Title

AN X-RAY MIROPROBE USING FOCUSSING OPTICS WITH A SYNCHROTRON RADIATION SOURCE

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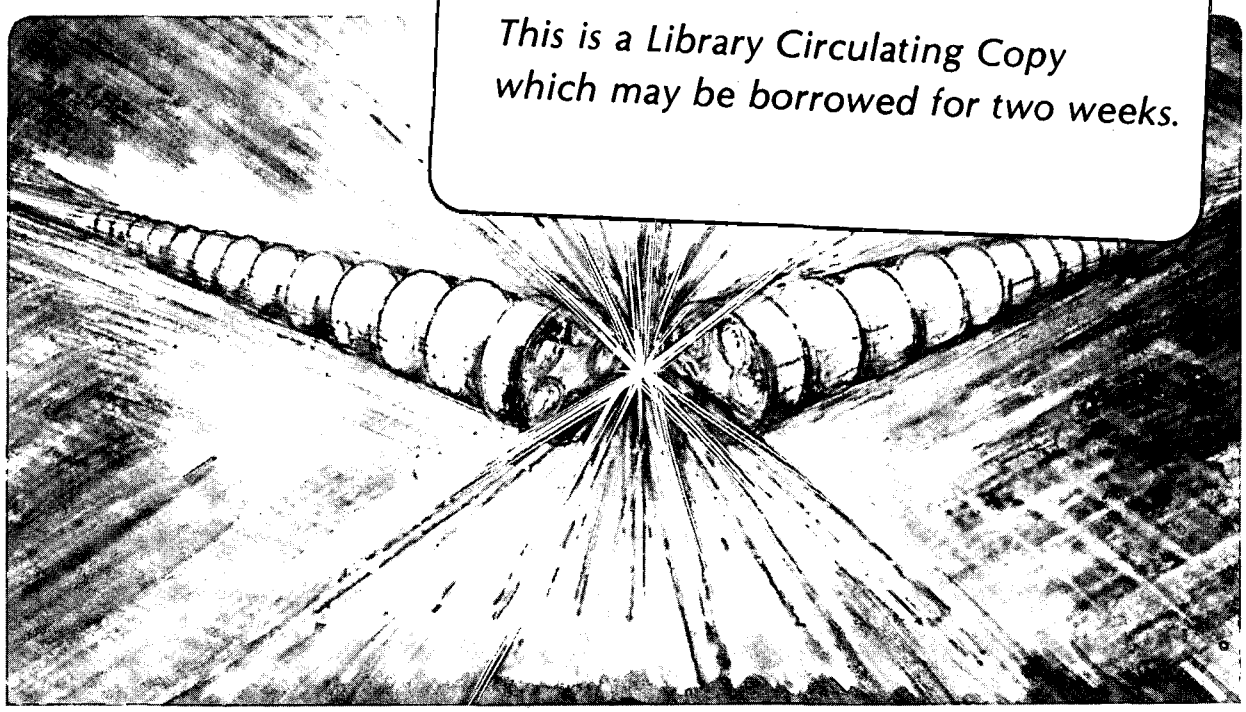

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ABSTRACT

An x-ray microprobe can be used to produce maps of the concentration of elements in a sample. Synchrotron radiation provides x-ray beams with enough intensity and collimation to make possible elemental images with femtogram sensitivity. The use of focussing x-ray mirrors made from synthetic multilayers with a synchrotron x-ray beam allows beam spot sizes of less than 10 μm x 10 μm to be produced. Since minimal sample preparation is required and a vacuum environment is not necessary, there will be a wide variety of applications for such microprobes.

INTRODUCTION

The availability of intense x-ray sources from synchrotron radiation sources permits the analysis of samples in many new ways. For example, an synchrotron radiation based x-ray microprobe allows the analysis of samples with higher spatial resolution and better elemental sensitivity than is possible with laboratory x-ray sources. In addition to the higher x-ray intensity obtained at synchrotron sources, the development of high efficiency x-ray mirrors using multilayer coated optical mirrors now 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. X-ray microprobes using synchrotron radiation will be useful in many fields because they provide a method to measure the concentration and spatial distribution of trace elements.

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 sensitive detector. Since the fluorescent x-ray counting rate is proportional to the concentration of each element in the volume of the sample irradiated by the x-ray beam, it is relatively easy to produce maps of the elemental concentration in a sample. Corrections for the x-ray absorption of the sample are usually made to obtain the final elemental concentrations.

