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DESIGN CRITERIA AND SENSITIVITY CALCULATIONS FOR MULTIELEMENTAL
TRACE ANALYSIS AT THE NSLS X-RAY MICROPROBE

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ABSTRACT

Synchrotron radiation from the National Synchrotron Light Source (NSLS) will be used for x-ray fluorescence elemental analysis at a spatial resolution of several micrometers. The initial phase in the development of the microprobe beam line will consist of obtaining a 30- μ m beam spot for application to scanning x-ray fluorescence analysis. The proposed beam line will have a multilayer monochromator and an ellipsoidal mirror to provide monochromatic x rays from 3-17 keV with 8:1 demagnification. Ray tracing was carried out to establish the flux of excitation photons at the target for different orientations of beam line components. These alternative layouts will be discussed in terms of optimizing experimental conditions and trace element sensitivities. Calculated sensitivities for thin biomedical and geological matrices will be presented.

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1. Introduction

Synchrotron radiation sources have recently been used to lower sensitivity limits for trace element x-ray fluorescence analysis in bulk materials (1-4). The introduction of dedicated synchrotron radiation sources with greatly increased brightness (photons/sec-source area-solid angle) promises to extend sensitivity limits for trace element analysis to spatial resolutions down to micrometer levels.

The first analytical microprobe using synchrotron radiation excitation was established at the Cambridge Electron Accelerator by Horowitz and Howell (5). They focussed the x-ray beam with a bent cylindrical mirror and defined a beam spot with a pinhole in front of the target. The pinhole was as small as 2 μm . The achieved sensitivities were in the range of 0.1- to 1% and were limited by the poor brightness of the source. Polack, et al. (6) applied synchrotron radiation to x-ray absorption microanalysis using radiography as a detection device. Grodzins (7) has compared the intrinsic sensitivities of electron, proton, and photon induced x-ray fluorescence microprobes and concluded that the photon microprobe is inherently the most sensitive provided a sufficient fluence of photons is available. The high brightnesses of the new dedicated synchrotron radiation sources promise to provide the photon fluences required to provide sub-ppm sensitivity levels at micrometer spatial resolution. Plans are being made to construct microprobe beamlines at the Synchrotron Radiation Source (SRS), Daresbury, England (8), at the

Photon Factory, Tsukuba, Japan (9), and at the National Synchrotron Light Source, Brookhaven National Laboratory. Also, Ice and Sparks (10) have proposed a system for focussing synchrotron radiation for use in an x-ray microprobe.

In this paper we describe the plans for the first phase of the x-ray microprobe beamline at the NSLS. The first phase beamline will be placed on an arc bending magnet source and will provide a beam spot of about 30 μm . The paper includes a discussion of beam optics, detection systems and the trace element sensitivity limits for representative biological and geological target matrices. A number of practical considerations will be included in the discussion, including the availability of space for detection equipment at the target with respect to neighboring beamlines and the location of pinholes in front of the target.

2. Beamline Optics

The design of the microprobe beamline was performed with the aid of a ray tracing program developed by Heald and Gordon (11) for use at the NSLS. The program selects rays coming out of the source by a Monte Carlo program. The vertical angle selection is made through the formalism of Green (12) and the horizontal angular dispersion of beam photons was taken to be uniformly distributed. The spatial distribution of the electron beam was assumed to be gaussian in both vertical and horizontal directions with a 4σ value of 1.5 mm. The design parameters were 0.5 mm and 1.5 mm for the vertical and

horizontal directions respectively, but experience with the commissioning of the 700 MeV ring at NSLS has indicated the use of the more conservative vertical distribution for the initial running periods. The formalism of Green was used to select the polarization status for each ray. The rays were then followed through an optical system consisting of slits, mirrors of varying shapes, and/or crystals and the spatial distribution of rays determined at any point along the beam axis. For the microprobe calculations, the program was iterated until 1,000 rays successfully traversed the beamline to the target.

The overall concept of the beamline consists of monochromating the beam with flat synthetic multilayer microstructures to provide wide energy bandwidths without introducing additional angular divergence characteristic of microcrystalline diffraction materials such as graphite. The monochromated beam is then focussed with an ellipsoidal mirror to produce the desired demagnification. The separation of the monochromating and demagnifying functions provides for a simpler system with which to begin our program. Also, the use of nondispersive multilayers allows a fixed beam spot on the target while changing the excitation energy. The range of excitation energies selected for these studies is 4- to 17 keV which allows for the excitation of all elements through uranium.

