Y-12

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OAK RIDGE Y-12 PLANT

LOCKHEED MARTIN

CRADA Final Report for CRADA Number Y-1294-0283

DEVELOPMENT OF IMPROVED X-RAY OPTICS FOR ANALYTICAL X-RAY MICROBEAMS

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I. Abstract

The purpose of this CRADA was to develop improved glass capillary, x-ray optics for analytical x-ray microbeam applications. X-Ray Optical Systems, Inc. (XOS) designed and fabricated capillary optics and LMES tested those optics for x-ray microanalytical applications using its unique X-Ray Microprobe. Tapered capillaries with 3-µm and 8-µm output openings were fabricated and tested. The tapered capillaries had better spectral quality for x-ray microfluorescence (XRMF) analysis, than non-tapered, straight capillaries that are currently used in the system. X-ray beam count-rates for the tapered capillaries were also greater than the straight capillaries. Two monolithic, polycapillary optics were fabricated and tested. The polycapillary optics produced focal spots of 40 and 100 µm. Beam intensities for the polycapillaries were, respectively, 44 and 18 times the intensities found in straight 50-µm and 100-µm capillaries. High-sensitivity scanning will be possible because of the enhanced intensity of the polycapillary optic. LMES and the DP program will benefit from improved capabilities for nondestructive x-ray microanalysis, while XOS will benefit from test results that will enhance the marketability of their products.

II. Objectives

The objective of this CRADA was to develop improved glass capillary, x-ray optics to enhance x-ray microfluorescence (XRMF) capabilities. XRMF offers significant advantages over traditional electron beam microanalysis for examining heterogeneous materials. For example, the penetrating power of the x-ray beam could allow simultaneous determinations of film thicknesses and impurity content at high spatial resolutions during the manufacture of integrated circuits. Analysis in air is possible with x-rays, and sample conductivity is not required. Thus, vacuum-sensitive materials or large parts can be analyzed in air. Ceramics and other non-conductors do not need to be coated with a conducting material for XRMF analysis. XRMF techniques have been used at the Y-12 Plant in applications ranging from nondestructive analysis of weapons components to phase mapping of heterogeneous materials. Due to limited x-ray flux, improved x-ray optics are needed to reduce the turnaround time and increase the reliability of the data.

XOS has unique expertise in the manufacture of single channel and multichannel (multicapillary) glass capillary, x-ray optics. The advanced glass capillary designs of XOS could lead to orders of magnitude improvement in the x-ray flux of the next generation of XRMF instrumentation. On the other hand, LMES has unique analytical XRMF capabilities and expertise. LMES developed an XRMF capability in a laboratory-based x-ray microprobe for the analysis of weapons materials and components. The Y-12 x-ray microprobe received the R&D 100 award based upon its unique method of attaining high x-ray brilliance. Analysis techniques are currently being developed with the x-ray microprobe, through an R&D task, to maintain the capability for production analysis and to develop instrumentation for use in a down-sized production environment. The unique XRMF capabilities possessed by LMES are also selling points for the technology transfer regional assistance program and work for others.

III. Discussion of Objectives

The CRADA objectives were met. Tapered capillaries were developed for the Y-12 x-ray microprobe that provide superior spectral performance, better spatial resolution, and better count rates than conventional, straight capillaries. In addition, polycapillary optics were developed with significantly improved intensity levels compared with conventional straight capillaries. The polycapillary optics will provide the capability for high-sensitivity, wide-area XRMF scanning.

IV. Benefits to Defense Programs

The improved x-ray, capillary optics provided additional leverage for the Nondestructive X-Ray Microanalysis task, currently funded by the Research and Development program. Potential applications of this technology include on-line microanalysis of materials and parts in a down-sized production environment. Improved x-ray microanalysis capabilities also provide selling points for technology transfer and work for others. X-Ray Optical Systems, Inc is the only commercial supplier of capillary optics that are specifically designed for the analytical x-ray market. This CRADA enhanced the viability of XOS and helped to ensure the continued development and supply of advanced optical elements for this important analytical technology.

V. Discussion of Work Accomplished

Development of Tapered Capillaries

The Y-12 x-ray microprobe is a laboratory instrument with a unique x-ray source, consisting of a glass, capillary tube close-coupled with a microfocal spot.[1] Cylindrical glass capillaries with inside diameters ranging from 4 μm to 100 μm have been used in the system.

Ray-tracing simulations were carried out to determine the optimum profile shape for a single capillary for this system. The profile shapes considered in the simulations were linear taper, elliptical taper, combinations of straight and linear taper, and combinations of straight and elliptical tapers. The simulations were carried out for exit diameters of 3 μm and 8 μm. Compared with the conventional cylindrical (straight) capillary, the simulations showed the highest gains in intensity for 3-μm exit diameters. Unfortunately, the profiles most difficult to fabricate generally yielded the highest gains. For example, a fully elliptically tapered capillary could provide a 16-fold increase in intensity over a straight 3-μm capillary. Such a capillary would be extremely difficult to fabricate. Linear tapers were chosen for this study because of the relative ease with which they could be fabricated.

Simulations of the linear tapers yielded gains of 1.5 for the 8-μm and 1.8 for the 3-μm output diameters. Theses were the maximum gains possisble, because the simulations assumed perfectly reflecting capillary walls and a perfectly tapered profile. Since these perfect conditions were difficult to obtain during fabrication, the gains were expected to be lower for the actual capillaries. Measurements were conducted at the Y-12 Site to assess the quality of the manufactured capillaries.

Testing of Tapered Capillaries

Both tapered capillaries were fabricated by pulling a straight, 23-μm capillary with an outside diameter of six millimeters. The tapered capillaries were tested by conducting edge scans to measure the output beam profile, by measuring the energy spectrum transmitted by the capillaries, by comparing beam count rates to those of straight capillaries, and by scanning specimens to construct XRMF images.

Edge scans of the 3-μm and 8-μm tapered capillaries are shown in Fig. 1 and 2. For both scans, the edge was positioned at approximately 0.2 mm from the end of the capillary. The first-derivative curve represents the profile of the x-ray beam. Half-widths derived from the first-derivative curves were 2.7 μm for the 3-μm capillary and 6.8 μm for the 8-μm capillary.

X-ray scatter spectra are shown in Figs. 3 and 4 for the tapered capillaries, compared with straight capillaries of similar sizes. Tapered capillaries show a greater reduction in high energies compared with straight capillaries. X-ray spectra transmitted through glass capillaries tend to emphasize lower energies because critical angles decrease as energy increases. A wider range of reflection angles is available to lower energies and, therefore, more photons with low energies are transmitted through the capillary channel.[2] Tapered capillaries discriminate against higher energies even more so than straight capillaries. Each reflection through a tapered capillary occurs at a higher angle than the previous reflection, thus restricting the range of reflection angles available to each photon even more than straight capillaries.

