X-RAY MICROPROBE FOR THE MICROCHARACTERIZATION OF MATERIALS

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ABSTRACT

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The unique properties of X rays offer many advantages over those of electrons and other charged particles for the microcharacterization of materials. X rays are more efficient in exciting characteristic X-ray fluorescence and produce higher fluorescent signal-to-background ratios than obtained with electrons. Detectable limits for X rays are a few parts per billion which are 10^{-3} to 10^{-5} lower than for electrons. Energy deposition in the sample from X rays is 10^{-3} to 10^{-6} less than for electrons for the same detectable concentration. High-brightness storage rings, especially in the 7 GeV class with undulators, will have sources as brilliant as the most advanced electron probes. The highly collimated X-ray beams from undulators simplify the X-ray optics required to produce submicron X-ray probes with fluxes comparable to electron sources. Such X-ray microprobes will also produce unprecedentedly low levels of detection in diffraction, EXAFS, Auger, and photoelectron spectroscopies for structural and chemical characterization and elemental identification. These major improvements in microcharacterization capabilities will have wide-ranging ramifications not only in materials science but also in physics, chemistry, geochemistry, biology, and medicine.

INTRODUCTION

Efforts to obtain micro-diffraction and micro-elemental analysis in order to understand the properties of matter have been made since the early part of this century when the first X-ray probes were constructed. Conferences have been held on the design and application of X-ray microprobe sources [1]. In the early 1950s, there was an upsurge in interest in microanalytical methods. Electron microprobes quickly became the instrument of choice. Electrons could easily be focused to spot sizes less than 1 μm -diam with enormous intensities compared to the weak X-ray sources then available. Though X-ray excitations were known to give a much better signal-to-background ratio, their generation required electron bombardment of a metal target with X rays emitted into 4π sr which then had to be gathered and focused to a small spot with inefficient X-ray optics. With the commercial availability of high-intensity and high-resolution electron microprobes, the unique properties of photons could not overcome their lack of intensity from weak sources. Interest in X rays as an excitation source for microprobe analysis faded, leaving electrons as the dominant microprobe source. It is a conservative estimate that 2500 electron probes and microscopes currently are in use for microcharacterization of matter in the United States. This represents an investment of \$1 billion or more in instrumentation alone. The wide usage of analytical microprobes is well documented in the several yearly conferences and journals of the electron microscopy and microprobe societies and attests to the great emphasis being placed by the scientific community on the need for microstructural characterization of matter.

With the advent of electron storage rings, an intense source of X rays has become available. The energy spectrum in the hard X-ray region is 10^4 to 10^6 times more brilliant than our conventional X-ray sources (2 kW to 60 kW dissipated by electrons impinging on metal targets). In fact, with magnetic devices especially suited for extracting the radiation from proposed low emittance storage rings, the spectral brilliance in units of

photons (or electrons) $s^{-1} mm^{-2} mrad^{-2}$ is near 10^{10} and approaches the brilliance of 3×10^{10} from the most advanced electron probes having field-emission electron guns [2-4]. This brightness is for the energy range from 1 keV to 35 keV from undulators on low-emittance electron storage rings in the 7 GeV energy range. This X-ray energy range covers the electron energy levels of the K- and/or L-shells for all the atoms and is most useful for EXAFS, fluorescent and diffraction analysis. Existing X-ray storage rings are about 10^{-3} to 10^{-6} less bright in this energy range.

As electron microprobes have clearly dominated the field of micro-characterization, the merits of the use of X rays for excitation of the sample will be compared to electrons. There are too many possible applications where microcharacterization is important to advancing our understanding of materials properties to be covered here. For more extensive information the reader should refer to the electron microscopy and microprobe literature and to Ref. 5. Actual applications of X-ray microprobes analysis are just beginning to emerge.

