

Surface elemental analysis with 1 mm spatial resolution for samples in ambient atmosphere using the AEXS instrument

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Abstract—Atmospheric Electron X-ray Spectrometer (AEXS) is a miniature instrument based on the excitation of XRF spectra from samples in planetary atmospheres *in situ* using a focused electron beam. Unlike in SEM, the samples are not drawn into the vacuum of the electron column due to the use of a thin electron transmissive membrane that isolates the vacuum within the AEXS electron column. The spectra are analyzed by using an energy-dispersive detector to determine surface elemental abundance for the irradiated spots with high-to-medium spatial resolution, enabling to assess sample heterogeneity.

The AEXS prototype has been demonstrated including characterization of the effect of the membrane on XRF spectra and developing a stand-alone 20keV probe sealed with a 500nm thick SiN membrane. The sealed probe requires no active pumping, and has been used for performing elemental analysis of NIST and USGS traceable standards with a good agreement with the certified composition for samples in up to about 90 Torr-cm thick atmospheres. The spatial resolution for the microprobe has been tested by resolving 1 mm size mineral grains for a Gabbro (Norite) sample - a big improvement in XRF instrument capabilities flown on previous NASA missions. The current effort aims to construct a portable instrument consisting of a stand-alone microprobe integrated with a high voltage power supply (HVPS), including a dielectric housing necessitated by low electrical strength at Mars atmosphere pressure. When implemented on a mobile platform, AEXS would be able to determine elemental composition of freshly exposed rock, as a part of a payload that would also include a visual light camera capable of imaging the area being analyzed. Though widely used in the laboratory SEM, electron excitation has not been previously used due to the difficulty of generating electron beams in ambient atmospheres. To decrease power consumption and mass, the thermionic emitters should be replaced with CNT based field-emitters, greatly simplifying power supply architecture.

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1. INTRODUCTION

AEXS^[1-4] is a miniature instrument based on excitation of XRF spectra from samples in planetary atmospheres to determine surface elemental composition *in situ* using a focused electron beam. The energy dispersive analysis of the XRF spectra (EDX) is similar to that in Scanning Electron Microscopy (SEM); the excitation has not been previously used for samples in ambient atmospheres due to the difficulty of generating electron beams in planetary atmosphere. The excitation in planetary atmosphere using the AEXS instrument is enabled by isolating the vacuum of the electron source with a thin electron-transmissive membrane, eliminating the need for the interrogated samples to be drawn into the source vacuum, active vacuum pumping, or sample manipulation. The spectra can be acquired from samples in their pristine state since they do not need to be coated with conductive material to prevent charging effects.

Two methods are currently available for analyzing samples at near-atmospheric pressure using electron beams. The AEXS, and the Environmental SEM (ESEM), 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. Although commercially available ESEM systems permit a smaller spot size than AEXS, the requirement for active vacuum pumping of multiple stages requires an elaborate vacuum system resulting in a much less portable instrument than could be obtained with a vacuum-isolated AEXS microprobe.

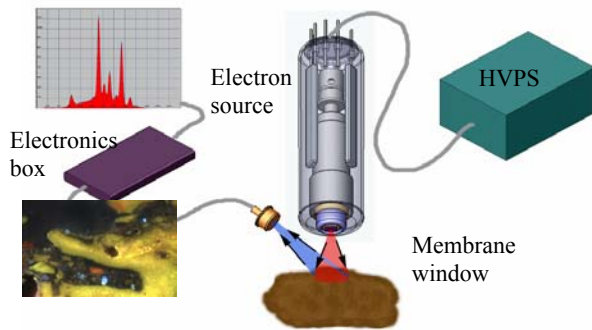


Fig. 1. AEXS instrument concept. The AEXS consists of a miniature, vacuum-encapsulated electron source, a high-voltage power supply, and XRF detector. The high energy (>15 keV) electron beam is transmitted through an electron-transmissive vacuum-isolation membrane into the ambient atmosphere to strike the sample, exciting characteristic XRF spectra for elemental analysis of the irradiated spot. The spot area can be adjusted from sub-millimeter to several centimeter size by changing the membrane-sample working distance. In the flight prototype AEXS, the electron source, high voltage multiplier (HVM), and XRF detector will be integrated in a miniature instrument head. The instrument head will be incorporated onto the instrument arm, and the control electronics placed inside the rover's warm box.

