Particulate Screening Using External micro-PIXE and Multivariate Statistical Analysis

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Abstract. The first experimental results are reported from an External micro-PIXE (XµPIXE) system designed to forensically analyze particulates on collection media. The system has demonstrated fixed in-air ~30μm focused spots of nA currents of 4.5 MeV protons. A specially designed computer automated system for targeting this beam on individual particulates has been developed that utilizes optically scanning imagery of samples collected onto Kapton films. Multivariate statistical analysis of the x-ray spectra from particle scans is performed using Sandia's Automated eXpert Spectral Image Analysis (AXSIA) program.

Keywords: particulates, particle-induced x-ray emission, multivariate statistical analysis, forensics

INTRODUCTION

Forensic analysis of particulates harvested from filters and other matrices is usually done by first screening to identify particles of interest (POIs) and then individually picking and analyzing these POIs in a labor-intensive process. Advances in µPIXE combined with Multivariate Statistical Data Analysis methods[1] offer new and complementary tools for automated nondestructive identification and characterization of POIs with high selectivity, specificity, and sensitivity. Recent results have demonstrated the capability to perform both in-vacuo and ex-vacuo analyses of field-collected samples[2]. These µPIXE techniques measure the major, minor and trace (ppm) element composition of particles and also allow the potential for ultra-trace (ppb) element analysis using mass spectrometry by locating, marking and extracting POIs in the collection media. Such measurements contain important information about the origin, processing and transportation of evidence collected at crime scenes or acts of terrorism.

The Sandia AXSIA[3] multivariate statistical analysis has already demonstrated the capability to automatically produce high quality elemental concentration images taken with µPIXE[1], and in this paper we show how AXSIA can also be used to classify the evidentiary value of particulates. A new ex-vacuo system is described that uses transmission XµPIXE geometry and a high resolution optical scanner for suspicious particle identification and stage navigation.
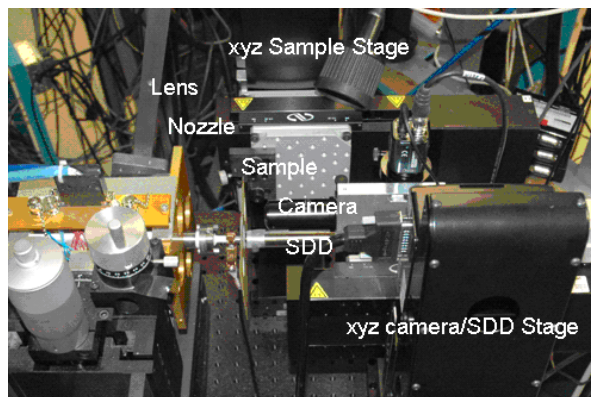

Figure 1. Photograph of the Sandia XµPIXE particulate analysis system.

HARDWARE

Overview

The XµPIXE system (see Figs. 1 and 2) is on the 45 degree left beamline of the Sandia Tandem-Pelletron. It uses a Martin lens to focus the 4.5 MeV protons accelerated by the tandem onto and through a 5-micron thick Al air-vacuum window. The beam then strikes the particulates mounted in a Kapton-foil sandwich targeting system (described below) which is positioned

only 1 mm from the nozzle to minimize beam spread from scattering in the exit foil and air-path. The beam loses ~0.1 MeV as it passes through this foil and the air gap to the sample. The proton beam loses another 0.3 MeV in transmission through the Kapton foil and, therefore, bombards the particles on the other side of this film with an energy of 4.1 MeV. The proton-induced x-rays from the particles exit the second,

downstream, Kapton foil and are detected by an XFlash[4] Silicon Drift Detector (SDD) also positioned just one mm from the foil to maximize solid angle.

The particulate targeting system and the SDD are each mounted and moved using their own precision xyz stages. The SDD xyz stage also holds a CCD microscope to view the position and focus of the proton beam on the quartz viewer.
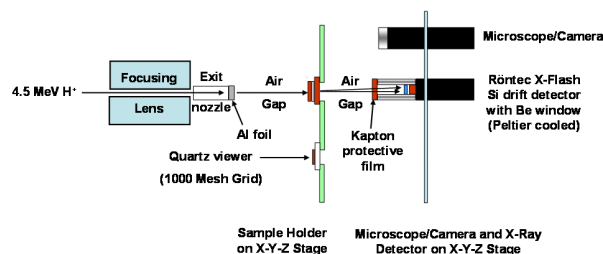

Figure 2. Schematic of XμPIXE system (not to scale).

