitable standards with well-constrained Fe^{3+} / Fe_{tot} ratios, and lower sensitivity at low Fe concentrations.

CONCLUSIONS

The properly standardized EDS analyses of a polished and carbon coated sample can provide comparable results with WDS data for simple mineral composition, without overlapping elements, at least, for concentration above 1 wt. % (Reed, 2005; Lavrent'ev et al., 2015). Given the higher spectral resolution and better detection limits of WDS compared to EDS, the wavelength-dispersive microanalysis is strongly recommended for the quantitative determination of the chemical composition of minerals with complex compositions, especially those containing elements with overlapping peaks in energy-dispersive spectra and has become an international standard in high-ranking mineralogical and geological journals. Moreover, owing to these advantages, WDS analyses are generally preferred by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association and are often essential for the successful approval of new mineral proposals.

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