DETECTION LIMITS WITH X RAYS VERSUS ELECTRONS

A standard definition of the minimum detectable mass fraction [6] based on Poisson counting statistics for 95% confidence in detection is

$$\text{Minimum Detectable Mass Fraction (MDMF)} = 3.29 C_Z(N_b)^{1/2}/N_s, \quad (1)$$

where C_Z is the mass fraction of element Z, N_b the background counts, and N_s the counts in the signal. To evaluate Eq. (1), we need to know the fluorescent cross sections to calculate the number of events in the signal and to evaluate the background. These data are presented in Figs. 1-3 [7].

Fig. 1. Fluorescence cross sections for the elements when excited by X rays, protons (H^+), and electrons (e) of varying energies (after Ref. 7).

Fig. 2. Thick-target fluorescence yields of pure elements for X rays, protons, and electrons of varying energies (after Ref. 7).

Fig. 3. Comparison of the fluorescent signal-to-background ratio for various excitation radiations; at a concentration of 10^{-6} gg^{-1} for an X-ray fluorescent radiation detection system with an energy resolution of the natural linewidth (after Ref. 7).

As shown in Figs. 1 and 2, the number of characteristic fluorescent events is typically 10 to 200 times larger for X-ray excitation than for the same number of electrons. As shown in Fig. 3 the fluorescent signal-to-background ratio is approximately 10^4 times larger for X-ray excitation than for electron excitation. This extremely favorable property of X rays derives from the fact that about 90% or more of the incident X-ray energy is dissipated by ionization of the inner shells which gives rise to the fluorescence of interest. In contrast, only 0.1% of the energy dissipated by electrons gives rise to the fluorescent radiation of interest. Much of their energy is consumed by interactions with the least-bound outer-shell electrons. The deceleration of the incident electrons in the target produces a broad spectrum Bremsstrahlung radiation which is responsible for most of the background beneath the fluorescent signals of interest.

With these greater signals and lower backgrounds we find that 10^{-3} fewer X rays than electrons are required for the same MDMF. In terms of energy deposited, electron energies from 20 keV to 100 keV usually exceed by three to ten times the ionization energy of the bound electron. X-ray energies between 2 keV to 33 keV can be chosen to lie just above the ionization energy. As 10^3 more electrons with energies from three to ten times those of X rays are required for the same MDMF, the energy deposited by electrons is 3×10^3 to 10^4 times that deposited by X rays in thick targets. For very thin targets where most of the incident electron energy is transmitted, even more of the incident X-ray energy would be transmitted with still less damage to the sample. In air-dried blood cells and 8 μm -thick tissue sections [8] exposed to synchrotron radiation and charged particles, X-ray fluences 10^2 to 10^3 times greater were required to produce similar damage. Therefore, X-radiation damage to the samples may be even orders of magnitude less than the comparison made here on the basis of energy deposition alone. Thus with X-ray excitation we have the important choice of being able to either lower the detectable limits for the same fluences or to reduce the radiation damage and heat deposited in the sample for the same MDMF. Since heating of metal and ceramic samples and both heating and radiation damage of organic samples is of primary concern in modern electron probes, X rays have a major advantage. Before we can make a direct comparison between modern electron microprobes and the proposed X-ray microprobe, we must determine how many X rays can be put into very small beams.