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. This system allows us to simultaneously measure the concentration of elements from K to Zn with a sensitivity of better than 50 fg in 60 sec.[1]

PROPERTIES OF SYNCHROTRON RADIATION

Development of synchrotron radiation sources such as the Stanford Synchrotron Radiation Laboratory (SSRL), the National Synchrotron Light Source (NSLS) and the Photon Factory in Japan (KEK) are beginning to provide x-ray sources with excellent properties. The potential of an x-ray microprobe using synchrotron radiation has been studied by many groups.[2-7] Some groups have used the white radiation beam from a synchrotron source with only minimal filtering and a pinhole optical system to obtain very high x-ray fluxes while others have used an x-ray monochromator to optimize the elemental sensitivity for particular elements. As well as the high intensity, the inherent collimation of the synchrotron x-ray beam allows focussing optics to be effectively used to produce small beam spot sizes. In addition, since these x-ray beams typically have a linear polarization of better than 94%, the detector background is reduced and elemental sensitivity enhanced if the fluorescent

detector is placed perpendicular to the incident beam and in the plane of polarization where the scattered x-ray intensity is decreased.

MULTILAYER X-RAY MIRRORS

Multilayer mirrors make excellent x-ray optical components. The mirror substrates are "super-polished" to have a low scatter finish that has been measured by optical interferometric techniques to have a microroughness of around 2 A° rms and a spherical radius that is accurate to about $\lambda/10$. A multilayer coating is placed on top of this substrate by depositing alternating layers of two elemental materials of very different atomic number (i.e. carbon and tungsten). These layers produce a periodically layered structure which diffracts x-rays much like a crystal.

These mirrors have two important properties. X-rays can be focussed with them: the curvature of the mirror substrate and the angle of glancing incidence together determine the focussing qualities of the mirror. The multilayer acts as a reflector for X-rays with the reflectivity reaching a maxima at angles of glancing incidence given by the Bragg relation:

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

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 angle of glancing incidence.

The very thin layers are deposited on the spherical mirrors using a dual source sputtering system. For the pair of multilayer mirrors used in this experiment the 2d spacings used were 58 and 87 A° for the first and second mirror respectively. These mirrors were designed to operate at 10 keV since at this energy elements from K to Zn can be measured with high sensitivity. The bandpass of multilayer mirrors is typically around 10 % while the bandpass of a silicon crystal monochromator is around 3×10^{-4}. Therefore a microprobe based on multilayer mirrors and operated with a "white" radiation x-ray beam gives much higher output fluxes than one based on silicon crystals. A bandpass of 10 % is almost optimum for x-ray microprobe since it allows the background under the fluorescent x-ray peaks to be reduced while simultaneously providing enough bandwidth at the incident x-ray energy to give very intense focussed beams.

A Kirkpatrick-Baez geometry was used to demagnify the x-ray source in both directions by a factor of over 300 since the distance from the synchrotron source was 22 m and the distance from the center of the second mirror to the focus point was 5.4 cm. The geometry of the mirrors is shown in Figure 1. This geometry has several advantages for microprobe applications. Since only on-axis performance is important in a scanning microprobe rather than performance over a large field of view, this geometry allows optics with a high demagnification with very little aberration (essentially only spherical aberation). The multilayer coating on the mirrors allows them to be used at

higher angles of glancing incidence than typical glancing mirror geometries. This therefore allows improved solid angle for a given length of mirror. Since spherical aberation increases as the square of the mirror length, multilayer mirrors also give improved spot size compared to conventional glancing incidence "total reflectors".

DESCRIPTION OF EXPERIMENT

Details of the initial operation of the microprobe have been presented elsewhere.[6,7] Figure 2 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 3 is a photograph of the new system. Six stepping motors are used to focus the mirrors. Two linear stages 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. Figure 4 shows a schematic top view of complete instrument. Just upstream of the mirror system are a pair of horizontal and vertical slits to collimate the incident beam to 0.5 mm x 0.5 mm. An ion chamber follows the slits to measure the incident x-ray flux. Following the mirror system is the sample stage system which is placed at 45 deg to the incident beam. An optical microscope with a long working distance lens is placed so that it can view the front of the sample and help in aligning the sample in the x-ray beam. A second ion chamber is placed downstream of the sample to measure the transmitted x-ray flux.

