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Title:

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Proceedings of the 1998 Denver X-ray Conference

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OPTIMIZING THE ELEMENTAL SENSITIVITY AND FOCAL SPOT SIZE OF A MONOLITHIC POLYCAPILLARY OPTIC USING MICRO-X-RAY FLUORESCENCE

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ABSTRACT

A commercial micro-X-ray fluorescence (MXRF) instrument with an aperture X-ray guide was used to compare elemental sensitivities and focal spot sizes with those obtained by focusing the source with a monolithic polycapillary optic retrofitted into the system. The capillary provided an intensity gain of 125 at 4 keV vs. using a pinhole beam collimator; however, this gain advantage declined with increasing analyte line energy as a result of the capillary being designed shorter than its optimal length to fit into the commercial instrument. A minimum capillary focal spot FWHM of 36 μm was achieved, whereas the smallest pinhole aperture available of 50 μm in diameter produced a focal spot width of 69 μm FWHM. Hence, better MXRF lateral resolution could be obtained with the capillary with a simultaneous improvement in elemental sensitivity.

INTRODUCTION

Recent micro-X-ray fluorescence (MXRF) reports using capillary optics with a laboratory-based source have demonstrated pronounced X-ray flux enhancements compared with utilizing traditional aperture collimators.¹⁻⁶ These studies all involved custom-built systems, however. In the present work, a monolithic polycapillary optic was designed to fit into a commercial MXRF instrument to increase elemental sensitivities while obtaining a small focal spot for elemental imaging applications. This study is relevant to the MXRF community using commercial aperture-based instruments because a higher primary X-ray flux can be achieved with a polycapillary optic than with pinhole beam collimators, but the flexibility of incorporating various sized apertures for large spot analyses is still maintained.

Polycapillary optics are ideal for analyzing heterogeneous samples with elemental domains on the order of a few hundred μm in diameter. With pinhole beam collimators, generating a beam diameter less than a few hundred μm results in a substantial loss of flux; however, no signal degradation occurs when the polycapillary spot size is adjusted. Single capillary optics can provide beam diameters of a few μm ,^{1,3,4,6} whereas polycapillary optics are limited to ~ 50 μm or larger; however, monolithic polycapillary optics offer much higher X-ray flux. Thus, for imaging samples with elemental domains >50 μm wide, monolithic polycapillary optics are better suited than single capillaries. The present work examines elemental sensitivities and focal spot sizes achieved using pinhole apertures versus a monolithic polycapillary optic to collimate the X-ray beam.

EXPERIMENTAL

Instrumentation. A majority of the data was acquired with a Kevex Omicron using a 100 W rhodium anode oriented 45 degrees to the sample stage. A liquid nitrogen-cooled Si(Li) detector was employed which was oriented 45° relative to the sample and contained an active

area of 50 mm². The sample stage was moved while the X-ray beam remained stationary, thereby scanning the X-ray beam across a sample.

Both monolithic polycapillary optics incorporated in this work were designed by X-ray Optical Systems, Inc. (XOS). A majority of the capillary data was acquired with an optic 29 mm long which was retrofitted into the Kevex Omicron, and plastic shims of various thicknesses were used for alignment with the source along the horizontal and vertical axes. Elemental sensitivities obtained using the 29 mm optic were compared with those using a 73 mm long optic. This data was acquired with a custom-built system at XOS incorporating a 5 W tungsten anode oriented 45° to the sample and a Si(Li) detector with a 10 mm² active area oriented 45° to the sample and 90° with the source. The source was moved with a x, y, z translator stage while the sample remained stationary.

To prepare the detector filter used in one MXRF imaging experiment, computer printer paper feeder ~100 μm thick with a 4 mm diameter hole was used as a support. Transparent tape was placed over one side of the hole, and 2 mg of CaCO₃ (Alpha) were spread evenly over the hole on the tape adhesive side and pressed to 10 tons under vacuum for 15 sec. Another piece of tape was then placed over the exposed CaCO₃ to contain it, and this filter was placed over the detector input aperture.

