

Elemental Surface Analysis at Ambient Pressure by Electron-Induced X-ray Fluorescence

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ABSTRACT

The development of a portable surface elemental analysis tool based on the excitation of characteristic x-rays at ambient pressure with an electron beam is described. This instrument relies on the use of a thin electron transmissive membrane to isolate the vacuum of the electron source from the ambient atmosphere. The major advantages offered by this instrument include rapid spectrum acquisition, non-destructive evaluation of elemental composition, no sample preparation, and high spatial resolution due to a small sampling spot size. The instrument proof-of-principle has been demonstrated by obtaining energy dispersive x-ray spectra from metal and mineral samples.

Rapid and nondestructive analyses of surface elemental composition in atmosphere can provide extremely useful information in the fields of mineralogy, materials science, and biology. Three excitation sources currently used for x-ray fluorescence analysis of surface composition in ambient pressure are: (i) a radioactive alpha particle source, (ii) an x-ray source, or (iii) a focused ion beam. Here we present the possibility of using a fourth technique, the excitation of characteristic x-ray fluorescence using a focused electron beam, which we have now demonstrated in ambient atmosphere. Electron beam excited Energy Dispersive X-ray Analysis (EDAX or EDX) is a widely accepted technique for determining the elemental surface composition of samples in vacuum, for example in analytical Scanning Electron Microscopy (SEM). It has, however, not been previously demonstrated in ambient atmosphere due to the difficulty of generating and transmitting electron beams through the atmosphere. In this work we present a proof-of-principle for a new instrument, the Atmospheric Electron X-ray Spectrometer (AEXS¹), that uses a thin electron-transmissive membrane to encapsulate the electron column, thus isolating the vacuum within the electron source from the ambient pressure. The focused electron beam is transmitted through the membrane, and impinges on the surface of the irradiated sample where it excites characteristic x-rays for elemental analysis. Using a prototype AEXS instrument with a 10 keV electron beam, we have performed surface elemental analysis for samples at one atmosphere pressure with an irradiated spot diameter of approximately 0.8 mm, and an analysis time as short as 100 seconds. Theoretical models predict further improvements for the performance of an optimized instrument.

Two methods are currently available for the analysis of samples at atmospheric pressures using electron beams. The method on which the AEXS is based utilizes a thin electron-transparent membrane strong enough to support a differential pressure of one atmosphere. This technique has been used in the past for electron beam charging of small particles for subsequent electrostatic deflection.² An alternative method for analysis at near-ambient pressure is the Environmental SEM (ESEM³), which employs a series of pressure-limiting apertures with pumping stages to isolate the electron source vacuum from the pressure in the sample chamber. Both approaches provide rapid analysis times, small irradiated spot size, and evaluation of both insulating and conducting samples is possible due to the charge neutralization provided by ionized ambient gas interacting with charges on the sample surfaces. We have investigated the AEXS technique because we expect it to result in a more compact instrument suitable for field deployment. Although the ESEM permits a smaller spot size than the AEXS, the requirement for active vacuum pumping of multiple stages is expected to result in a much more elaborate vacuum system and hence much less portable instrument.

The AEXS concept is shown schematically in Figure 1. An electron gun is mounted in a vacuum enclosure (or tube) that is isolated from the ambient atmosphere by a thin electron-transmissive membrane. We use a thermionic electron source to generate and accelerate the electrons, and electrostatic lenses to focus this beam onto the surface of a sample in the ambient atmosphere. Because of its critical role, the membrane properties were investigated prior to incorporation into the AEXS. A series of experiments determined that the 1 mm x 1 mm membrane is capable of isolating high vacuum, is able

to withstand differential pressure in excess of one atmosphere, survive vibrational shocks, and has high electron transmissivity. High electron transmissivity was modeled with Monte Carlo simulations⁴ and was demonstrated using both SEM and laboratory AEXS-based setups. Figure 2 shows the predicted transmissivity and beam spreading due to scattering events as a function of the working distance between the membrane and the target at one atmosphere pressure for a 200 nm thick silicon nitride (SiN) membrane. For example, for 10 keV electrons at 1 mm working distance, the predicted transmissivity is 80% and the predicted irradiated spot diameter is 0.6 mm, whereas at 2 mm working distance the predicted diameter is 1 mm. Here, the spot size was defined as the arithmetic average of distances from the beam center at which the electrons impinge on the sample. As expected, the transmissivity increases and spot size decreases with increasing electron energy. Note that within the experimental error, the measured spot size at 2 mm agrees with theoretical predictions.

