

Guest Forum

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Confocal Micro X-ray Fluorescence 3D Elemental Imaging For Materials Characterization



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Confocal micro X-ray fluorescence is a new instrumental method for materials characterization. In a confocal geometry, the excitation and detection regions are bound by the same foci and therefore, share the same focal spot. This confocal arrangement is achieved by using two monolithic polycapillaries; one focuses the x-rays to a focal spot and the second optic is oriented on the detector side for emission collection from the focal spot. An advantage of the confocal geometry is the capability of scanning the sampling volume in the x, y, or z direction and subsequently producing a 3D elemental distribution. In this presentation, the performance of the confocal micro x-ray fluorescence microscope and its application capabilities are determined.

Background

Confocal micro x-ray fluorescence (CMXRF) is a relatively new analytical concept for materials characterization^[1-7]. The power of CMXRF arises from the use of the monolithic polycapillary optics. These x-ray optics provide an intense x-ray flux at the focal spot and enables spatially resolved elemental analysis with high sensitivity. Fundamentally, the instrument is quite simple however it is different in that it incorporates two polycapillary optics, as opposed to only one in typical MXRF. One optic is used to spatially restrict and focus the x-rays from the x-ray tube. The second optic is used to collect and direct the x-rays onto the detector. The region of focal spot overlap of the two optics is the confocal region. Figure 1 shows a red circle which indicates the confocal region. The advantage of the confocal approach for materials characterization is the ability to obtain elemental information nondestructively in three dimensions. This means the elemental composition can be mapped below the surface of the material. Elemental mapping below the surface is achieved by moving the confocal volume in a plane, collecting an x,y map of the elemental distribution. Then the confocal spot is

incremented deeper into the sample, typically 50 micrometers and another x,y map would again be collected. This process is repeated until the critical depth of the analyte has been reached. The critical depth is the maximum extent into the sample the confocal volume can be probed before the detected x-ray signal reaches zero. The critical depth is completely sample dependent and can range from very low depth penetration for a sintered uranium sample, to the full working distance of the microscope of 10 mm for low density aerogels. The x,y maps at the different z depths are then stacked into a 3 dimensional image of the elemental distribution. It must be recognized that the analyte signal intensity will be affected by the overlying layers for both the excitation and detection schemes. Since the composition of the overlying layers is known, the absorption effects can be modeled. In this report, only the raw elemental signal is visualized.

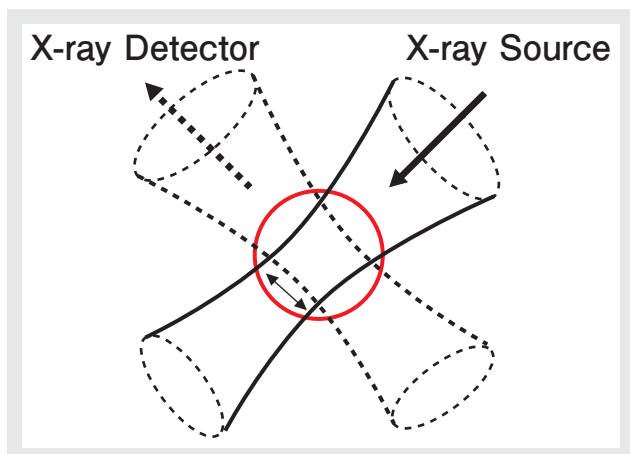


Figure 1 Diagram of confocal concept showing overlap of the excitation focal spot with the detector focal spot

Experimental

The prototype CMXRF instrument was designed and built by X-ray Optical Systems, Inc., (XOS) East Greenbush, NY, USA. The instrument is shown in Figure 2. The x-ray tube is a 50 W silver anode X-Beam (XOS) which has the polycapillary optic incorporated directly with the x-ray tube. An XLG high-voltage power supply (Spellman High Voltage Co.) provides the 50 kV and 0.5 mA for the x-ray tube. This minimizes a number of alignment issues. The detector is an Amptek (Bedford, MA) model XR-100CR which is a solid state pin diode detector. The optics are a pair of monolithic polycapillaries(XOS) with a focal spot size of around 30 micrometers and a working distance of 10 mm. The angle between the source and detector is approximately 60° which is well below the typical 90°. The difference in source detector angle was to improve depth penetration into the samples. As a consequence the shape of the confocal volume as measured with tantalum foil (10 micrometers thick) profiles is 30 x 30 x 60 micrometers

giving it an elliptical shape instead of a spherical shape. The sample is placed on a stage with x, y, and z scanning capability (model 850G Newport Corp.) controlled by XOS software. The collected x,y maps at different z depths are rendered using MATLAB (The Mathworks Inc.). Visualization of the data in three dimensions provides the most useful and visually powerful information. Once the data has been imported into MATLAB, an array of useful data processing can be done to generate a variety of elemental images in addition to the 3D images.