Samples. Line scans to determine the capillary optic focal spot size were performed by rastering a tungsten foil knife edge across the X-ray beam in 10 μm steps at 10 sec/step acquisition times, and the tungsten L_α peak intensity was integrated at each point versus distance. The source was operated at 20 kV and 1 mA, and the sample was analyzed in air. The focal spot size of a 50 μm aperture, which was the smallest available pinhole aperture, was determined by performing a line scan of the same tungsten foil edge using the above parameters. The sample was moved as close to the aperture as allowable with the Omicron instrument to minimize beam divergence.

Source scatter spectra were obtained from a piece of plexiglas to compare the source energy distribution profile using the 29 mm capillary optic vs. the 50 μm aperture. These spectra were acquired at 20 kV and 0.5 mA in air with a 2000 sec scan time.

A standard reference material (SRM) 1832 was purchased from the National Institute of Standards and Technology (NIST) for examining elemental sensitivities. This SRM consisted of a silica-based glass film 0.55 μm thick homogeneously doped with several elements at the weight percent level and deposited on a polycarbonate filter. Spectra were acquired from the sample using a 300 μm aperture to collimate the source vs. using the 29 mm long capillary. The sample was examined under helium for 1000 sec, and the source was run at 20 kV and 1 mA.

To measure the MXRF gallium sensitivity, gallium distribution maps were acquired from the interior of a cylindrical pellet consisting of 2% Ga₂O₃ in a CeO₂ matrix which was reduced in 6% hydrogen in argon for 0.5 h at 1000°C. To examine the interior, the pellet was cut in half parallel to the long cylinder axis using a diamond saw. Further details of the sample preparation can be found in an earlier publication.⁷ All MXRF images were acquired using the Kevex Omicron Xmap software with the sample in air and continuously rastered across the X-ray beam. All images consisted of 256 x 256 pixels and were acquired with equal scan times of ~ 4 h. For the image acquired using the capillary without a detector filter, the source was run at 20 kV and 0.57 mA (50% detector dead time). A focal spot width of 36 μm FWHM was determined using the W L_α line. When the detector filter was implemented, the maximum source power at 20 kV of 64 W (3.2 mA current) was used. Above ~20 kV X-rays penetrated the capillary without focusing. Therefore, higher voltages could not be utilized, but when the 50 μm aperture was

used, the source was run at the maximum power of 100 W (50 kV and 2 mA) to optimize the gallium sensitivity.

To compare elemental sensitivity vs. energy for the two different length capillary optics, source scatter spectra were acquired from plexiglas using the XOS customized MXRF system with the sample in air and the source run at 50 kV and 0.1 mA. The spectra were acquired for 100 sec each.

A gallium/cerium microspot sample was prepared by grinding 50 wt % CeO₂ (Alfa) and 50 wt % Ga₂O₃ (Alfa) with a mortar and pestle, and 2 mg of this powder were spread over a 200 μm wide 0.004 in. thick molybdenum aperture (Ernest F. Fullam, Inc.). The powder was pressed into the aperture at 2 tons for 15 sec under vacuum, and the side opposite that pressed was analyzed for gallium and cerium. Spectra were acquired for 100 sec in air using both the XOS 29 mm and 73 mm long capillaries. The 29 mm capillary spectrum was only obtained at 20 kV and 0.1 mA due to the loss of X-ray focusing above 20 kV, while the 73 mm optic spectra were acquired at both 20 and 50 kV using 0.1 mA.

RESULTS AND DISCUSSION

Because polycapillary optics provide high X-ray flux in a small spot, they offer excellent elemental sensitivities from heterogeneous samples containing elemental microdomains, especially if the domains are approximately the same size as the focal spot. This is because the domains are irradiated with a very high X-ray flux. Hence, determining the focal spot size of the 29 mm capillary used with the Kevex Omicron instrument was important and was carried out by varying the distance (*z*) between the optic exit window and a tungsten knife edge while acquiring line scans as a function of this distance. Line scans were performed by rastering the tungsten edge through the X-ray beam and integrating the tungsten L α peak (8.4 keV) vs. lateral position. The beam spot FWHM was then determined at each *z* position and plotted vs. *z* (relative sample stage position; figure 1). From this graph, a minimum spot size of 36 μm FWHM was found. When the 50 μm aperture was used instead of the capillary, a 69 μm FWHM focal spot size was observed. Thus, the capillary provided a focal spot almost half that produced with the aperture, but considerably higher X-ray flux was obtained within the focal spot as will be discussed in more detail later.