X-RAY INTENSITIES FROM UNDULATORS ON LOW EMITTANCE STORAGE RINGS

With the proposed X-ray intensities from undulators on low emittance storage rings [2,3], fluxes are predicted to be on the order of 10^{15} X-rays s^{-1} in an energy bandwidth, $\Delta E/E$, of 0.1%. Projections of an electron source size in the storage ring of $2\sigma_x = 0.8$ mm and $2\sigma_y = 0.14$ mm and divergences of about 40 μ rad in both horizontal and vertical planes for undulators produce a brilliance approaching 10^{18} X rays s^{-1} mm $^{-2}$ mrad $^{-2}$ in a 0.1% energy bandwidth. Actual X-ray-focusing optics [9] have been fabricated and shown to have demagnifications of 287:1 with about 25% reflection efficiencies. Because of the small divergence of undulator radiation, X-ray optics can intercept the entire emittance and both focus and monochromatize with high efficiency. This small divergence lessens the demands on the optics since only a small area is illuminated. For example, the 40 μ rad divergence from a practical undulator produces a beam only about 1 mm-diam at 25 m from the source. We base the following arguments for the intensities obtainable for an X-ray microprobe on low emittance storage rings on a demagnification of 100:1. A demagnification of 100:1 results in a probe size of about 2×8 μ m 2 , and further reduction is achieved by pinholes in heavy metal foils. The estimate of the intensity available is conservative. Other optical systems could improve the intensities by about 10^2 [9,10,11]. The predicted intensities are given in Table I. Comparisons are made between photon fluxes from the brightest storage rings being proposed and the most intense electron microprobe sources. Note that the spread in electron energy is listed as 1 eV as voltage regulation approaches that fluctuation. For X-ray undulators, typical units of flux are given for 0.1% bandwidth or 10 eV spread for 10 keV X rays.

Table I. Comparison of X-ray microprobe intensities from undulators on a 7 GeV storage with a modern high brightness electron probe source.

	10 keV X-rays 7 GeV, 100 mA undulator	100 keV e $^{-}$ Electron microprobe
Brightness photons or e $^{-}$ /s mm 2 mrad 2	$1 \times 10^{15}{}^{a,b,c}$	$3 \times 10^{15}{}^d$
	$\frac{1 \times 10^{15}}{(3.2 \mu\text{m})^2 \text{ s } 10 \text{ eV}}$	
	$\frac{1 \times 10^{15}}{\mu\text{m}^2 \text{ s } 10 \text{ eV}}$	$\frac{6 \times 10^{12}e}{\mu\text{m}^2 \text{ s eV}}$
Intensity P or e $^{-}$ /area s	$\frac{3 \times 10^{11}}{(500 \text{ \AA})^2 \text{ s } 10 \text{ eV}}$	$\frac{6 \times 10^{11}e,f}{(500 \text{ \AA})^2 \text{ s eV}}$
		$\frac{6 \times 10^{10}f}{(30 \text{ \AA})^2 \text{ s eV}}$
		$\frac{10^{10}f}{(4 \text{ \AA})^2 \text{ s eV}}$

^aNational Synchrotron Light Source, Planned Evolution of NSLS, October 1983.

^bH. Wiedemann, Nucl. Instr. and Methods in Phys. Res. A266, 24 (1988).

^cG. K. Shenoy, P. J. Viccra, and D. M. Mills, Argonne National Laboratory Report ANL-88-19 (October 1988).

^dN. J. Zaluzec, Quantitative X-ray Microanalysis: Instrumental Considerations and Applications to Materials Science, Chapter 4, pp. 121-67 in *Introduction to Analytical Electron Microscopy*, J. J. Hern, J. I. Goldstein, and D. C. Joy, eds., New York: Plenum Press, 1979.

^eLaB $_6$ electron source.

^fField emission source.

At 0.1% bandwidth (10 eV at 10 keV), the brilliance of undulators will match that available from the most advanced electron probes. Though undulators peak the intensity at harmonic energy intervals, energies ranging from 2 keV to 40 keV would be available from the first through third harmonic. For fluorescent excitation, large energy spreads of $\Delta E/E = 1$ are acceptable [7]. For Bragg diffraction to identify the compounds present, a $\Delta E/E = 10^{-2}$ to 10^{-3} is useful. For microprobe EXAFS analysis and photoelectron spectroscopy, $\Delta E/E$ should be 10^{-4} to 10^{-5} to match the energy width of the electron energy levels. These various energy resolutions can be achieved with presently available optics from multilayers to nearly perfect crystals, and the microprobe energy resolution tailored to meet the experimental needs of a variety of applications.

