

X-Ray Microanalysis in the Variable Pressure (Environmental) Scanning Electron Microscope

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Electron-excited x-ray microanalysis performed in the variable pressure and environmental scanning electron microscope is subject to additional artifacts beyond those encountered in the conventional scanning electron microscope. Gas scattering leads to direct contributions to the spectrum from the environmental gas, as well as remote generation of x rays by electrons scattered out of the focussed beam. The analyst can exert some degree of control over these artifacts, but depending on the exact situation, spurious elements can appear at the trace (< 0.01 mass fraction), minor (0.01 mass fraction to 0.1 mass fraction), or even major (> 0.1 mass fraction)

levels. Dispersed particle samples give the least compromised results, while fine scale microstructures are the most severely compromised. Procedures to optimize the situation based upon specimen preparation as well as spectral processing are described.

Key words: energy dispersive x-ray spectrometry; environmental scanning electron microscopy (ESEM); variable pressure scanning electron microscopy (VP-SEM); x-ray mapping; x-ray microanalysis; x-ray spectrometry.

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1. Introduction

Characterization of chemical microstructure is one of the most important applications of the conventional scanning electron microscope (SEM) equipped with an energy dispersive x-ray spectrometer (EDS) [1]. Interest in electron-excited x-ray microanalysis is potentially even greater in the variable pressure (VPSEM) and environmental scanning electron microscopes (ESEM) where dynamic chemical experiments can be conducted. The distinction between the VP-SEM and ESEM is made on the basis of achieving gas pressures that can maintain an equilibrium between water vapor and liquid water. With sample cooling to 2 °C, this equilibrium can be established at approximately 660 Pa. An arbitrary division between ESEM and VPSEM can be made at 100 Pa. X-ray microanalysis performed in the VPSEM-ESEM is subject to additional conditions and constraints that arise from the presence of the environmental gas and its influence on the primary electron beam. Figure 1 shows schematically the effects of elastic and inelastic scattering of the beam electrons by the gas atoms. The major consequence of inelastic scattering is the generation of characteristic and continuum (bremsstrahlung) x rays from the gas atoms that contribute to the measured Si-EDS spectrum. X-ray production is a relatively rare event, suffered by one in 10^6 electrons or fewer. Most electrons do not suffer significant energy loss from inelastic interactions.

The consequences of elastic scattering are the reduction of beam current within the focused probe and redistribution of this current to form a wide "skirt" around the beam, significantly degrading the spatial resolution

