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Application of Synchrotron Radiation to Elemental Analysis*

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The use of a synchrotron storage ring as a high brightness source for production of monoergic, variable energy, and highly polarized x-ray beams promises to revolutionize the field of elemental analysis. The results of exploratory work using the Cornell synchrotron facility, CHESS, will be described. Design considerations and features of the new X-Ray Microprobe Facility now under construction at the Brookhaven National Synchrotron Light Source will be presented. This facility will be used for bulk analysis and for microanalysis with an initial spatial resolution of the order of 30 μm .

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1. Introduction

Determination of the elemental composition of materials by x-ray fluorescence (XRF) techniques is a well established method. The development of synchrotron radiation x-ray sources capable of producing high intensity x-ray beams in the energy range from 1-20 keV now makes possible major improvements in the capabilities of the XRF method. The several distinctive features of the synchrotron source compared to ordinary x-ray tubes make it plausible to use a distinctive acronym for it, namely, SXRF, for synchrotron x-ray fluorescence.

Only a few experiments have been devoted to the topic to the present time. Sparks [1] has reviewed the situation and technique up to 1980 in a comprehensive way and has presented numerous examples of spectra obtained from diverse samples. Gentry et al. [2] have applied the technique in a search for superheavy elements. Experiments done at the Cornell High Energy Synchrotron Source (CHESS) have been reported by Hanson et al. [3], at the Daresbury Synchrotron Radiation Source (SRS) by Prins and Van der Heide [4], at the Stanford Synchrotron Radiation Laboratory by Gilfrich et al. [5,6] and at BESY by Knochel et al. [7]. At this conference there are comparisons with other methods of excitation [8], and results on the analysis of coal samples [9] are presented. Estimates of ultimate detection sensitivities have been given by Sparks [1] and by Gordon [10]. The use of the synchrotron source for a x-ray microprobe has been discussed by Sparks [1], Howells and Hastings [11], and by Prins and Kuiper [12]. It is now clear that the intensive use of synchrotron

radiation in the near future will have substantial impact on many aspects of trace element measurements.

In this paper results of experiments which bear on several aspects of SXRF will be presented. The design philosophy for a dedicated x-ray microbeam facility at Brookhaven National Synchrotron Light Source (NSLS) will also be considered.

2. Investigation of Radiation Damage Effects

Any probe which produces ionizing radiation damages the sample being investigated. The total number of photons which strike the sample when synchrotron radiation is used can be quite high. For example, the NSLS can easily produce a fluence of 10^{18} monochromatic photons/cm² in the course of an irradiation of a few hundred seconds. While some attention has been paid to radiation effects at lower fluence levels by Chance et al. [13], there has been no investigation of effects at the higher levels. In previous experiments [14,15] studies have been made on the effect of d, t, ³He and ⁴He bombardment on human blood cells. Sparks [1] has considered the situation and estimated that photons in the keV region should be less damaging by a factor of 10^{-4} than MeV protons when comparison is made for the same minimum detectable limit of included trace elements.

In this present experiment we have investigated the effect of white radiation from the CHESS facility on the morphology of human blood cells and several different types of tissues. The beam incident on the sample had passed through about 3 meters of helium at

atmospheric pressure, two Be windows each 508 μm thick, and 50.8 μm of Al and 10 cm of air. The energy spectrum of the radiation produced by CHESS and the total transmission of the four absorbers are shown in fig. 1. The resulting energy spectrum for the beam on the target is shown in fig. 2. The average photon energy for this spectrum is 15 keV.

The samples were air-dried red and white blood cells and various 30- μm thick microtomed tissue specimens mounted on glass microscope slides. Irradiations were made for periods up to 3.3×10^4 seconds. The photons were produced at an electron energy of about 5.27 GeV with average beam currents of about 6 mA. The total fluence of photons striking the samples could then be found by an integration of the spectrum shown in fig. 2. The intensity shown there is integrated over the entire vertical emission angle of the beam. In order to estimate the vertical intensity distribution, the approximate size of the source, 1 mm FWHM, was convoluted with a Gaussian of 1.9 mm FWHM calculated from the formalism of Green [16]. The resulting intensity distribution is shown in fig. 3. With this information the fluence on the sample can be calculated as a function of distance from the median plane. A careful examination of the samples was made with both optical and electron microscopes. The detailed results will be presented elsewhere [17]. As a summary of the experiment we show the damage to polymorphic leukocytes as a function of the photon fluence in fig. 4 as seen by SEM. Also included in the figure are comparable results for bombardment by 1.7-MeV protons [15]. It can be seen that,

in both cases, the ultimate course of damage is very similar, with the nucleus of the leukocyte more resistant to damage than the cytoplasm. It can be seen that the proton fluence is about a factor of 10^2 less than for photons for equivalent degrees of damage. This is consistent with the observation of Sparks cited above, when differences in x-ray production cross sections are taken into account. For leukocytes, at least, irradiations should be restricted to perhaps 10^{17} photons/cm² if excessive damage is to be avoided. This value of fluence can be easily obtained with the National Synchrotron Light Source, NSLS, and other high brightness machines, and hence, radiation damage effects should be considered in the design of experiments dealing with SXRF trace element measurements. The work reported here was done in a parasitic mode at CHESS. Further systematic exploration of the effects noted here would be useful.

