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Measurements of the effective atomic numbers of minerals using bremsstrahlung produced by low-energy electrons

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ABSTRACT

The accuracy of a method for measuring the effective atomic numbers of minerals using bremsstrahlung intensities has been investigated. The method is independent of detector-efficiency and maximum accelerating voltage. In order to test the method, experiments were performed which involved low-energy electrons incident on thick malachite, pyrite, and galena targets. The resultant thick-target bremsstrahlung was compared to bremsstrahlung produced using a standard target, and experimental effective atomic numbers were calculated using data from a previous study (in which the Z-dependence of thick-target bremsstrahlung was studied). Comparisons of the results to theoretical values suggest that the method has potential for implementation in energy-dispersive X-ray spectroscopy systems.

1. Introduction

Many scanning electron microscopes (SEMs) also have energy-dispersive X-ray analysis (EDX) capabilities, which are commonly used to analyze mineral and geological samples. However, EDX analysis has several quantitative measurement issues, some of which are due to resolution limitations of the X-ray detector used, as well as limitations related to the maximum accelerating voltage of the SEM. As EDX analysis involves the identification of elements using characteristic X-rays, it is susceptible to error due to poor detector resolution, which can lead to characteristic peak overlap in X-ray spectra and X-ray peak misidentification, which is common for minor and trace elements [1]. Furthermore, EDX analysis is dependent on the maximum accelerating voltage of the SEM. The use of a low accelerating voltage restricts the atomic shells which can be ionized, which reduces the number of characteristic X-rays available for EDX analysis [2]. In the present work, we describe an experimental method that is practically independent of detector-resolution and maximum accelerating voltage, which can be used to measure the effective atomic numbers of mineral and geological samples using bremsstrahlung intensities rather than characteristic X-ray intensities (both of which are included in the spectra produced using EDX). This alternative method for measuring the effective atomic numbers of geological samples is particularly well-suited for situations involving low-energy electron beam analysis (≤ 5 keV), which has been shown to lead to improved spatial resolution, a reduced probability of beam damage, and the minimization of charging effects [3].

It should be noted that the method described here for measuring the effective atomic number of geological samples is only applicable for situations involving so-called “thick-target bremsstrahlung.” This type of bremsstrahlung, emitted by incident electrons that eventually come to rest within the target, involves a target that is sufficiently thick that most of the interactions between the incident electrons and the target-atoms occur after the electrons have already been deflected due to previous interactions and lost energy. Thick-target bremsstrahlung production is a complex process, and can be difficult to model theoretically, as factors such as the absorption and deflection of bremsstrahlung photons by target-atoms and bremsstrahlung emitted by secondary electrons also play significant roles [4]. The resultant X-ray spectra are much different than so-called “thin-target bremsstrahlung” spectra, which approximate the spectra that result when an electron is incident on an isolated target-atom. Due to the aforementioned complexity of thick-target bremsstrahlung production, empirical and semi-empirical methods, such as the one described here, are quicker and much simpler to use than Monte Carlo methods. Furthermore, Monte Carlo programs such as PENELOPE and GEANT4 only simulate ordinary bremsstrahlung (emitted by electrons incident on the target) and not bremsstrahlung emitted by atomic electrons in the target as the atoms are polarized by the Coulomb fields of the incident electrons (often referred to as polarizational or atomic bremsstrahlung). Theoretical [5] and experimental [6] results suggest that polarizational bremsstrahlung can make significant contributions to the total bremsstrahlung spectrum, especially at low photon-energies.

The principal objective of the experiments described here was to determine whether the effective atomic numbers of mineral samples

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could be accurately measured by comparing the intensities of the bremsstrahlung produced using the mineral samples to the intensity of the bremsstrahlung produced using a high-purity target with a known composition and effective atomic number. The potential accuracy of the method was investigated by comparing the minerals' experimentally-measured effective atomic numbers (Z_{exp}) to the theoretical values (Z_{the}) obtained using an equation from Ref. [7].

2. Experimental methods

In the experiments described herein, electrons were accelerated to kinetic energies of 5 keV using an ELS5000 electron source (PSP Vacuum Technology, UK). The targets, which consisted of 1 mm-thick slabs of malachite ($Cu_2CO_3(OH)_2$), pyrite (FeS_2), and galena (PbS), were oriented at an angle of 45° relative to the electron beam. The thicknesses of the targets used were much greater than the 5 keV-electron CSDA ranges for their respective materials (thick-target bremsstrahlung is essentially independent of target-thickness once the thickness is greater than the CSDA range of the incident electrons). All data presented here were normalized by the total number of electrons incident on the targets. The numbers of electrons absorbed by the targets were measured using a current integrator, and the numbers of electrons incident on the targets were determined by accounting for backscattered electrons. Backscattering coefficients were calculated using an expression taken from Ref. [8]. Pressures in the aluminum target cell were between 1.1×10^{-5} torr and 7.0×10^{-5} torr during the experiments. X-rays were detected using a Si(Li) detector (Princeton Gamma-Tech, USA), oriented at an angle of 90° relative to the electron beam (thick-target bremsstrahlung is essentially emitted isotropically, except at photon energies near the Duane-Hunt limit [9]). Bremsstrahlung intensities were determined by summing the numbers of photons detected in an energy range Δk (approximately 7 eV), centered at a photon energy, k. The energy resolution of the detector was measured to be approximately 200 eV at 5.89 keV. The relative positions of the electron beam, targets, and X-ray detector were the same during each of the experiments.

