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Optimizing detector geometry for trace element mapping by X-ray fluorescence

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ABSTRACT

Trace metals play critical roles in a variety of systems, ranging from cells to photovoltaics. X-Ray Fluorescence (XRF) microscopy using X-ray excitation provides one of the highest sensitivities available for imaging the distribution of trace metals at sub-100 nm resolution. With the growing availability and increasing performance of synchrotron light source based instruments and X-ray nanofocusing optics, and with improvements in energy-dispersive XRF detectors, what are the factors that limit trace element detectability? To address this question, we describe an analytical model for the total signal incident on XRF detectors with various geometries, including the spectral response of energy dispersive detectors. This model agrees well with experimentally recorded X-ray fluorescence spectra, and involves much shorter calculation times than with Monte Carlo simulations. With such a model, one can estimate the signal when a trace element is illuminated with an X-ray beam, and when just the surrounding non-fluorescent material is illuminated. From this signal difference, a contrast parameter can be calculated and this can in turn be used to calculate the signal-to-noise ratio (S/N) for detecting a certain elemental concentration. We apply this model to the detection of trace amounts of zinc in biological materials, and to the detection of small quantities of arsenic in semiconductors. We conclude that increased detector collection solid angle is (nearly) always advantageous even when considering the scattered signal. However, given the choice between a smaller detector at 90° to the beam versus a larger detector at 180° (in a backscatter-like geometry), the 90° detector is better for trace element detection in thick samples, while the larger detector in 180° geometry is better suited to trace element detection in thin samples.

1. Introduction

Trace elements play an important role in many aspects of our world. Cells and organisms require trace metals for their normal function; for example, roughly one-third of all proteins require a metal atom or cofactor to function properly. However, excess exposure to, deficiency of, or disregulation of trace metals are all implicated in various diseases; several examples have been investigated by X-ray fluorescence microscopy [1–5]. Trace elements in the environment can affect the functioning of microbes, animals, and plants [6–8]. In manufactured materials such as polycrystalline photovoltaics, trace metals can significantly degrade device performance [9,10]; in the semiconductor devices that pervade our lives, trace elements such as arsenic are essential for device operation. Trace elements even control the color and perceived value of gemstones.

There are a wide variety of techniques for measuring trace elemental distribution, including mass spectrometry (for example with micrometer-scale matrix-assisted laser desorption, or nanoscale focused ion beam desorption) and atomic emission spectroscopy. The measurement of characteristic X-ray emission lines (X-ray fluorescence, or XRF) is among the most sensitive, and moreover one can stimulate XRF in a relatively non-destructive manner. For XRF measurements, one must remove core shell electrons so that fluorescence is generated as electrons from less strongly bound states drop down to fill the vacancy. Inner-shell ionization is usually accomplished by using proton, electron or X-ray probes. With Proton-Induced X-ray Emission (PIXE) [11,12], one has the advantage that the high mass of protons leads to relatively low continuum background emission, so X-ray fluorescence lines are readily detectable above a very low background

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signal; the downside is that the proton mass also leads to considerably more specimen damage than one would have using excitation beams with lower momentum transfer. Electron Probe Micro-Analysis (EPMA) [13,14] are based on scanning electron microscopes equipped with energy or wavelength dispersive fluorescence detectors; they impart less damage to the specimen, but weaker fluorescence lines can become obscured by the continuum background signal, spatial resolution can be affected by electron beam sidescattering, and typically thin sections are required. By using focused X-ray beams to remove core level electrons via X-ray absorption, one has the advantage that there is a much lower background signal leading to improved trace element sensitivity at reduced radiation dose [15–18], as well as no beam blurring due to beam scattering. We therefore concentrate in this paper on a more detailed examination of trace element analysis in X-ray microprobes.

While the general advantageous properties of XRF analysis in X-ray microprobes are well-known [19], a detailed understanding involves a sequence of interactions as will be shown below. The best approach is to fully account for all possible interactions in Monte Carlo simulations, and considerable success has been obtained with excellent agreement with experiments. These include fundamental momentum based Monte Carlo simulations intended for general scattering phenomena, like GEANT4 [20] and its derivatives [21,22], and more specific interaction cross-section based simulations for energy-dispersive XRF (ED-XRF) spectrometers [23–28]. However, while Monte Carlo simulations can deliver a very detailed view of what can be expected from one or a few experimental configurations, we consider here an analytical approach which allows for more rapid exploration of a greater range of experimental parameters. Since there have been new developments in fast data collection with scanned beams [29], and fluorescence detectors with new geometries and data acquisition strategies [30–32], this faster analytical approach provides a tool to explore a wider range of experimental configurations so as to optimize trace element analysis for a different specimen types and using different types of detectors. We compare our approach against Monte Carlo simulations and also against experimental data, and find a very satisfactory agreement. We then apply this approach to consider trace element detection in two example specimens shown in Fig. 1:

