https://doi.org/10.1017/S1551929500059770 Published online by Cambridge University Press

Confocal Micro X-Ray Fluorescence: A New Paradigm in Materials Characterization

Brian M. Patterson, George J. Havrilla, Kimberly A. DeFriend
Los Alamos National Laboratory, Los Alamos, NM
bpatterson@lanl.gov

Introduction:

Micro x-ray fluorescence (MXRF) is a microscopic analysis and imaging technique that is used to characterize the elements in a material non-destructively. Micro XRF instruments use an x-ray source to shine x-rays on a sample, and a detector to detect the characteristic x-rays given off. These fluorescent x-rays have very specific energies corresponding to specific electron energy transitions. Therefore, it is possible to detect and identify all of the elements present in a sample (typically above sodium) as well as measure their concentrations. This technique is widely used for the characterization of materials including polymer[1] and metallic foams, powder samples, forensics applications, geological samples, works of art and nuclear fuels[2]. Commercial MXRF instruments use a fused silica optic (mono or polycapillary) to focus the x-rays on the sample with no optic on the detector (Figure 1a). In this geometry, it is possible to raster the sample in two dimensions to collect the x-ray fluorescent signal as a function of position and generate a 2D map, identifying the elements present, their locations, and their relative and absolute abundances. While very useful, this geometry provides *x-y* mapping of the sample only, it does not provide signal discrimination versus depth.

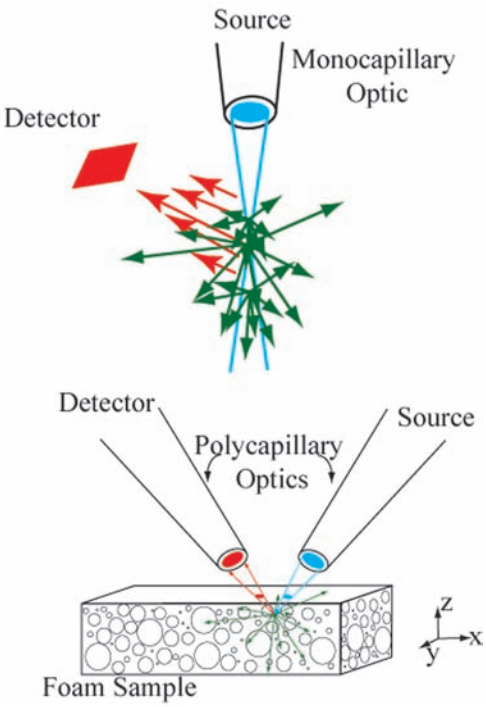

Figure 1: Top cartoon is the layout of a typical MXRF instrument showing an optic on the source but none on the detector. Fluorescent x-rays are detected even from the out of focus regions. The lower cartoon shows the optical geometry of a confocal MXRF instrument with an additional optic on the detector. Only fluorescent and scattered x-rays from the overlapping foci are detected.

As an improvement upon this design, confocal micro x-ray fluorescence (confocal MXRF) adds a new 'dimension' to this materials characterization technique by adding an optic on the detector. The foci of the two optics overlap in 3D space (Figure 1b), which can be useful for two purposes. The first is that any natural x-ray emission from a radioactive sample emitted off axis from the detector optic is rejected, reducing the background and improving the signal-to-noise when characterizing these samples. The second is that only the x-rays emitted from within the overlapping foci are measured, therefore a true 3D measurement is possible. By moving the sample through the confocal x-ray beam in the *x, y* and *z* directions, a 3D elemental map of the sample is possible, nondestructively providing elemental distribution and concentration. As an additional capability, the amount of x-ray scatter from low-density materials is proportional to the mass of material within the confocal volume, since this volume is measureable; the amount of scatter is proportional to the density of the material at that specific location. Confocal MXRF is useful for measuring the density of the material in 3D.

