TRACE ELEMENT MEASUREMENTS USING WHITE SYNCHROTRON RADIATION


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Synchrotron radiation, when used for X-ray fluorescence (XRF) has several advantages over conventional X-ray sources. Our group at Brookhaven National Laboratory is developing the equipment and expertise to make XRF measurements with synchrotron radiation. The apparatus is briefly described, along with the alignment techniques. Some minimum detectable limits for trace elements in thin biological standards measured with white light irradiations are presented.

1. Introduction

We are presently developing and using beam line X-26C at the National Synchrotron Light Source (NSLS) for X-ray fluorescence measurements using synchrotron radiation (referred to as SRIXE for synchrotron radiation induced X-ray emission). Monochromation and focussing capabilities are also being developed for this beam line and for X-26A, a beam line which will be dedicated for X-ray microprobe fluorescence [1]. However, since we are presently using white light radiation for our measurements the emphasis of this paper will be on this aspect of the technique.

The advantages of using synchrotron radiation for X-ray fluorescence have been discussed in depth in previous publications [2-11]. Briefly, electron synchrotron storage rings emit X-rays at brightnesses several orders of magnitude greater than conventional X-ray sources. This many-fold increase in intensity means that not only can we analyze samples faster, but we can, and many times are required to, analyze structures of the samples that are physically smaller than structures that can be analyzed with conventional X-ray fluorescence (XRF). In addition, the higher intensities of photons allows for monochromation of the beams while still maintaining usable fluxes. The intensity attribute is complemented by low beam divergences, so the X-ray beam can be brought over distances of meters while maintaining integrity of the beam. This brilliance makes focussing the beam feasible. Another attribute of particular importance is the high degree of polarization of the photon beam in the plane of the electron orbit. By placing a detector at 90° to the direction of incidence, in the plane of the electron orbit, the number of X-rays scattered into the detector can be minimized [12,13].

2. Experimental apparatus

A schematic of the experimental apparatus is illustrated in fig. 1. The photon beam passes through a 20 m UHV beam pipe, containing two 250 μm thick Be windows. The beam size is defined with 0.8 mm thick Ta slits mounted on four stepper-motor driven linear feedthroughs. After the beam is apertured, it passes through a helium filled ion chamber which provides the normalization of the fluorescence spectra to the incident number of photons. The (parallel) plates of this ion chamber are 8 cm in length. Filtering of the incident photon beam occurs after the ion chamber. Samples are mounted nominally at 45° to the beam on a stepper-motor driven stage assembly equipped with X, Y, Z and θ motion. This stage has 1 μm size steps in the X, Y, Z directions. The X-rays are counted with a 3 mm thick Si(Li) detector (145 eV resolution at 5.9 keV) placed at 90° to the beam. The data are
acquired with a LeCroy 3500 analyzer which is controlled by a DEC microVAX II computer. Data is transferred directly to the microVAX II from the LeCroy. All of the stepping motors are likewise driven with the microVAX II.

3. Alignment procedures

Because of the low divergence and high natural collimation of the photon beam, at 20 m from the source most of the beam is confined within 5 mm either side of the plane of the electron orbit (the vertical direction which is described with the angle $\psi$). From a line source all of the photons will be 100% polarized (electric field vectors in the plane of the electron orbit) in the mid-plane. This is illustrated in fig. 2, which shows plots of the parallel, perpendicular, and total number of photons emitted into the vertical opening angle $\Delta\psi$ about the center line of the beam for several energies. These curves were calculated assuming a line source for the electron beam and integrating over increments in $\Delta\psi$ of 0.004 mrad. Fig. 2 illustrates gradients, in vertical displacement for both intensity and relative polarization. Therefore, in order to maintain the maximum intensities of fluorescent peaks and minimum scattering, the alignment between the beam, target and detector is important. For realistic sources the electron beam will be larger than a line (for the NSLS $4\sigma$ is on
the order of 0.5 mm) so the best polarization will be on the order of 98%.

Alignment is a two step process. The first step is to establish the center of the beam. There are two procedures that we regularly use. The first procedure is to set an SCA window about a high energy X-ray (> 20 keV) and slowly move a small particle producing the desired X-ray through the beam while performing an MCS scan. This scan provides a vertical map of the beam flux integrated in energy over the fluorescence cross sections. Typical scans using gold, palladium and iodine are shown in fig. 3. As can be seen from these scans, the spectral maps made with the higher energy photons are narrower than the maps made with the lower energy photons. This is, of course, due to the smaller opening angles for the higher energy X-rays as illustrated in figure 2. These scans show raw data, and if the backgrounds were subtracted, the shapes from the spectral maps would become more apparent. The abrupt cutoffs are from fixed apertures upstream of the apparatus. The second, and simpler, procedure uses the peak to background ratio of the palladium Kα peak in a fluorescence spectrum from a synthetic pyrrhotite (FeS) sample doped with 1000 ppm palladium. If the peak to background ratio is above 10.5:1, we consider the alignment to be a "good" alignment. After the center of the beam is found, a general alignment of the appropriate angles between the orbit plane, detector, sample stage, and viewing system is established. For this general alignment we use diffraction spots of white light by a (111) oriented single crystal of silicon, as described by Sutton et al. [14]. The peak to background ratio of the palladium in pyrrhotite is checked to assure proper alignment of the beam has been maintained.