The suppression of the high energy spectra has the advantage, in x-ray fluorescence, of making the x-ray beam more monochromatic. Absorption corrections in quantitative analysis are more accurate with a monochromatic beam. In addition, pencil-beam radiography and tomography results are expected to be improved because of the suppression of increased count rates due to high energy components in the beam.

Gain measurements for the tapered capillaries consisted of comparing the intensities cobalt k-alpha fluorescence, from a pure cobalt specimen, with that from straight capillaries. The results were gains of 1.4 for the 8-μm capillary and 1.5 for the 3-μm case. These results were very close to the expected values.

An advantage of the tapered capillaries in the Y-12 microprobe is the potential additional stability offered by the large entrance diameter with respect to small focal-spot drift. With straight capillaries, focal-spot drift caused the output flux to decrease during the time needed to complete data collection. Fig. 5 shows a comparison of source scans of the 3-μm tapered and straight capillaries. The greater profile widths and flatter tops of the source scans of the tapered capillary suggested that the assumption of greater stability was correct. The greater stability of the output flux has since been confirmed by analysis of element-distribution data scans.

Monolithic Polycapillary Optics

Monolithic polycapillary optics (MPO) are x-ray focusing optics, consisting of hundreds of strands of fused glass fibers that are formed into a near-elliptical longitudinal profile. Each strand of glass contains thousands of hollow, hexagonal channels, each just a few microns in diameter. X-rays from a point source are transmitted down the channels by total reflection, converging to a focal point several millimeters from the end of the capillary bundle. The MPO optics were expected to produce very high intensities at energies from 4 to 20 keV.

Two MPOs were made for testing at the Y-12 Site. Edge scans, given in Figs. 6 and 7, showed focal spot widths of approximately 40 and 100 microns for capillaries S06 and S11, respectively. Intensity gains, with respect to comparable straight monocapillaries, were 18 for S11 and 44 for S06. Gains were determined from the fluorescence of elements in the NIST SRM 1832 and 1833 thin-film standards.

The spectra of the NIST SRM 1833 sample from the MPO capillaries are given in Figs. 8 and 9, compared with corresponding spectra from straight capillaries. The MPO capillaries exhibited apparently greater count rates at energies greater than 8 keV, the energy of the kα line of the copper anode, due to summing in the detector counting train. S06 also showed higher background below 8 keV than the corresponding 50-μm straight capillary. This was caused by the fact that higher energies were less efficiently transmitted through S06 that lower energies because of the greater bending radius of the optic.

As an example of the use of MPO optics in x-ray microfluorescence analysis, Fig. 10 shows scans, made with S06, of element distributions in a dried microdrop of NIST SRM 1643c on a thin membrane. SRM 1643c contains ppb amounts of Fe, Mn, Cr, V and other metals, and ppm quantities of Ca. The microdrop provided a basis for testing and comparing detection sensitivities for x-ray microbeam techniques. The ppb elements in the microdrop were difficult to detect using conventional capillary or pinhole x-ray optics, because of low intensities and high backgrounds. However, the high intensity produced by the MPO optic made possible the use of a thick nickel filter to reduce the energies transmitted through the capillary, while still maintaining adequate intensity at 8 keV and above. X-rays below 8 keV contribute to the background under the first row transition series elements, making them difficult to detect.

Although chemical homogeneity was necessary for the comparison, Fig. 10 shows that the distribution of elements was not homogeneous. Most of the elements had low areas near the center of the microdrop. The copper scatter image suggested that an inclusion consisting of lower atomic number elements occupied the center area of the drop. In addition, one portion of the microdrop was high in Ti, although Ti was not listed as a constituent on the NIST certification of SRM 1632c. Fe and V were also associated with the high Ti area.

VI. <u>Inventions</u>

No inventions were made or reported as a result of work done under this CRADA agreement.

VII. <u>Assessment of commercialization possibilities</u>

X-Ray Optical Systems, Inc designs and fabricates glass capillary optics for x-ray applications. This CRADA has shown that tapered capillaries and MPO capillaries have advantages for use in x-ray microfluorescence analytical applications. It is anticipated that publications of these results will enhance the commercialization prospects of XOS capillaries in the analytical x-ray community.

VIII. <u>Plans for Future Collaborations</u>

Although there are no definite plans for future collaborations, XOS and LMES have agreed, in principle, to pursue further opportunities for joint work.

IX. <u>Conclusions.</u>

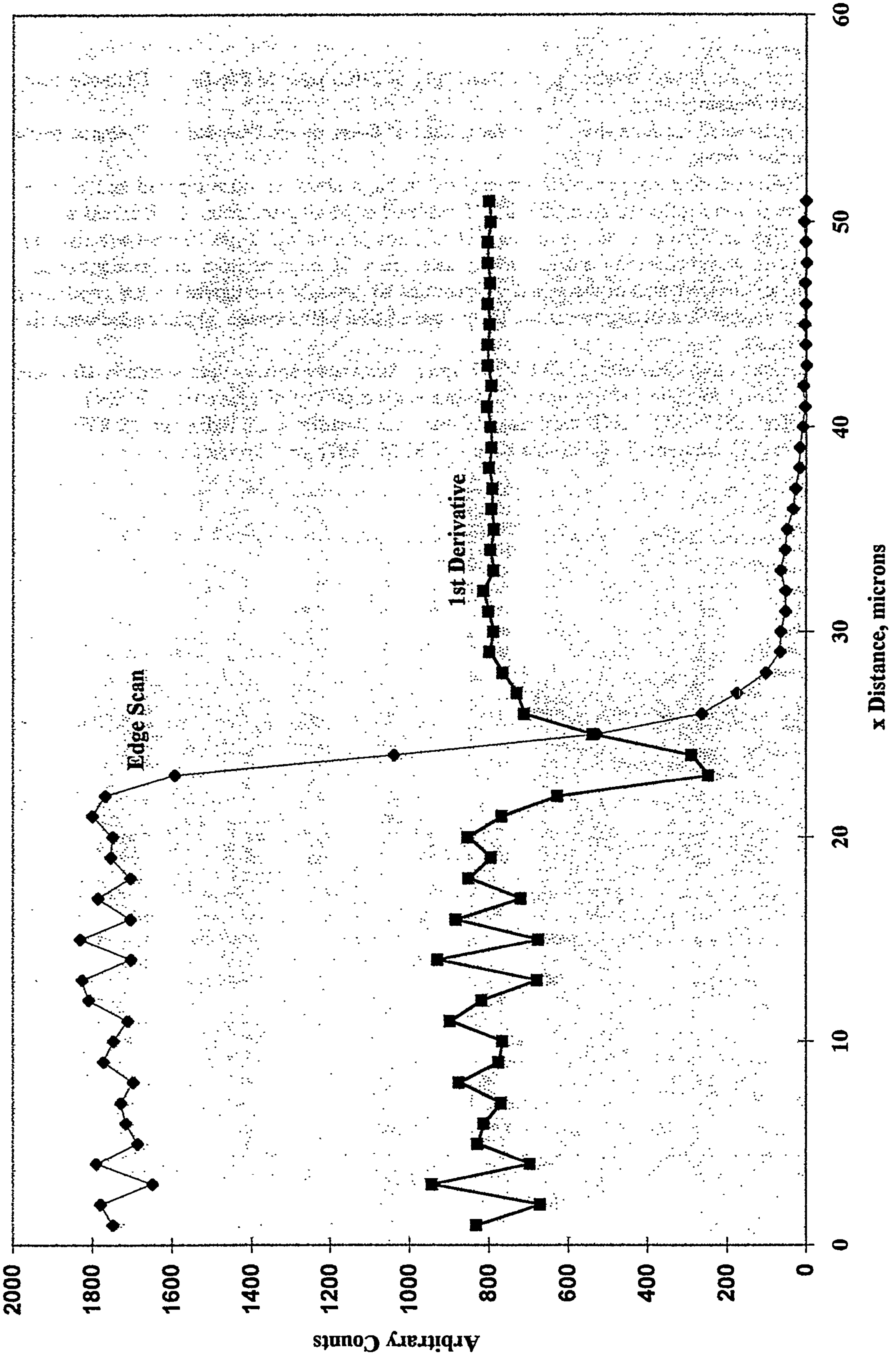
Advanced glass capillary optics were designed, fabricated and tested to assess their applicability to x-ray microfluorescence analysis. Tapered capillaries were found to offer superior spectral performance and greater intensities than conventional straight capillaries. Monolithic polycapillary optics provided significantly improved intensities and were advantageous in mapping minor to trace elements. This CRADA provided XOS with important market data while helping to assure LMES and DP of continued development and supply of advanced capillary optics for the nondestructive x-ray microanalysis technology.