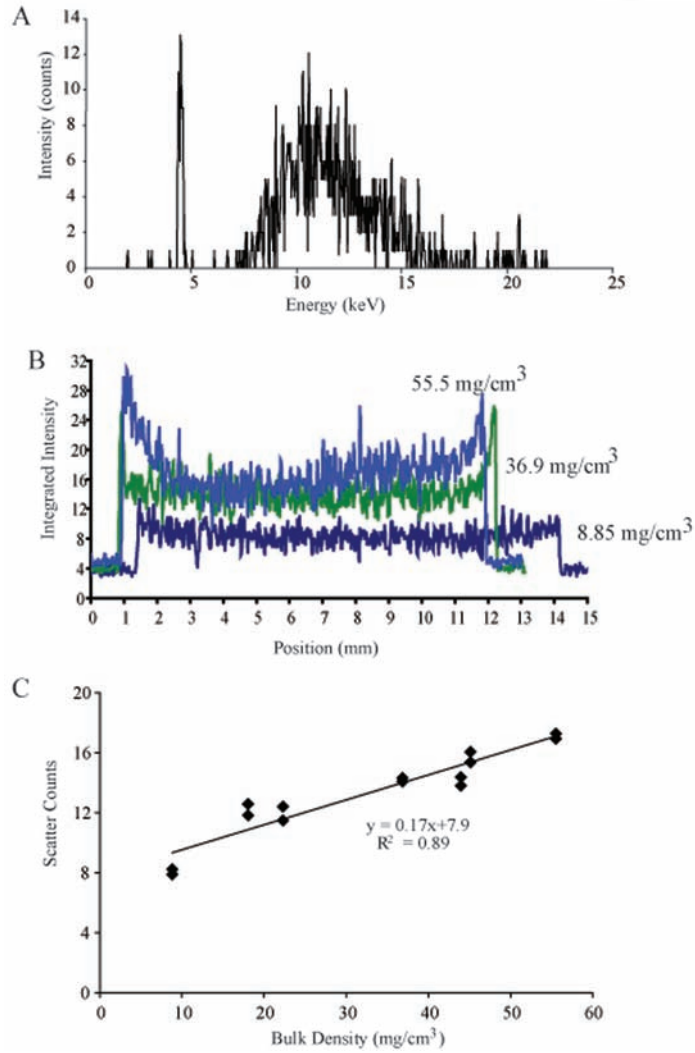

Figure 2: A) X-ray scatter spectrum indicating region of interest for the following figures. B) Line profiles of 8 (bottom), 37 (middle) and 55 (top) mg/cm^3 cast aerogels showing higher density gradients at the surfaces. C) Correlation of measured bulk density versus x-ray scatter intensity for a variety of cast aerogels.

As a proof of operation, several samples will be illustrated including using the scatter to quantitatively measure the density of silica aerogels, using the x-ray scatter to identify the voids in a silicone foam material in 3D and finally to collect 3D elemental image of a surface mount resistor for an integrated circuit.

Instrument:

The current prototype bench top design (X-ray Optical Systems, (XOS), East Greenbush, NY), except for the associated electronics, fits on a 2' by 2' optical bread board, and is housed and interlocked inside a cabinet. There is currently no vacuum chamber. The instrument uses an XOS X-beam Ag tube powered by a Spellman XLG power supply (25 W max) as the source, with an Amptek Si pin diode (XR-

Would You Bet Your Company's Reputation on Your EDS Results? We Did.

Place Your Bet at M&M Booth 1122

We've Expanded Our Product Range with the Most Powerful SDD for EDS

- ***New*** **Apollo Silicon Drift Detector Enables Complete Spectrum Maps to be Collected in Seconds**
- ***New*** **Hikari High Speed EBSD Detector**
- **Seamless Integration of EDS, EBSD, and WDS**

The original expectations of the development of the Silicon Drift Detector are now achievable with the EDAX Apollo SDD. Fulfilling the promise of the new technology, the Apollo SDD is capable of collecting high count rates with excellent resolution in an LN_2 free environment. The Apollo SDD, when seamlessly integrated with the LambdaSpec WDS and the Hikari EBSD Detector, provides the ultimate in high speed analysis.

Results with Confidence…Even Faster

The Apollo SDD is the latest innovation from EDAX. As the world's leader in Electron Beam Microanalysis, EDAX continues to raise the performance standard with features that provide faster results that you can trust to be complete and accurate.

For more information on EDAX's latest product developments visit our web site at ***www.EDAX.com/NEW*** *or call* ***1-201-529-4880****.*