1. “Bio” specimen: this sample consists of a 20 nm thick layer with the stochiometric elemental distribution of a typical protein ($C_{30}H_{50}O_{10}N_9S$) containing 0.01% Zn by weight, sandwiched between two water layers of varying thickness so as to comprise a specified total sample thickness. This sample approximates a small organelle within a cell, where Zn can play roles in fertilization and signaling (see for example [33]).
2. “Chip” specimen: this sample consists of a 0.5 nm thick layer of As on top of a Si crystal with specified thickness. Arsenic is a common dopant used in semiconductor integrated circuits, or silicon “chips.”

We will refer to these “bio” and “chip” specimens below.

2. X-ray fluorescence and signal estimates

Because synchrotron light sources usually make use of magnetic beam deflections in the horizontal plane, most beamlines (X-ray beam delivery systems) produce X-ray beams that are linearly polarized in the horizontal direction. With these polarized beams, there is a minimum in the elastic and inelastic (or Compton) scattering cross section at 90° from the incident beam direction, so that detectors mounted in the 90° configuration (Fig. 2) see a minimum of scattered photons as a background signal. It is for this reason that most synchrotron XRF microprobes are operated in the 90° geometry, in spite of associated inconveniences as discussed in Section 2.2. With detectors in the 90° geometry, increasing the detector's solid angle coverage will increase the strength of the detected fluorescence signals, but it will also increase the scattering background signal. How does this scale with fluorescence detector aperture? Is there an optimum solid angle of acceptance? In addition, newer detector options have emerged: one is the Maia detector [31,34,32], which is typically deployed in the 180° geometry, so that it is equipped with a hole in its center to allow the X-ray nanofocused beam to reach the specimen. What are the advantages and drawbacks of this geometry? These are some of the questions we wish to address.

We consider below several factors that lead to the final detected signal and background in XRF analysis:

- Scattering of the incident X-ray beam. While elastic or Rayleigh scattering is completely polarization dependent and minimized to zero at 90° to the polarized incident X-ray beam, inelastic or Compton X-ray scattering has a different distribution as described by Klein and Nishina [35,36] combined with the incoherent scattering function [37], which contains both polarization dependent and independent components leading to a non-zero minimum at 90° to the polarized incident X-ray beam (Fig. 3).
- Absorption by the atoms to be detected, and the emission of X-ray fluorescent photons versus Auger electrons [38,39] as well as their possible reabsorption.
- The response of energy-dispersive X-ray detectors, including energy spread and incomplete charge collection.

With an estimate of detected signal and background in hand, we can estimate the signal-to-noise ratio (S/N) and then estimate the number of incident photons that are required for trace element detection.

2.1. Signal-to-noise ratio

Our goal is to provide estimates on imaging particular elemental features in the presence of noise due to photon statistics and due to background signals. Following an approach outlined by Glaeser [40] and developed further by Sayre et al. [41,42], our calculations are based on $\bar{n}$ photons incident, and then comparing measurements when a particular feature is present (in which case we measure a mean image intensity of $\bar{n}I_p$ photons,

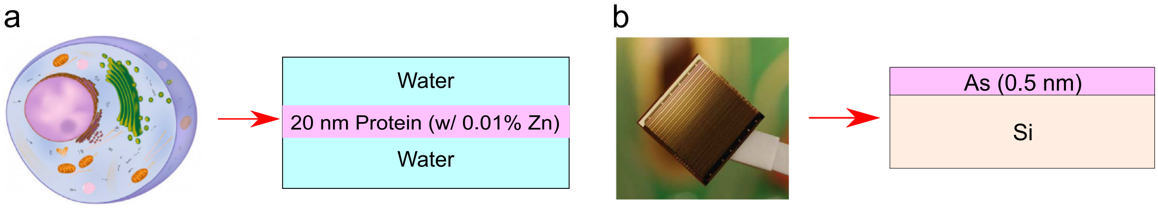

Fig. 1. Two models used as test samples. (a) The “Bio” sample consists of a thin (20 nm) protein layer with 0.01 wt% of Zn sandwiched between two layers of water to comprise a total sample thickness. (b) The “Chip” modeled semiconductor sample consists of a 0.5 nm thick layer of As on top of a Si layer with specified thickness.