While bremsstrahlung intensity is approximately proportional to Z^2 (where Z is the atomic number of the target) for incident electron energies greater than 10 keV [10], the intensity is less dependent on the atomic number of the target at lower incident electron energies [11]. For an incident electron energy (E_o), the bremsstrahlung spectral photon distribution is:

$$S(k,Z,E_0) = K(k,E_0)Z^n \tag{1}$$

where Z is the atomic number of the target, K(k, E_o) is a proportionality constant, and n is the index value of the Z-dependence [12]. The index values (n) used here for various photon-to-electron energy ratios (k/E_o) were taken from the experimental results of Czarnecki et al. [11]. As the index values taken from Czarnecki et al. [11] were measured without correcting for self-absorption effects, the effects of self-absorption (which are dependent on a material's atomic number) are already incorporated into the index values. Similarly, polarizational bremsstrahlung contributions and contributions from secondary electrons are already incorporated into the index values, as well.

Values of Z_{the} were calculated using an equation from Markowicz and Van Grieken [7]:

$$Z_{the} = \frac{\sum \frac{w_i Z_i^2}{A_i}}{\sum \frac{w_i Z_i}{A_i}} \tag{2}$$

where w_i, Z_i, and A_i are the weight fraction, atomic number, and atomic mass of the *i*th element, respectively.

The values of Z_{exp} were calculated using the equation:

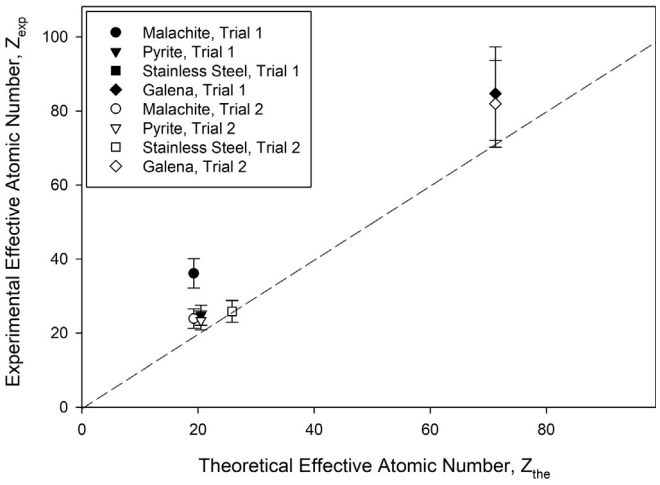

Fig. 1. Comparison of the experimental (Z_{exp}) and theoretical (Z_{the}) atomic numbers of the mineral samples (and the stainless steel target) for $k/E_o = 0.85$. The dashed line in the figure has a slope of unity.

$$Z_{exp} = \sqrt[n]{S(k,Z,E_0) \Big/ \left[\frac{S_{SS}(k,Z,E_0)}{25.85^n}\right]} \tag{3}$$

where S_{SS}(k, Z, E_o) is the normalized bremsstrahlung spectral photon distribution obtained using a 0.5 mm-thick, high-purity stainless steel target (Alfa Aesar, USA) of known composition (Fe: 70 wt%, Cr: 19 wt %, and Ni: 11 wt%), with an effective atomic number of 25.85 (calculated using Eq. (2)). Measurements of Z_{exp} made using this method are independent of factors such as detector efficiency and solid angle (as the positions of the electron beam, targets, and X-ray detector were the same during all of the experiments), thus eliminating uncertainty contributions from these factors.

Uncertainties in the Z_{exp} values shown here were calculated by summing statistical uncertainty, estimated uncertainty in backscattering coefficients, estimated uncertainty in background subtraction, uncertainties in index values, and uncertainties in the total number of incident electrons in quadrature. The error bars in all figures shown correspond to one standard deviation.

3. Results and discussion

Figs. 1–3 are comparisons of the experimental (Z_{exp}) and theoretical (Z_{the}) effective atomic numbers of the mineral targets for k/E_o = values

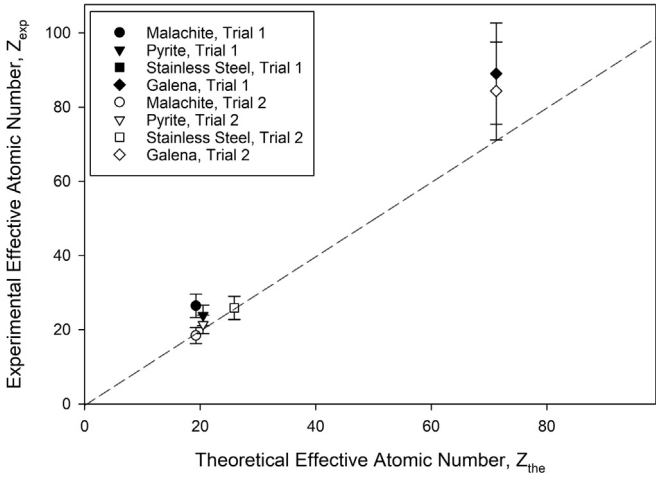

Fig. 2. Comparison of the experimental (Z_{exp}) and theoretical (Z_{the}) atomic numbers of the mineral samples (and the stainless steel target) for $k/E_o = 0.90$. The dashed line in the figure has a slope of unity.