EDAX®
advanced microanalysis solutions
AMETEK®
MATERIALS ANALYSIS DIVISION

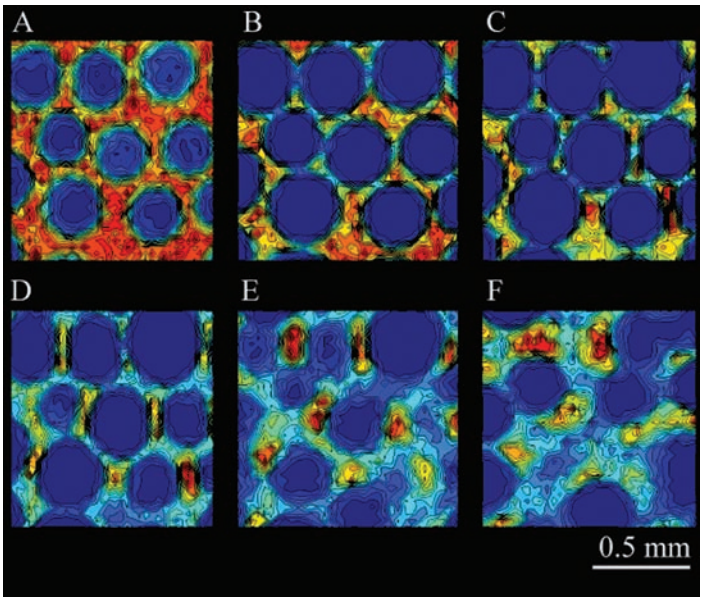

Figure 3: Array of sequential x-y contour plots displaced in z direction using region of interest indicated in Figure 2A. Pixel size (x-y) is 30 µm and z step size (from A-B, B-C, etc.) is 50 µm. Each slice took approximately 30 minutes to collect with a 1 second dwell at each location. There are 20 contour lines in each plot which are not of fixed intensity values from plot to plot.

100CR) as the detector. A monolithic polycapillary is used for each of the source and detector optics with an angle between the optics of 60 degrees, providing a spatial resolution of 30 × 30 × 65 micrometers as measured with the Ta L_α line. The center axis of each of the optics cuts the sample plane along the surface normal. The 60° angle between the optics is used for better depth penetration. Using polycapillary optics with a focal spot as small as 15 µm and mounting them 90° to each other, (45° from the surface normal) improves the spatial resolution and circularizes the confocal probe volume. Samples are mounted on three Newport 850G stages. The associated electronics are mounted on a single rack below the instrument. The instrument is controlled by a Dell computer running proprietary XOS software.

This instrument geometry enables the collection of MXRF spectra at a single point or line scans as either *x, y*, or depth profiles, *z*, as well as collect 2D regions of interest elemental maps at selected depths below the surface of the sample. These 2D slices can then be stacked into a full 3D image of the sample. Without the vacuum purge, elements with an atomic number greater than potassium can be identified and mapped. However, even low atomic number samples can be characterized and mapped based upon x-ray scatter. The confocal volume can be useful for density measurements of low atomic number matrices such as foams and aerogels. The amount of scatter produced by the sample (Figure 2) is dependent upon the mass of material within the confocal volume. Since the volume of the confocal beam is fixed, the amount of scatter is proportional to density. The 3D data is plotted using Matlab (Mathworks).

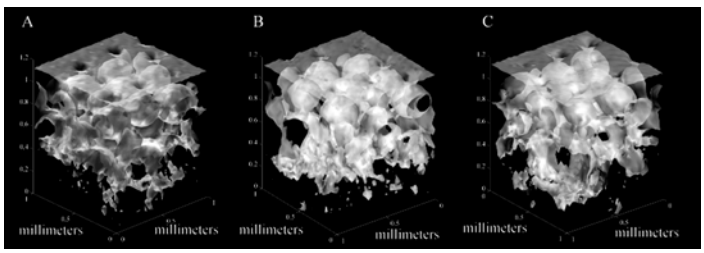

Figure 4: 3D constructs of PDMS foam scatter data from Figure 3. Each 3D image is rotated 90° counter clock-wise (A-C). Plot is 1 mm³. No modeling of x-ray attenuation is shown. Information is being collected from 1-mm depth, but signal is below user selected isovalue threshold of 20 counts.

Results:

Several cast aerogel samples with densities measuring between 10- 55 mg/cm³ were examined. These aerogels were cylindrical in shape and were mounted vertically with a flat surface pointing up. This orientation kept the beam path distance through the sample constant as the sample was moved through the beam. Measuring the x-ray scatter (Figure2a) for 4 seconds at each point (Figure 2b) and collecting a cross section profile can be used to measure the bulk density of an aerogel as well as density variations throughout the sample[3]. We have found good correlation between the amount of scatter in the center of the sample versus the density of the sample measured using a shadow graph and an analytical balance (Figure 2c). A higher density or 'skin' of aerogel has been measured on all aerogel samples examined. This 'skin' density is not seen on other samples such as polystyrene foams with similar densities and geometries. Work is ongoing with this phenomenon using confocal MXRF as well as micro-CT and is probably due to void collapse of the aerogel at the surface.

