Uses of Synchrotron Radiation

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INTRODUCTION

X-ray fluorescence has long been used as a technique for
elemental analysis. Within the past decade technological advances
brought about the ability to perform trace element analysis in
bulk samples using electrons, protons, heavy ions and x-ray tube
photons as excitation sources. Furthermore, the ability to focus
charged particle beams allowed major and minor elemental analysis
with spatial resolutions in the micrometer and sub-micrometer
range.

X-ray fluorescence techniques have a number of features that
make them attractive for application to biomedical samples,
including: they are non-destructive; they are absolute techniques
(as is neutron activation analysis) wherein cross sections and
absorption coefficients are known and standards are used for
geometry determinations; the chemical form of the trace element
will not affect the analysis as it could in techniques using ion
sources; only small amounts of sample are required and these can
be prepared with a minimum of handling; fine spatial resolution
and mapping of elemental distributions in a sample is possible;
and sensitivity is a continuous and slowly varying function of
atomic number.

In the past few years synchrotron radiation x-ray sources
have been developed and, because of their properties, their use
can improve the sensitivity for trace element analysis by two to
three orders of magnitude. Also, synchrotron radiation will make
possible an x-ray microprobe with resolution in the micrometer
range. The National Synchrotron Light Source (NSLS), a dedicated
synchrotron radiation source recently built at Brookhaven National
Laboratory, will have a facility for trace element analysis by
x-ray fluorescence and will be available to all interested users.

SYNCHROTRON RADIATION

Properties

Synchrotron radiation is light emitted by electrons when being accelerated toward the center in a circular orbit. The electrons emit the radiation at every point along the orbit with an angular distribution characteristic of dipole radiation in the reference frame of the electron. At relativistic energies $(E \gg m_0 c^2)$ the radiation pattern in the laboratory frame of reference is strongly peaked in the forward direction tangential to the electron orbit with a vertical angular divergence of $1/\gamma$, where γ is the ratio of the electron energy to its rest mass. For the 2.5 GeV NSLS x-ray ring, the vertical angular divergence of the x-ray beam is about 0.1 mrad, or a height of 2 mm at 20 m from the source. This small divergence and the high brightness (photons/s/mm^2/ster) will allow for the development of an x-ray microprobe, as indicated by Sparks[10] and as discussed in the next paper by Grodzins. Some of the properties of synchrotron radiation[11] and their importance for trace element analysis are:

1) A broad and continuous energy spectrum from which the desired excitation energy may be selected by appropriate monochromators. Using wide bandwidth monochromators, it is possible to obtain tunable x-ray beams with photon intensities many orders of magnitude greater than that of characteristics lines of x-ray tubes.

2) A stable beam intensity which decays with a half-life of about eight hours. The NSLS, as are all synchrotron light sources, is a storage ring that maintains a constant energy circulating electron beam that decays slowly in intensity because of scattering by residual gas molecules in the chamber.

3) A high brightness which permits the use of a microprobe. For the NSLS, the eletron beam distribution is gaussian and the 4σ size is 0.4 mm high and 1.3 mm wide. The high brightness will allow the use of wavelength dispersive detectors.

4) The light is predominantly linearly polarized in the plane of the electron orbit, thereby reducing scattering backgrounds when observing the target at 90° to the beam in the horizontal plane. This is of particular importance when using Si(Li) solid state detectors.

5) There is relatively low energy deposition in targets when compared to that of charged particle excitation at similar sensitivities.

6) The availability of appreciable flux within narrow energy bandwidths allows for chemical speciation at trace levels by measurement of chemical shifts in the absorption edge energies.

The usable energy range for the NSLS extends to about 20 keV when the energy of the electron beam is 2.5 GeV. Both the intensity and energy of the x-rays can beincreased greatly by the use of a wiggler, which is a multipole magnet installed in the straight section of the electron storage ring. The wiggler bends the beam out of its normal path with a small radius of curvature and then bends it back to the original path. By this process the energy spectrum of the emitted photons is shifted to higher energies by a factor equal to the ratio of magnetic field strengths for the wiggler and ring magnets. Using 60,000 gauss superconducting 6-pole magnets, the NSLS will provide useful intensities as high as 100 keV, enough to produce K excitation in the heavy elements through radon. The height of the oscillation of the electron path in the wiggler is less than 1 mm, which will make the source only slightly extended compared to that of the ring magnet source.