It should be emphasized that these studies do not bear on the effect of synchrotron radiation in living cells, nor do they address the threshold observed by mass loss effects as noted by various EM investigators at which some trace element mobility may be suspected.

3. Trace Element Determinations

An investigation of various aspects of trace element determinations with synchrotron radiation was made with monochromatic radiation from the CHESS facility. The experimental arrangement was made as simple as possible for these first runs. The general idea was to ascertain the detection limits which could be obtained with a

Si(Li) detector at various photon energies and to obtain spectra for a variety of materials. A discussion of the results obtained for a set of coal samples is given elsewhere in these proceedings by Chen et al. [9]. An earlier account of this work has been given by Hanson et al. [3].

A channel cut Si crystal monochromator was used to obtain monochromatic radiation. A 254- μ m Be window was used to allow extraction of the photon beam into air. The beam size at the entrance to the hutch could be defined in horizontal and vertical directions by a set of adjustable x and y slits. The Si(Li) detector was 30 mm² in area placed at 90° to the incident beam 1.3 cm from the sample. The samples were mounted on a pair of stepper motor driven slides which gave control over the x - y positioning of the target. The storage ring generally operated at 5.27 GeV with initial currents of 15 mA. A collimator of Lucite was used to define the region of space viewed by the Si(Li) detector. The targets were viewed with an optical microscope and TV camera. The beam position was determined by scanning a copper knife edge past the beam and measuring the intensity of the Cu K_α line as a function of position. It was thus possible to measure the composition of heterogeneous samples, such as the coal, at particular points of interest.

The Si(Li) detector and its cryostat were about 55 cm in overall length and, when placed at 90° to the incident beam, could not be moved further than 1.3 cm from the beam because of the physical limitations of the hutch. This did not permit maximum advantage to be

taken of the beam polarization. The optimum geometry for the detector was determined by counting the number of Compton and elastic events produced by interactions with air in the photon path as a function of scattering angle and vertical displacement from the median plane of the monochromatic photon beam. Normalization was done relative to the Ar K x rays produced. The results as a function of scattering angle, θ , are shown in fig. 5. The expected parallel polarization for the beam is roughly 3%. This experiment measured the polarization since the number of scattered events at 90° is proportional to the number of photons, $N_\perp$, polarized perpendicular to the scattering plane and proportional to the Compton and elastic differential scattering cross sections. The total number of K x-ray events is proportional to the photoelectric cross section and to the total number of photons with polarizations both parallel and perpendicular to the scattering plane. The finite size of the solid angle subtended means some Compton and elastic scattering will occur from the parallel polarized portion of the photons. This scattering is proportional to $\cos \theta$. The results as a function of vertical displacement are shown in fig. 6. As shown in fig. 6, the percentage of perpendicularly polarized photons increases rapidly as a function of vertical displacement. It is important to position the detector carefully to take maximum advantage of the synchrotron radiation polarization since Compton and elastic scattering are a large component of the total detector counting rate and since incomplete charge collection gives background pulses at lower energies.

A spectrum obtained by Sparks et al. [1] for orchard leaves fluoresced by 37-keV photons is shown in fig. 7 and is to be contrasted with the spectrum obtained in the present work at 13.0 keV (fig. 8). The relative intensities of the various elements observed, iron for example, change markedly. Several elements, such as Pb, can be fluoresced at 37 keV, but not at 13 keV. Thus, by varying the photon energy carefully, elements can be excited selectively, and interferences, such as exist for As and Pb when observed with Si(Li) detectors, can be easily resolved.

The variation of MDL for trace elements in a thick sample of NBS orchard leaves, SRM 1571, as a function of atomic number, Z , has been shown by Hanson et al. [3] for several incident photon energies. In fig. 9 the minimum MDL obtained at various photon energies is shown as a function of Z . These are runs made for 300 sec with the conditions described above. This includes differences which arise from changes in the photon intensity as a function of beam current at different photon energies.