Sample Collection and Mounting

Particulate samples are collected using a 1" diameter, 25 micron thick Kapton disk with Si adhesive ("Kapton PostIt") which is then attached to another 228 micron thick Kapton backing that is 2" on a side. This sandwiched sample is mounted on a specially manufactured circuit board that has a 1" circular opening and fiducial marks built into the mount. The three fiducials are shown in Figure 3 and
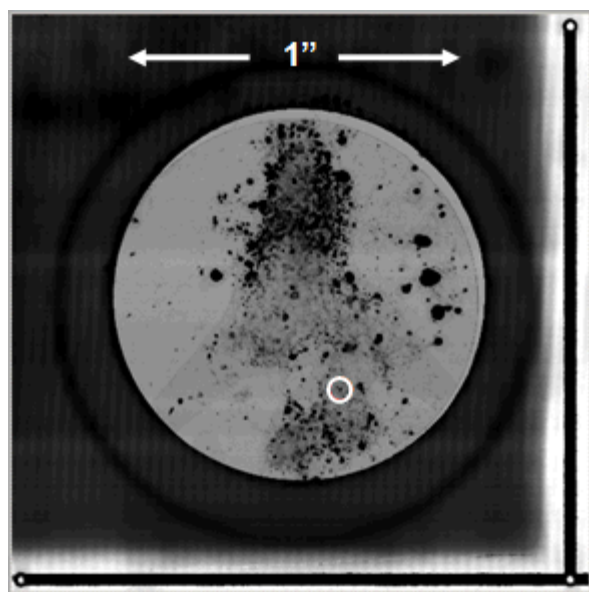

Figure 3. Photograph of particulate mounting system. The particulates were provided by INL[5] and contained Pitchblende particles mixed into NIST[6] Peruvian dirt. A particle containing uranium is circled in white. The fiducial marks which are through holes built in to the PC board are used for alignment and can be seen in the lower left and right, and upper right.

are in the lower left, lower right, and upper right of the image. A quartz viewer and TEM grid is also mounted on this board permanently for purposes of focusing the beam and determining the beam position.

Optical Scanning

It is clear from the beam-target-detector geometry that the sample cannot be observed during the analysis. As a result, the sample is first scanned using a high resolution 4096x4096 (5um pixels) optical scanner, and this image stored by a frame grabber. The Kapton-sandwiched samples are attached to a standard PC board (see Fig. 3) and mounted onto a computer controlled precision xyz stage. The second xyz stage moves a CCD-equipped optical microscope into focus along the position of the beam when placed on the quartz viewer. The Martin quadrupole double magnetic lens is used to focus the beam on this quartz viewer. Typically beams less than 50 microns in diameter are obtained and the position of the beam as seen on this quartz is recorded. The board is moved and centered on each fiducial mark surrounding the Kapton particulate sample. Each of these positions are recorded and matched to the scanned image of the sample. At this point, the position of the beam on the sample is determined from the scanned image and the position of the xyz stage, ameliorating the need for direct viewing, and simplifying the navigation of the fixed focused proton beam from particle to particle.
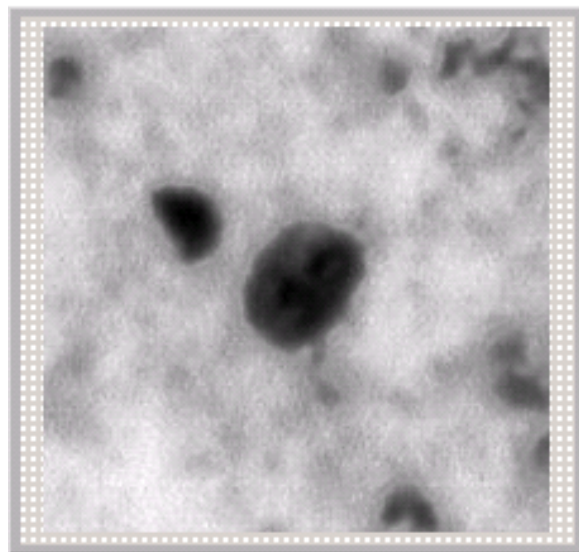
The individual particles to analyze can now be

Figure 4. Blowup of the image of particle #47 taken from the scanned image.

selected either manually from the scanned image or automatically by filtering their images in the LabView Program "XuPIXE"[7]. At this point, the only image filters being used are the bitmap intensity of the pixels in the scanned image of each particle and the area of these particles in units of pixels. For the particle

analysis described here, 50 particles were manually selected from the scan region to analyze.

