

June 3, 1988

To be published in the Proceedings of the XXIII School on Physics, Zakopane, Poland April 16-30, 1988.

BNL-41371

CONF-8804154--

Roles of Scattered Radiation in SRIXE

A.L. Hanson

Brookhaven National Laboratory, Upton, New York 11973, USA

BNL--41371

DE88 012140

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Research supported by the Processes and Techniques Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy, Contract No. DE-AC02-76CH00016 and by the US National Institutes of Health as a National Biotechnology Resource Center under Grant RR01838-02.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Roles of Scattered Radiation in SRIXE

A.L. Hanson

Brookhaven National Laboratory, Upton, New York 11973, USA

Scattering Processes

Synchrotron Radiation Induced X-Ray Emission (SRIXE) is an analytical technique for trace element measurements^(1,2,3,4,5,6,7). In short it is x-ray fluorescence with electron storage ring generated x rays (i.e. synchrotron radiation). When used for fluorescence, synchrotron radiation has many advantages over tube generated x rays. The advantages of synchrotron radiation include extremely high intensity and high degree of polarization of the x rays. The polarization properties of the x rays can be utilized to reduce the amount of x rays scattered into the detector therefore reducing the background in the spectra.

The energies of x rays that we deal with in SRIXE are in the keV and tens of keV range. Therefore only x-ray interactions with atomic electrons need to be considered in this work. When an x ray in the keV range interacts with an atom it can remove an electron, i.e. the photoelectric effect, or it can scatter. Scattering is either a coherent or an incoherent event. Coherent scattering can only result in a change of direction of the photon, that is scattering without a change of either the phase or energy of the photon. Hence, the coherent scattering is necessary for x-ray diffraction. The incoherent scattering results in a change of phase of the photon and, in this energy range, a measureable energy shift. Incoherently scattered x rays cannot result in x-ray diffraction. Since the scattering of x rays is a major source of background in SRIXE spectra, the scattering affects the minimum detectable limits (MDL's) available with the technique. Understanding the scattering processes and how far the scattering can be reduced is important. Since we will always have some level of scattered radiation, it is important to consider whether the scattered radiation can be utilized for some aspect of the analyses. In many SRIXE applications, especially those biological in nature, the thickness and mass of the samples are small so there is little attenuation of the x-ray beam. Therefore fluctuations in the thickness need to be accounted for. It is proposed to use the intensity of scattered radiation for this purpose.

As an example, a typical measurement made at our SRIXE beam line (X-26) at the U.S. National Synchrotron Light Source at BNL with unfocussed "white" radiation (that is no monochromation of the x rays) 20 meters from the storage ring uses an apertured beam between $50 \times 50 \mu\text{m}$ to $250 \times 250 \mu\text{m}$. Biological samples are usually sectioned to thicknesses between 10 and $30 \mu\text{m}$. Such thin sections pose problems for normalization of fluorescent peak areas since regional and sample to sample fluctuations in sample thickness may be significant with respect to the nominal thickness of the samples. If the attenuation is small, scattered radiation can be used to monitor the fluctuations in thickness since the number of scattered photons is proportional to the number of incident x rays and the number of electrons in the sample within the beam spot.

One of the assets of synchrotron radiation is that it has an inherently high degree of linear polarization in the plane of the electron orbit. This simply means that there is a net alignment of the electric field vectors in a particular direction. If the electron beam in the storage ring would be a line source then the x rays would theoretically have 100%

of their electric field vectors in the plane of the electron orbit. The terms "parallel" and "perpendicular" are actually determined by placement of a detector with respect to the net polarization of the photon beam. For synchrotron radiation the "parallel" direction is defined to be when a detector is placed in the plane of polarization. The "perpendicular" direction is 90° out of this plane. By placing the detector in the plane of polarization the amount of radiation scattered into the detector can be greatly reduced. For linearly polarized x rays, the basic equation ruling this behavior is:

$$\frac{d\sigma}{d\Omega} \propto \cos^2 \alpha \quad (1)$$

where $\cos(\alpha)$ is the scalar product between the electric field vectors of the incident and scattered x rays. For parallel scattering α is equal to the scattering angle so $\frac{d\sigma}{d\Omega} = 0$ directly into 90° . For perpendicular scattering α is always 0° so the scattering is isotropic. Since we can assume the photons are linearly polarized, the effective cross section is simply a sum of (1) the cross section for "parallel" scattering weighted by the fraction of electric field vectors projected onto the "parallel" plane, and (2) the cross section for "perpendicular" scattering weighted by the fraction of electric field vectors projected onto the "perpendicular" plane.