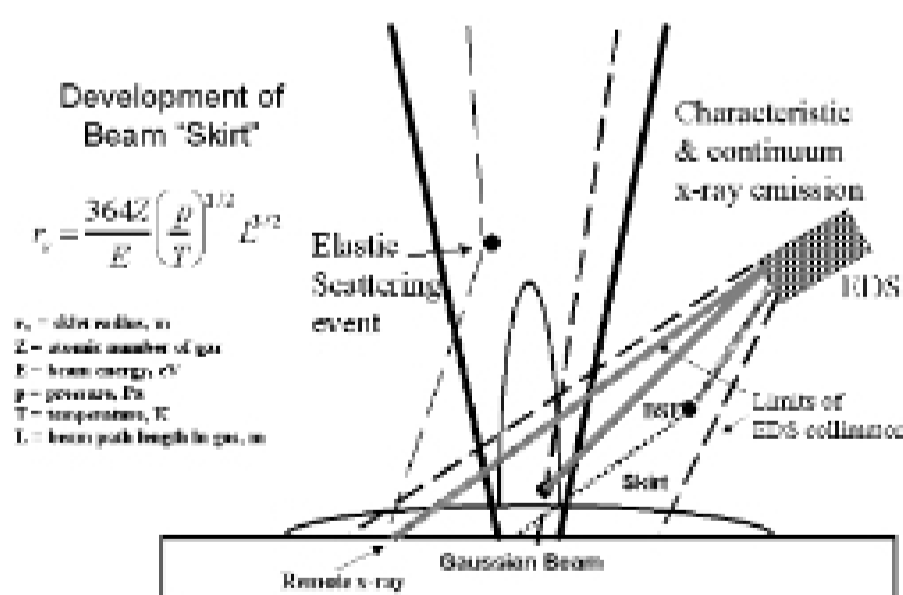


Fig 1. Schematic diagram illustrating formation of electron scattering "skirt" around the unscattered beam in a VPSEM-ESEM. Elastic scattering leads to transfer of electrons from the focused beam to the skirt. Inelastic scattering leads to inner shell ionization and subsequent emission of characteristic x rays from the gas, which will be collected by the EDS if emitted into the solid angle defined by the collimator.

of x-ray microanalysis. These gas-scattering effects can greatly alter the results achieved with x-ray microanalysis in the VPSEM-ESEM compared to performing a similar x-ray measurement in a conventional SEM under high vacuum conditions, given that the specimen would be compatible with high vacuum. This paper will consider the special aspects of x-ray spectrometry and microanalysis performed in the VPSEM-ESEM, especially the impact of gas scattering on spectrum quality, methods of specimen preparation to minimize the effects of gas scattering, practical aspects of qualitative and quantitative x-ray microanalysis, and prospects for future improvements in this area.

2. X-Ray Spectrometry in the VPSEM-ESEM

Electron-excited x-ray spectrometry performed with wavelength dispersive spectrometry (WDS) and/or semiconductor energy dispersive spectrometry (Si-EDS) in the SEM is a mature technique that is widely employed across many of the sciences [1]. Specimen excitation with a focussed electron beam at a fixed position can achieve lateral spatial resolution down to approximately 1 μm or less, depending on the beam energy and the exact composition of the specimen at the beam location. WDS and Si-EDS have critical strengths and weaknesses (e.g., resolution, spectral coverage, limits of detection, speed of photon processing, etc.) that are mutually supportive, so that combined Si-EDS-WDS instruments represent the most sophisticated level of this instrumentation in conventional SEM applications [1]. Because of the constraints imposed by the more aggressive environment of the VPSEM-ESEM, virtually all x-ray spectrometry in these instruments has been performed with Si-EDS, usually equipped with a vacuum isolation window that is resistant to water vapor. WDS could, in principle, be incorporated, but the special optical focusing properties of WDS demand precise positioning of the electron-excited x-ray source, and the diffractors of the WDS would require special protection to avoid degradation from exposure to the environmental gas. In this paper, we will consider only Si-EDS for performing x-ray spectrometry in the VPSEM-ESEM.

After recording an x-ray spectrum at a fixed beam location, the x-ray microanalysis procedure consists of two distinct stages:

(1) Qualitative analysis: The x-ray peaks are assigned to specific elemental constituents, and the broad categorization of major, minor, and trace is applied to each constituent so identified. These terms are defined (arbitrarily) as:

Major: $C > 0.1$ mass fraction (> 10 weight percent)

Minor: $0.01 \leq C \leq 0.1$ mass fraction (1 to 10 weight percent)

Trace: $C < 0.01$ mass fraction (< 1 weight percent)

(2) Quantitative analysis: A numerical value is assigned to the concentration, along with a statistical measure of the precision as a measure of repeatability and of expected accuracy.

A separate procedure, x -ray mapping, involves measuring x -ray intensities while the beam is scanned in a regular array of locations to form an image that depicts the spatial distribution of elemental constituents.

In the following discussion, we must also be aware that Si-EDS conducted under conventional high vacuum conditions is itself subject to artifacts (e.g., escape peaks, coincidence or sum peaks, and remote excitation due to backscattered electrons and rescattering of BSEs in the specimen chamber) that must be understood and corrected to achieve optimum results. In the following discussion, an understanding of EDS artifacts in conventional high vacuum operation will be assumed. A large literature on SEM/EDS exists that describes all aspects of the measurement science of the technique, including spectral artifacts, peak identification, various mathematical peak modeling procedures for separating peak and background, accuracy of quantitative analysis, limits of detection, etc. (for comprehensive treatments, see Refs. [1,2,3]). This literature forms the basis for proceeding with Si-EDS in the VPSEM-ESEM.