References

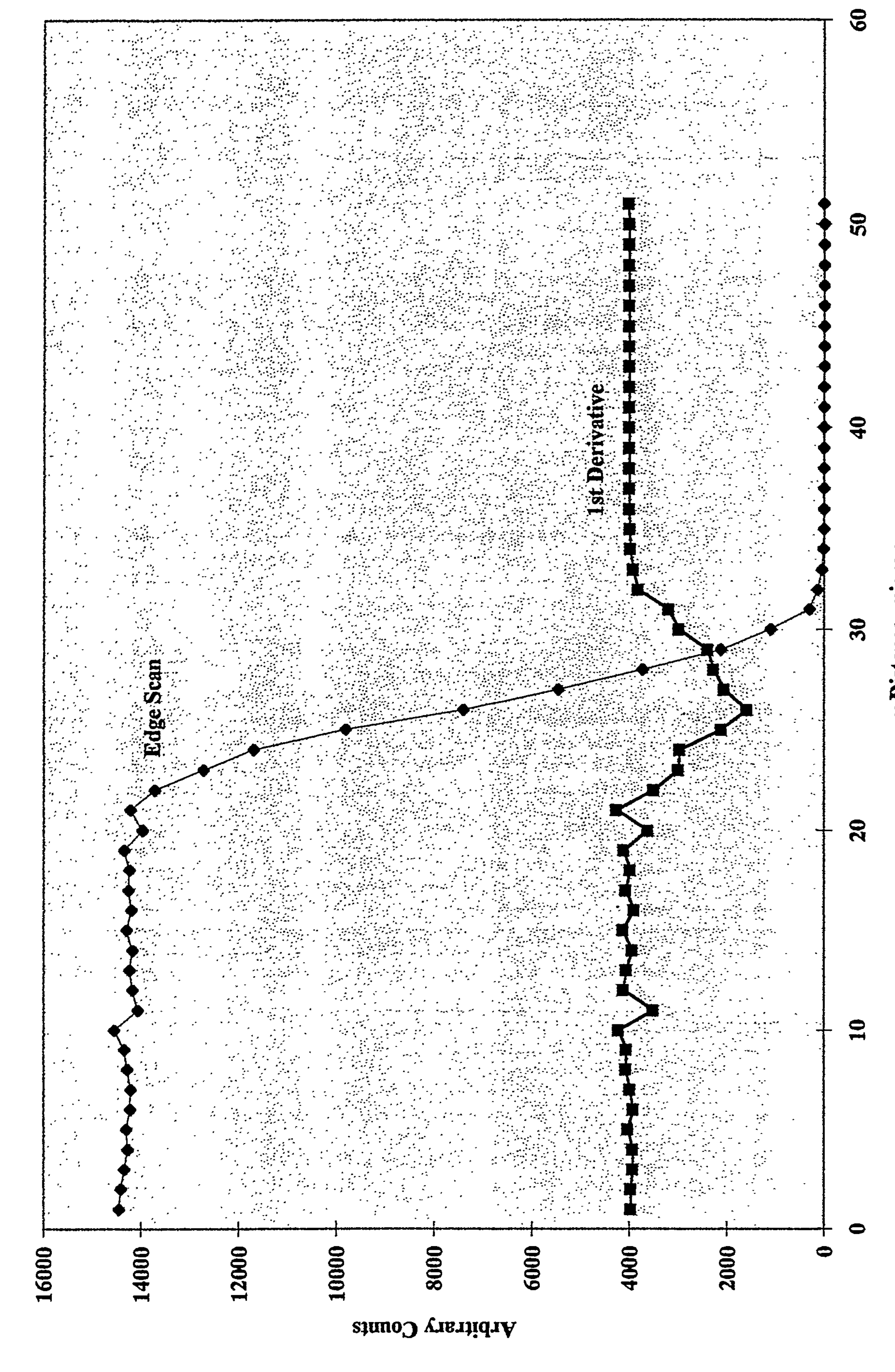
1. D. A. Carpenter, M. A. Taylor, and R. L. Lawson; "High Resolution X-Ray Microfluorescence Imaging with a Laboratory-Based Instrument," *J. Trace and Microprobe Tech., 13(2),* 141-161 (1995).
2. D. A. Carpenter; "Improved Laboratory X-Ray Source for Microfluorescence Analysis," *X-Ray Spectrometry, 18*, 253-257, (1989).