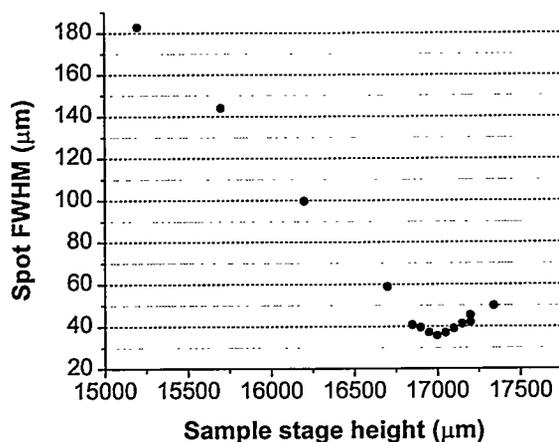


Figure 1. Polycapillary focal spot width vs. relative sample stage position.

The focal spot size of a polycapillary optic is not only determined by the optic to sample distance but is also energy dependent. In addition to tungsten, line scans using the capillary were performed across aluminum and zirconium knife edges. The focal spot size FWHMs determined for the aluminum $K\alpha$ (1.5 keV) and zirconium $K\alpha$ (15.8 keV) lines were 66 μm and 22 μm respectively. Including the 36 μm FWHM spot found for tungsten, this data clearly indicates that the focal spot size is inversely proportional to energy. Hence, for imaging the distribution of an element in a sample by MXRF, a line scan should be performed using a knife edge of either the element being analyzed or a material with a line close in energy to that of the analyte.

Rhodium source scatter spectra were acquired from plexiglas to compare the energy distribution profile irradiating the sample using the capillary to that with a 50 μm aperture collimator. The capillary spectrum was then divided by the aperture spectrum to generate a capillary intensity gain curve (figure 2). The calcium $K\alpha$, gallium $K\alpha$, and cerium $L\alpha$ absorption edges are marked on this curve because they will be discussed later. A maximum capillary intensity gain of ~ 125 was found at 4 keV, but this sensitivity advantage diminished at higher energies to a gain of only 2.5 at 16 keV. This high energy filter effect resulted from the capillary being designed shorter than its optimum length to fit into the Omicron instrument. With a short optic, there is a considerable bending angle in the individual capillary fibers at the entrance to the optic, and high energy X-rays have a shallower acceptance angle for total reflection than low energy photons. Therefore, high energy X-rays will only reflect along the innermost capillary fibers and exit the optic, while low energy photons can reflect along both the inner and some outer fibers resulting in a higher transmission efficiency. The fibers in a longer optic, however, are bent less at the input window which provides a greater acceptance angle for high energy X-rays and therefore greater transmission efficiency.

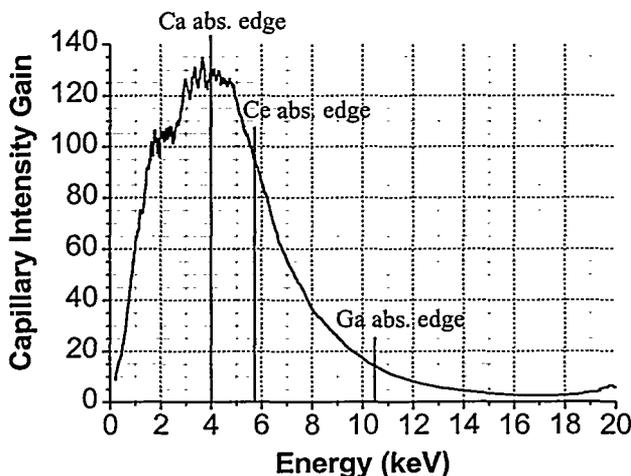


Figure 2. Capillary plexiglas spectrum intensity gain curve vs. 50 μm aperture.