X-ray production cross sections and backgrounds

X-ray production cross sections (the probability, in appropriate units, that an interaction between a projectile particle and a target atom wil result in a fluorescence x-ray) for x-ray excitation are greater than for charged particle excitation. Since synchrotron radiatior can be tuned to the optimum energy, conditions can be attained in which the ratio of the photon-induced cross section to the particle-ir'iced cross section as a function of atomic number, Z, ranges between ten for low Z elements and one thousand for high Z elements. Photon cross sections are greatest for excitation of atoms whose ionization energies are closest to the exciting photon energy and decrease as the ionization energy lessens, i.e., as one goes to lower Z elements. This trend is opposite to that for charged particle excitation. Generally, elements of low Z are in greatest abundance and those of high Z are of lower abundance. Since the detector response is the product of the abundance and cross sections, photon excitation tends to equalize the elemental responses in the detector across the periodic table, whereas charged particles exhibit very large signals for low Z elements and thereby limit the sensitivity for high Z elements.

The principal limitation to sensitivity is the background radiation through its effect on the signal to noise (S/N) ratio. In charged particle excitation, bremsstrahlung radiation, produced by the slowing down of electrons produced and stopped in the target sample, is most evident in the low energy portion of the x-ray spectrum and limits sensitivities in the low Z region. The limitation for higher Z elemental sensitivities is limited by lower cross sections and beam intensity limitations due to sample heating. For x-ray tube excitation using energy dispersive detectors (e.g. Si(Li)), total count rates are very high because of elastic and inelastic scattering of the incident unpolarized

radiation. Also, properties of Si(Li) detectors cause some background throughout the x-ray spectrum(6). The scattered radiation is the limiting factor for bulk analysis by x-ray tube excitation. Synchrotron-radiation induced x-ray fluorescence analysis is not as limited because the incident radiation is highly linearly polarized and the scattering is minimized by viewing the fluorescence at 90° to the beam in the horizontal plane. The angular distribution of the fluorescent radiation is isotropic and, therefore, the S/N ratio is considerably greater using synchrotron radiation. In addition, the much more intense photon beams from storage rings permits the use of lower geometry wavelength dispersive detectors, which eliminates elastic and Compton scattering backgrounds completely. In this case the principal background radiation originates with the slowing down of photoelectrons produced in the sample matrix elements.

Sensitivity of synchrotron radiation induced XRF analysis

Gordon(5) recently made sensitivity calculations for multielemental trace analysis by synchrotron radiation induced x-ray fluorescence analysis. These calculations are based on a beam line consisting of the following components: an excitation source which is the NSLS 2.5 GeV electron beam, which at 20 m from the source will provide a photon beam 2 mm high and 20 mm wide for a 1 mrad horizontal acceptance angle; a tunable wide energy bandwidth monochromator with 10% resolution and 50% reflectivity; a thin sample target of 2 mg/cm^2 thickness and consisting of a carbon matrix; and a wavelength dispersive detector system consisting of as many as twenty-eight fixed crystal spectrometers and which has been commercially available for a number of years.

The sensitivity is defined according to the criteria of Currie(3) and in this case is given as the sensitivity for which the standard deviation of the measurement is 10%. The detection limits will be a factor of three to five lower than the sensitivity. Results of these calculations are shown in Fig. 1. Each curve represents the sensitivity for multielemental trace analysis using monochromatic radiation of the energy indicated for both K- and L-shell excitation. The time for the measurement is one minute. The rapid fall-off in sensitivity for lower Z values is due to lower cross sections when the ionization energy becomes much less than the photon energy used for the excitation, absorption of fluorescent x-rays by the sample, and low fluorescence yields for the low Z elements. The sensitivity curve for measuring one element at a time (by tuning the monochromator to select an excitation energy just above the absorption edge) can be constructed by connecting the lower extremities of the curves. The upward curvature of this constructed curve with Z reflects the fall-off of photon intensity for the light source at higher energies. The energy deposition rates for the assumed intensities are 0.13, 0.013, and 0.0021 watts/cm^2 for 5, 10, and 15 keV