XuPIXE analysis

The Proton-Induced X-ray Emission (PIXE) x-rays are detected in the forward direction (i.e., same direction as the proton beam) in a 5 mm^2 Silicon Drift Detector (SDD) which is placed 1.5 mm downstream from the sample. The x-rays and protons that are transmitted from the sample must pass through an additional 228 micron Kapton film. This film stops all of the protons so that they do not reach the SDD where they could cause damage. Because of the thickness of these two Kapton films (totaling 458 microns), only x-rays with energies greater than 3.5 keV reach the detector and this currently limits the detection of elements higher than calcium in the periodic table. On the other hand,

various peaks in the spectra. The scan/analyze function is then engaged and 4096 multichannel spectra are collected for each particle. The spectra are automatically recorded together with the position and magnified image of the each particle analyzed taken from the scanned image (see Figure 4 which is particle #47 and discovered to contain U). The PIXE spectrum taken for this particle, albeit with a longer run, is shown in figure 5. The x-axis is in units of keV. The uranium L x-rays are seen at 13.6, 16.7, 17.2 and 20.2 keV. These spectra have been fit with the GeoPIXE[8] program and converted to un-normalized concentrations in Fig. 6. The time required to scan to each of the 50 particles and "find" this one U particle only took a matter of minutes.
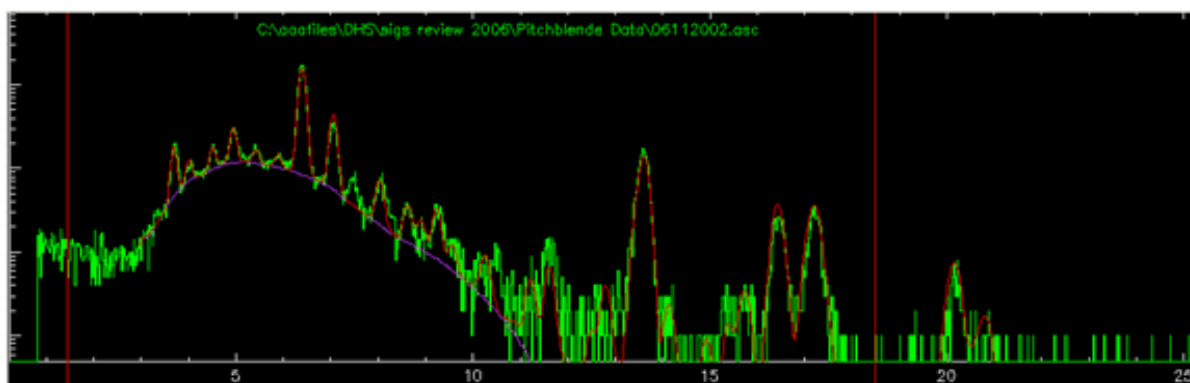

Figure 5. XµPIXE spectrum of particle # 47.

the alternative of not using these extra downstream Kapton films would jeopardize the expensive XFlash detector.

After the selecting the particles to be analyzed, the amount of time to spend collecting x-ray spectra from each particle is entered into the program. Several regions-of-interest (ROI) are defined to give a crude analysis of the number of x-ray counts collected from
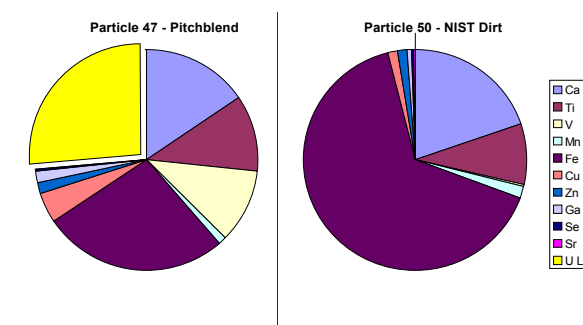

Figure 6. GeoPIXE analysis of particles #47 and #50 showing that #47 definitely contains a large fraction of U.