The AEXS instrument prototype has been developed in several stages. The viability of Silicon Nitride (SiN) membranes has been demonstrated under the NASA's PIDDP'98 funding. The membranes were 200 nm and 500 nm thick SiN windows defined within (1.5 mm)² rectangular openings in Si chip using standard photolithography and reactive ion (RIE) and wet chemical etching techniques.^[1,4] The windows have high electron transmission (> 90%), yet are strong enough to support up to one atmosphere differential pressure while maintaining a high vacuum within an electron column. The excitation of Cathodo-Luminescence (CL) spectra has been investigated under the ASTID'02 program.^[3] The development of a stand-alone microprobe, and demonstration of AEXS capabilities through XRF data acquisition using textured mineral samples has been funded by MIDP'03 program. The hardware development relied on assembly of a series of increasingly integrated setups. The first setup used an actively pumped vacuum chamber with a 10 keV electron tube incorporated into a high vacuum feed-through at one end and a SiN bearing window at the opposite end; the setup was used to demonstrate the ability of the transmitted electrons to excite XRF spectra in the outside, 760 Torr pressure Earth atmosphere. The next setup had the membrane attached directly to the exit aperture of a 10 keV gun operated under the support of a high vacuum pump. The most recently constructed breadboard instrument consists of a "stand-alone" microprobe with the electron-optics column encapsulated within a glass envelope sealed with a specially designed glass-tube attachment that incorporates the membrane bearing Si chip. The stand-alone probe requires

no active pumping, making it possible to develop a compact, low mass instrument suitable for *in situ* observations for NASA missions.

2. AEXS MICROPROBE

The stand-alone microprobe is shown in Fig. 2. In our early work with the 10keV tube,^{2,3} the Si chip was bonded directly to the glass tube, resulting in a large mismatch in the Coefficient of Thermal Expansion (CTE) between the lead-glass envelope and the Si chip, imparting large stresses during the thermal processing, evacuation, and subsequent field use. The mismatch was reduced by using a progressively graded CTE seal, leading to improved robustness. For the 20keV tube, we specify the glass materials to be CTE-matched to Si. The electron gun is mounted on a 7052 glass stem containing an evacuation port. The tube is sealed using a Kovar/Pyrex/Si attachment

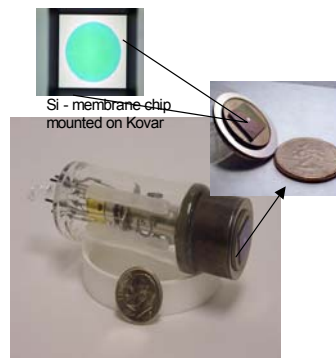


Fig 2. Vacuum-isolated 20keV electron gun

fabricated using a JPL developed process. A commercially available glass-to-Kovar transition sleeve is glass-blown to the stem/gun subassembly. In a separate process, the Si chip is anodically bonded to a Kovar disc (see the inset in Figure 2). The assembly process is completed by laser welding the Kovar sleeve to the Kovar disc-Si chip subassembly. Following

the welding, the electron gun is evacuated, baked out at 375 deg C and vacuum processed to a final pressure in the 10⁻⁸ Torr range, and the evacuation port is "pinched-off" by flame sealing the exhaust tubing, creating a stand-alone vacuum-sealed electron source.

3. THE EFFECT OF THE MEMBRANE AND EXTERNAL ATMOSPHERE ON EDX ANALYSIS

Unlike in SEM, the electron interaction with the traversed medium (membrane and external atmosphere) affects the EDX analysis.

To determine the membrane effect on the analysis, experiments were conducted within SEM with the membrane intercepting the probing beam. The main results are summarized in Fig 3. The electron transmissivity exceeds 90 % for all working distances less than 10 cm. The beam width widens due to elastic collisions with the intercepted medium. The Monte-Carlo simulated^[5] beam shape is fitted by a Gaussian (standard deviation $\sigma = 0.4$ cm) in Fig 3b, and the simulated widths are compared with the experimental values obtained using knife-edge type

experiments in SEM in Fig 3c. The standard deviation varied from about 0.6 mm to 1.8 mm when the working distance varied from 2.5 mm to 8 mm. The predicted spot size (defined as equal twice the standard deviation) is about 6 mm at 1 cm, and 6 cm 10 cm working distance, for 20kV electrons at 7 Torr pressure.