Gas scattering of the primary beam is the single most important difference between performing x -ray spectrometry with the conventional low pressure (i.e., high vacuum) SEM and with the elevated pressure (low vacuum) VPSEM-ESEM instruments. X -ray spectrometry performed in the VPSEM-ESEM must inevitably be compromised because of gas scattering compared to the "ideal" situation in the conventional high vacuum SEM. The key problem to consider for practical microanalysis in the VPSEM-ESEM is determining the concentration level of the analyte in the specimen (major, minor, or trace) for which the results can be trusted.

2.1 Extraneous X-Ray Peak(s) Due to the Environmental Gas

X -ray spectrometry in the VPSEM-ESEM is subject to additional artifacts beyond those familiar in conventional SEM/EDS. These artifacts are directly related to the presence of the environmental gas. The inevitable gas scattering, both elastic and inelastic, of a fraction of the primary beam electrons has a significant and frequently severe impact on both qualitative and quantitative Si-EDS x -ray microanalysis in the VPSEM-ESEM. Considering first the case of inelastic scattering, both

characteristic and continuum (bremsstrahlung) x rays are produced by the incident beam electrons during interactions with the environmental gas atoms. Moreover, the beam electrons that backscatter from the specimen can also undergo inelastic scattering events with the environmental gas atoms, further contributing to the measured x -ray spectrum. Although the density of atoms in the gas is very low compared to the atom density in the solid specimen, the volume of the gas which lies within the solid angle of collection of the Si-EDS, even when properly collimated, is quite large. The EDS accepts x rays from most of the gas path length of the beam from the final pressure limiting aperture to the specimen, a distance of several millimeters. The volume above the specimen into which the backscattered electrons are emitted (following a cosine distribution for a specimen surface placed normal to the beam) is also within the acceptance of the Si-EDS for the majority of BSEs, with only those lost which are emitted as a result of beam electrons scattered so far out into the skirt that they re-emerge as BSE outside the collimated acceptance area of the Si-EDS.

Figure 2 (a) shows Si-EDS spectra obtained as a function of water vapor pressure from a pure carbon disk (2.5 cm in diameter) bombarded with 20 keV electrons with a beam gas path length of 6 mm. The artifact oxygen contribution is barely detectable at the base pressure (≈ 50 Pa), but develops into an easily detectable peak at 133 Pa (1 torr) and above. Figure 2 (b) shows a plot of the O/C peak intensity ratio as a function of the pressure. Depending on the pressure, the environmental gas can be detected in the x -ray spectrum as an apparent major, minor, or trace constituent relative to the legitimate peak from the target. At the highest pressure used (2800 Pa = 21 torr), the oxygen peak intensity reached more than 70 % of the C K peak intensity from the carbon target. Close examination of Figure 2 (a) reveals that initially the oxygen intensity increases with increasing water vapor pressure with a gradual lowering of the carbon peak relative to the measurement at base pressure. At the highest pressure, the carbon peak is substantially reduced in intensity compared to the base level. This reduction in carbon x -ray intensity occurs because of elastic scattering into the skirt at distances beyond the acceptance of the EDS collimator (see next section) rather than from energy loss. Below approximately 10 Pa (0.1 torr), the contribution of the environmental gas to the x -ray spectrum becomes negligible. When He-H₂ gas mixtures are used instead of H₂O or air, extraneous x rays from the gas can be eliminated because of the lack of measurable x -ray emission from these atoms. There is still a contribution to the composite spectrum from continuum x rays produced from this gas mixture. For equivalent gas densities, the intensity of this extraneous