The results reported here were acquired during an experiment at the LBL/EXXON beamline of the Stanford Synchrotron Radiation Laboratory (SSRL) in November,1987. The insertion device for this is beamline is a 54 pole permanent wiggler magnet that was operated at 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 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/sec at 10 keV photons was measured in a spot size 8 μm x 18 μm. Although this intensity was not as high as that obtained at NSLS (3 x 10^9/sec at 10 keV), it was still possible to analyze an interesting variety of samples. 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" marks on different papers were scanned. These fox marks 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 marks. Some resemble brown or grey circular stains with a diameter of about 1 mm. Others are more irregular and diffused and look like mold growth. Fox marks of the first type on five different papers were scanned in the microprobe. In all marks scanned it was found that near the center of the stain there was a small area in which the x-ray microprobe measured a high concentration of iron. Figure 5 shows a one dimensional scan across one of these marks. A scan in the other direction was similar. From the figure it can be seen that the mark is less than 50 μm in diameter and that the concentration of iron was 91 $\mu g/cm^2$. This is the concentration expected if the particle is a circular iron containing particle. These marks, therefore, probably come from small iron or iron oxide particles that were imbedded in the paper when it was made. With time the iron has probably oxidized in the presence of moisture in the air and the iron oxide has slowly diffused through the paper - staining the paper as it moved.

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

The second problem that was examined was the possible characterization of documents by measuring the elemental profile of the ink used in the document. The small spot size of this x-ray microprobe is useful in this study since the amount of ink is small relative to the paper background. To demonstrate this application, a scan across a line in a signature of an old document was taken. Figure 6 shows the energy spectrum 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. The maximum concentration of iron along the scan was 43 $\mu g/cm^2$. This is how the ink might be expected to concentrate as it dried and was "wicked" toward the edges of the line.

Improvement of X-Ray Optics

The present microprobe optics which uses spherical mirrors represents an approximation to an ideal ellipsoid. Spherical mirrors do not yield perfect point to point focusing. In fact, with the current geometry and assuming uniform reflectivity across the mirror, a point source produces a distance of 25 μm between the extreme rays in the image plane. However, the intensity distribution is such that 50% of the total intensity is within a beam size of about 6 μm. This agrees well with the beam

size that we have obtained at NSLS using spherical mirrors and including the x-ray beam spot size. To improve the spot size it is necessary produce mirrors that are elliptical rather than spherical. However, the high cost of manufacturing precise non-spherical mirrors, make using these custom made mirrors currently impractical. We have therefore decided to try to make elliptical mirrors by deforming a selected region of flow glass as discussed by Underwood.[8] With this in mind, we have calculated the point distribution function for a mirror with similar size as the ones we are using but bent to a closer form of the desired ellipsoid form. The distance between extreme rays in the image plane from a point source in this case is reduced to about 8 μm and the size of beam that contains 50% intensity is just about 1 μm. This size is still larger than the physical optical limit of this system. Further reduction of the beam spot size is possible but would be much harder. In order to achieve a beam spot of micron size, a small size source is needed as well. With a demagnification of few hundred, we can not use a source size that is bigger then a few hundred microns. In some cases, therefore, the emitance of the storage ring produces an limit on the focused beam size. If a pinhole is placed upstream in the beamline, and the x-ray mirrors are used to demagnify the pinhole a very small spot size is possible but with significantly reduced x-ray flux. This option may be useful for some experiments where imaging of only major elemants is desired.

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 a adequate intensity to measure femtogram amounts of elements from K to Zn in less than 60 sec.

As a example of the application of this probe, fox marks and ink lines on paper samples were examined. Some of the fox marks were determined to have a small iron containing particle near the center of the stain with a diameter of less than 50 μm. In other more diffuse fox marks, 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 historic and artistic documents to measure the elemental composition of the inks used. Since the x-ray flux is not high enough to cause any radiation damage, there is no 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 many biological studies that could be undertaken. Since the sample does not have to be in a vacuum, the spectrum of samples that can be studied by such microprobes is very broad.

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FIGURES

Figure 1. Schematic layout of x-ray microprobe.

Figure 2. Photograph of one of the multilayer coated spherical mirrors installed in its flexure pivot mount.

Figure 3. Photograph of the Kirkpatrick-Baez mirror system that has remotely controlled adjustments of the position and angle of both mirrors.

Figure 4. Schematic top view of x-ray microprobe showing the position of the different components of the system.

Figure 5. One-dimensional scan of a "fox" mark on an old document. A scan in the other direction gave a similar profile.

Figure 6. One-dimensional scan of across an ink line on a document.

