A new EPMA method for fast trace element analysis in simple matrices

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ABSTRACT

It is well known that trace element sensitivity in electron probe microanalysis (EPMA) is limited by intrinsic random variation in the X-ray continuum background and weak signals at low concentrations. The continuum portion of the background is produced by deceleration of the electron beam by the Coulombic field of the specimen atoms. In addition to the continuum, the background also includes interferences from secondary emission lines, “holes” in the continuum from secondary Bragg diffraction, non-linear curvature of the wavelength-dispersive spectrometer (WDS) continuum and other background artifacts. Typically, the background must be characterized with sufficient precision (along with the peak intensity of the emission line of interest, to obtain the net intensity for subsequent quantification), to attain reasonable accuracy for quantification of the elements of interest. Traditionally we characterize these background intensities by measuring on either side of the emission line and interpolate the intensity underneath the peak to obtain the net intensity. Instead, by applying the mean atomic number (MAN) background calibration curve method proposed in this paper for the background intensity correction, such background measurement artifacts are avoided through identification of outliers within a set of standards. We divide the analytical uncertainty of the MAN background calibration between precision errors and accuracy errors. The precision errors of the MAN background calibration are smaller than direct background measurement, if the mean atomic number of the sample matrix is precisely known. For a simple matrix and a suitable blank standard, a high-precision blank correction can offset the accuracy component of the MAN uncertainty. Use of the blank-corrected-MAN background calibration can further improve our measurement precision for trace elements compared to traditional off-peak measurements because the background determination is not limited by continuum X-ray counting statistics. For trace element mapping of a simple matrix, the background variance due to major element heterogeneity is exceedingly small and high-precision two-dimensional background correction is possible.

Keywords: EPMA, quantitative analysis, microanalysis, trace elements, sensitivity, accuracy, X-ray mapping

INTRODUCTION

Traditionally electron probe microanalysis (EPMA) has relied upon precise characterization of the continuum intensities adjacent to the emission line of interest for determination of the background under the peak, through interpolation of the off-peak intensities. Recent improvements including new hardware designs with large area Bragg crystals, new software methods implementing exponential and polynomial interpolations to more accurately characterize the curvature of the background, and aggregated spectrometer signals to improve sensitivity, have enabled the EPMA to attain detection limits as low as 2 to 3 ppm in some materials (Donovan et al. 2011).

The traditional off-peak method requires careful selection of background positions to avoid spectral interferences from secondary emission lines near the off-peak intensity positions, and various continuum artifacts (Kato and Suzuki 2014). For trace element characterization, the traditional off-peak method generally requires careful study of a wide swath of the emitted continuum spectrum by means of high-precision WDS scans, which can be quite time consuming. Such spectrometer scanning techniques are particularly time consuming when WDS scans are performed with a precision similar to subsequent trace quantification measurements, to avoid secondary emission lines from other elements when selecting off-peak measurement positions. Unfortunately, even high-sensitivity and time-consuming wavelength scans may not suffice for some samples where the inhomogeneity of major and/or minor elements may introduce unanticipated off-peak interferences on the pre-specified off-peak positions, which may result in significant inaccuracies in the background determination underneath the peak of interest.

Recent work on a new multi-point background method where multiple high-precision off-peak measurements (essentially a sparse high sensitivity wavelength scan combined with typical quantitative peak intensity measurements), for subsequent “iterative” determination of the optimum background positions based on statistical considerations, has been developed for complex matrices where such off-peak interferences are variable in complex materials such