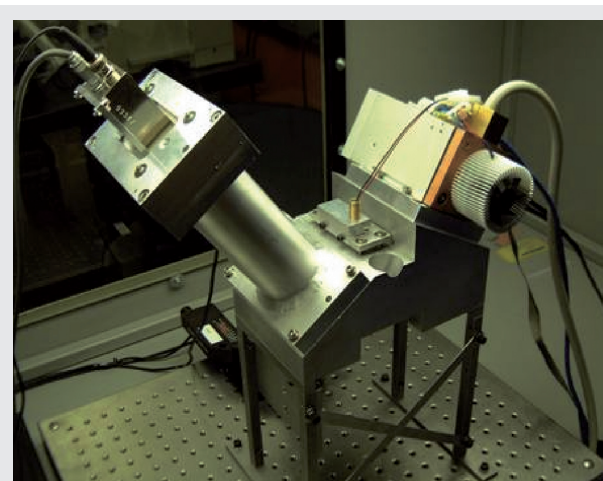


Figure 2 Picture of prototype CMXRF instrument

Results

The simplest demonstration of subsurface elemental information is a depth profile. The confocal volume is moved in a line scan from above the surface to a selected depth. Figure 3 shows a cross section of a paint chip with an accompanying depth profile through the surface. The elemental profiles of the paint pigments show some of the layering of the different paints. Due to the large z profile

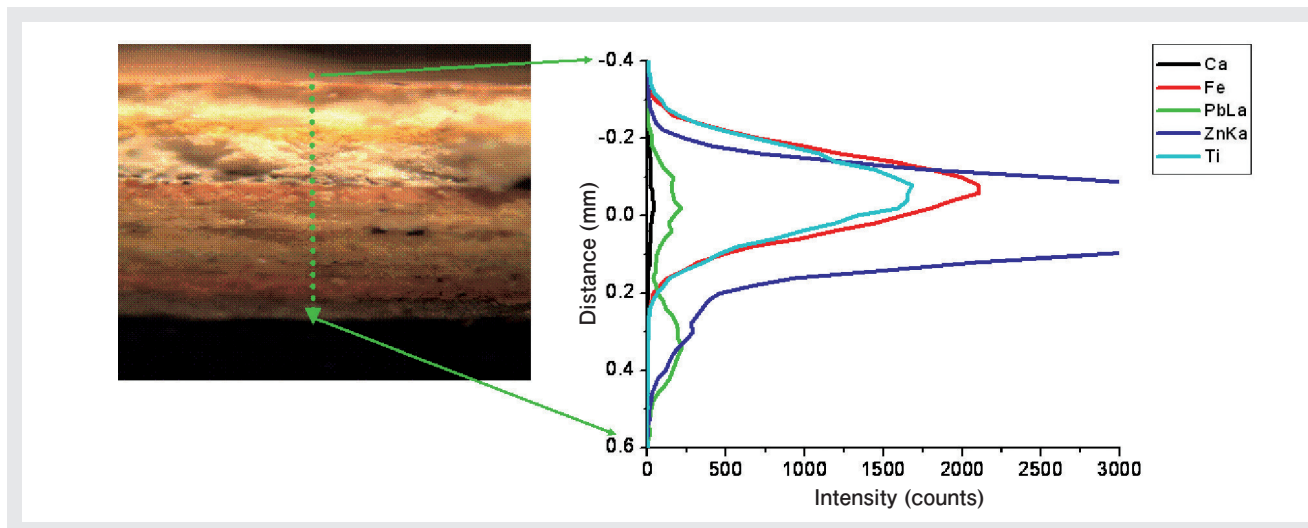


Figure 3 Picture of cross section of paint chip
The green dashed line indicates the depth profile through the top surface of the paint chip. The elemental distributions are shown on the right for the paint pigments.