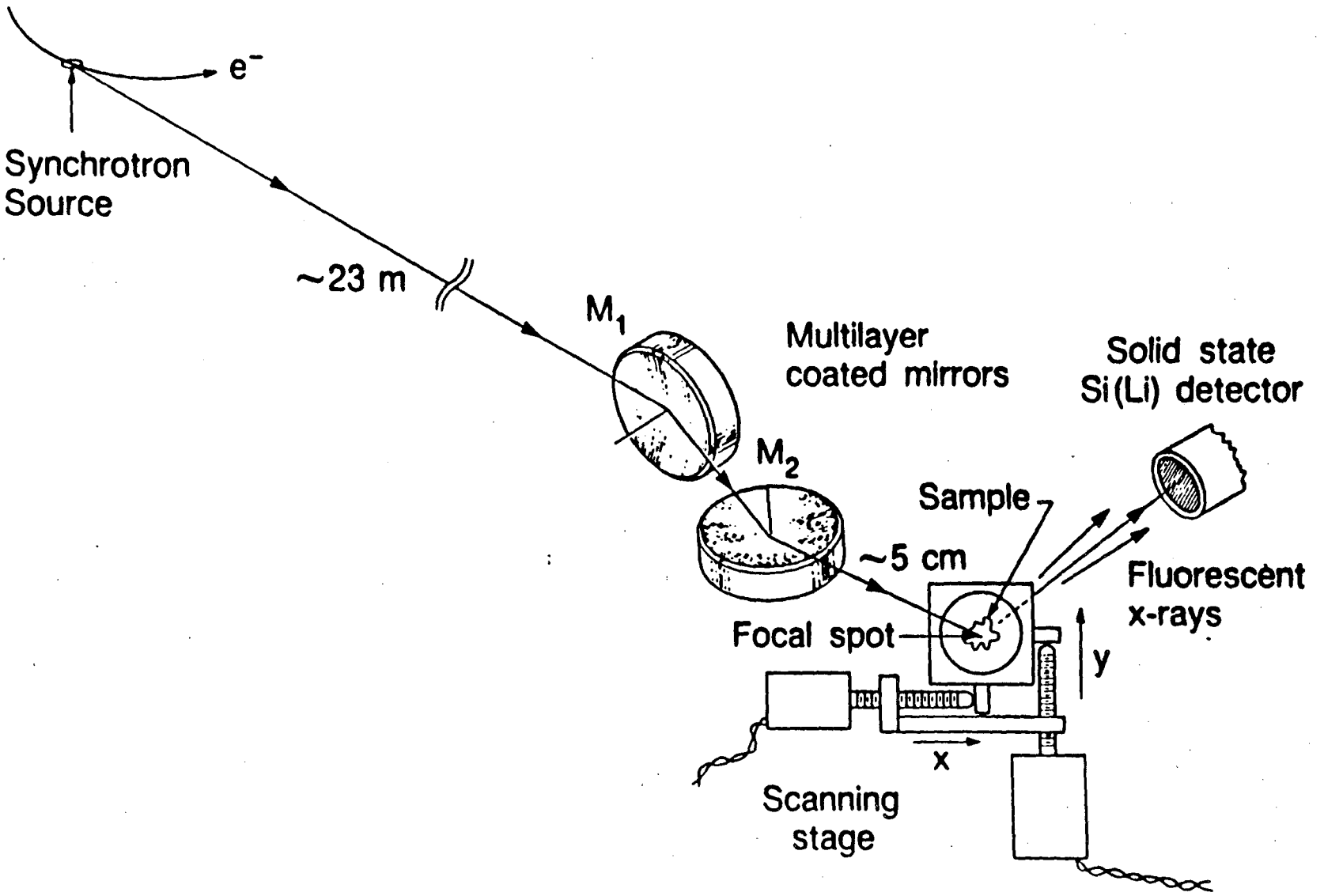
e⁻
Synchrotron
Source
~23 m
M1
Multilayer
coated mirrors
Solid state
Si(Li) detector
M2
Sample
~5 cm
Fluorescent
x-rays
Focal spot
y
x
Scanning
stage