irradiations, respectively. No heating problem is anticipated, particularly if the irradiations are carried out in air or a helium atmosphere. Calculations are also performed for a Si(Li) energy dispersive detector system. For such calculations it was necessary to restrict the vertical acceptance angle in order to minimize vertical polarization and its related high scattering backgrounds. For one minute irradiations, sensitivities were in the 0.2 to 0.5 ppm with minimum detectable levels (MDL) a factor of 3 to 5 less.
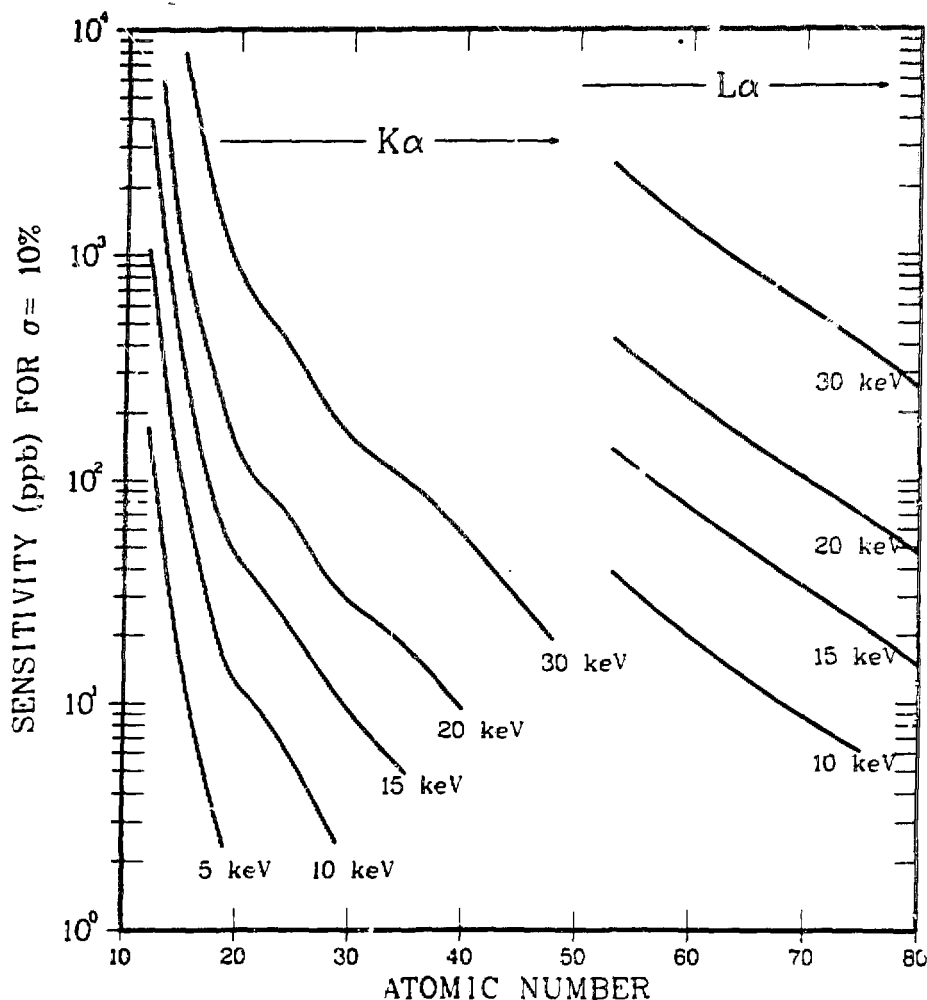

Figure 1. Quantitation limits for $2mg/cm^2$ carbon matrix sample using a wavelength dispersive detector system and a one-minute irradiation (after Gordon, ref 5).

Chemical speciation

X-ray fluorescence techniques for trace element analysis do not normally yield information concerning the chemical nature of the elements being determined, although wavelength-dispersive detection systems have been used to extract this type of information from energy shifts in the fluorescence of major and, sometimes, minor constituents. However, the high intensities available at the NSLS and the ability to obtain less than 1 eV resolution for the excitation energy, allows the determination of the absorption edge energy for a particular trace element by scanning through the absorption edge and observing the energy at which there is an abrupt increase of fluorescence. Generally, more oxidized species of a particular element will show absorption edges at higher energies because of lesser shielding of the ionized electrons by the valence electrons. The position of the absorption edge is compared with those of model compounds covering the entire range of oxidation states of the element in question and determining where the absorption edge of the sample falls compared to those of the model compounds. This type of speciation experiment can be performed for elements at the 10 ppm concentration level. An example of the technique has been demonstrated by a study of molybdenum in nitrogenase(2).