The coherent scattering of x rays by free electrons is known as Thomson scattering and the differential cross section is given by:

$$\frac{d\sigma}{d\Omega}_{Th} = r_o^2 \cos^2 \alpha \quad (2)$$

Where r_o^2 is the classical radius of the electron. The bound electron counterpart to Thomson scattering is known as Rayleigh scattering and its cross section is given by the atomic form factor approximation:

$$\frac{d\sigma}{d\Omega}_R = f(q, Z)^2 r_o^2 \cos^2 \alpha \quad (3)$$

where f is the atomic form factor, q is the momentum transfer, $q = \frac{\sin(\frac{\theta}{2})}{\lambda}$, θ is the scattering angle, and Z is the atomic number of the target. The true definition of f is:

$$f^2 = \frac{\frac{d\sigma}{d\Omega}_R}{\frac{d\sigma}{d\Omega}_{Th}} \quad (4)$$

Tables of $f(q, Z)$ are generated from wave functions of the atomic electrons. When $q = 0$, $f = Z$, and for large values of q , f approaches 0. Therefore the coherent scattering is strongly forward peaked and becomes more so as the energy of the photon increases. Since the differential Rayleigh cross section for 100% parallel polarized photons is 0 directly into 90° , we can always improve our peak to Rayleigh scattering ratio as the detector aperture is reduced. This is because the fluorescence radiation is isotropic and therefore is proportional to the solid angle.

The incoherent scattering of x rays by free electrons is known as Compton scattering. The cross section can be given by the Klein-Nishina formula:

$$\frac{d\sigma}{d\Omega}_{KN} = \frac{r_o^2}{4} \left(\frac{K}{K_o} \right)^2 \left[\frac{K}{K_o} + \frac{K_o}{K} + 4\cos^2 \alpha - 2 \right] \quad (5)$$

$$\frac{K}{K_0} = \frac{1}{1 + \frac{E_0}{m_0 c^2} (1 - \cos \theta)} \quad (6)$$

The Klein-Nishina formula is a modification of the Thomson formula. In the low energy limit:

$$\frac{d\sigma(E=0)}{d\Omega}{}_{KN} = \frac{d\sigma}{d\Omega}{}_{Th} \quad (7)$$

The terms $[\frac{K}{K_0} + \frac{K_0}{K} + -2]$ are sometimes known as the "depolarization terms" since they are independent of the polarization of the incident photons and result in a portion of the scattered x rays being unpolarized. Because of these depolarization terms, the Klein-Nishina differential cross section, unlike the differential Thomson cross section, is not equal to zero directly into 90° . This means that in contrast to Rayleigh scattering, we will eventually reach a limit in the improvement of the peak to background ratio as the detector aperture is reduced. From equation (6) it can be seen that $\frac{K}{K_0}$ is a slowly varying function of energy, and decreases with energy. However, the sum of the depolarization terms increases as the square of the photon energy. The bound electron counterpart is sometimes known as "Compton" scattering, "atomic Compton" scattering, "inelastic" scattering and "incoherent" scattering. This cross section is given by the incoherent scattering function approximation, which is the Klein-Nishina cross section modified by the incoherent scattering function $S(q,Z)$:

$$\frac{d\sigma}{d\Omega}{}_{aC} = S(q,Z) \frac{d\sigma}{d\Omega}{}_{KN} \quad (8)$$

When the energy and momentum transfer is too small to excite an atom, the scattering can only be coherent. When the energy and momentum transfer becomes large enough to remove the electron, or move it to a more loosely bound state, the scattering becomes more incoherent. Therefore the Rayleigh and atomic Compton scattering processes are competitive processes. In calculating $S(q,Z)$, the first order approximation is:

$$S = Z - \frac{f^2}{Z} \quad (9)$$

The properties of S are such that S approaches 0 for small values of q and approaches Z for large values of q . Tabulations of f and S can be found in references (8) and (9).

