LBL-27103

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Accelerator & Fusion Research Division

Center X-Ray Optics

Presented at the 37th Annual Denver X-Ray Conference,
Steamboat, CO, August 1–5, 1988

X-Ray Microprobe Studies Using Multilayer Focussing Optics

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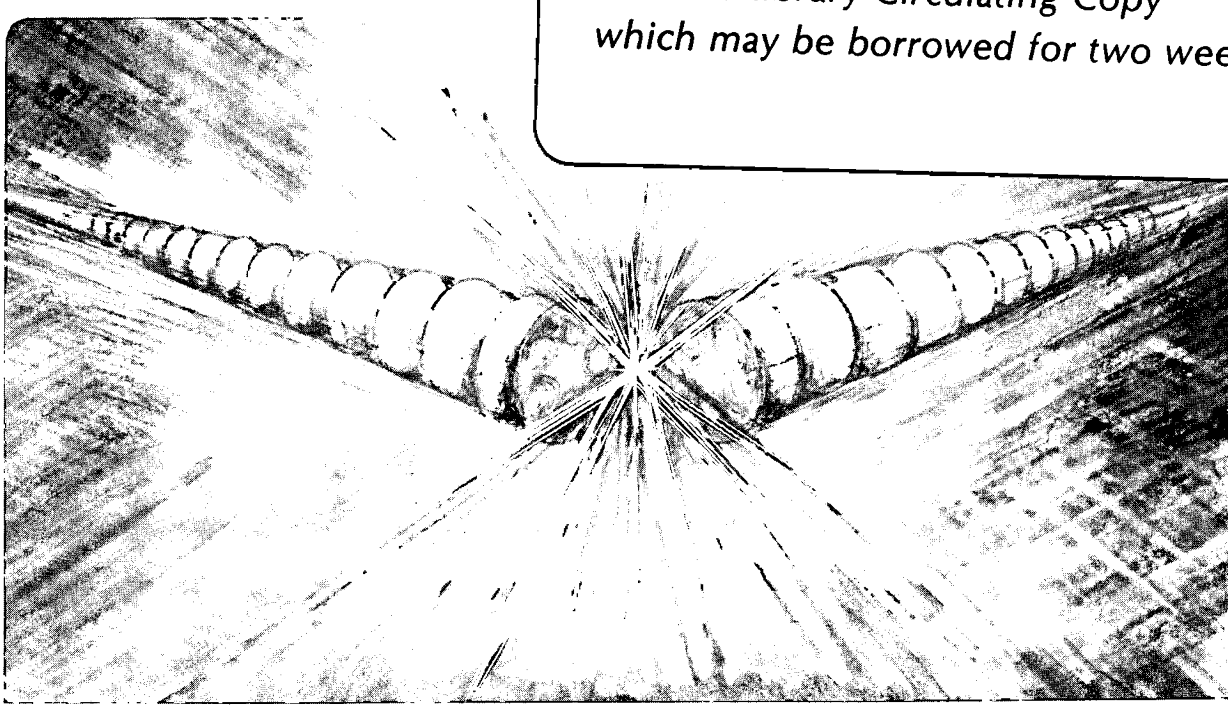
August 1988



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

X-RAY MICROPROBE STUDIES USING MULTILAYER FOCUSSING OPTICS

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INTRODUCTION

The availability of intense x-rays from synchrotron radiation sources permits the elemental analysis of samples in new ways. An x-ray microprobe using these sources allows the analysis of much smaller samples with greatly improved elemental sensitivity.[1] In addition to the higher x-ray intensity obtained at synchrotron sources, the development of high efficiency x-ray reflectors using multilayer coated optical mirrors permits the achievement of spot sizes of less than 10 μm x 10 μm with enough x-ray intensity to simultaneously measure femtogram quantities of many elements in less than one minute. Since samples to be studied in an x-ray microprobe do not have to be placed in a vacuum, almost any sample can be conveniently analyzed. With an x-ray microprobe it is possible to obtain elemental distributions of elements in one, two or even three dimensions.

In an x-ray microprobe a beam of x-rays is either collimated or focussed to a fine spot which is then scanned over the specimen. The characteristic fluorescent x-rays excited in the specimen are then detected using an energy or wavelength dispersive detector. In our system we use a synchrotron radiation x-ray beam as the source of x-rays, a pair of multilayer mirrors to focus the x-rays, and a Si(Li) detector to measure the fluorescent x-rays. It allows us to simultaneously measure the concentration of elements from K to Zn with a sensitivity of better than 50 fg in 60 sec.