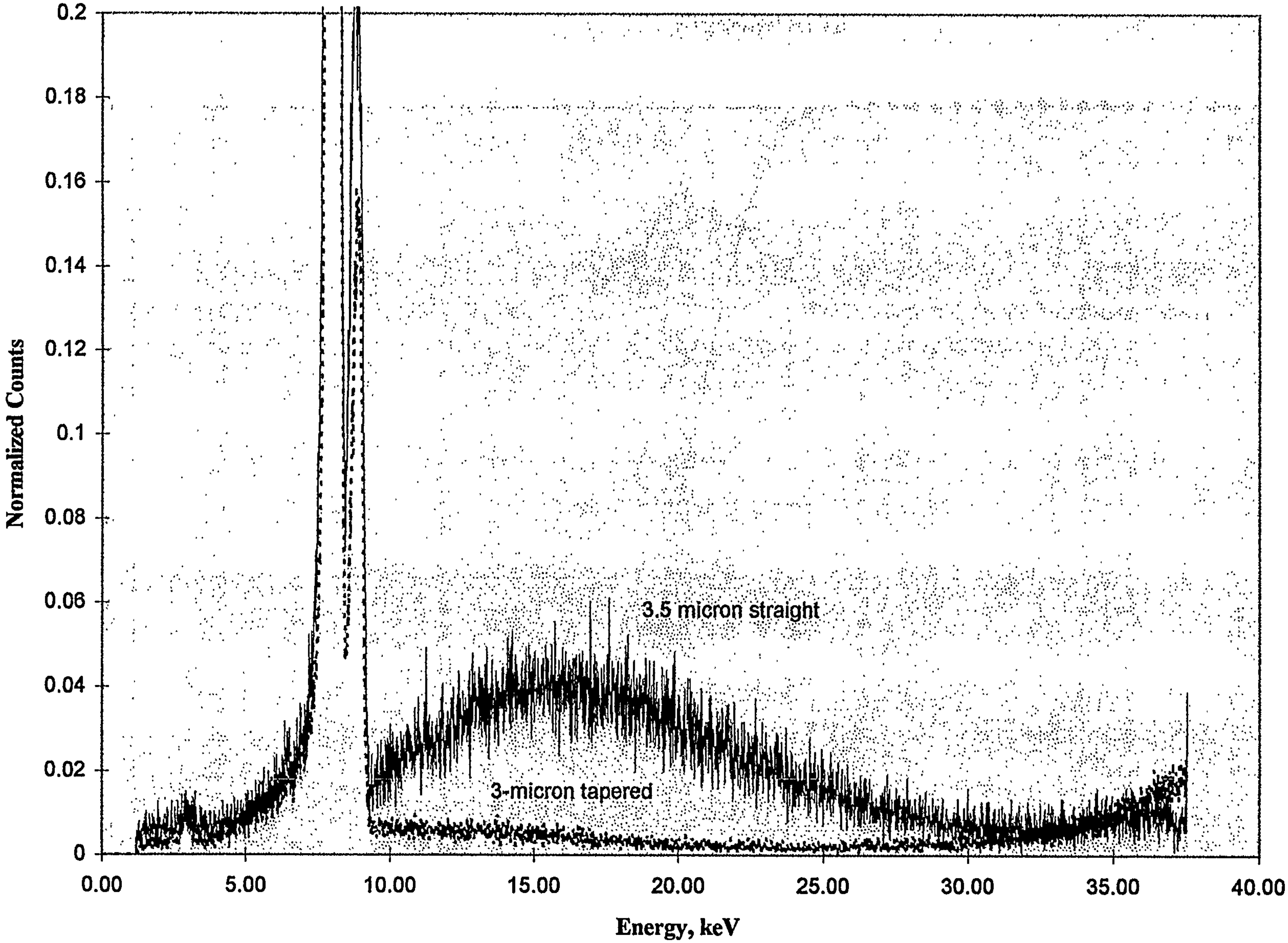
Figures:

1. Knife edge scan and first derivative at the focal spot of 3-µm tapered capillary. Distance between data points is one micron.
2. Knife edge scan and first derivative at the focal spot of 8-µm tapered capillary. Distance between data points is one micron.
3. Spectra of radiation from copper anode transmitted through nominal 3-µm tapered and straight capillaries. Spectra were reflected from teflon and detected at 90 degrees from the incident beam.
4. Spectra of radiation from copper anode transmitted through nominal 8-µm tapered and straight capillaries. Spectra were reflected from teflon and detected at 90 degrees from the incident beam.
5. Comparisons of source scans in the x and y directions for straight and tapered 3-µm capillaries.
6. Knife edge scan and first derivative at the focal spot of S06 MPO optic. Distance between data points is 10 microns.
7. Knife edge scan at the focal spot of S11 MPO optic. Distance between data points is 10 microns.
8. Spectra of SRM 1833 (S06 MPO optic and 50-µm monocapillary; Cu radiation, 30 kV).
9. Spectra of SRM 1833 (S11 MPO optic and 100-µm monocapillary, Cu radiation, 30 kV).
10. XRMF images of elements in dried microdrop of SRM 1632c on Moxtex film.