The electrons impinging on a sample generate characteristic x-rays, which are analyzed to determine the elemental composition of the irradiated spot. Electron induced x-ray generation is efficient, resulting in predicted spectrum acquisition times shorter than 100 seconds (assuming 10 μ A beam current and 10,000 counts per spectrum). The x-rays are detected by a cooled silicon *p* type-intrinsic-*n* type (PIN) diode x-ray detector. Recently, it has become possible to miniaturize these detector systems without significantly compromising their energy resolution, as the cooling systems have been miniaturized. Thus the concept of a portable surface analysis instrument is realistic

The proof-of-principle of the AEXS concept has been demonstrated by using laboratory apparatus with the same components as in Figure 1, with the addition of a turbo-molecular high vacuum pump to maintain the vacuum enclosure pressure at approximately 10^{-6} Torr. The electronics include a silicon PIN diode x-ray detector cooled to 255K, a shaping amplifier, and a high voltage power supply to accelerate and focus the electrons. The membrane was low-stress 200 nm thick SiN. The membrane was fabricated by using low pressure chemical vapor deposition of a 200 nm thick pinhole free SiN film on both sides of a 400 μ m thick Silicon wafer. One side of the wafer was coated with photoresist, and 1.5 mm x 1.5 mm openings were created using optical photolithography. The SiN film within these openings was removed with reactive ion etching. The photoresist was removed and the wafer was back-etched in potassium hydroxide (KOH) up to the etch-resistant top SiN film, leaving a pyramidal shaped etch-resistant SiN covered silicon support frame for mechanical strength. The frame was attached to a stainless steel flange using Epotech⁵ type H20E silver epoxy. The final membrane size is 1 mm x 1 mm.

Electron transmission through the membrane was first confirmed by introducing a sample coated with a ZnO phosphor into the path of the electron beam. A significant reduction in the phosphorescence was observed when a 5 μ m thick polycarbonate film was introduced between the membrane and the phosphor. Following this preliminary observation, we proceeded to obtain x-ray spectra from metals. To verify that the observed fluorescence was indeed excited by the electrons, a 5 μ m thick polycarbonate film was inserted between the membrane and the target, resulting in a strong reduction of

the characteristic x-ray signal. When, however, the polycarbonate film was inserted between the target and the x-ray detector, only very slight reduction was observed. These results confirm that the excitation particles are electrons.

The irradiated spot size was roughly determined by observing the luminous spot on the phosphor screen. A diameter between 0.5 mm and 1.5 mm was observed at 2 mm working distance. It should be noted that both electrons and x-rays can excite phosphorescence. Due to the inevitable presence of spurious x-rays, the measured diameter provides us with an upper limit to the electron spot size.

The x-ray detector and field effect transistor preamplifier used in these experiments was manufactured by the Amptek⁶ Corporation and cooled using a Peltier cooler. The detector was calibrated by using an Am x-ray fluorescing source. X-ray spectra from this target were collected with a commercial KeveX EDX system, and compared with the AEXS spectra. The comparison was used to identify known spectral peaks, and these peaks were used to calibrate the energy scale of the acquired data.

The calibrated system was then used to analyze metal and mineral samples in atmosphere. One of these was a 99.99% pure Ti sample mechanically polished with 800 grit sandpaper. The sample was placed at 2 mm from the membrane, and the x-ray spectrum was compared to that from a SEM-mounted EDX analysis system. Figures 3a and 3b show this comparison. Figure 3a shows the spectrum taken in the SEM, and Figure 3b shows that taken with the AEXS. Note that the two clearly discernible peaks (Ti $K\alpha$ and Ti $K\beta$) in Figure 3a are observed as a single, slightly shifted peak with a small shoulder in Figure 3b. The peaks are more resolved in the SEM due to greater detector sensitivity. The AEXS detector is cooled to 255 K, whereas the SEM detector is cooled to 77 K.

In summary we have demonstrated rapid acquisition of spatially resolved x-ray spectra for surface elemental analysis by measurement with the prototype AEXS instrument. By using a 10 keV electron beam and a 2 mm working distance in one atmosphere, the irradiated spot size was between 0.5 mm and 1.5 mm, and the analysis time was as short as 100 seconds. We expect this new analysis tool to find its place among other ambient pressure surface analysis systems, such as external micro ion-beam analysis (X-MIBA⁷), external nuclear reaction analysis (X-NRA), external Rutherford backscattering spectrometry (X-RBS), and x-ray fluorescence (XRF) instruments.⁸ Portable instruments, such as the MCA-4000⁹, analyze surface regions of dimensions of several square centimeters. Comparable laboratory techniques such as X-MIBA provide focused beams for surface analysis with spatial resolutions as small as several square μm but require large stationary instruments. The portability and resolution of the AEXS fills the gap between non-portable, high resolution laboratory instruments and portable, low resolution *in-situ* instruments such as the Alpha Proton X-ray Spectrometer (APXS¹⁰) used in the 1997 Mars Pathfinder mission. Our simulation models predict that the figures of merit will be improved by increasing the energy of the irradiating electrons, by reducing the working distance, and by working in reduced atmospheres such as Mars ambient. In Mars atmosphere (approximately 7 Torr) a 25 keV beam has been

predicted¹¹ to resolve areas as small as 100 μm at 2 mm working distance, thus offering the potential for a compact instrument for performing rapid *in-situ* surface analysis at medium spatial resolution.