Figure 1

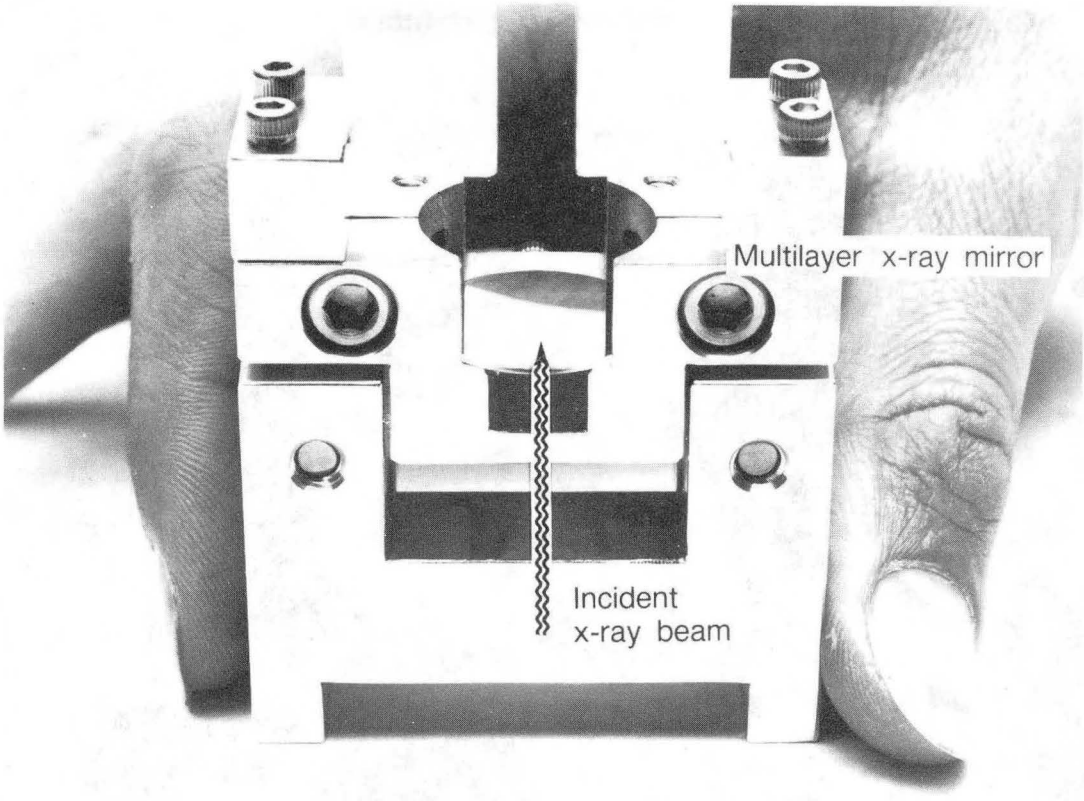

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Figure 2