To compare actual elemental sensitivities achieved with the optic to those with an aperture collimator, NIST SRM 1832 was analyzed. A 300 μm aperture was used because at the time the data was acquired, the capillary focal spot diameter was ~ 300 μm ; however, a considerably smaller focal spot was obtained in later experiments as already discussed. Figure 3 is a plot of elemental peak intensities vs. energy acquired with the capillary divided by those obtained with the aperture. For the sodium and silicon K lines, a gain of ~ 7 was achieved with the capillary

(which would have been considerably larger if a smaller aperture had been utilized). However, as previously discussed, the capillary high energy filter effect resulted in a loss in gain at higher energies.

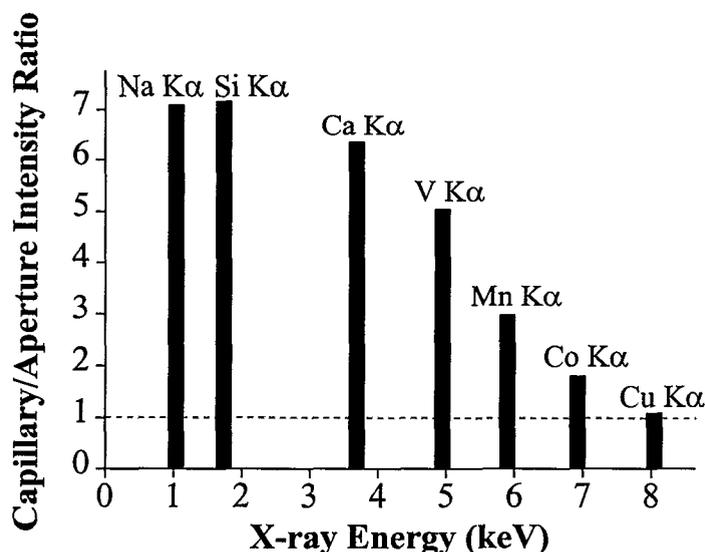


Figure 3. SRM 1832 capillary/300 μm aperture elemental intensity ratios.

The authors were interested in improving the Omicron MXRF gallium sensitivity using the capillary for reasons discussed in a prior article.⁷ The gallium distribution was imaged from the internal cross section of a pellet containing 2% Ga_2O_3 in CeO_2 starting material reduced in hydrogen, and these gallium maps were compared between using the 50 μm aperture and the capillary (figure 4). Numerous gallium inclusions were observed throughout the pellet, but because the gallium absorption edge at 10.4 keV is in the low region of the capillary gain curve (figure 2), only a marginal improvement in the gallium microdomain sensitivity was observed with the capillary (figure 4b) vs. with the aperture (figure 4a). However, calcium has an absorption edge at 4 keV which corresponds to the maximum region of the capillary gain curve (figure 2), and calcium impurities were found in the sample and imaged with both the 50 μm aperture (figure 5a) and the capillary (figure 5b). While no calcium was found when the aperture was employed, the capillary image exhibited numerous domains, demonstrating the capillary's excellent low energy sensitivity.

To improve the capillary high energy sensitivity, a new system could be designed (or the current instrument greatly modified) to accommodate a longer capillary optic, or a detector filter could be implemented. The latter option is considerably cheaper and less time consuming, and was therefore pursued. For the gallium/cerium pellet, the cerium signal was saturating the detector electronics before a maximum source current could be used since the matrix was CeO_2 and the capillary cerium L line sensitivity was high. The basis for using a detector filter was to attenuate the cerium peak and allow the current to be maximized to boost the gallium signal. A CaCO_3 filter was placed between the sample and detector. Calcium was chosen because it absorbs the Ce L peak very effectively but does not attenuate the higher energy gallium K line as

extensively. With the cerium signal substantially attenuated, the source current was maximized resulting in over a twofold increase in the gallium peak intensity.