SPATIAL RESOLUTION

Inherently, X-ray excitation for microprobe analysis offers the highest spatial resolution in thick samples of any radiation because the low-scattering cross section for X rays limits the lateral spreading of the beam in the sample. However, X rays are more difficult to focus, and their source size is larger. Electron field-emission source sizes approach 10 Å-diam and can be focused to diameters of atomic dimensions. However, lateral spreading of the electrons in matter produce interaction regions of about 1 µm-diam in thick samples [12]. Electron-probe analysis of ferrous materials having specimen thicknesses of 1000 Å to 2000 Å produce an interaction region of approximately 500 Å-diam even though the incident probe diameter is much less. Diffraction limits and beam penetration may keep the useful X-ray probe diameter to 500 Å and greater [11]. An X-ray microprobe with a beam diameter of 500 Å to 1 µm would compete favorably with the spatial resolution of electron microprobes in a great majority of the samples of interest. Because X rays have greater penetrating power than electrons, the convergence angle of the X rays at a demagnification of 100:1 places a limit of about 10 µm to the depth of beam penetration in the sample before divergence of the X-ray beam in the sample exceeds the intended probe size of 1 µm diam.

FLUORESCENT DETECTION LIMITS

To determine the fluorescent detection limits from Eq. (1), we use the data presented in Figs. 1-3 and Table I. We assume a fluorescent detection system equipped with a crystal analyzer intercepting 10^{-3} of the total solid angle and with an energy resolution matching the K_{α} or L_{α} fluorescent energy widths. In this case MDMF is about 10^{-4} times less than for the best electrons probes with similar wavelength dispersive optics.

As the detection of elements at interfaces is important to many materials problems, we calculate the detectable levels for a planar distribution of elements. Assume that one monolayer of an impurity element replaces one 2 Å-wide atomic plane. For an X-ray probe diameter of 1 µm², 5000 atomic planes end-on would be irradiated by the beam. Since one of the atomic planes out of 5000 consists of impurity atoms, the concentration of the impurity is 2×10^{-4} gg⁻¹ in the volume irradiated by the probe. This assumes that none of the impurity exists outside the boundary. Since the MDMF is 10.5×10^{-9} gg⁻¹ s⁻¹, then the detection of 5×10^{-5} of a monolayer s⁻¹ of impurity is feasible. However, in most materials we expect some of the impurity to be distributed in the matrix. Typical elemental concentrations of 2×10^{-3} to 10^{-4} gg⁻¹ are used to affect grain-boundary behavior. Plotted in Fig. 4 are the calculated profiles of X-ray-probe scans for an iron sample containing 0.1 wt % titanium uniformly distributed in the matrix and with one monolayer of titanium in the grain boundary. The shape and size of the microprobe beam can be defined by pinhole apertures to

Fig. 4. Calculated fluorescent intensity profile for an X-ray microprobe scan over a grain boundary containing a monolayer of titanium when the iron matrix contains 0.1 wt % titanium (after Ref. 5).

better match the geometry of the interface to improve the contrast and lower the detectable limit. For this case of titanium in iron where 0.1 wt % of the same impurity is in the matrix, the minimum detectable impurity with the plane of the grain boundary parallel to the direction of the probe (end on) is 5×10^{-3} of a monolayer for both the $1 \mu\text{m}^2$ and $500 \text{ \AA}^2$ probes. As predicted by Eq. (1) a decrease in the probe diameter does not change the detectable limits for a line distribution since the signal decreases linearly and the background decreases as the square of the probe size. If the region next to the boundary is denuded of the impurity, then the smaller probe size has the advantage of better providing the spatial resolution to determine that information. The rectangular-shaped probe has a detectable limit of 6×10^{-6} of a monolayer in the presence of 0.1 wt % in the matrix. Typical experience with advanced analytical electron probes is that 0.1 monolayer of impurity at a boundary is at the detection limit [13]. For typical surface sensitive electron excited Auger spectroscopy the detection limit is about 0.01 of a monolayer [5].