The main problem with this approach is that we have claimed that for any given Z , the only variable needed to describe changes in f and S is the momentum transfer q . This assumption is not valid in the vicinity of absorption edges and the errors introduced can be large. The coherent scattering of x rays when the energy of the incident x ray is in the vicinity of absorption edges is many times referred to as anomalous scattering^(10,11). The problems of scattering when the energy is near an absorption edge also affects the incoherent cross section.

One virtue of using synchrotron radiation for fluorescence is that the intensity of the radiation is high enough that the radiation can be monochromated and still have useable intensities of radiation. Therefore if we are analyzing a matrix which has major or minor concentrations of elements that can be fluoresced, we can eliminate the characteristic radiation of the major/minor element by tuning the monochromator to an energy just below the

absorption edge of that element. In this case, the photoelectric effect is not energetically possible. However, the x ray can excite the electron into an unfilled bound state. We have now created an excited neutral atom as opposed to an ion excited with an inner shell vacancy. This results in an electronic transition that is the same as we observe in the photoelectric effect, however, the energy of the photon is different due shifting of the electronic energy states of the target atoms. This process is known as resonant Raman scattering. The x rays emitted from this process are shifted to lower energies and have an apparently broad peaks. The cross section for this scattering is large, larger than the Rayleigh or atomic Compton cross section^(12,13).

As was discussed before, the scattered radiation can be greatly reduced by placement of the detector at 90° to the x-ray beam in the plane of the electron orbit. Since the scattering cross section is rapidly changing about zero with scattering angle in that plane, the approximation, $\frac{d\sigma}{d\Omega}$, for the total cross section for scattering into a finite sized detector aperture, is not valid. Therefore the cross section must be integrated over the solid angle of the detector. The Rayleigh scattering cross section, integrated over the solid angle of a circular aperture has been shown to be⁽¹⁴⁾:

$$\sigma_R = \pi r_o^2 f^2 \left[(1 - H^2) \left(\frac{4}{3} - \frac{\cos^3 t}{3} - \cos t \right) + 2H^2 \left(\frac{2}{3} + \frac{\cos^3 t}{3} - \cos t \right) \right] \quad (10)$$

where $t = \arctan(r/R)$, the detector aspect ratio, $r =$ radius of the aperture, and $R =$ distance from the point of scatter to the aperture. The function H^2 is determined by the placement of the detector with respect to the point of scatter and with respect to the plane of polarization:

$$1 - H^2 = 1 - \sin^2 \theta^* \cos^2 \psi^*$$

The angle θ^* is the scattering angle and the angle ψ^* includes the polarization of the x rays and includes the placement of the detector with respect to the reference plane of polarization.

As was illustrated in ref. (14), the integration of the atomic Compton cross section over solid angle is not so easy since the integration is greatly hampered by the $(\frac{K}{K_o})$ terms. However if we make the approximation that $(\frac{K}{K_o})$ is a slowly varying function of angle, then we can treat it as a constant with respect to the integration. In this case the atomic Compton cross section can be approximated with⁽¹⁵⁾:

$$\sigma_{aC} = r_o^2 S(q, Z) (eqn(12) + eqn(13)) \quad (11)$$

$$\pi(1 - \cos t) \left(\frac{K}{K_o} \right)^2 \left(\frac{K}{K_o} + \frac{K_o}{K} - 2 \right) \quad (12)$$

$$\pi \left(\frac{K}{K_o} \right)^2 \left[(1 - H^2) \left(\frac{4}{3} - \frac{\cos^3 t}{3} - \cos t \right) + 2H^2 \left(\frac{2}{3} + \frac{\cos^3 t}{3} - \cos t \right) \right] \quad (13)$$

Using Scattered Radiation for Normalization

SRIXE measurements of trace elements do not determine elemental concentrations but rather the number of atoms of a given element within the beam. In order to convert from the number of atoms to concentration we must determine the total number of atoms in the sample within the beam. This must be done either by calculating the number of atoms on an absolute basis by or comparing to an appropriate standard. Since the amount of scattered radiation is proportional to the number of electrons irradiated by the x-ray beam, measuring the scattered radiation can be used to determine the actual sample mass in the beam (thickness) or to monitor the fluctuations in the mass (thickness). Now we must consider some of the pitfalls involved with attempting to measure and use the measurements of the scattered radiation.