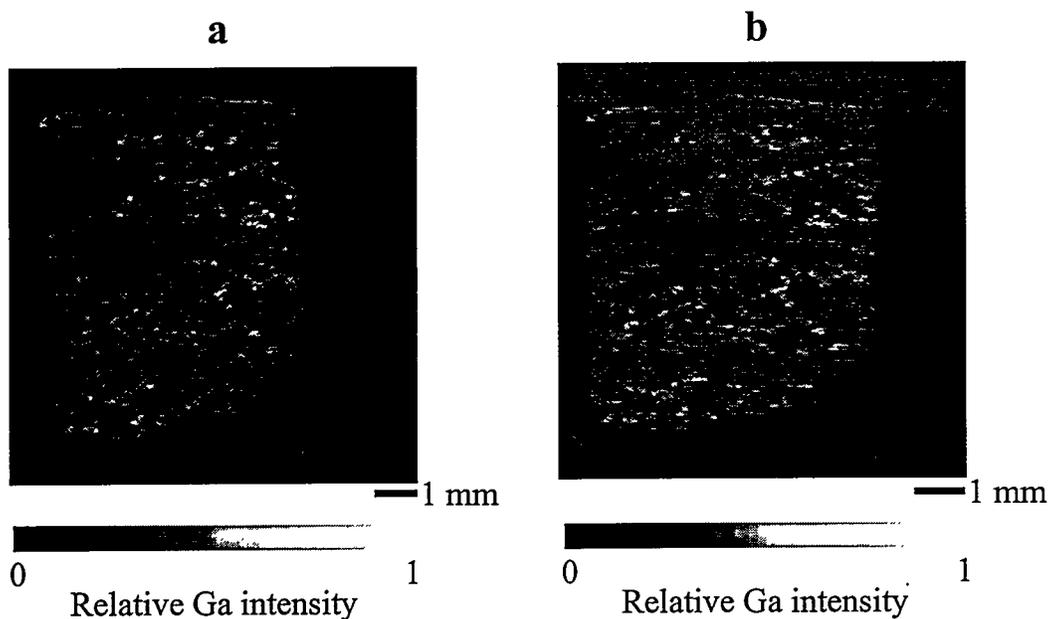


Figure 4. Gallium images from the interior of the gallium/cerium pellet reduced at 1000°C using (a) the 50 μm aperture collimator and (b) the polycapillary optic.

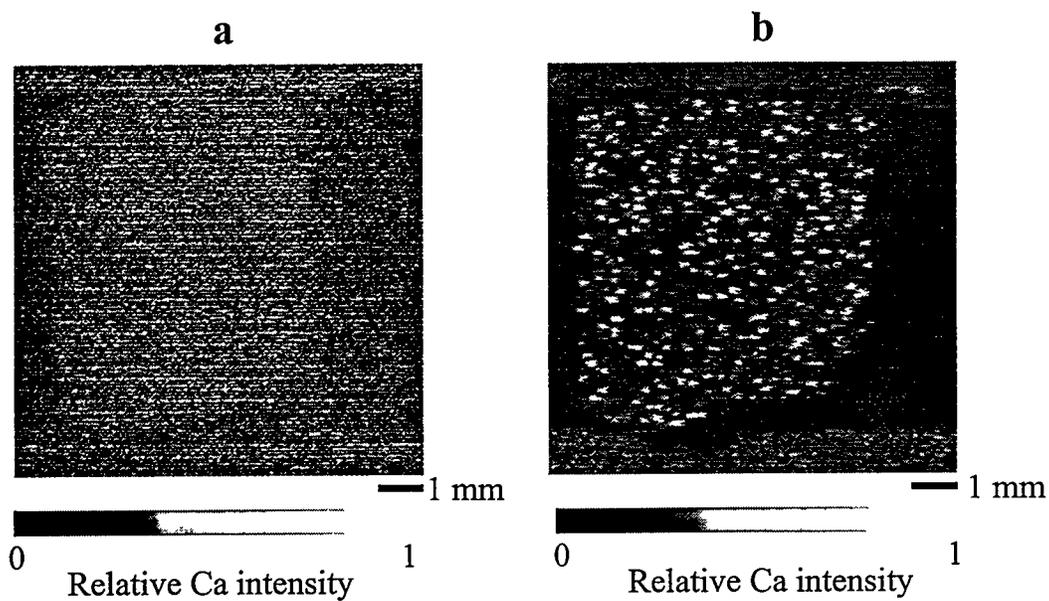


Figure 5. Calcium impurity images from the interior of the gallium/cerium pellet reduced at 1000°C using (a) the 50 μm aperture collimator and (b) the polycapillary optic.