DIFFRACTION AND EXAFS ANALYSIS

X rays also have some advantages over electrons when used for diffraction. Diffraction measurements provide important information such as the crystal structure, compound identification, and how the geometrical arrangements of the atoms deviate from perfect periodicity. For the same number of 10 keV X rays or electrons impinging on a metal sample, the X rays are approximately 200 times more likely than electrons to undergo a useful elastic-scattering event. Electrons are most likely to lose energy by straggling energy-loss processes adding to the unwanted background unless removed by energy-analysis spectrometers. Electrons are also more likely to undergo multiple-scattering events in thick foils which complicate the interpretation of the measured diffraction pattern [14]. X-ray microprobes permit the use of thicker samples reducing the problem of defect migration to interfaces and strain relief which can be a problem in thin samples.

With the criteria expressed in Eq. (1), the MDMF by diffraction with a μm^2 X-ray probe in 1 s is:

10^{-2} of a monolayer, 1.6×10^3 atoms in a particle, and 28-Å-diam particle.

This is a conservative estimate, since an experiment with less flux but for the favorable case of a monolayer of lead deposited on the surface of a copper single crystal produced a minimum detectable coverage of approximately 10^{-3} of a monolayer from the observed 5×10^6 signal counts s^{-1} with a signal to background of 500:1 [15]. For amorphous materials, the diffuse scattering from only six monolayers of matter could be measured with a $1 \mu\text{m}$ -diam probe. Recent X-ray diffuse-scattering measurements from thin amorphous layers convinced those authors to predict that analysis of 100 Å films is feasible even at intensities 10^{-3} of those proposed for the microprobe [16].

Among the most prominent applications of synchrotron radiation in the X-ray-energy region is the measurement of the extended X-ray absorption fine structure (EXAFS) [17]. Such measurements permit the determination of the average number of near-neighboring atoms and average bond distances about a central atom whose absorption edge is scanned by changing the X-ray energy. The ability to determine the chemical environment of a particular element at low concentrations has resulted in major contributions to our understanding of the role of minor elements in matter [18]. The projected 3×10^{10} photons s^{-1} (eV) $^{-1}$ for a 500 Å-diam probe would extend the ability to make EXAFS measurements on extremely small quantities of matter containing minor elements at concentrations as low as 100 ppb.

MICROPROBE RESULTS

The earliest application of synchrotron radiation to microprobe measurements was by Horowitz and Howell in about 1971 [19]. They achieved $2 \mu\text{m}$ resolution and rastered samples in front of the beam but reported no detectable limits. This work was followed in 1977 with a quantitative analysis of the detection limits for a probe area of 0.45 mm^2 containing 2×10^{11} X rays s^{-1} of 37 keV energy from the SPEAR storage ring at the Stanford Synchrotron Radiation Laboratory [20]. The detectable limit in one second was found to be 10^{10} atoms of cadmium though the solid state detector energy resolution was sacrificed (450 eV at 39.2 keV) to achieve high counting rates.

More recent developments in X-ray optics and improved storage ring brightness have resulted in beam dimensions of $10 \mu\text{m} \times 10 \mu\text{m}$ containing fluxes of 3×10^9 X rays s^{-1} of 10 keV energy [9,21]. Fluorescent detection limits of 2×10^{-15} g in 60-s counting times were reported. An example of this work is shown in Fig. 5 where the elemental variation along a blue-green algae strand is plotted.

In a microprobe experiment where the beam was formed by a $25 \mu\text{m}$ -diam pinhole placed at the focus of an optical system with a magnification of unity, a flux of 10^7 X rays s^{-1} at 8 keV were obtained [22]. This $25 \mu\text{m}$ -diam collimated X-ray beam was used to measure the Bragg diffraction from a

Fig. 5. Energy spectra as a function of position obtained at $10\text{-}\mu\text{m}$ intervals along a filament of blue-green algae. The variation of iron along the filament is highlighted (after Ref. 21).