Experimental results

Figure 2 illustrates the use of synchrotron radiation for trace element analysis. The BNL Applied Physics Group performed a set of preliminary experiments(7) at the Cornell High Energy Synchrotron Source (CHESS). The conditions were not ideal for trace element analysis because the high resolution monochromator $(\Delta E/E=10^{-4})$ limited the transmitted beam intensity and physical restraints on detector geometry did not permit full utilization of the beam polarization. In Fig. 2(a) the target was a thin Orchard Leaves Standard (NBS 1571) and was irradiated for 5 min at 9.15 keV. This energy ionized the K-shell of Cu but not that of Zn. For this run the MDL for Cu is 350 ppb and for Ni is 120 ppb. One advantage of the tunability is illustrated in Fig. 2(b) where the same sample was irradiated with 13.00 keV x rays. Additional peaks for Zn, As and, questionably, for Hg are seen. Usually, x-ray fluorescence spectra show an overlap between As $K\alpha$ and Pb $L\alpha$ peaks. In this case, however, the 13.00 keV x rays were not energetic enough to cause Pb L-shell excitation and, therefore, the As K peak appears without any contribution from Pb. Likewise the L-shell spectra for heavy elements can be simplified by exciting only the L_{III} subshell but not the $L_{I,II}$ subshells. In this case the principal peaks that would appear are the $L\alpha$ and $L\beta_2$ peaks while the $L\beta_{1,3,4}$ and $L\gamma$ peaks would be absent.

(a)

10000

COUNTS

1000

100

10

E(incident): 9.15 KeV

P(0.21%)
S(2300)
Cl(700)
Ar(air)
K(1.47%)
Ca
Ti
Cr(2.3)
Mn(91)
Fe(300)
Ni(1.3)
Cu(12)
INCIDENT PHOTON SCATTERING

(b)

E(incident): 13.0 KeV

10000

COUNTS

1000

100

10

Zn(25)
As(4)
INCIDENT PHOTON SCATTERING

PHOTON ENERGY (KeV)
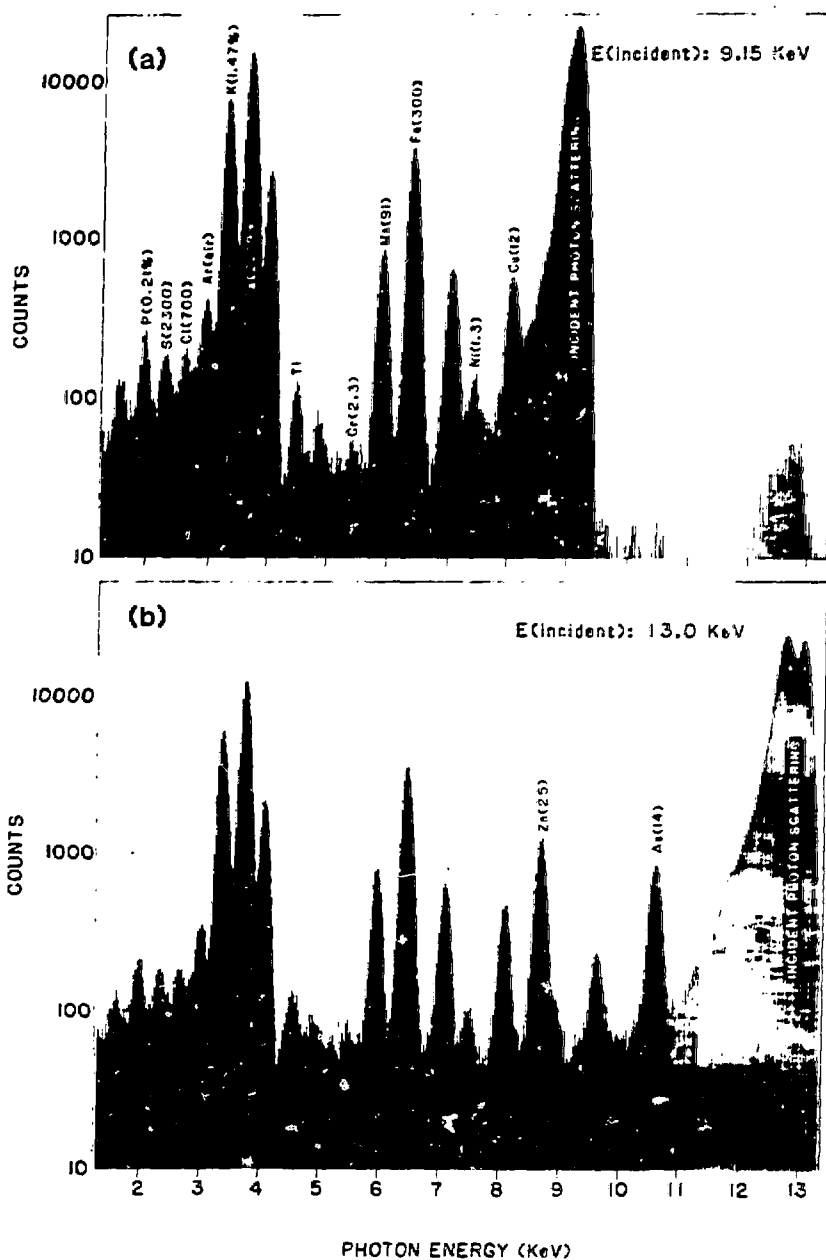
2   3   4   5   6   7   8   9   10   11   12   13

Figure 2. X-ray fluorescence spectra obtained for Orchard
Leaves Standard NBS 1571 (1 mg/cm^2 thickness) in 5-minute
irradiations.