Table 1

<table>
<thead>
<tr>
<th>Identification</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Br</th>
<th>Sr</th>
<th>Cd</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gelatin</td>
<td>0.22</td>
<td>0.17</td>
<td>0.26</td>
<td>0.26</td>
<td>0.88</td>
<td>0.32</td>
<td>0.56</td>
<td>0.73</td>
<td>4.2</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NIES-CRM-5</td>
<td>0.8</td>
<td>0.17</td>
<td>0.25</td>
<td>0.26</td>
<td>0.88</td>
<td>0.32</td>
<td>0.56</td>
<td>0.73</td>
<td>4.2</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NIES-CRM-1</td>
<td>0.84</td>
<td>0.18</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.16</td>
<td>0.24</td>
<td>0.24</td>
<td>0.16</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Identification slits (μm x μm)</th>
<th>Target thickness</th>
<th>Beam filter (μm Al)</th>
<th>Detector filter (μm Kapton)</th>
<th>Detector aperture (mm)</th>
<th>Detector distance (mm)</th>
<th>Counting time (s, live)</th>
<th>Ion chamber (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gelatin 100 x 100</td>
<td>30 μm (wet)</td>
<td>100</td>
<td>50</td>
<td>3</td>
<td>40</td>
<td>300</td>
<td>1.7</td>
</tr>
<tr>
<td>NIES-CRM-5 50 x 50</td>
<td>0.25 mm</td>
<td>100</td>
<td>100</td>
<td>3</td>
<td>40</td>
<td>600</td>
<td>0.5</td>
</tr>
<tr>
<td>NIES-CRM-1 50 x 50</td>
<td>1 mm</td>
<td>200</td>
<td>32</td>
<td>3</td>
<td>40</td>
<td>1900</td>
<td>0.09</td>
</tr>
</tbody>
</table>

a) The MDLs are based on the wet weight which is 75% water. The MDLs for the dry weight will be 4 times higher.
4. MDLs

When using white light for X-ray fluorescence, the spectrum of the photon beam as it strikes the target is important since it not only fluoresces the target atoms, but the photon scatter reproduces the incident spectrum of the beam, shifted in energy by the Compton scattering. With white light it is often necessary to filter the incident beam with 25–600 μm aluminum. The purpose of using filters is to help reduce the amount of low energy scatter and some major (or minor) element fluorescence. This reduces the total count rate that the detector must process, while hopefully not significantly reducing the number of fluorescent X-rays of interest. Care must be taken in choosing appropriate filters since the effects of the filters are not only to reduce the number of scattered low energy photons, but also to reduce the number of photons at energies that most efficiently fluoresce the atoms of interest. Therefore we have a trade-off between a reduction in background and a loss of fluorescent X-rays. As long as the fluorescent yield does not fall off faster than the square of the scattered radiation under the peak, there will be a net improvement in the minimum detectable limits (MDLs).

We have prepared some thin organic standards by dissolving 10 ppm V, Fe, Zn, Pb, Br, Sr, and Cd in undialized gelatin (20% gelatin, J.T. Baker, 5% glycerol, 75% water). The samples were then sliced with a cryomicrotome to 30 μm thickness, mounted on 7 μm polyimide film, then freeze-dried. Fig. 4 shows spectra of the gelatin standard containing no overlapping peaks. The blank gelatin contains K, Ca, and about 1 ppm Fe, Ni, Zn and Sr. The measured MDLs for the spiked elements are shown in table 1. Also shown on this table are the measured MDLs from 0.5 mm thick, pressed NIES-CRM-1 Pepperbush and NIES-CRM-5 Hair Standards.

5. Discussion

The MDLs reported in table 1 include all the parameters that should be necessary to determine what is expected for a given (similar) measurement. Our experience to date is that the measurement many times determines the maximum beam spot size that will be used. A comparison with previously reported values for MDLs is not always easy since many of the parameters of the measurements were not included. Many variables affect the measurements, which include: (1) White light vs monochromated light. (With white light we increase the background from scattered radiation, and with monochromatic we reduce the number of X-rays available for fluorescense.) (2) When using monochromated light, what is the band pass (ΔE/E) of the monochromator, since the band pass limits the flux. (3) With monochromated light, what is the relation between the energy of the monochromated X-rays and the fluorescence edge of the element(s) of interest. Using energies at the absorption edges of the elements, the Compton scattered photons interfere many times with the fluorescent peaks increasing the background. The energy difference between the Compton scatter peak and the Rayleigh peak becomes more pronounced with higher photon energies, so the Compton scatter peak causes more interferences when measuring higher energy photons. (4) The size of
the beam spot. (5) With white light, the composition and thickness of the primary beam filter alters the incident spectra and therefore the spectra of the scattered radiation. (6) The composition and thickness of the matrix determine not only the background due to scatter, but thicker matrices can cause substantial attenuation of the fluorescent photons. (7) The total number of photons, and their spectra, that strike the sample determine not only the number of fluorescent events, but will also determine the number of scatter events.

The measurements of MDLs reported by Iida et al. [15] and Knöchel et al. [8,9] were made maintaining maximum intensity of photons into the detector. To achieve this they increased the beam aperture size as thicker filters were added. By reporting the results in this way MDLs expressed in ppm may be lowered, but when expressed in picograms the MDLs will go up. As an example Iida et al. measured metals on chelated resins and analyzed with 0 and 280 μm thick aluminum filters. For zinc they measured MDLs of 550 and 170 ppb for the two filters, respectively. However, to achieve this their irradiation area was increased from 0.35 × 10⁻² to 2.8 × 10⁻² mm². The MDL in absolute number of zinc atoms that can be fluoresced went from 0.13 to 0.34 pg. Knöchel et al. used filters between 0 and 8 mm thick aluminum. They did not mention the beam sizes used, but did mention that they increased the beam aperture size to account for the loss in beam intensity.

It is our suggestion that the field adopts reporting the experimental parameters listed in this paper when presenting data in order to make results more understandable to potential users.

References