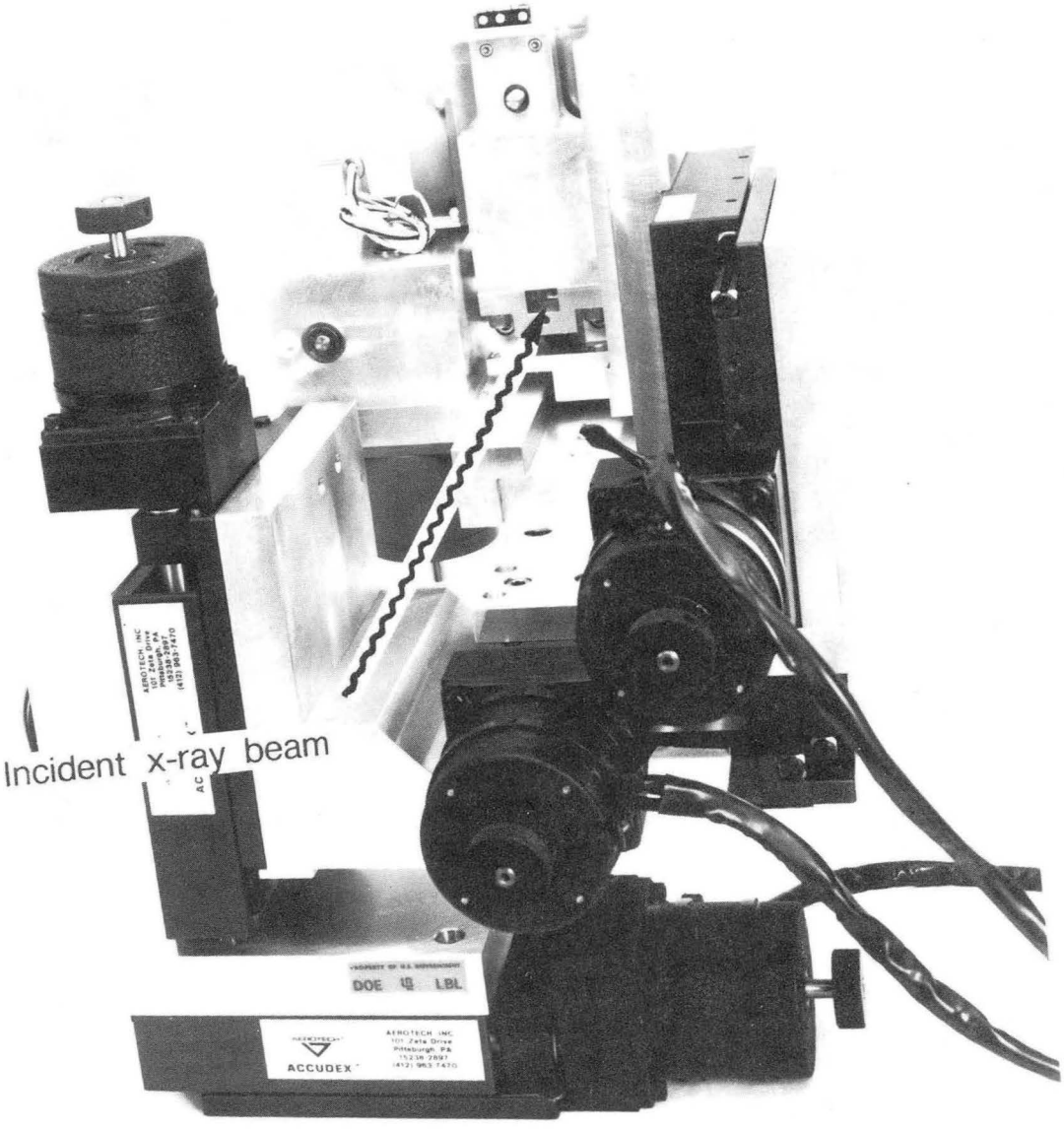

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Figure 