FOCUSSING X-RAYS WITH MULTILAYER MIRRORS

Multilayer mirrors make excellent x-ray optical components. The mirrors are "super-polished" to have a low scatter finish that has been measured by optical interferometric techniques to have a microroughness of around 2 Å RMS. A multilayer coating is placed on top of this substrate by depositing alternate layers of two elemental materials of very different atomic number (i.e. carbon and tungsten). These layers produce a periodic lattice which diffracts x-rays.

These mirrors have two important properties. X-rays can be focussed with them since the substrate can be properly figured. The curvature of the mirror substrate determines the focussing qualities of the mirror. The reflectivity of a multilayer reaches a maximum at an angle of incidence given by the Bragg relation:

$$n\lambda = 2(d_A + d_B)sin\theta = 2dsin\theta$$

where λ is the wavelength of the photons, d is the multilayer period (the sum of the thicknesses of the two component layers A and B) and θ is the glancing angle of incidence. The layers are deposited using a dual source sputtering system and are very thin. For the proper operation of the focusing system, the d spacings of the multilayer must be adjusted to reflect x-rays of given energy at selected angles. In this experiment the d spacings for the two mirrors were 58 Å and 87 Å respectively. The bandpass of our mirrors were measured to be 10% at 10 keV.

To achieve focussing in two directions a Kirkpatrick-Baez geometry was used to demagnify the x-ray source by a factor of over 200 in both directions. This geometry has several advantages for microprobe applications. Since only on-axis aberrations are important in a microprobe rather than aberrations over a large field of view, this geometry allows optics with a high demagnification with very little aberration. The multilayer coating on the mirrors allows them to be used at larger angles than the critical angle of total external reflection. This therefore allows improved solid angle for a given length of mirror. Because the multilayers limit the energy bandpass to 10%, the elemental sensitivity is better than a pinhole or glancing incidence mirror system since the background under the fluorescent x-ray peaks is much lower.

DESCRIPTION OF EXPERIMENT

Details of the initial operation of the microprobe have been presented elsewhere.[2-4] Figure 1 shows how one of the spherical mirrors is mounted with a flexure hinge and a sine bar arm to allow its angle to be varied. The mirror assembly has recently been redesigned and Figure 2 shows the new system. Six stepping motors are used to focus the mirrors. Two linear stages (not shown) permit the height and horizontal position of the pair of mirrors to be set. Another two linear stages allow the distance of each mirror from the sample to be adjusted. The last two stepping motors are used to set the angle of incidence of each mirror.

The results reported here were acquired during an experiment at the LBL/EXXON beamline of the Stanford Synchrotron Radiation Laboratory (SSRL) in November, 1987. This beamline is powered by a 54 pole wiggler magnet that had a magnet field of 0.8 Tesla. During this run the electron storage ring operated at 3.0 GeV at a current of around 30 mA. On this beamline it is not possible to obtain a white radiation beam as we have done at the Brookhaven National Light Source (NSLS). Instead it was necessary to use the installed beamline monochromator which uses a pair a Si<111> crystals to produce a 10 keV beam with bandpass of less than 4 eV. This significantly reduced the x-ray flux that was produced at the sample. The beam flux was measured using a set of NBS thin glass Standard Reference Materials. A flux of 5 x 10^8 10 keV photons/sec was measured in a spot size 20 μm x 10 μm. Although this intensity was not as high as that obtained at NSLS (3 x 10^9 photons/sec at 10 keV), it was still possible to analyze a variety of interesting samples.

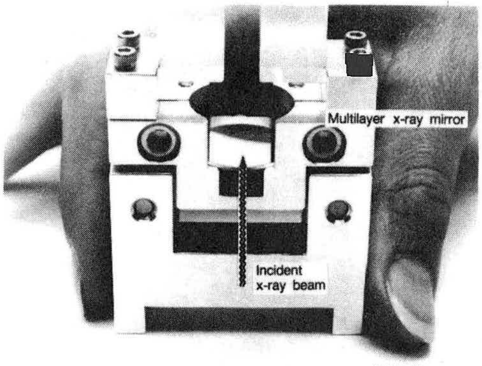

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Figure 1. Picture of a multilayer coated mirror with the mirror holding block.

