Solving the iron quantification problem in low-kV EPMA: An essential step toward improved analytical spatial resolution in electron probe microanalysis—Fe-sulfides

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ABSTRACT

The use of the field emission gun in scanning electron microscopy permits the imaging of sub-micrometer-size features. However, achieving sub-micrometer analytical spatial resolution in electron probe microanalysis (EPMA) requires both reducing the electron beam size and reducing the accelerating voltage to achieve the desired sub-micrometer interaction volume. The resulting quantification of the first-row transition metals at low accelerating voltage, i.e., below 7–8 kV, is problematic as the main characteristic X-ray lines (Kα) cannot be excited at these conditions. Furthermore, the use of the La and Lβ soft X-ray lines for quantification is complicated by bonding and self-absorption effects resulting in not-yet-determined mass absorption coefficients and hence in the failure of the traditional matrix correction procedure. We propose two methods to circumvent these low-kilovolt (low-kV) analysis limitations: using the non-traditional FeLα line and using universal calibration curves for the more traditional FeLα and Lβ lines. These methods were successfully applied to Fe-sulfide minerals showing accurate quantification results by EPMA at reduced kV, necessary for accurate quantification of sub-micrometer sulfide grains.

Keywords: EPMA, sulfides, low kV, iron, microprobe, SXES, EMPA, X-ray

INTRODUCTION

Electron probe microanalysis (EPMA) is a characterization technique that is routinely used for qualitative and quantitative analysis of micrometer-sized volumes. The technique has seen many significant advances in the last decades (Llovet et al. 2021). One of them has been developing and integrating Schottky field emission guns (FEGs) in microprobe instruments. These types of electron sources produce a stable, bright, and narrow electron beam, resulting in a smaller beam diameter compared to tungsten and LaB₆ sources and hence offer a significant increase in the spatial imaging resolution. However, to better use this resolution improvement for quantitative purposes, it is also essential that the electron beam energy is reduced, typically from the traditional 15 or 20 kV to 7–8 kV or less. The combination of reduced beam size through the availability of FEGs and reduced electron interaction volume through using lower beam energy then permits the possible successful analysis and quantification of sub-micrometer features.

Figure 1 illustrates this for the FeKα and La X-ray production volume diameters in FeS₂, using the Monte Carlo code PENEPMA/PENELOPE (Llovet and Salvat 2017; Salvat 2019). By decreasing the accelerating voltage from 20 to 7 kV (assuming an electron beam diameter of 80 nm), the diameter of the contour delimiting an area where 99% of the considered X-rays are produced is reduced from 3 μm to about 0.75 μm, as shown on Figure 1. Hence, the analytical spatial resolution is increased by a factor of 4. Reducing the beam diameter will only reduce the X-ray production volume’s diameter by the same amount, therefore not drastically improving the analytical resolution. The critical parameter governing the analytical spatial resolution is the accelerating voltage. It is worth noting that at 10 and 20 kV, the diameter of the X-ray production volume for the FeKα and La X-ray lines are similar, as summarized in Table 1. However, at 7 kV the maximum of the produced X-ray intensity for the FeLα X-ray line is about three times higher than the maximum of the produced X-ray intensity for FeKα X-ray line at 10 kV.

We are not, however, the first to investigate the use of low-voltage (or low-kV) EPMA for sulfides. Desborough et al. (1971) ran a successful series of experiments, measuring SKα at 6 kV on the USGS ARL EMX electron probe. The goal was not to improve the analytical spatial resolution but rather that of effectively eliminating matrix effects. Using a suite of synthetic in-house sulfide reference materials (Czamanske and Ingamells 1970), they concluded that “a linear calibration curve relating X-ray intensity to sulfur concentration eliminates the need for using complex computer corrections required at higher operating voltages”—recall the state of computing five decades ago.

DIFFICULTIES OF EPMA AT A LOW ACCELERATING VOLTAGE

Two methods can be distinguished to improve the analytical spatial resolution in EPMA (and, as demonstrated by Desborough et al. 1971, reduce the magnitude of the matrix correction for some elements): low overvoltage and low voltage. The low overvoltage approach employs lowering the accelerating voltage, or electron beam energy, to just above the ionization energy required to produce the X-ray transition of interest (i.e., low overvoltage), such as 8–10 kV for the FeKα X-ray line. The beam electrons have enough energy to produce the ionization only in a very small volume near the landing point of the electron beam, resulting in...