APPLICATIONS

The importance of a number of trace elements in the proper functioning of living systems has been evident for many years. Within more recent times, the number of trace elements shown to be important, either as beneficial or as toxic agents, has increased dramatically to include most of the common elements. Furthermore, the interrelationships among trace elements have been shown to be important in living systems. The treatment of abnormalities in the concentration level of a particular trace element can affect the levels of other trace elements to produce undesirable side effects. Therefore, it is desirable to use a multielemental technique which is rapid, uses targeting techniques requiring little handling, and which is relatively insensitive to chemical constituency and matrix effects. A unique feature of x-ray fluorescence analysis is the ability to determine precisely ratios of elemental concentrations in systems of biomedical interest, particularly for neighboring elements (e.g., Cu/Zn, Hg/Pb) or elements with similar characteristic x-ray energies (e.g., Se/Pb), for which systematic errors would cancel. The application of synchrotron radiation to microprobe analysis will be presented later in this workshop. Some examples of proposed applications of bulk sample analysis using synchrotron radiation are:

1) the establishment of base-line concentration levels for all possible elements in human organ tissue and blood components as outlined in the Proceedings of the Workshop on Mineral Content in Human Tissues(8). The synchrotron radiation x-ray fluorescence technique is particularly capable for this type of study since it is rapid, requires a minimum of processing of samples, and is very sensitive for almost all elements. Great care would have to be taken as to methods of sample homogeneity and sampling. Although the time that could be allotted to this type of study would represent a relatively small part of such a large project, synchrotron radiation XRF would be a valuable technique complimenting the other techniques to be utilized.

2) the study of the relationship between trace element concentrations in tissue and carcinogenicity. Many observations have been reported, both epidemiological and experimental, suggesting a number of trace elements originating in the diet or as environmental pollutants have a role in the pathogenesis of cancer(4). Virtually all elements in the periodic table have been tested to some degree, including the rare earths, which are now being used more extensively in industry. It is clear the chemical form of the element is important as is the method of uptake. Some non-carcinogenetic elements are important in that their deficiencies can contribute to

development of neoplasms. Thus, a study of specific relationships between cancer and elemental concentrations (and chemical speciation) in tissue should be explored.

3) the rapid analysis of diet material in human nutrition studies. In the past, analysis for trace amounts of chromium in tissue and diet material has proved particularly troublesome. Synchrotron radiation XRF is able to quantitate chromium levels as much lower concentration levels than those that are now achievable.

4) a variety of problems that can be studied through use of an x-ray microprobe. The microprobe is not the subject of this particular paper, but it might be well to list a few examples of such studies. These include analyses of individual cells, components of blood; the localization and quantitation of enzymes and co-factors; the detection, quantitation and localization of cellular transport systems; and the analysis of living cells using newly developed wet cells(1).

5) the study of zinc metabolism in humans and its relationship to disease. These studies would include the investigation of zinc metabolism in sickle cell disease, experimental production of zinc deficiency in man in order to define zinc-related parameters for zinc requirements in man, and the study of the relation between zinc and chronic renal disease(9). Inasmuch as several trace elements compete with each other for similar binding sites and biological interactions have been well recognized, the use of a multielemental technique for samples of 1 ng to 500 ng is required.

NSLS AS A USERS FACILITY

The NSLS x-ray source, as well as a smaller storage ring for the production and utilization of vacuum ultraviolet radiation, is a national users' facility and as such is available under certain conditions to all researchers from universities, industry and national laboratories. There will be eventually over fifty beam lines at the x-ray ring with one or two being devoted exclusively to x-ray fluorescence analysis. The beam line will be used for experimentation in the geological and material sciences as well as the biomedical sciences. An operating group made up of the BNL Applied Physics Group and a number of researchers from outside BNL will be responsible for construction and operation of the XRF beam line. At least 25% of the useful operating time will be available to occasional users upon the submission to and the approval by the NSLS Program Advisory Committee. The XRF operating group will be responsible for aiding the visiting researcher with the operation

of the equipment. The beam time for all visitors is witnout charge for all publishable, non-proprietary research. Brookhaven National Laboratory has a long history of operating user facilities and is well equipped to aid visitors with experimental equipment and their auxiliary needs. Funding for travel to BNL and living expenses for the purpose of performing analyses is to be provided by the individual researchers.

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