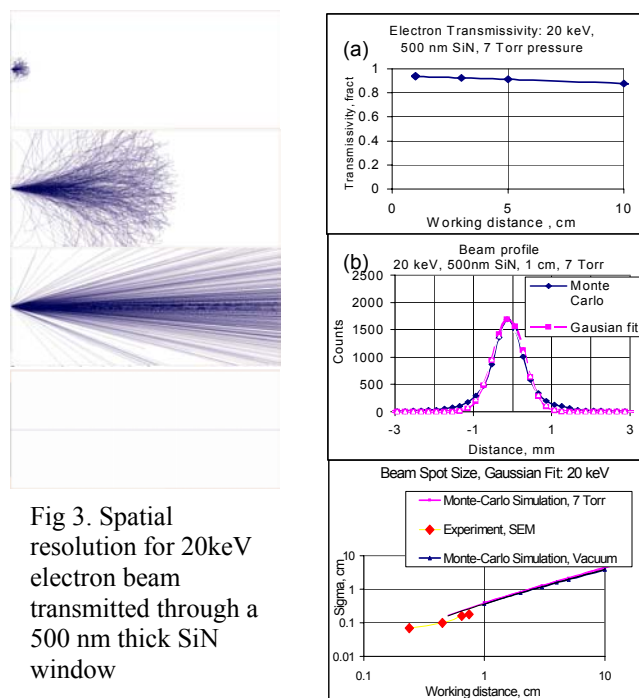


Fig 3. Spatial resolution for 20keV electron beam transmitted through a 500 nm thick SiN window

The effect of the external atmosphere (atmosphere outside the sealed microprobe) was investigated by irradiating targets inside an environmental chamber that has been constructed to simulate the effect of reduced atmosphere pressure on the acquired spectra. The electron microprobe, the irradiated samples and XRF detector were all placed into the chamber. To determine accuracy limits for the elemental composition, XRF spectra were collected from a number traceable standards (metal NIST and mineral standards of

known composition) as well as more complex mineral powder USGS standards at various atmosphere thickness. The detector was a Peltier-cooled PIN diode Amptek Inc.^[6] detector that was used on the Mars Pathfinder APXS.^[7] instrument (FWHM of 253 eV@5.9 keV). The membrane-to-sample working distance was ~ 1 cm, sample-to-detector distance ~ 3 cm, the spectra acquisition time ~ 100 seconds using a 1 μ A beam current (the same as in SEM). The spectra were analyzed using a commercially available EDX Quantification software acquired from IXRF corporation,^[8] The abundances were determined by “standard-less” quantification (ie no side-by-side standards were provided).

Table 1 shows the results for a BCR-2 (Basalt, Columbia River) sample,^[9] for a set of Nitrogen pressures varying from 10⁻⁴ Torr to 200 Torr. The experimentally determined composition (in weight %) is compared to certified composition for all analyzed elements, including the abundant (Si, Fe, Al and Ca, with K α lines well above the detection cutoff of the Be- window), light (Na, Mg, with K α lines near the Be-window cutoff), less abundant (K and Ti at 1.5 %), and trace elements (Mn, P, Ba, and V, with less than .15 % abundance). By comparing the composition for elements other than the light elements, the detection limit was several %, similar to that in SEM. Si, Fe, Al and Ca were detected at all pressures. Ti and K were also detected, albeit with a large relative error at some pressures. Table 1 lists the absolute abundance, the relative errors (the normalized difference between the certified and determined values) were generally larger for trace (TR) and light (cutoff, CF) elements than for more abundant elements: The trace elements were detected in some but not all cases, and for the light elements, K α lines (at 1.041 keV and 1.254 keV for Na and Mg, respectively) are effectively cut-off from detection due to strong attenuation by the detector’s 12 μ m thick Be window. The “un-detectables” (mostly Oxygen, since the elements are present as oxides) comprise about 46% of the BCR-2 sample by weight. The difference (for the detectable elements) between the certified and derived abundance increases with increasing pressure; the absolute difference was as large as 5% (of weight) for Fe, and less

Table 1. Elemental abundance of BCR-2 sample vs pressure: Comparison with the certified composition. CF = elements with the characteristic X-ray energy near the detector Be window cut-off energy. TR = trace element below the detection limit