3

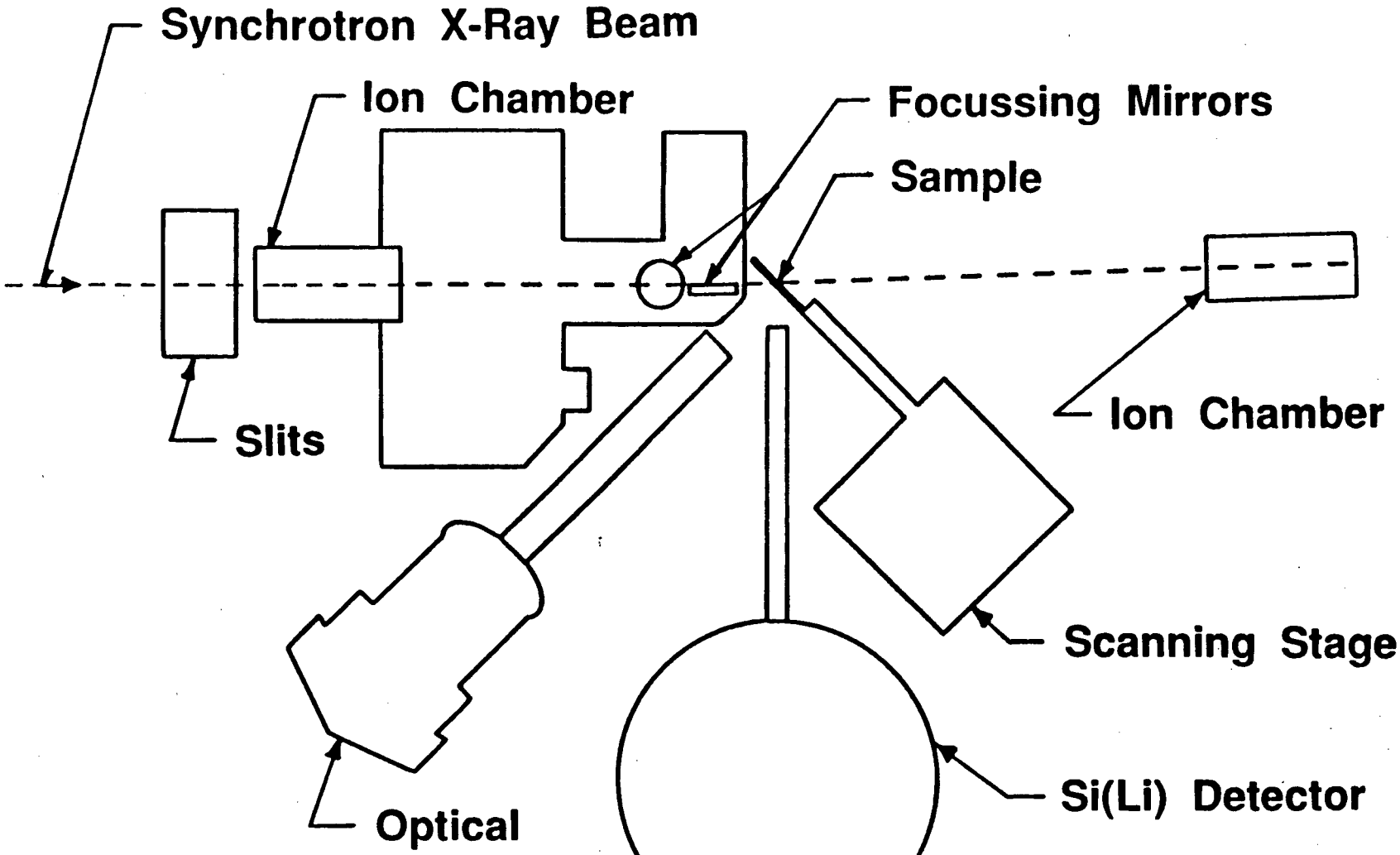
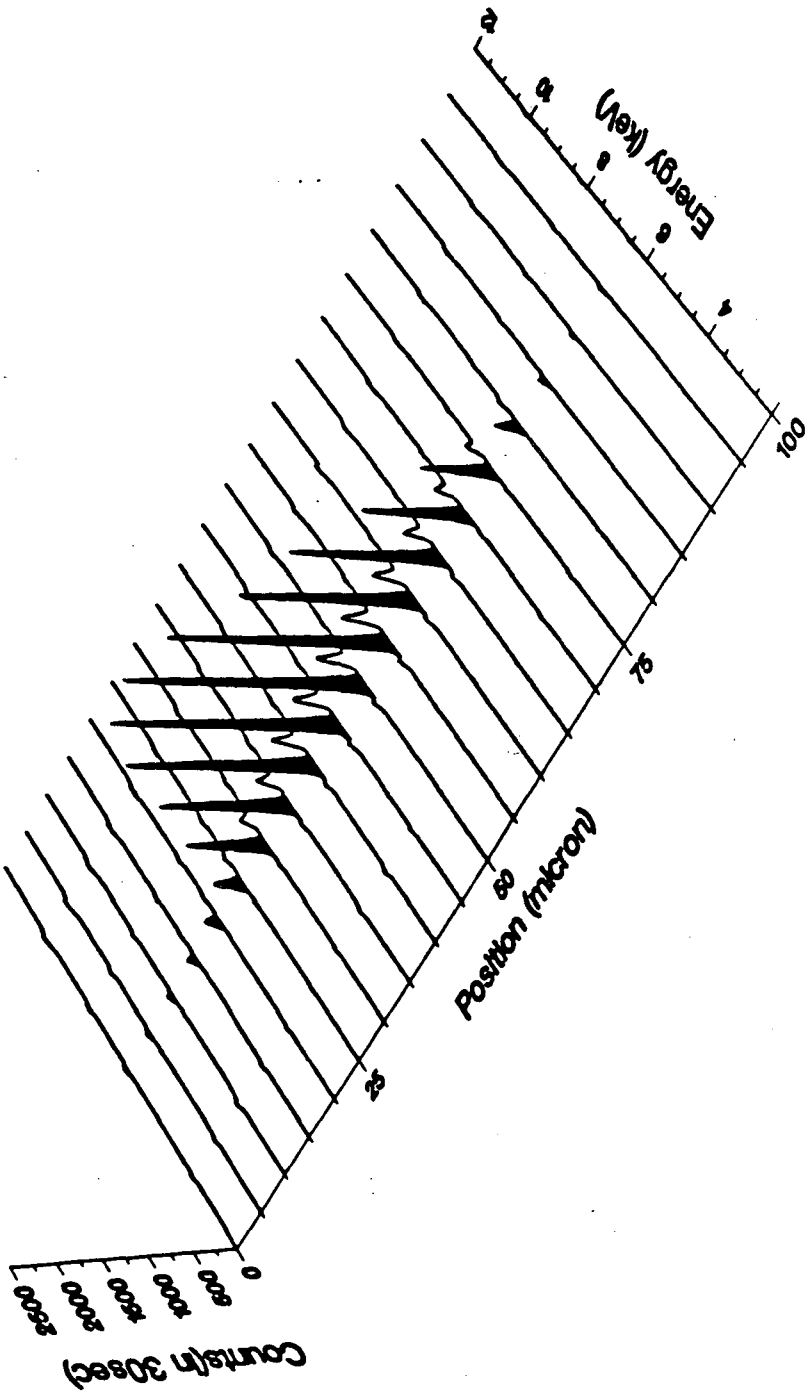