If we try to calculate the total number of atoms within the photon beam we must rely on a measurement of both the amount of scattered radiation and the number of photons that struck the target. For our particular beam line, the x-ray beam intensity is monitored with a helium filled ionization chamber from which only current is measured. Helium is used because it is the only gas that is linear with the beam intensity in this intensity region. While ionization chambers are useful as relative intensity monitors it is very difficult to extract exact white light "intensities" from them since white light implies a broad energy spectrum of the photons. First problem is, each energy photon interacts differently with the gas in the ionization chamber and we only measure a current from the chamber, but not a spectrum. Second, helium itself is problematic since small amounts of contaminating gases can provide contributions to the current signals that are significant compared to the contributions from the helium itself. Third, we do not know the energy distribution of photons in the ionization chamber, even if the theoretical calculations of the x ray emission from the electron beam are exact. The photons in our beam line pass through two beryllium windows of 250 μm nominal thickness. These windows, which are common in x-ray synchrotron radiation work, separate the experimental vacuum system from the storage ring vacuum system. These windows help protect our experimental system from what is happening on the other side of the shielding wall. The uncertainty in the thickness of the beryllium windows are 10%. The current from the ionization chamber is proportional to the integral of the energy distribution weighted by the cross section for the photoelectric effect and the incoherent scattering cross section. The photoelectric cross section is highest where the uncertainty in the intensity, due to the uncertainty in the thickness (and oxidation) of the beryllium windows, is highest. This aspect alone results in uncertainties in the absolute "intensity" of at least 20%. Fourth, the accuracy of the absolute scattering cross sections (for scattering by the target) need to be questioned. There is no "rule of thumb" as to a general level of accuracy of the cross sections since there is energy, angle, and Z dependence on the cross sections. The estimates of accuracy range from less than 1% to sometimes as high as 30%. The particular tables of scattering functions give estimates of expected accuracies of the tables for several energy and Z ranges. Fifth, in order to determine the scattering cross section we must assume both a major and minor element composition of the target and the polarization of the x-ray beam.

From these arguments we must conclude that the errors in absolute calculations of the number of atoms within our (white light) beam would be much larger than what would be acceptable for normalization. Therefore normalization to scattered radiation should be on a relative or comparative basis.

With equations 10 and 11 we can assess errors from our knowledge of the absolute polarization (δP about P) and absolute placement of our detector ($\delta\theta^*$ about θ^* and $\delta\psi^*$ about ψ^*)⁽¹⁶⁾. One significant source of error is from our knowledge of the polarization of the x-ray beam. If the x-ray beam has a polarization of $98\% \pm 1\%$ then the uncertainty in measuring the scattered radiation at 90° is 50%, just from the uncertainty in the polarization. This is because the scattering is totally dominated by the perpendicular component of the x rays. The total scattering cross section is determined by $(0.02 \pm 0.01)\sigma_\perp$. Even if the beam is 95% polarized a 1% uncertainty in knowing the polarization results in a 20% uncertainty in the measurement of the scattered radiation. Therefore measurement of the scattered radiation should not be made with the same detector that the fluorescence radiation is measured with.

Measuring scattered radiation at forward angles is a measurement of the coherently scattered radiation. Measurement of coherently scattered radiation from organic materials in the forward direction should be avoided since there are problems with diffraction effects⁽¹⁷⁾. For normalization purposes the incoherently scattered radiation should be measured at backward angles in order to achieve the lowest level of errors⁽¹⁸⁾.

Conclusions

The scattering of x rays is the major source of background and hence is a limiting factor in the minimum detectable limits available with SRIXE measurements. The scattering can be utilized for normalizing the net peak areas to fluctuations in sample thickness or mass on a relative basis or on a comparative basis. Even then measurement of the scattered x rays should be made at backward angles. Measurement at forward angles should be avoided because of diffraction problems. The uncertainties in the measurement of an absolute "intensity" of the x rays can be extremely large.

Acknowledgements

The author would like to thank M. Meron, J. Pounds, and B. Johnson for commenting on the manuscript. Research supported by the Processes and Techniques Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy, Contract No. DE-AC02-76CH00016 and by the US National Institutes of Health as a National Biotechnology Resource Center under Grant RR01838-02.