niobium single crystal in the vicinity of a niobium hydride precipitate. X-ray rocking angle measurements were made to measure the tilt of the niobium crystal planes caused by the growth of the niobium hydride particle. The data are shown in Fig. 6 where the rocking curves are plotted as a function of position, Z, as the beam is stepped over the embedded particle. From data such as these and measurements of the Bragg positions, strain distributions can be determined. Sufficient X-ray flux is available from this simple optical arrangement for Bragg diffraction with beams as small as $0.5\text{ }\mu\text{m}$ in diameter since single crystal diffraction is an efficient process reflecting between 0.1 and 10% of the incident flux. With undulator sources on low emittance storage rings, detection by Bragg diffraction will be possible for single particles of matter no larger than about $30\text{ }\text{\AA}$ in diameter.

Fig. 6. X-ray diffraction rocking curves taken at 0.2-mm intervals show how the niobium crystal lattice is tilted in the vicinity of a NbH particle. Note also that the rocking curves broaden as the particle is approached (after Ref. 22).

With similar pinhole X-ray optics, X-ray tomography was performed on the abdomen of a bee. Iron fluorescence excited by 9 keV X rays collimated to a $150\text{ }\mu\text{m}$ -diam beam was used to map the iron distribution throughout a transverse cross section of the abdomen [23]. Such a tomograph is shown in Fig. 7 where the change in the iron fluorescent intensity is depicted by the vertical scale. X-ray tomography with submicron beams will have many applications in biological, polymer, and ceramic type materials.

Fig. 7. Iron distribution in the circular cross section of the abdomen of a bee. Some internal organs are found to contain high concentrations of iron. The outer ring depicts the smaller concentrations found in the body wall (after Ref. 23).

CONCLUSION

Though the application of X-ray microprobe analysis is still in its infancy, the scientific promise is so appealing that high brilliance X-ray sources will be forthcoming. Table II compares some of the properties of X rays with those from electrons for the case of fluorescence. It takes little imagination to recognize the revolutionary impact on materials science that will arise when detection limits at surfaces, interfaces, and in bulk are reduced by 10^3 or more. As segregation of elements to defects is the rule, mapping their segregation behavior is essential to understanding their role on the physical and chemical properties of matter.

Though fluorescence detection has been emphasized here, compound identification by Bragg scattering, strain mapping about crack fronts, determining the structure of grain boundaries, and a host of other applications are obvious [5]. An X-ray fluorescent, diffraction, and EXAFS microprobe that can operate in environments such as air, moisture, or through millimeter thick water films opens the door to much new scientific progress. A scanning photoelectron microscope is being proposed in which the spot size on the sample will be diffraction limited to about 250 Å in diameter [24].

Table II. Comparison of the characteristics of an X-ray fluorescent microprobe on proposed low emittance storage rings with those of the most advanced electron microprobes for fluorescent chemical analysis on thick samples (after Ref. 5).

Characteristics	X rays	Electrons
Minimum detectable mass fraction s^{-1} for 1 μm -diam probe	0.01 ppm	50 ppm
Minimum detectable mass s^{-1} for 500 Å probe	250 atoms	10,000 atoms
Minimum spatial resolution (samples $\geq 1 \mu\text{m}$ thick)	~ 500 Å	10^3 to 10^4 Å
Minimum spatial resolution (samples 100 Å to 2000 Å thick)	~ 500 Å	10 to 500 Å
Number of electrons and X rays for the same MDMF	1	10^3
Number of energy units deposited in thick targets for same MDMF	1	10^3 to 10^4
Operating atmosphere	air, gas, water, vapors	vacuum
Relative signal to background (contrast)	10^4	1
Accuracy for quantitative analysis { similar standards pure element standards	$\sim 1\%$ $\sim 5\%$	$\sim 5\%$ $\sim 10\%$
Relative fluorescent cross section	10 to 200	1
Relative thick-target fluorescent yields	10 to 150	1
Charge collection on electrically insulating samples	negligible	must be coated with conducting film

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