Figure 6a is the gallium distribution from the gallium/cerium reduced pellet using the capillary without the detector filter, and figure 6b is an image of the same sample but with the

detector filter used. The gallium domain sensitivity was enhanced when the filter was utilized, and figure 7 demonstrates the marked gallium sensitivity improvement achieved with the capillary and filter (figure 7a) compared with using the 50 μm aperture (figure 7b). The 50 μm aperture image was acquired at 50 kV, while the capillary image was obtained at only 20 kV because above 20 kV X-rays penetrate through the capillary without focusing. Yet, even at a lower voltage, the capillary image contrast was considerably better than that in the aperture image.

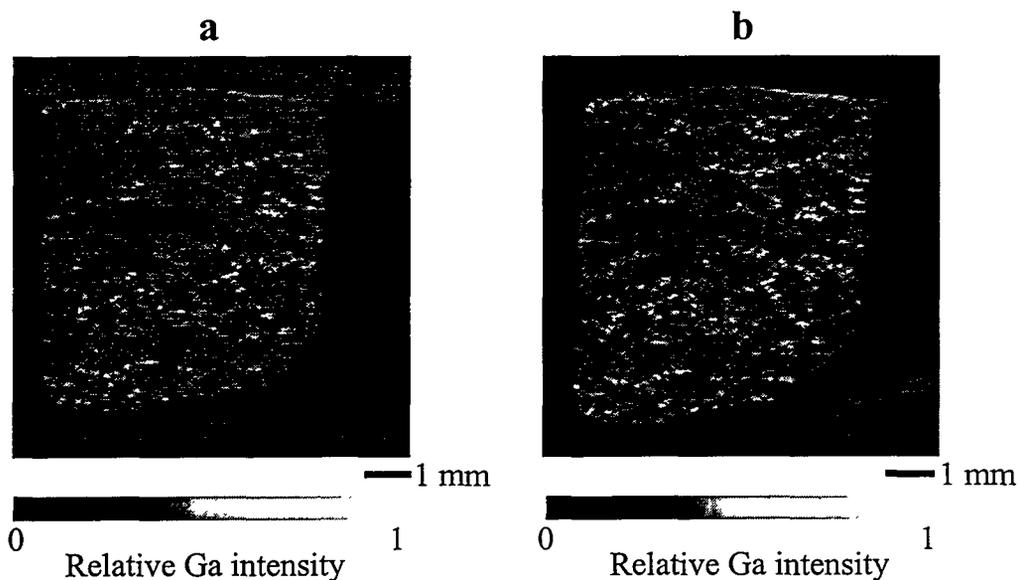


Figure 6. Gallium images from the interior of the gallium/cerium pellet reduced at 1000°C using (a) the polycapillary optic and (b) the polycapillary optic with a detector filter.