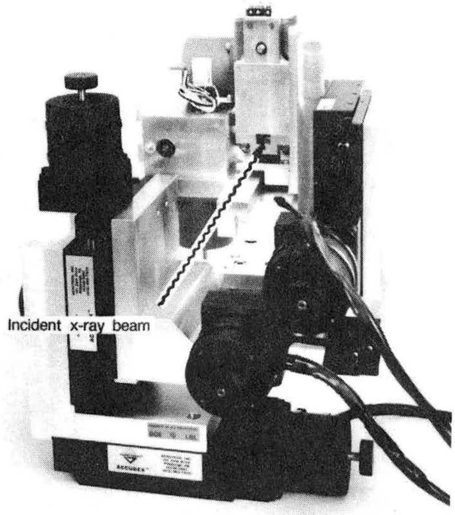

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Figure 2. Overview of the microprobe mirror assembly. Four motors are used to set the incidence angles and positions along the beam direction for the two mirrors to achieve proper focusing.

The beam spot size was measured by scanning a cross hair made from 8 μm diameter gold coated tungsten wire and measuring the transmitted radiation using an ion chamber. This allowed the position and angle of both mirrors to be optimized rapidly for best focus.

RESULTS

A variety of paper and ink samples obtained from the conservation department of the Fine Arts Museum in San Francisco were measured. A special mounting frame was built using plastic frames and small permanent magnets to hold these paper samples.

A series of stains or "fox" spots on different papers were scanned. These fox spots are a problem in art conservation since they grow as the document ages and can seriously degrade the appearance of the document. There are two types of fox spots. Some look like brown or grey circular stains with a diameter of about 1 mm. Others are more irregular and diffused and look like a mold growth. Fox spots of the first type on several different papers were scanned in the microprobe. In all spots scanned it was found that near the center of the stain there was a small area in which the x-ray microprobe measured relatively large quantities of iron. Figure 3 shows a one dimensional scan across one of these spots. A scan in the other direction was similar. From the figure it can be seen that the spot is less than 50 μm in diameter and that the highest Fe elemental density is 130 $\mu g/cm^2$. These spots, therefore, probably come from small iron particles that were imbedded in the paper when it was made. With time the iron has oxidized in the presence of moisture in the air.The oxide slowly diffuses through the paper result the coloring of the surroundings.

On the other hand, when fox spots of the other more diffuse kind were scanned, no increase in any of the elements from K to Zn was measured. These spots are therefore more likely of an organic rather than metallic origin.

The second problem that was examined was whether the x-ray microprobe can measure the components of ink and separate them from the paper back-

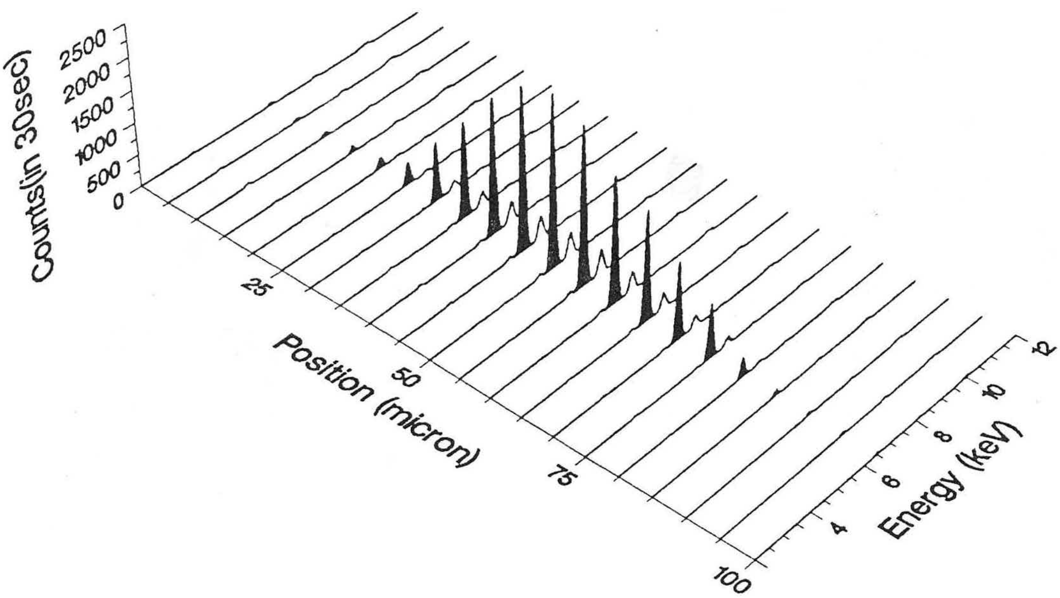

Figure 3. A scan across the "fox" spot shown very localized and quite concentrated elemental Fe distribution. The highest peak correspond to an elemental density of 130 $\mu g/cm^2$.

ground. Small spot size is important for this experiment since the concentrations of ink relative to the paper is small. To study application of the microprobe to this type of problem, a scan across a line in a signature of an old document was taken. Figure 4 shows the energy spectra taken at each point across the line. There is clearly iron in the ink and it has an interesting distribution. It shows that the Fe concentration increases when the ink line is approached and that it has two maxima on either edge of the line. This is how the ink might be expected to concentrate as it dried.