		Composition, Weight, %									
Element		Certifd	Vac	3 Torr	7 Torr	12 Torr	34 Torr	63 Torr	94 Torr	130 Torr	200 Torr
Si	Detected	25.3	28.89	28.56	28.95	28.45	26.68	27.11	26.00	23.23	17.28
Fe	"	9.65	12.07	11.52	12.30	12.69	13.14	14.08	14.88	17.25	23.18
Al	"	7.14	6.10	6.57	5.93	5.74	5.12	4.44	3.57	3.30	0.72
Ca	"	5.09	4.85	5.10	5.30	5.18	6.53	6.29	6.77	6.87	6.38
K	"	1.49	1.56	1.81	1.24	1.21	2.35	1.21	1.26	0.88	0.87
Ti	"	1.35	1.19	1.14	0.89	1.21	0.81	1.30	1.18	1.41	1.43
Na	NC	2.34	0.03	0.03	0.00	0.00	0.00	0.07	0.04	0.00	0.00
Mg	"	2.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.13
Mn	TR	0.152	0.12	0.11	0.18	0.24	0.13	0.24	0.24	0.89	1.47
P	"	0.15	0.00	0.00	0.00	0.01	0.00	0.09	0.40	0.61	1.03
Ba	"	0.0683	0.00	0.00	0.00	0.20	0.00	0.00	0.44	0.00	1.22
V	"	0.0416	0.13	0.09	0.13	0.00	0.17	0.10	0.14	0.49	1.23

for other elements, at pressures up to about 90 Torr.

At higher (>90 Torr-cm) atmosphere thickness, the discrepancy between the certified and experimental abundance becomes greater than 50% for most of the analyzed elements. The disagreement is due to the neglect by EDX software of the effect of atmosphere and membrane on the analysis. Electron interaction with the membrane and atmosphere leads to spectral and spatial dispersion of the incident beam. The relatively good agreement between the derived and certified compositions using the SEM/EDX software package with no corrections for the non-monochromatic beam, is due to the fact that the spectral distribution of the incident electrons remains strongly peaked (at least until 90 Torr-cm).

4. RESOLVING MINERAL GRAINS

To test the AEXS ability to resolve mineral “grains”, the tube was also used to excite XRF spectra from a number of complex rocks. Rock samples containing mm-scale size mineral grains of unknown composition were placed on top of a moving stage in the chamber. By moving the samples underneath the electron beam (producing beam scanning), regions with different elemental abundance on the sample surface were differentiated with ~ 1mm spatial resolution, a big improvement over a several cm-scale spatial resolution of the APXS instrument on MER.^[10]

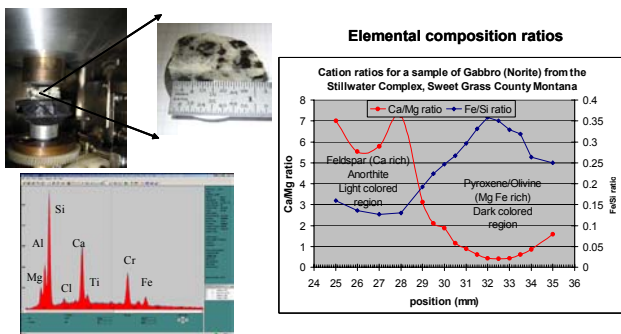


Fig 4. Spatially resolved measurements for Gabbro (Norite) sample. Mg & Fe rich areas were differentiated from Ca & Al rich areas (in 0.5 mm steps). These results were obtained using a newer Amptek detector with 1.49 eV FWHM, and thinner detector window (8 μm Be).

Figure 4 shows a Gabbro (Norite) sample from the Stillwater Complex, Sweet Grass County Montana, which contained mineral grains of 1 to 3 mm in size. The stage was stepped in 0.5 mm increments. Mg & Fe rich areas were differentiated from Ca & Al rich areas with about 1.5 mm spatial resolution. This is the first demonstration of the ability of any XRF instrument to map composition with better than several cm-scale spatial resolution. Other XRF instruments (APXS, flown on Pathfinder and MER) or the Chemin (selected for MSL mission), are essentially bulk analysis instruments. Resolving the elemental composition spatially may give clues about sample’s geologic origin. The environmental chamber does not allow us to “see” the exact probed location by the electron beam. Having determined

the achievable spatial resolution, Fig 5 shows the simulated (using averaged EDX data from SEM) maps for AEXS beam with 1mm spatial resolution. The simulated “AEXS” maps mimic the spatially distribution of the EDX data well.