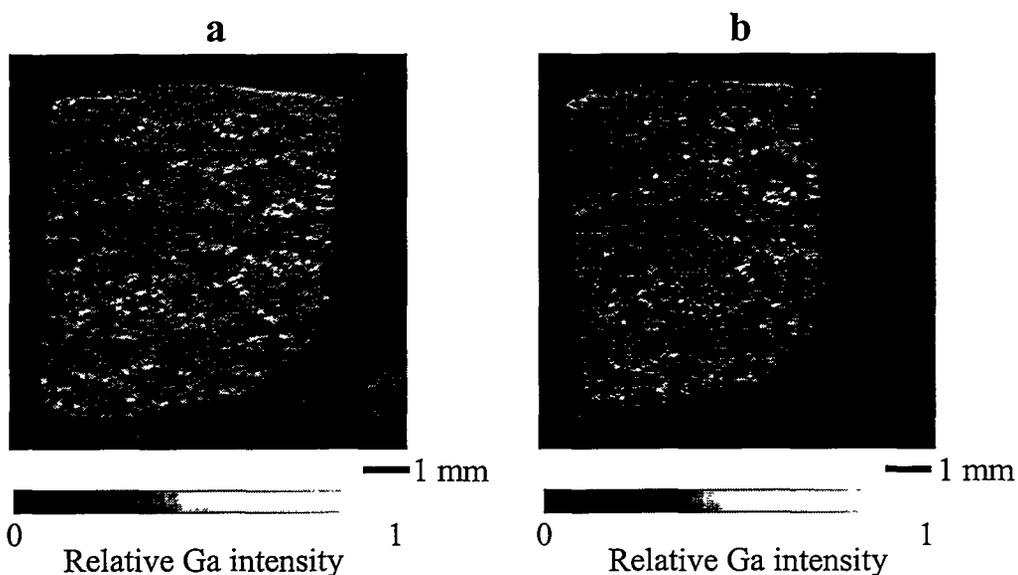


Figure 7. Gallium images from the interior of the gallium/cerium pellet reduced at 1000°C using (a) the polycapillary optic with a detector filter and (b) the 50 μm aperture.

As previously discussed, the short 29 mm optic used with the Omicron hindered transmission of high energy X-ray photons. Thus, experiments were performed to compare the energy throughput of this optic with a more ideal optic 73 mm in length. This data was acquired at XOS using their custom-built XRF system. The tungsten source scatter spectra from plexiglas were obtained using each optic to focus the primary beam, and the 73 mm optic spectrum was divided by the 29 mm optic spectrum to generate an intensity gain curve for the longer optic (figure 8). An intensity gain of ~ 4.5 was obtained with the 73 mm optic at 15 keV, and this gain would have extended to even higher energies if the high energy X-rays did not penetrate the short 29 mm optic without total reflection. These high energy photons were not focused and, therefore, could not be used for MXRF imaging, but they did contribute to a higher net flux than that achieved with the 73 mm optic. Hence, the 73 mm gain curve declined at higher energies (gain < 1 above ~ 22 keV). This high energy penetration problem did not occur with the longer optic, however. Thus, this optic could be used for imaging even at high source voltages.

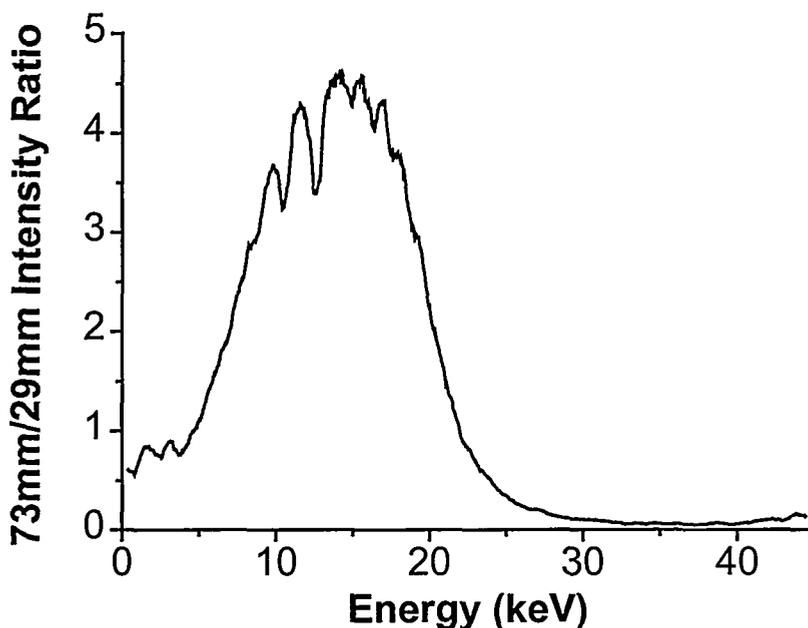


Figure 8. Tungsten source scatter spectra off plexiglas using 73 mm long capillary optic divided by the spectra acquired with the 29 mm capillary.