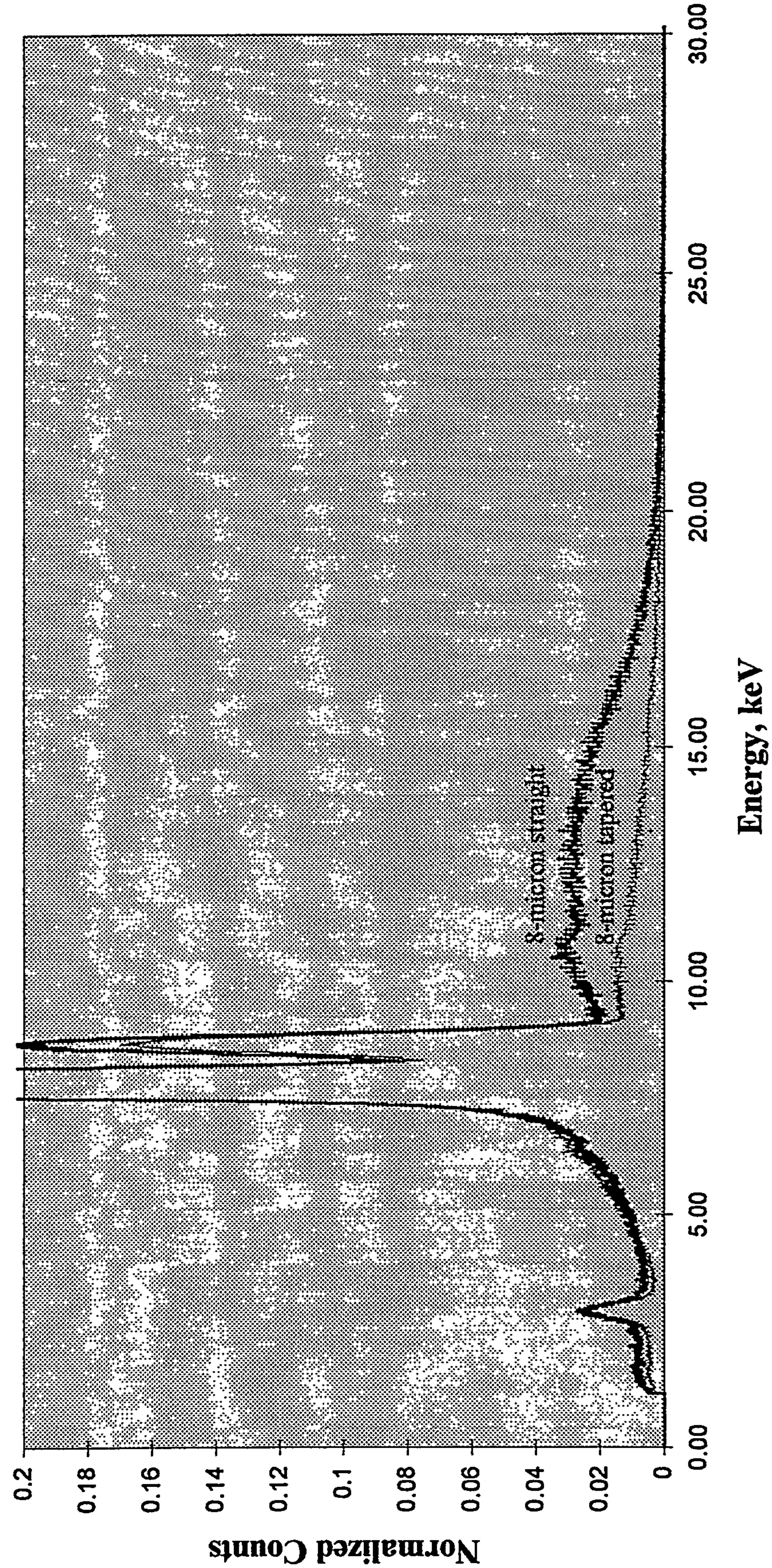


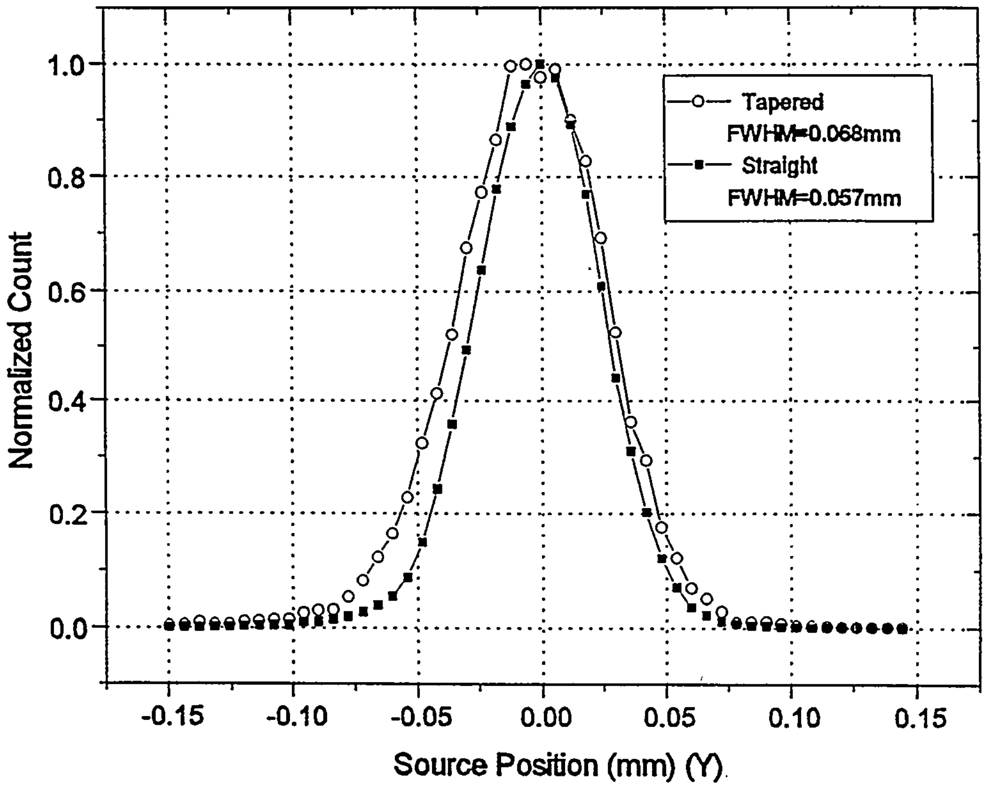
Edge Scan
1st Derivative
Arbitrary Counts
x Distance, microns
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0
10
20
30
40
50
60

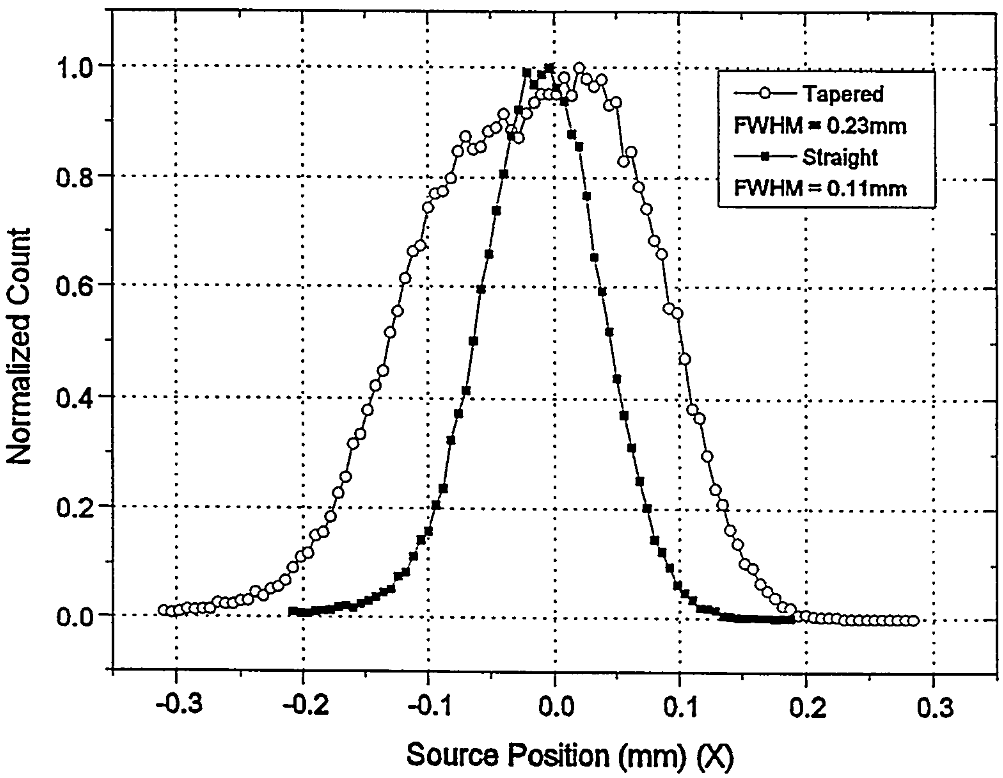

Edge Scan
1st Derivative
Arbitrary Counts
x Distance, micron
16000
14000
12000
10000
8000
6000
4000
2000
0
0
10
20
30
40
50
60