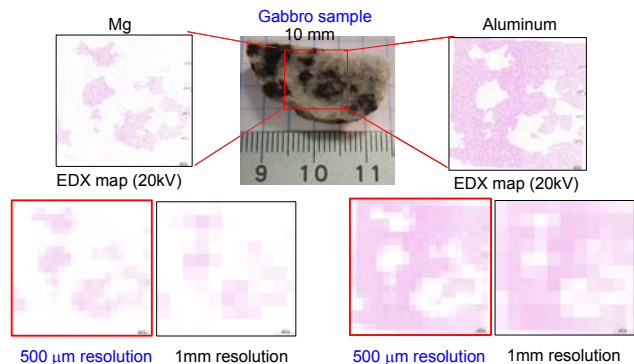
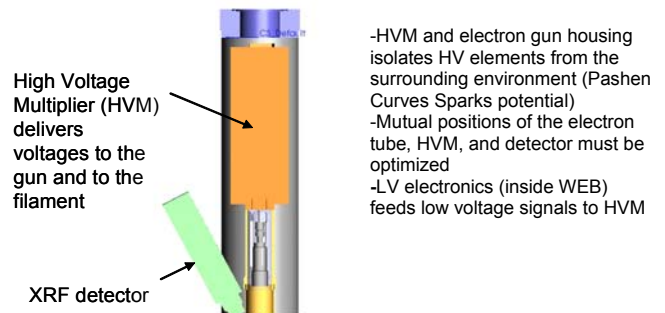


Fig. 5. Simulation of spatial maps obtained with 1 mm (and 500 μm) spatial resolution compared to EDX data in SEM for Gabbro sample.

5. INSTRUMENT HEAD

Reliability tests for the sealed microprobe were conducted including thermal cycling (-65 to +120C) and vibrational tests, with no adverse affects observed for microprobe operation after the testing. Figure 6 shows a rendering of the envisioned instrument head. The instrument head integrates a high voltage multiplier (HVM) that delivers voltages to the tube’s electrodes and to the filament heating power supply. The development of the power supply is currently ongoing, scheduled in several phases at JPL. The

Portable AEXS concept



Aerosino's 50keV X-ray tube

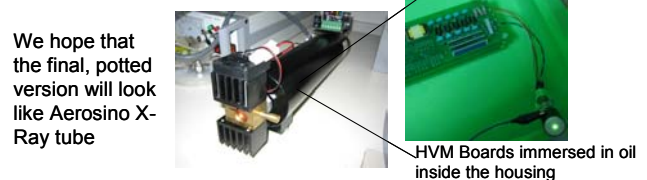


Fig 6. Dielectric Insulation for High Voltage (HV) elements for extreme environment operation (low pressure- Mars 7 Torr; and low temperature, -135C to + 65C for rover arm).

development includes design and fabrication of the electronic boards, development of a dielectric housing envelope (necessitated by low electrical strength of the Mars atmosphere pressure) for the HVM and electron microprobe, and instrument head design for low temperature operation.

6. CONCLUSIONS

AEXS is an *in situ* instrument for the determination of surface elemental composition using energy-dispersive XRF analysis, for samples in planetary atmosphere with no or little sample preparation, and no active vacuum support. The stand-alone microprobe was used to determine elemental composition for several mineral standards with a good agreement (4%) in up to 90 Torr-cm thick atmosphere, and resolve mineral grains from inhomogeneous rocks with 1.5 mm spatial resolution. This is the first demonstration of the ability of any XRF instrument to map elemental composition with better than several cm-scale spatial resolution. The potential for miniaturization addresses the need of planetary missions for *in situ* analysis tools, complementary to other, essentially bulk analysis XRF instruments. Table 2 summarizes merit parameters for the AEXS and compares them with the APXS and the CheMin XRF/XRD instrument. Resolving the elemental composition spatially may give clues about samples geological origin.

Table 2. Merits of electron-induced excitation with other *in-situ* excitation methods of XRF (*assumes CNT-emitter primary source)

Property for XRF excitation	CNT-array emitters*	XRF/XRD *	APXS (MER)
Excitation particles	Electrons	X-ray photons	α -particles
Spectrum acquisition time	< 30 sec	5 min/30min	0.5 hour
Energy per acquired spectrum	< 30 J	300 J/2000 J	500 J (includes electronics)
Scanning ability	Electronic	Mechanical	None
Spatial resolution	Several ten μm^2 to cm^2	$\sim \text{mm}^2\text{-cm}^2$	$\sim \text{cm}^2$
Can be turned off during operation	Yes	Yes	No: radioactive

When implemented on an instrument arm, AEXS would be a part of a payload that would also include a visual light camera capable of imaging the area being analyzed. The spectral fidelity is expected to improve further with the planned use of the Ketek detector (that was used on MER). In our future work, we would like to replace the tube's thermionic emitter with Carbon-nanotube-based field-emitters, greatly simplifying the power supply architecture, resulting in significantly lower power consumption, size, and mass.

7. ACKNOWLEDGMENTS

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