CONCLUSIONS

The synchrotron radiation based x-ray microprobe using multilayer focussing optics provides a new analytical tool that can be used to study a wide variety of samples. The Kirkpatrick-Baez mirror geometry allows an x-ray beam with an adequate intensity to measure femtogram amounts of elements from K to Zn in less than 60 sec.

As an example of the application of this probe, fox spots and ink lines on paper samples were examined. Some of the fox spots were determined to have a small metallic particle near the center of the stain with a diameter of less than 50 μm. In other more diffused fox spots, no increase in elements from K to Zn was measured. A scan across an ink line showed that the microprobe has excellent sensitivity to inks containing elements from K to Zn.

There are many possible applications of this probe. One example would be the study of the "Vinland" map. There is a controversy about the authenticity of this document.[5,6] If titanium dioxide particles are present in the ink it would tend to indicate that the document is not very old. With the x-ray microprobe it is possible to study different points along the ink lines

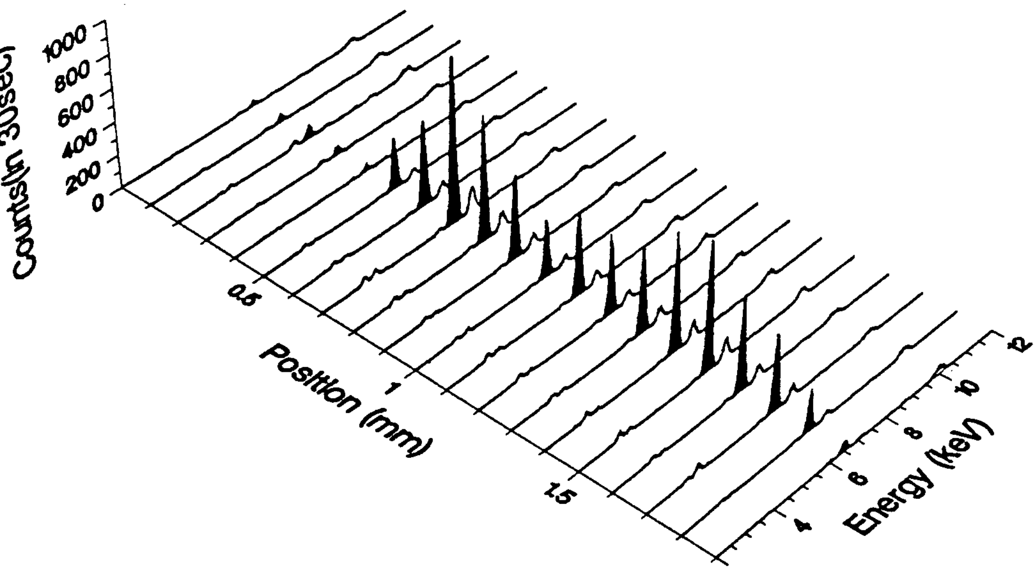

Figure 4. Scan across a dried ink line. It is interesting to notice the uneven distribution of Fe across the line. Upon drying, the liquid ink tend to get thicker at the outside edge and therefore result in a higher Fe concentration. The highest peak correspond to an Fe density of 60 $\mu g/cm^2$.

to see if titanium dioxide particles are present and if so what their sizes might be. Since the x-ray flux is not that high, there is no radiation damage to precious art documents that might be scanned with this probe.

It is also possible to reduce the spot size of this microprobe using improved multilayer mirrors. If spot sizes close to 1 μm x 1 μm can be achieved, there are a large number of biological studies that could be undertaken. Since the sample does not have to be in a vacuum, almost any sample can be scanned. The use of multilayer mirrors with laboratory x-ray sources is also being studied.

ACKNOWLEDGEMENTS

The authors wish to thank P. Batson and R. Delano for their help with the mechanical parts of this experiment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract DE-AC03-76SF00098. The experiment was carried out at the SSRL which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

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