The monochromator will consist of a pair of flat multilayer microstructures of alternating tungsten and carbon deposits. The number and thickness of the deposits will be such as to provide energy

bandwidths of about 2% and a transmission efficiency of 50%. A grazing incidence totally reflecting mirror has been chosen as the focussing element for the first phase of microprobe development (13,14). The mirror will be platinum coated and the angle of incidence will be 5 mrad, which will allow for total reflection of energies to about 17 keV. There are a number of physical constraints which dictate the size and placement of the mirror. First, the state of the art of mirror construction is such that the specified tangential slope error in the meridian plane be $< 5 \mu\text{rad}$. The slope error leads to a blurring of the image at the focal point. The minimum radius of curvature in the sagittal plane is 10 mm. The design parameters for the 4σ size of the electron beam cross section is $500 \times 1200 \mu\text{m}^2$. The fractional amount of allowable "blurring" ($f = \text{blur circle dia.}/\text{image dia.}$) in the image spot caused by the maximum slope error was set at $f = 1/4$. These constraints lead to the selection of an ellipsoidal mirror of 1/8 magnification with a major axis length of 9000 mm and a minor axis of 28.3 mm. The mirror must be 300 mm in length to accept most of the vertical angular divergence of the x-ray beam.

A physical restraint on the placement of components is the proximity to neighboring beamlines at the NSLS. With the target at 9000 mm downstream from the electron source, a Si(Li) detector in the preferred horizontal plane at 90° to the beam is allowed a maximum of 1200 mm. More space could be achieved by moving the focal point of the mirror further downstream at the cost of reducing the photon brightness at the source focal point of the mirror.

Two possible configurations are illustrated in fig. 2. The first includes the 1:8 ellipsoidal mirror at 8000 mm and a 30 μm pinhole at 4 mm upstream of the target (PH configuration). The second includes a 240 μm square collimator at 6000 mm, the same ellipsoidal mirror at 14000 mm and no pinhole at the target (CO configuration). Fig. 1 also shows, in shading, the area of the electron beam source which contributes photons to the 30 μm for each of the options. Note that for the CO option, photons originate over the whole source and the horizontal acceptance angle is restricted to 0.15 mrad. For the PH case photons originate only in the center 240 μm and the horizontal acceptance angle can be as large as 1 mrad. Therefore the angular divergence at the target is greater for the PH case than for the CO case.

The photon distribution at the 9000 mm has a size of $240\text{-} \times 240 \mu\text{m}^2$, thereby requiring a pinhole (e.g. 100 μm gold) at the target to define a $30\text{-} \times 30 \mu\text{m}^2$ beam spot. Fig. 1 illustrates the photon distribution for transmission at 10 keV through 20- and 30 μm square holes at varying distances upstream of the target. The edges appear to be quite diffuse for pinholes at a position of 4 mm.

There is an important experimental advantage that results from a placement such as the CO option. If a $240\text{-} \times 240 \mu\text{m}^2$ collimator were placed at the source focal point of the mirror, a 30 μm beam spot would be obtained at the target without using a spot-defining pinhole at the target. The collimator would be placed at least 6000 mm from the electron source because of the space required by the front end and

the shield wall. The elimination of a pinhole at the target would facilitate the telescopic viewing of the target.

The intensities shown in table 1 are for photons passing through the nominal 30 μm square target area for the NSLS design electron beam current of 500 nA and a 4 electron beam cross section of $1.5 \times 1.5 \text{ mm}^2$.

3. Sensitivity calculations

The criteria used for defining quantitation levels ($\sigma=10\%$) and minimum detectable levels (MDL) for trace elemental analysis were summarized in a previous paper by Gordon (15) as were the sources for the fluorescence production cross sections and scattering cross sections. The backgrounds considered in the use of solid state detectors originate in incomplete charge collection from both Compton and Rayleigh scattering and in bremsstrahlung from photoelectrons produced in the target by the excitation radiation. At a 90° viewing angle in the horizontal plane, the small angle approximation to scattered photons entering a detector of radius r at a distance R , where $\theta=r/R$, is:

$$\sigma(\parallel) \approx (3/16) \sigma_0 \theta^4 \quad \text{horizontal polarization}$$

$$\sigma(\perp) \approx (3/8) \sigma_0 \theta^2 \quad \text{vertical polarization}$$

where σ_0 is the total Compton and Rayleigh scattering cross section summed over all angles. The Rayleigh scattering at 90° is an upper limit because the angular dependences of the atomic form factors, which are strongly peaked in the forward directions, were omitted from consideration. At the energies considered here, the form factors for Compton scattering do not play a role.

The background when using crystal spectrometers was considered to be the bremsstrahlung originating in the target. The scanning wavelength dispersive spectrometer considered in these calculations is that described by Wagman, et al. (16). The system uses Johann focussing optics with a PET crystal for fluorescence energies below 4 keV and a LiF(200) crystal for energies above 4 keV. Slit-to-crystal distances vary from 6- to 20 cm and overall geometric efficiencies vary from 5×10^{-4} to 4×10^{-3} at resolutions of 2 eV at low Z to 220 eV for the BrK α line.

Sensitivity calculations were made for both the PH and CO options described above. For the CO series the 240 μm square collimator at 6000 mm sees rays that originate from the whole electron beam source area and any ray passing through the collimator will be focussed to the 30 μm target area. This comparison of the two configurations assumes a perfectly aligned and stationary electron beam orbit. Fluctuations in the beam position with time would have a greater effect in reducing photon beam intensity in the PH series than in the CO series.