SOFTWARE

We have previously reported[1] the use of the multivariate spectral analysis program AXSIA (Automated eXpert Spectral Image Analysis) developed at Sandia to quantitatively analyze micro-PIXE data maps. Such automated multivariate statistical analyses are useful for converting very large amounts of data into a smaller, more manageable number of chemical components (spectra and images) that are needed to describe the PIXE maps. AXSIA can be used to classify the different types of particles identified using the XµPIXE system. In conventional PIXE analysis, the data set consists of x-ray spectra vs. (x,y)-pixelized position; in the case of AXSIA, the data are processed according to x-ray spectra vs. particle number.

A second particle sample was prepared to test the use of AXSIA and consisted of fine Ta and CoNiCr particles, again collected on the Kapton PostIts. As before, a number of particles were selected for analysis from the scanned image, but in this case the individual
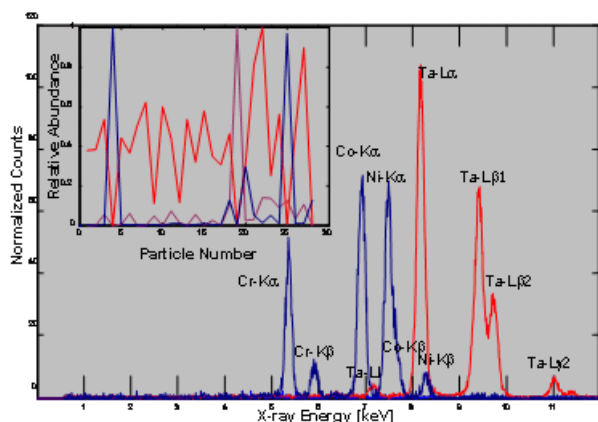
Figure 7. Two PIXE spectral shapes automatically determined by AXSIA, and (in the inset) the relative weighting of these spectra vs. particle number.

particle selection was automatic and based on size. The PIXE spectra were collected with approximately 10 second exposures on each particle so the experiment only took ~5 minutes. The spectra and particle number were input into the AXSIA program which identified two principle component spectra shapes and produced the results in Figure 7. Note that the program knows nothing about x-ray spectra *a priori* and factored these two spectral shapes from the data, automatically identifying and separating the CoNiCr particles from the Ta ones. This demonstrates that individual POIs (e.g., radiological particles of forensic interest) could just as easily have been separated from the rest. This analysis took only a fraction of a second, signifying the potential of AXSIA for automatically classifying the forensic value of even more complex sample sets.

CONCLUSIONS AND FUTURE DIRECTIONS

While these first results of using the XµPIXE system to find trace amounts of nuclear material in environmental samples is very encouraging, more needs to be done to transform XµPIXE from being a physics technique into a practical forensics analysis tool. Some of the improvements planned include:

1. Automated identification of suspicious particles: this could include, but not be limited to, determining other parameters about the particle beyond size such as:
   a. Sphericity
   b. Center of gravity
   c. Higher moments of optical density
   d. Color
2. Add the AXSIA program to the "XµPIXE" program to automatically correlate and classify the composition of each particle analyzed according to its threat potential, during the experiment.
3. Regarding the analysis, the XµPIXE geometry is in transmission so the protons excite x-rays on the side of the particle that is away from the detector. This means that the PIXE x-rays must pass through the particles with some absorption depending on the particle thickness and geometry. For example, there would be a difference between a particle that is a cube vs. a sphere vs. a thin pancake. While GeoPIXE can handle such an analysis, we need to find a way to automatically input this particulate-shape data into GeoPIXE.
4. A method to automatically "mark" the Kapton in the vicinity of suspicious particles needs to be developed together with techniques to then extract these them for more sensitive analyses using, for example, mass spectrometry. Much of the forensic value is contained in the ultra trace elements found in such samples and, unfortunately, we found XµPIXE incapable of such high sensitivity.
5. We need to develop a standard way of collecting samples that will be accepted by field agents.

ACKNOWLEDGEMENTS

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