of the confocal volume the individual paint layers, which are around 15-20 micrometers thick, cannot be resolved. The top surface layer of paint is titanium with iron. Evidently there is rusting occurring and the iron is migrating through the paint layers. Zinc is another top coat component, while lead appears in 2 layers. However a key feature of the depth profile is the raw elemental signal can be detected well below 600 micrometers in depth. The lead signal in particular is clearly visible at the 400-500 micrometer depth. This is an indication of the early lead based paint pigment as well as the penetrating power of the Pb $L\alpha$ line through the overlying pigment layers. This elemental depth profile was done nondestructively and without any sample preparation. The raw elemental intensity data provides a wealth of information regarding the paint pigment layers. While the individual layers are not resolved there is sufficient information regarding the layering of the paints as well as some depth information. With the appropriate modeling of signal absorption, more realistic elemental intensities can be obtained which can be used to more accurately measure relative, qualitative and quantitative elemental compositions.

One potential application of CMXRF is to study the distribution of elements in the environment. One model system is the deposition of an aqueous metal onto a substrate such as a mineral surface. Aqueous cobalt will precipitate onto a marble surface and oxidize, changing from a 2+ to 3+ oxidation state. This transformation can be seen visually as shown in Figure 4. Since marble has some porosity, the thickness of the cobalt surface layer as well as the depth of penetration into the marble is of interest. As shown in Figure 5, a 3D representation of the cobalt distribution both on the surface of the marble and below the surface, CMXRF can provide nondestructive elemental maps to show the distribution of cobalt on the surface and below. The cobalt has penetrated the surface of the marble several hundred micrometers into the marble substrate. There are obvious areas where the cobalt has not deposited. This is more clearly illustrated in Figure 6 which includes the elements calcium, titanium and iron. Evidently the cobalt does not deposit or penetrate in the areas where there are inclusions of these elements. The CMXRF 3D imaging provides unique information on the cobalt deposition which cannot be attained with any other technology.

In the development of high surface area porous electrodes for a variety of applications which include advanced batteries, supercapacitors and electrocatalysts, the objective is to increase the surface area of the electrodes

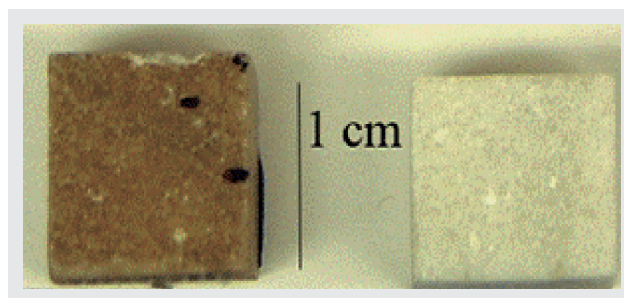


Figure 4 A marble cube is shown on the right and a specimen which was exposed to aqueous cobalt solution and then air dried is on the left

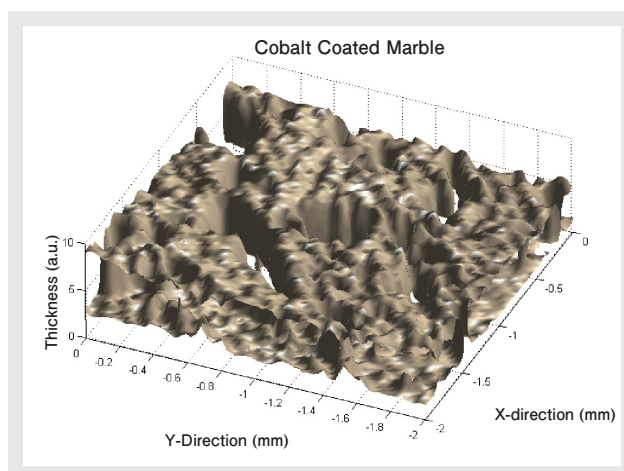


Figure 5 3D cobalt elemental image of cobalt deposition and penetration into marble substrate