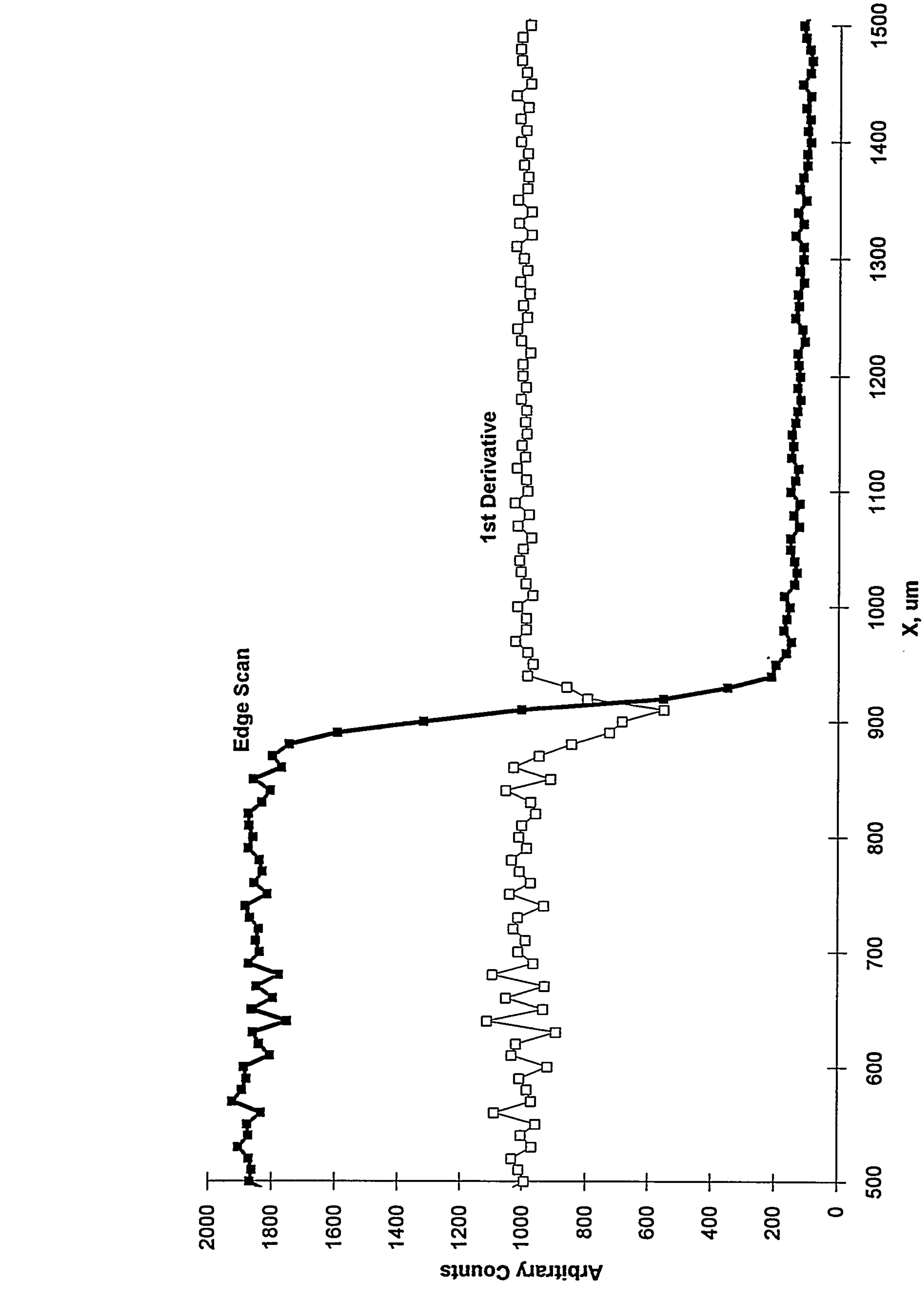


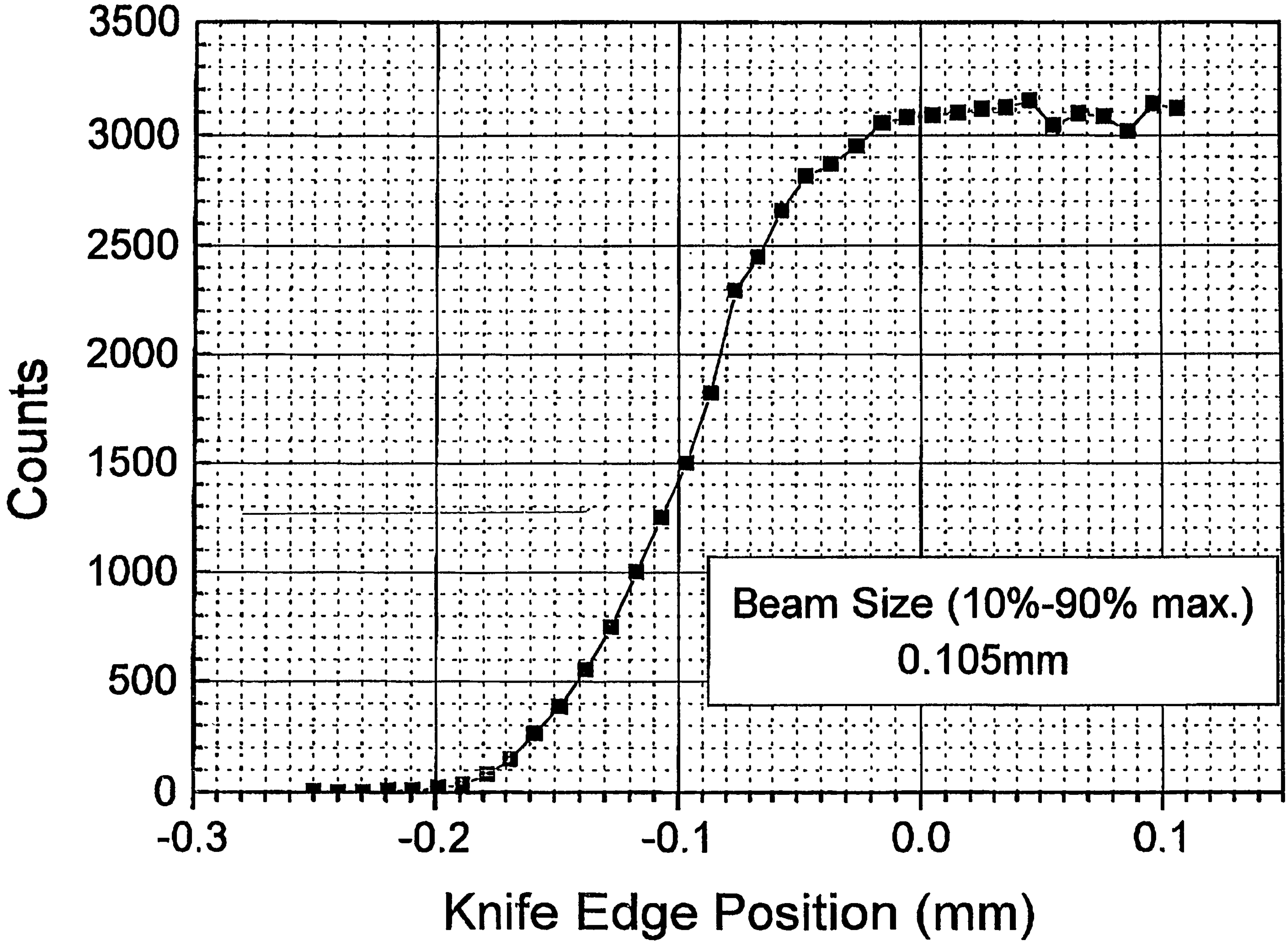
Normalized Counts
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
3.5 micron straight
3-micron tapered
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
Energy, keV