Synchrotron X-Ray Beam
Ion Chamber
Focussing Mirrors
Sample
Slits
Ion Chamber
Scanning Stage
Optical
Microscope
Si(Li) Detector

Figure 4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800
1200
1600
2000
Position (mikron)
25
50
75
100
Energy (keV)
4
6
8
10
12

Figure 5

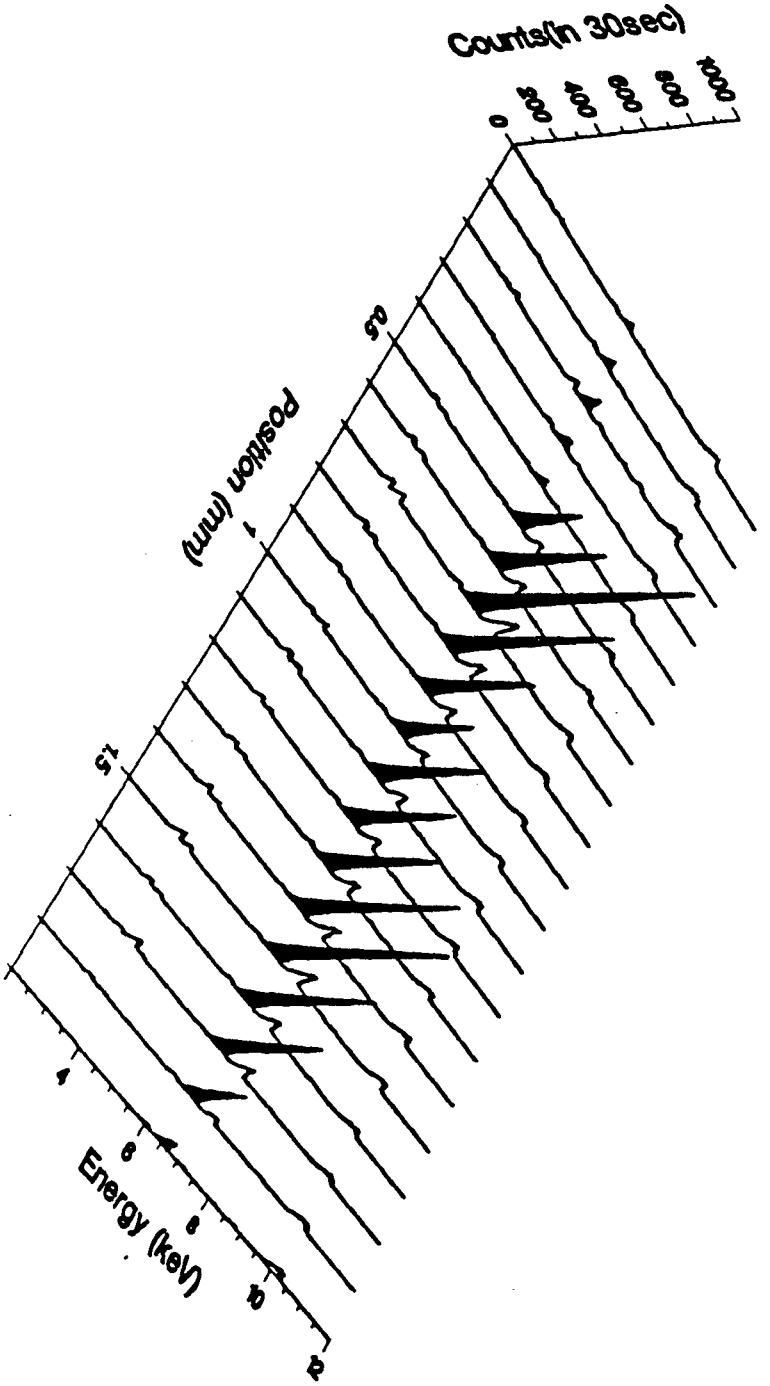
Counts(in 30sec)
0
200
400
600
800
1000
Position (mm)
1
.5
15
Energy (KeV)
4
6
8
10
12

Figure 6

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