The two sample matrices chosen for these sensitivity calculations are 2 mg/cm² thick carbon on a 1 mg/cm² thick carbon backing and 3 mg/cm² thick USGS rock standard BCR-1 with no backing. These matrices represent biomedical and geochemical samples, respectively. The incident and fluorescent radiation each were oriented at 45° to the target surface. Corrections were made for the absorption of the incident radiation as well as for the emerging fluorescent radiation. Multiple scattering in the thin targets was not included in the calculations, nor was secondary excitation by the fluorescent radiation.

4. Results and discussion

The results of the sensitivity calculations are illustrated in figs. 3-5. Quantitation levels for irradiations at 10 keV are included in the figures. The calculations for the Si(Li) detector system were performed for a sample-detector distance of 10 cm and a 60 s irradiation period as representative of a single measurement of a small sample. Fig. 3 shows results for a 1 s irradiation at 10 keV as a representative of operating in a scanning mode with a rate of 1 s/pixel. Under those conditions, a 1 mm² area would be scanned in 20 m. The calculations for the wavelength dispersive detector systems were made for 5 s irradiation periods representing a convenient rate for scanning a spectrum. Fig. 3 shows results for determination of a carbon matrix using a Si(Li) detector in the PH series. Because a limit of 10,000 c/s was placed on the rate of scattered count

accumulation, the required electron beam current stored in the ring was considerably less than the design current of 500 mA. For example, with a carbon sample the detector would reach saturation for a storage ring current of 17 mA at 4 keV to 485 mA at 20 keV. For BCR-1 the current would range from 7 mA at 4 keV to 300 mA at 20 keV. Since the potential design current is not required in this configuration, it is possible to consider increasing the fraction of horizontally polarized photons at the expense of reducing the total flux of photons from the source. By inserting a $0.5 \times 10 \text{ mm}^2$ collimator at 7000 mm, the fraction of horizontally polarized photons at 10 keV increases from about 0.96 to over 0.99. For a carbon matrix the useable ring current increases from 76 mA with full detector saturation to 500 mA with a detector saturation factor of 0.27. The calculations for use of a collimator with 10 keV excitation energy are included in fig. 3 and show an improvement in MDL of a factor of 3.5.

Figs. 4 and 5 show results obtained using wavelength dispersive detector systems in the PH series. The discontinuity in the K-shell curves are due to the change in analyzing crystal from PET to Li(200) at about 4 keV. The use of crystal spectrometers is indicated for taking full advantage of the storage ring capabilities.

As discussed above, the CO option has a $240 \text{ }\mu\text{m}$ square collimator placed at 6000 mm downstream from the electron source and acts as a source focal point for the 1:8 ellipsoidal mirror placed at 14000 mm. The photons passing through the collimator are then focussed in a $30 \text{ }\mu\text{m}$ beam spot at 15000 mm without the use of a constricting pinhole

in front of the target. For a carbon matrix using a WDS, the CO option results in sensitivity levels which are generally a factor of three higher than the PH option over the 6- to 15 keV excitation energy range. For the Si(Li) detector system, the CO option has a higher sensitivity level by a factor of 1.6 compared with the PH option at 15 keV, but actually has a lower sensitivity level at 6 keV. This is due to the collimator of the CO option acting as a filter for the vertically polarized x rays, which at 6 keV, has a larger vertical dispersion compared to higher excitation energies.

The PH option will be tested first since it makes the most efficient use of the available photon intensity, and the disadvantages of working with a pinhole and in a constrained area are probably not insurmountable. The CO option remains available, however, since the conversion only involves movement of the mirror and detection system downstream. The experimental program will also investigate other focussing options, such as those of Ice and Sparks (10), which appear to be more complex, but which promise larger photon fluences. Further demagnification of the beam spot to $\sim 3 \mu\text{m}$, will use an aperture at the image focus of the ellipsoidal mirror as the object for the optical components which will produce the smaller beam spot.

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Table 1. Microprobe photon intensities in 30 μm beam spot

<u>Energy</u> <u>(keV)</u>	<u>Intensity</u> <u>(photons/sec)</u>	
	<u>PH Series</u>	<u>CO Series</u>
4	7.30×10^{12}	8.45×10^{11}
6	6.41	7.53
8	5.23	6.30
10	3.98	5.08
15	1.91	2.51
10 ^{a)}	1.39	
a) additional $0.5 \times 10 \text{ mm}^2$ collimator at 7000 mm.		

FIGURE CAPTIONS

- Figure 1. Schematic diagram of PH and CO configurations for microprobe beamline. The shaded portions of the source indicate the area from which photons can originate and also strike target within a 30 μm beam spot.
- Figure 2. Ray-tracing-derived distributions of photons striking the target through 20- and 30 μm pinholes at various upstream positions. The distribution for the CO option is included.
- Figure 3. Minimum detectable levels and quantitation limits for a 2 mg/cm^2 carbon matrix using a Si(Li) detector.
- Figure 4. Minimum detectable levels and quantitation limits for a 2 mg/cm^2 carbon matrix using a wavelength dispersive detector.
- Figure 5. Minimum detectable levels and quantitation limits for a 3 mg/cm^2 rock standard (BCR-1) using a wavelength dispersive detector.

PH Configuration

CO Configuration

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5