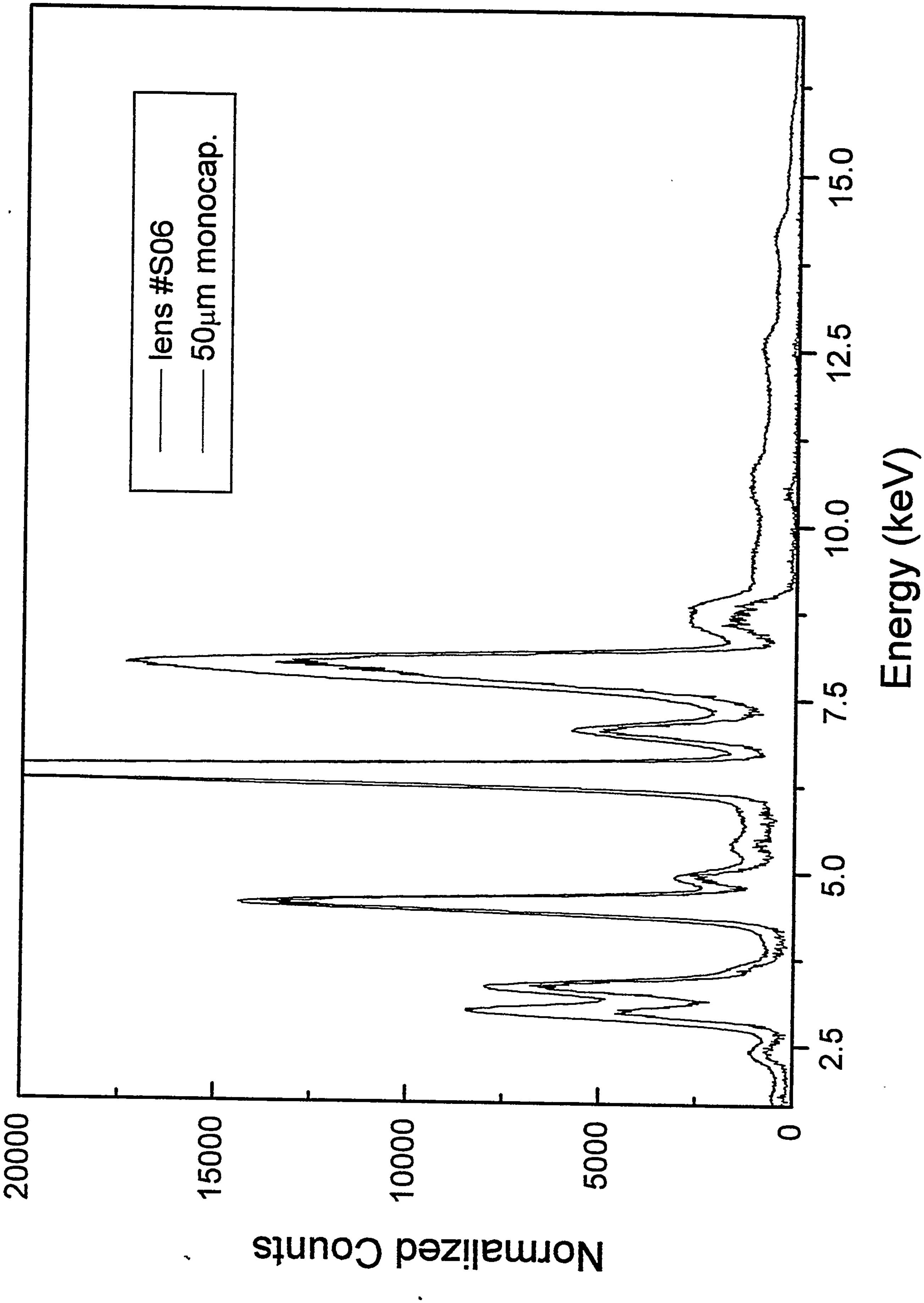

Normalized Counts
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0.00
5.00
10.00
15.00
20.00
25.00
30.00
Energy, keV
8-micron straight
8-micron tapered