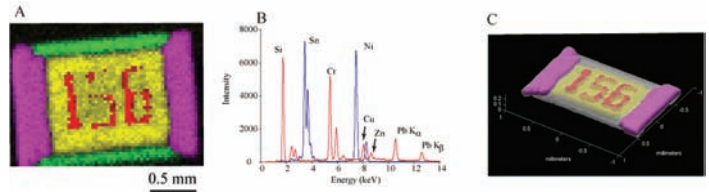

Figure 5: A) MXRF image of resistor using an EDAX Eagle II. Ti = red, Pb = yellow, Al= green, and Sn/Ni in pink. B) Spectra of the center (red) and edge (blue) of the resistor using the Eagle MXRF. Center spectrum indicates the presence of Si, Cr, Cu, Zn, and Pb. Edge spectrum shows Sn and Ni. A spectrum collected with the confocal would be exactly the same except that Al and Si peaks would not be present. C). 3D rendering of elemental images from the confocal MXRF. The same colors as A are used. Al is not identified by the confocal MXRF instrument, but is detected by its x-ray scatter shown as gray.

A piece of polydimethylsiloxane foam was also examined using confocal MXRF. Slices at various '*z*' locations were collected (Figure 3) and stacked into a single 3D image (Figure 4). As the sample is raised higher into the beam to collect information at depth, the x-ray scatter signal is attenuated by the upper layers, leading to the overall intensity dropping below the chosen cutoff isovalue and the sample is no longer resolvable. The image was plotted using Matlab with no data treatment or compensation for attenuation. There is still useful x-ray scatter signal at over 2 mm below the sample surface, and could be plotted with a signal attenuation correction versus depth. Current work is ongoing characterizing these foams using FT-IR, XRF, and micro-CT.

As a third example, a surface mount resistor for an integrated circuit is shown illustrating the ability of confocal MXRF to image a sample in 3D based solely on the elemental signal. Data was collected with a 1 second integration of each 50 × 83 *x, y* data points and 11 total slices in *z*. All spacing's were 30 µm in all three dimensions. Each slice required approximately 2 hours to collect, 22 hours for the entire data set. Eleven regions of interest were collected simultaneously, representing, the full range of channels, which were assigned to the elements Sn, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb. The regions of interest and their corresponding energies that were mapped out are shown in Table 1, below. Understanding the distributions of lead and tin are important for mitigation of tin whisker formation which

cannot be measured in 3D using any other bench top technique nondestructively.

Table 1: Regions of Interest and their Corresponding Energies

Element	Detector Channels	Energy Range (keV)
Scatter	0-1022	0-36.7
Sn	85-115	2.9-4.04
Ti	127-137	4.4-4.8
Cr	137-152	4.8-5.3
Mn	152-164	5.4-5.8
Fe	168-178	5.9-6.3
Ni	192-209	6.8-7.4
Cu	209-225	7.4-8.2
Zn	251-275	8.9-9.8
Pb	281-307	10-10.9

Conclusions:

Confocal micro x-ray fluorescence offers a previously unobtainable dimension to the elemental characterization of a material. Using this technique the sample does not need to be put under a vacuum, no coatings are needed, such as in electron beam techniques, and most importantly, 3D elemental information can be extracted from the sample non-destructively. Either samples can continue to be examined using other techniques or, the same sample that is examined can later be used in the field. Further developments to this technique focus primarily upon the construction of a second-generation instrument with fully automated data acquisition, a vacuum chamber for identifying and measuring low atomic number elements in samples, and automated data processing. Data processing may include full 3D mapping based upon region of interest, and full spectral mapping. Full spectral mapping/imaging has already shown great utility in many other techniques such as XRF and EDS, FT-IR, and UV/Vis fluorescence and can be used beyond simple elemental mapping. Full spectral imaging is often used to create maps of chemical phases. Confocal MXRF has demonstrated considerable characterization utility and yet it still offers undiscovered potential for further developments. The relative low cost and exciting capabilities of this technique, offers new opportunities for materials characterization. ■

Acknowledgments:

The authors wish to thank Brent Espinoza for making the silica aerogels. This work was funded by the ICF and Enhanced Surveillance Campaign programs. Los Alamos National Laboratory is operated by Los Alamos National Security LLC under contract number DE AC52-06NA25396 for the US Department of Energy.

References:

1. B. M. Patterson, G. J. Havrilla, and J. R. Schoonover, *Appl. Spectrosc.* **60**, 10, 1103 (2006).
2. G. J. Havrilla, Abstracts of Papers, 223rd ACS National Meeting, Orlando, FL, United States, April 7-11, 2002, NUCL (2002).
3. P. A. Keiter and G. A. Kyrala, *Review of Scientific Instruments* **75**, 10, Pt. 2, 4057 (2004).