It is interesting to compare the results with those obtained with a standard XRF source which uses a tungsten tube for x-ray production. In this case a 30-KVCP voltage and electron current of 4 mA was used. The x rays were filtered with a 150- μ m Mo absorber (graded with Ni and Al) to produce a spectrum from 13 keV to 20 keV. In fig. 10 the results for XRF and SXRF at 24.9 keV are compared. It can be seen that the MDLs are comparable. However, run times for the

XRF work are longer by a factor of 24. The brightness of the SXRF is also much better so that smaller samples can be handled. The feature of good spatial resolution can be very useful and in fact is demonstrated in the measurements on coal samples done during the course of this work, which are reported by Chen et al. [9].

Several biological samples were also run. In this case total fluences used were far below those found to cause severe damage effects, as mentioned in Section 2. For this work 5×10^{11} photons/cm² was the maximum fluence used. Hence, it can be concluded that MDLs in the 100-ppb range can be easily obtained with Si(Li) detectors at low fluences. Increasing fluences and reducing spatial extent of the beam to permit the use of crystal spectrometers or to obtain better spatial resolution will make it necessary to consider damage effects in more detail. There appear to be no reasons to suspect that the calculated MDL values will not be attainable in the future with optimized experimental conditions.

4. Design of X-Ray Microprobe Facility at the NSLS

The design of new generation synchrotron storage rings, such as the National Synchrotron Light Source (NSLS) at Brookhaven, gives promise of x-ray sources of unique brightness. We have therefore begun a project to utilize the NSLS for a beam line devoted to x-ray microanalysis projects. A multifaceted research program is planned with work on (a) development of analytical techniques using synchrotron radiation; (b) several projects relating to the

geosciences, and (c) applications in biomedical areas such as nutrition, toxicology, and trace elements in the environment.

The NSLS x-ray ring is not yet operational, and for this reason a conservative, phased approach has been taken in the design stage. The x-ray ring has been designed for operation at 2.5 GeV with a critical wavelength, λ_c , of .25 nm. The design current is 500 mA, but during the initial commissioning stages we have assumed operating currents more like 10 mA. In our phased approach, the resolution sought during Phase I is roughly 30 μm , consistent with the x-ray fluxes available and limited by the design of a low scatter slit. When the operation gives fluxes nearer the design figures, Phase II with resolutions in the range from 1-10 μm will be provided. Phase III, to be accomplished some time in the future with new instrumentation and based on a wiggler source, would aim at obtaining resolutions below 1 μm .

The NSLS is well suited as an x-ray source for this type of application. Details of the machine parameters are given by Van Steenberg, et al. [18]. There are several important factors to emphasize. One factor is the range of x-ray energies that will be available. The NSLS has high fluxes at photon energies in excess of 16 keV even if only the standard arc source (bending magnet) is considered. It will be possible with this maximum energy to span the entire periodic table covering either K- or L-shell excitation. The use of a high field wiggler to increase the energy range would make it possible to use K-shell excitation over a wider span of elements for

less ambiguous identification. The most important factor for consideration in the performance of a microprobe is the brightness of the source. In this case the NSLS is, in principle, superior to other running storage rings, or those under construction. The caveat is, of course, that these specifications must still be demonstrated in practice.

The design of synchrotron microprobes proposed in the past have presented a variety of solutions to the problem. In our approach we have attempted an approach which separates functions as much as possible. This means that the first stage of the system is a monochromator followed by a focussing mirror. This is intended to produce an image of the source, of roughly $1500 \mu\text{m} \times 500 \mu\text{m}$, at a position in the experimental hutch where it will be available for experimental use. Because of the geometry of the system the mirror is chosen to give a demagnification, about a factor of 4, so that the image size becomes about $375 \times 125 \mu\text{m}^2$. A greater demagnification would be desirable, but hardware and space considerations may limit the useful value to roughly 4.

The monochromator to be used represents a balance of throughput and resolution. Use of the microprobe for chemical speciation measurements would require a monochromator capable of high energy resolution. However, the most important consideration for trace element measurements is to obtain high transmission with less severe requirements on resolution. For this reason a multilayer two-crystal monochromator with resolution, $\Delta E/E \approx .01$ to $.02$, and a peak

reflectivity around 65% will be used. Attention to the mechanical design of the monochromator will make it possible to interchange the multilayers to provide perfect crystals with high resolution, but a concomitant loss of throughput. Another important aspect of this monochromator will be the production of a spot with essentially a fixed spatial position as a function of photon energy. Power dissipation of the multilayer monochromator is believed adequate to provide stable operation of these surfaces. Further, it should be noted that focussing of a monochromatised beam considerably eases the power stress on the system optics. Since this will hold true for the image as well, a great convenience for the experimental apparatus will result. An ellipsoidal or toroidal mirror, after the monochromator, will be used to produce the focussed spot, with a 1.2 mr acceptance in the sagittal plane (horizontal) and collecting the full vertical emittance of the source.