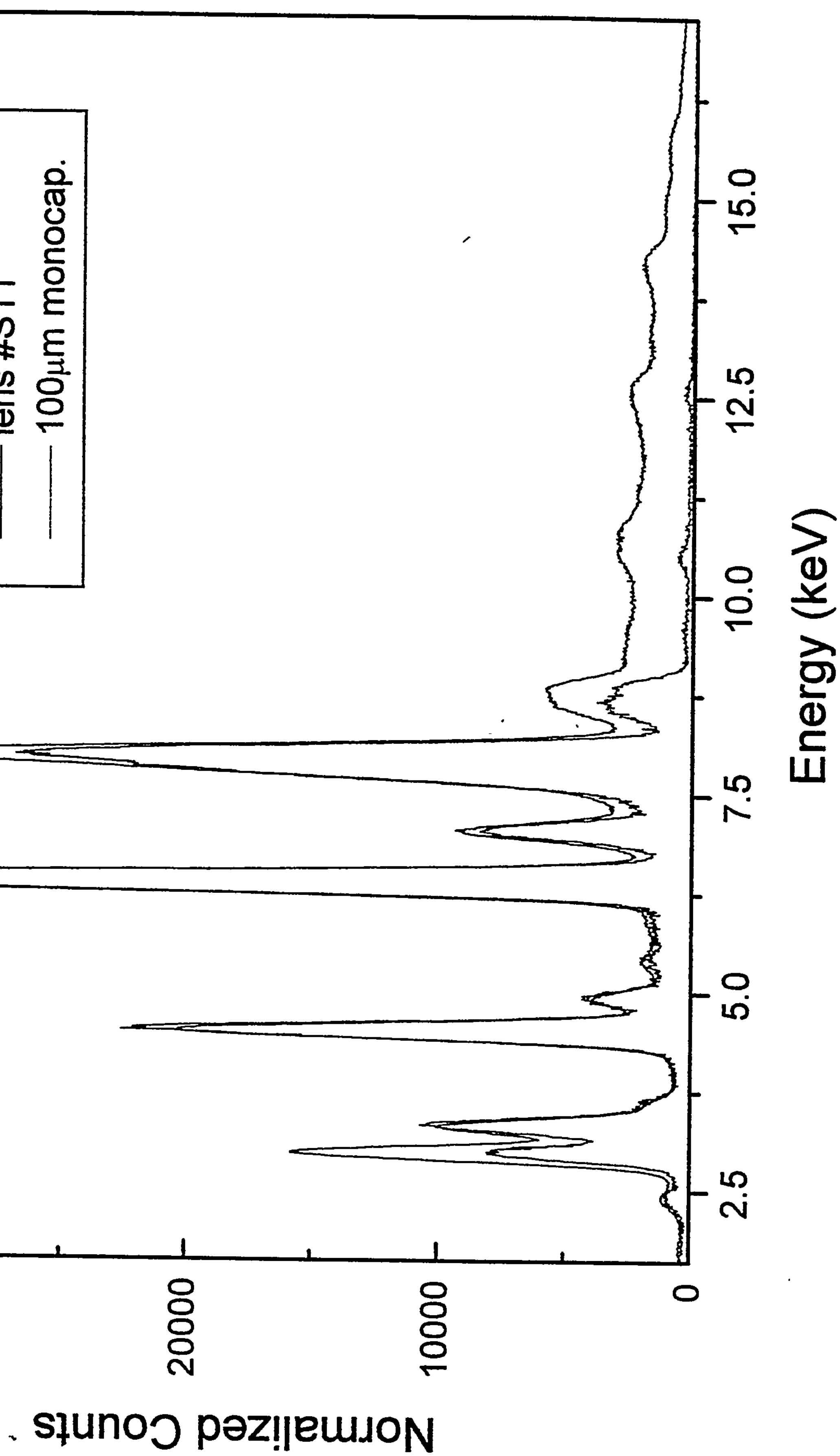

Normalized Count
1.0
0.8
0.6
0.4
0.2
0.0
-0.15
-0.10
-0.05
0.00
0.05
0.10
0.15
Source Position (mm) (Y)
Tapered
FWHM=0.068mm
Straight
FWHM=0.057mm


Normalized Count
1.0
0.8
0.6
0.4
0.2
0.0
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.3
Source Position (mm) (X)
Tapered
FWHM = 0.23mm
Straight
FWHM = 0.11mm


Edge Scan
1st Derivative
Arbitrary Counts
X, um
2000
1800
1600
1400
1200
1000
800
600
400
200
0
500
600
700
800
900
1000
1100
1200
1300
1400
1500


Counts
3500
3000
2500
2000
1500
1000
500
0
-0.3
-0.2
-0.1
0.0
0.1
Knife Edge Position (mm)
Beam Size (10%-90% max.)
0.105mm


lens #S06
50μm monocap.
Normalized Counts
0
5000
10000
15000
20000
2.5
5.0
7.5
10.0
12.5
15.0
Energy (keV)



lens #S11
100μm monocap.
Energy (keV)
Normalized Counts
0
10000
20000
30000
2.5
5.0
7.5
10.0
12.5
15.0

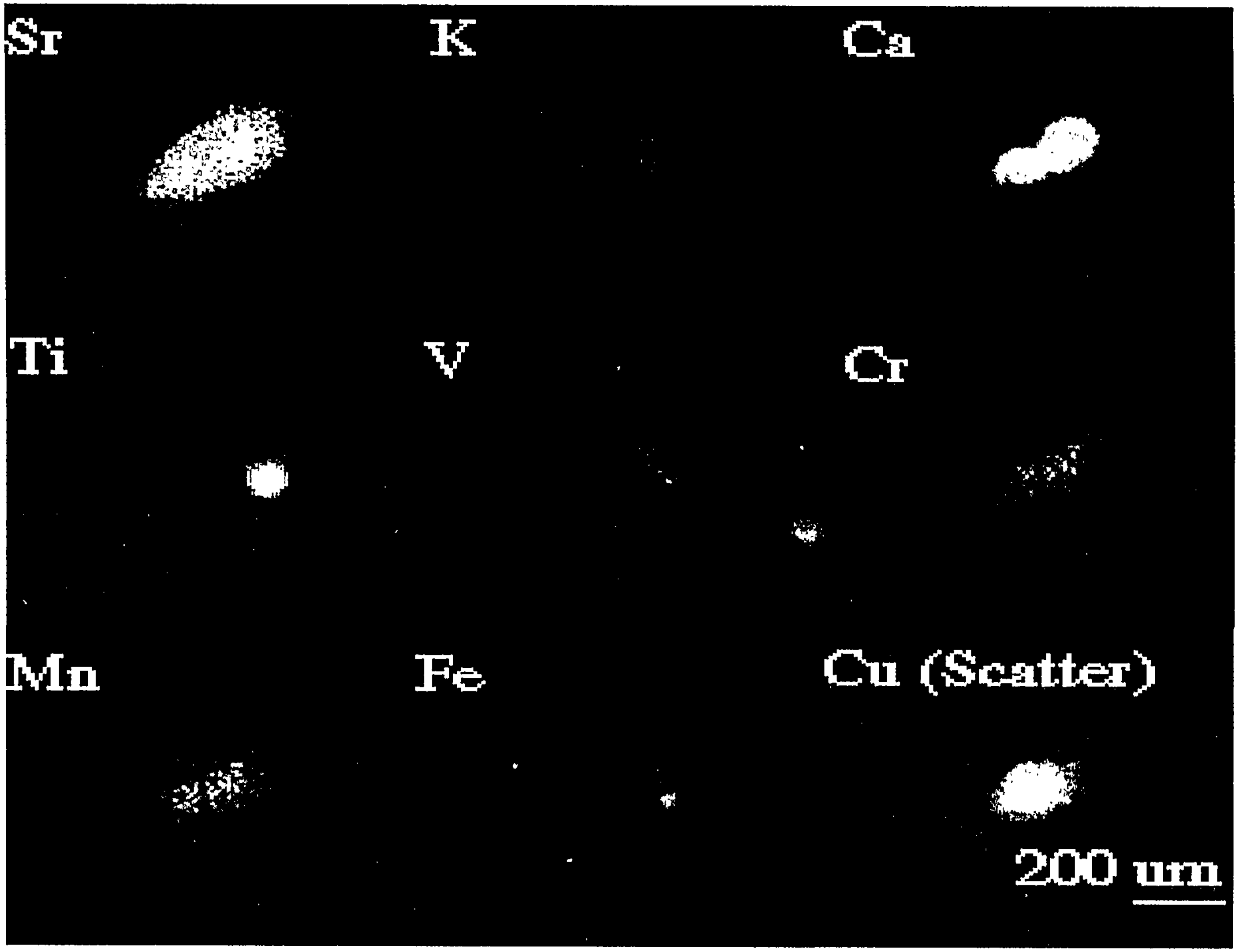


Figure 10 XRMF images of elements in dried microdrop of SRM 1632c on Moxtex film

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