References

1. J.R. Chen, E.C.T. Chao, J.A. Minkin, J.M. Back, W.C. Bagby, M.L. Rivers, S.R. Sutton, A.L. Hanson, and K.W. Jones, "Determination of the Occurrence of Gold in an Unoxidized Carlin-type Ore Sample Using Synchrotron Radiation", NIM B22 (1987) 394-400.
2. A.L. Hanson, H.W. Kraner, K.W. Jones, B.M. Gordon, R.E. Mills and J.R. Chen, "Trace Element Measurements with Synchrotron Radiation", IEEE Trans. Nucl. Sci. NS-30 (1983), 1339-1342.
3. A.L. Hanson, K.W. Jones, B.M. Gordon, J.G. Pounds, W.M. Kwiatek, G.J. Long, M.L. Rivers, and S.R. Sutton, "Trace Element Measurements Using White Synchrotron Radiation", NIM B24/25 (1987) 400-404.
4. J.M. Jaklevic, R.D. Giaque, and A.C. Thompson, "Quantitative X-Ray Fluorescence Analysis Using Monochromatic Synchrotron Radiation", NIM B10/11 (1985) 303-308.
5. A. Iida, A. Yoshinaga, K. Sakurai, and Y. Goshi, "Synchrotron Radiation Excited X-Ray Fluorescence Analysis Using Total Reflection of X-Rays", Anal. Chem. 58 (1986) 394-397
6. P. Ketelsen, A. Knochel, and W. Petersen, "Synchrotron Radiation Excited X-Ray Fluorescence Analysis Using a Graphite Monochromator", F.Z. Anal. Chem. 323 (1986) 807-810.
7. S.R. Sutton, M.L. Rivers, and J.V. Smith, "Applications of Synchrotron X-Ray Fluorescence to Extraterrestrial Materials", NIM B24/25 (1987) 405-409.
8. J.H. Hubbell, Wm.J. Veigele, E.A. Briggs, R.T. Brown, D.T. Cromer and R.J. Howerton, "Atomic Form Factors, Incoherent Scattering Functions and Photon Scattering Cross Sections", J. Phys. Chem. Ref. Data 4 (1975) 471.
9. J.H. Hubbell and I. Øverbø, "Relativistic Atomic Form Factors and Photon Coherent Scattering Cross Sections", J. Phys. Chem. Ref. Data 8 (1979) 69.
10. G. Basavaraju, Lynn Kissel, John. C. Parker, R.H. Pratt, S.C. Roy, and S.K. Sen Gupta, "Rayleigh Scattering by Atomic Ions of Low Nuclear Charge", Phys.Rev.34 (1986) 1905.
11. P.P. Kane, L. Kissell, R.H. Pratt and S.C. Roy, "Elastic Scattering of γ -Rays and X-Rays by Atoms", Physics Reports 140 (1986) 75-159.
12. J.M. Jaklevic, R.D. Giaque, and A.C. Thompson, "Resonant Raman Scattering as a Source of Increased Background in Synchrotron Excited X-Ray Fluorescence", Anal. Chem., 60 (1988) 482-484.
13. C.J. Sparks, Jr., "Inelastic Resonance Emission of X Rays: Anomalous Scattering Associated with Anomalous Dispersion", PRL 33 (1974) 262-264.
14. A.L. Hanson, "The Calculation of Coherent and Incoherent Scattering Cross Sections for Polarized X-Rays into an Arbitrarily Placed Circular Aperture", NIM A264 (1988) 471-483.
15. A.L. Hanson, "An Easy and Accurate Approximation to the Integrated Compton Cross Section for the Scattering of Polarized X-Rays into an Arbitrarily Placed Circular Aperture", NIM A264 (1988) 484-487.
16. A.L. Hanson, and M. Meron, "Errors Associated with the Measurement of Scattered Polarized X Rays", NIM A264 (1988) 484-487.
17. J. Kosanetzky, B. Knoerr, G. Harding, and U. Neitzel, "X-Ray Diffraction Measurements of Some Plastic Materials and Body Tissues", Med. Phys. 14 (1987) 526-531.