The first operation of the system will coincide with the initial commissioning period of the x-ray ring. If we assume that the ring will run at around 2.5 GeV at 10 mA current during this time, it should be possible to provide about 6×10^{11} photons/(sec-mm²) at an energy of 8 keV or about 5.8×10^8 photons/sec in a 30 μ m square spot. These figures should be increased by 50 to give the values appropriate to NSLS operation at design level of 2.5 GeV and 500 mA current. Such fluences are adequate for trace element measurements with sensitivities close to the ppb region, as demonstrated by the experiments discussed above, and by the estimates of Sparks [1] and Gordon [10].

The design of the actual exit slit system will draw on the existing experience of Sparks [1] and the slits used at CHESS. The use of variable aperture slits is desirable since the requirements of individual experiments for particular beam configurations will vary substantially. This can be achieved either by mechanically adjustable apertures or by interchangeable slit assemblies.

The design of actual experimental equipment to be used with the microprobe is beyond the scope of this paper. However, there is one important consideration that needs to be stressed. Namely, the photon beam will have an appreciable divergence at the final image position in the experimental hutch, ≈ 5 mr, in the sagittal plane. The size of the beam will increase by about $5 \mu\text{m}$ per millimeter past the defining slit. The sample must therefore be placed within a few mm of it if good spatial definition is to be maintained. This is a nuisance, but is no different from the corresponding situation with proton microprobes.

In later Phase II development, it is planned to add a further stage of demagnification to attain an image size of about $5 \mu\text{m}$. The instrument will probably be in the Kirkpatrick-Baez configuration discussed by Howells and Hastings [11].

5. Conclusions

Several groups have now investigated some of the problems that are involved in measurements of trace element concentrations with synchrotron radiation. The values of minimum detectable limits that

have been reported are roughly in the range of 100-200 ppb between Ti and Mo using K-shell excitation and between Yb and U using L-shell excitation. These results were obtained under a wide variety of experimental conditions. Thus far no detailed investigation of the various effects limiting the sensitivity has been carried out, and further work is necessary to understand the ultimate limitation of the SXRF technique. Recent calculations have shown ultimate sensitivities should be lower than the 100-200 ppb state-of-the-art limits. Similarly, questions of radiation damage in biological and organic materials have barely been raised and must be considered for each particular experiment. Further work will be essential, particularly for future experiments with x-ray microprobes where fluences will be high.

These initial experiments have shown that SXRF has extremely important implications for scientific fields which require rapid, sensitive, multielemental analytical measurements. The development and applications of SXRF as the newer facilities become available in the near future will therefore be rapid and extensive.

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Figure Captions

1. Energy spectrum of photons obtained from the CHES facility at about 5.3 GeV. The transmission of Be, Al and air absorbers traversed by the photons before reaching the sample is also shown.
2. Energy spectrum of filtered white beam from the CHES facility at about 5.3 GeV.
3. Vertical intensity distribution of 5.3-GeV photon beam from CHES. A source size of 1 mm has been included.
4. Radiation damage to blood cells from filtered white radiation is shown in a) for a fluence of about 2×10^{19} photons/cm². The damage from 200-keV tritons is shown in b) for a fluence of 6×10^{16} tritons/cm² (taken from ref. 14). The scales of the two photographs are slightly different.
5. Intensity distribution of the Compton + elastic scattering of 13.0 keV photons produced by 5.3-GeV electrons is shown as a function of observation angle. The solid curve is the calculated polarization assuming an electron beam of negligible height. The experimental values have been normalized to the calculations.
6. Intensity distribution of Compton + elastic scattering is shown as a function of distance normal to the median plane of the beam. The solid curve is the calculated polarization assuming an electron beam of negligible height. The experimental values have been normalized to the calculations.

7. Spectrum of x rays produced by fluorescence of 37-keV x rays by NBS SRM 1571 orchard leaves (see Sparks et al., ref. 1). Concentrations in ppm are indicated with numbers in the figure.
8. Spectrum of x rays produced by fluorescence of NBS SRM 1571 orchard leaves by 13.0-keV x rays.
9. Summary of the minimum detectable limits for K-x rays observed at various incident photon energies as a function of Z.
10. Comparison of minimum detectable limits for XRF and SXRF obtained for two specific experimental arrangements. Details are given in the text.

Figure 1

Figure 2

Figure 3

10 μm

0 10 20 μm

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10