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FIGURE CAPTIONS

Fig. 1. The AEXS instrument concept with the major components: encapsulated electron source with membrane, power supply, and x-ray detector system.

Fig. 2. Predicted electron (a) transmissivity and (b) spot size as a function of the working distance at one atmosphere pressure for a 200 nm thick SiN membrane. Note that the measured spot size (\blacklozenge designates experimental data taken at 10 keV and 2 mm working distance) agrees with the predicted spot size within the experimental error.

Fig. 3. Acquired x-ray spectrum from an irradiated Ti sample by 10 keV electron beam in (a) SEM, and (b) laboratory AEXS. Since the beam current was not measured, the number of counts for SEM and AEXS measurements has not been correlated. The particular spectrum acquisition time in the AEXS was 1000 seconds; however, similar spectra were obtained with times as short as 100 seconds.

Figure 1

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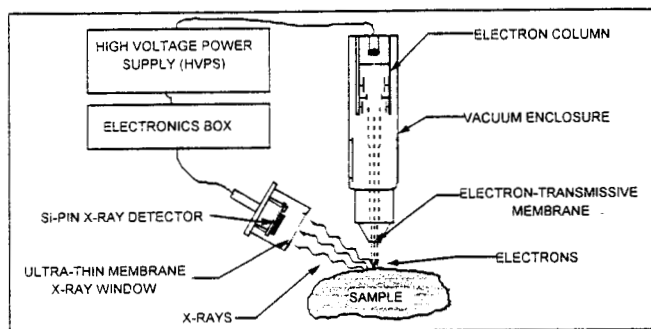


Figure 2

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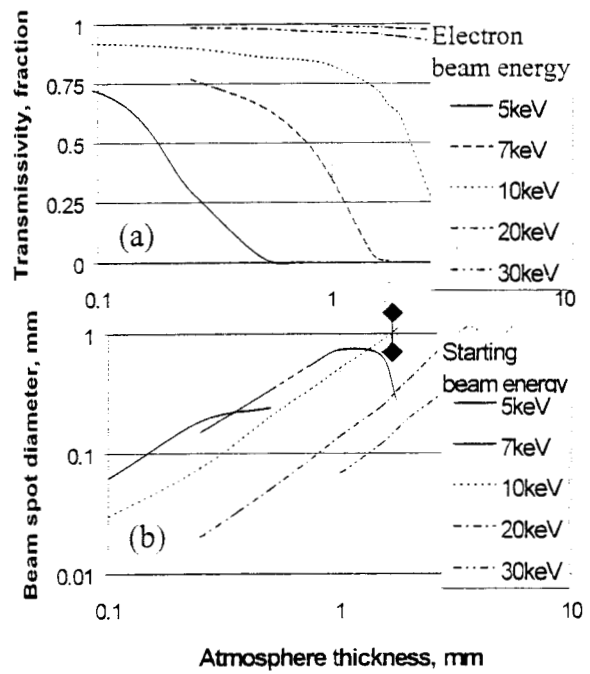


Figure 3a.

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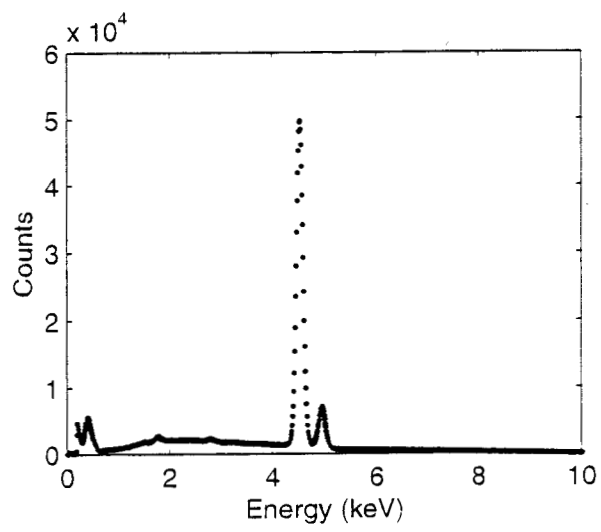


Figure 3b.

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