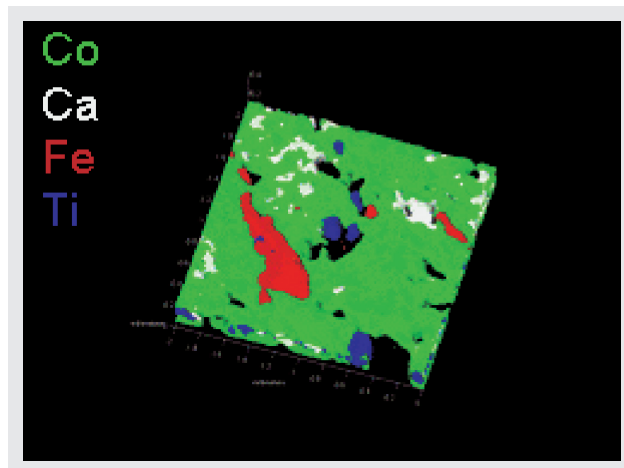


Figure 6 CMXRF elemental images of cobalt (green) on marble substrate, with calcium (white), iron (red) and titanium (blue) areas indicating different mineral phases where the cobalt did not deposit

and thereby increase their performance application. Recent work by Campbell et al.^[8] has demonstrated the use of silica templates in electrodepositing nickel nanowires onto the surface of nickel foam electrodes. Initially 2D MXRF was done to image the distribution of cobalt nanowires (cobalt was used instead of nickel to provide elemental contrast). While the MXRF elemental

maps showed apparent uniform distribution of the nanowires on the surface of the nickel foam substrate, there was still the issue of coverage within the network of the nickel foam ligaments^[8]. CMXRF elemental imaging was done on a 1 mm³ volume of the cobalt nanowire coated nickel foam substrate. The 3D image of the data is shown in Figure 7. The 3D elemental image shows both the nickel foam as the teal blue core of the structure. The pink color is the cobalt elemental distribution of the nanowires on the surface. While this image is only the raw elemental intensities, the distribution of cobalt over the surface of the nickel substrate foam appears to be homogenous. The 3D elemental image can also be rotated to inspect the underside of the nickel foam ligaments. The elemental signal is decreasing with depth due to the aforementioned attenuation by the overlying structures. This is seen in the partial ligaments at the bottom of the image. In this image, there were 34 x 34 x 34 steps with step sizes of 30 x 30 x 50 micrometers. This generated 30,000 voxels of data using a dwell time of 1 sec per point. Each x,y slice took 30 minutes to acquire, with a total data acquisition time of 13 hours. These 3D elemental images produce large amounts of data. However the information obtained from these measurements cannot be duplicated with other technology.

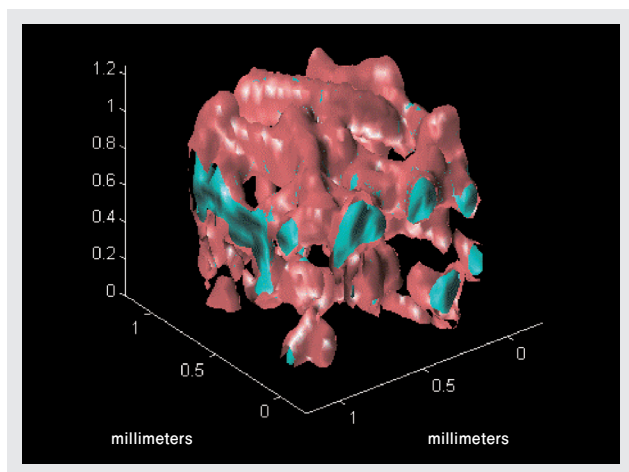


Figure 7 3D elemental image of nickel foam (teal) core with cobalt nanowires (pink) on the surface

Conclusion

Confocal MXRF offers new capabilities not found with conventional analytical instrumentation for materials characterization. In these few examples, a simple elemental depth profile, the cobalt deposition onto a marble substrate and the distribution of cobalt nanowires on a nickel foam substrate all show unique elemental and structurally related information which cannot be obtained with any other elemental analysis technique in a nondestructive manner. There are substantial

opportunities for improving the data acquisition, data processing and visualization of the information obtained from this 3D elemental imaging approach. Even with the long data collection times, the information obtained overwhelms the time involved. The future for continued development and increasing use of CMXRF for materials characterization appears very promising and full of potential.

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