Since improving the gallium sensitivity in the gallium/cerium pellet sample was important, studies were undertaken to quantify the gallium $K\alpha$ line using the two capillaries. A 200 μm diameter spot consisting of 50 wt.% Ga_2O_3 and 50 wt.% CeO_2 was analyzed, and the cerium $L\alpha$ and gallium $K\alpha$ lines are presented in figure 9. (The sample was prepared only slightly larger than the focal spot so that the same region would be examined with both capillaries.) The gallium peak intensity using the 73 mm optic at 20 kV was 4.6 times that using the 29 mm optic, and it was 8.1 times greater at 50 kV than the short optic at 20 kV. This illustrates the marked

contrast improvement which can be expected in gallium images of the gallium/cerium pellet using the longer ideal optic. (Note that the two capillaries were not compared at 50 kV because the higher energy X-rays generated would penetrate the short optic without focusing.)

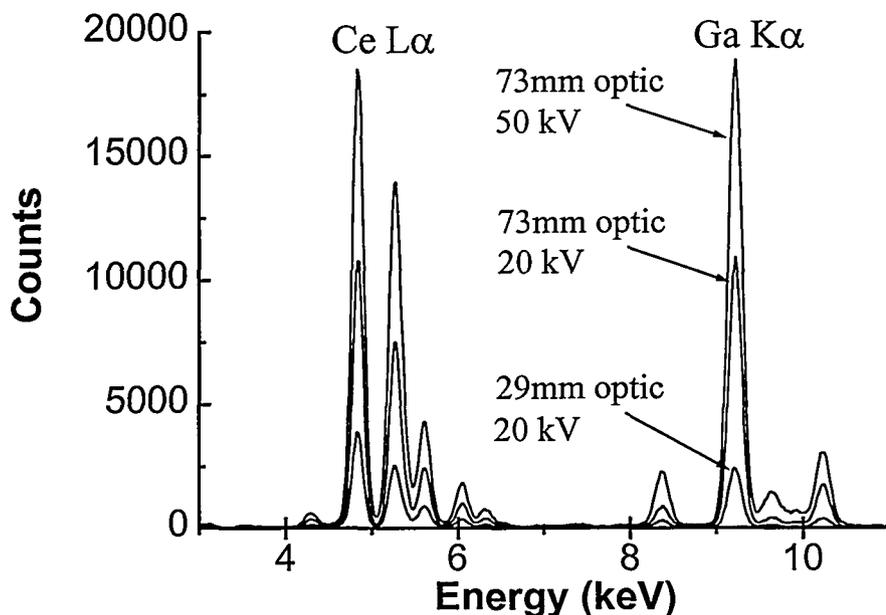


Figure 9. 50% Ga, 50% Ce 200 μm spot analysis comparing 73 mm optic to 29 mm optic.

As has been reiterated throughout this work, the short length of the 29 mm capillary hindered its high energy transmission efficiency, and using a longer optic will improve this efficiency. In addition, the source emission spot size was too large ($\sim 250 \mu\text{m}$ in diameter). Using a smaller source size will also aid in obtaining better high energy throughput. Finally, the distance between the capillary input and the source was not optimized because of instrumental geometric constraints when retrofitting the optic into the Omicron, resulting in a lower than optimal flux irradiating the sample. If this distance could be controlled, the total flux would be increased. Thus, by designing a new instrument or greatly modifying the current one, a dramatic improvement in the high energy transmission efficiency and net flux would be obtained.

CONCLUSIONS

A monolithic polycapillary optic was successfully retrofitted into the commercial Kevex Omicron MXRF system. For analyte lines below $\sim 5 \text{ keV}$, an intensity gain of two orders of magnitude was achieved compared with using a pinhole beam collimator. Simultaneously, the focal spot width for the capillary was almost half that of the pinhole aperture, leading to improved spatial resolution when performing elemental imaging. The capillary intensity gain vs. the aperture markedly declined with increasing analyte energy due to instrumental geometric constraints mandating that the capillary be made shorter than its ideal length, but implementing a

detector filter improved the high energy signal. For analyzing a wide array of sample types, though, a new MXRF system will need to be designed to accommodate a longer optic.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Darryl Butt and Dr. Youngsoo Park for providing the gallium/cerium pellet and the Department of Energy office of fissile materials disposition for funding. Los Alamos is operated by the University of California for the Department of Energy. Identification of specific vendors is not an endorsement of particular instrumentation.

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