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## Application of Synchrotron Radiation to X-Ray Fluorescence Analysis of Trace Elements

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## Application of synchrotron radiation to x-ray fluorescence analysis of trace elements

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Abstract

The development of synchrotron radiation x-ray sources has provided the means to greatly extend the capabilities of x-ray fluorescence analysis for determinations of trace element concentrations. A brief description of synchrotron radiation properties provides a background for a discussion of the improved detection limits compared to existing x-ray fluorescence techniques. Calculated detection limits for x-ray microprobes with micrometer spatial resolutions are described and compared with experimental results beginning to appear from a number of laboratories. The current activities and future plans for a dedicated x-ray microprobe beam line at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory are presented.

Introduction

X-ray fluorescence has long been used as a technique for trace element analysis. Excitation of target atoms has included irradiation by electrons, protons and heavier charged ions, and x-ray tube photons. The ability to focus the charged particles led to the development and use of microprobes with spatial resolutions in the micrometer range for charged ions and in the sub-micrometer range for electrons. Within the past few years, high-energy electron storage rings have been developed as sources of intense synchrotron radiation x-rays. Using appropriate monochromators, it is possible to obtain energy-tunable x-ray beams with photon intensities up to five orders of magnitude greater than those of the characteristic lines from x-ray tubes.<sup>1</sup> With these sources, the x-ray fluorescence technique for elemental analysis has improved dramatically, and the development of an x-ray microprobe with properties similar to probes that use charged particles for excitation has been made possible.

Synchrotron radiation is light emitted by electrons as they are accelerated, usually in a circular orbit. At relativistic energies the radiation pattern in the laboratory frame is strongly peaked in the forward direction with a vertical divergence of  $1/\gamma$ , where  $\gamma$  is the ratio of the electron mass to its rest mass. For the NSLS at Brookhaven National Laboratory, the 2.5-GeV electron storage ring provides an x-ray beam with a vertical divergence of about 0.2 mrad, or a height of 4 mm at 20 m from the source. This small divergence and small source size (0.5 mm x 1.5 mm, 4 $\sigma$ ) provide a high brilliance source and, with further focussing, allow for the development of an x-ray microprobe. Some of the properties of synchrotron radiation useful for x-ray fluorescence analysis include: 1) a broad and continuous energy spectrum ("white light") from which the desired excitation energy may be selected by monochromators; 2) a stable beam intensity which decays with a half-life of about eight hours; 3) the light is predominately 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; 4) there is relatively low-energy deposition in targets when compared to that of charged particle excitation at similar beam fluences; 5) the availability of intense flux within narrow and tunable energy bandwidths allows for chemical speciation at trace levels by measurement of chemical shifts in absorption edge energies as well as structure changes in the absorption edge.

Synchrotron radiation may be used for both bulk analysis and microprobe analysis with irradiation areas ranging from approximately 1 cm<sup>2</sup> for bulk analysis to the order of 1- to 5- $\mu$ m square for microprobe analysis. The technique requires minimum handling of samples and can be carried out in vacuum or in the atmosphere. Wet samples can also be analyzed.

Sensitivity

Calculations for detection and quantitation limits using synchrotron radiation-induced x-ray fluorescence analysis (SRIKE) for both bulk and microprobe analysis have been published previously.<sup>2,3</sup> The technique is limited by the photon fluence on the target and the efficiency rate capability of the detection system. A solid state detector is limited by a background distributed through the whole fluorescence energy spectrum and the large count rates from the Rayleigh and Compton scattering peaks. The use of white light, although providing a much greater fluence of photons introduces continuous scattering backgrounds throughout the energy spectrum. In both monochromatic and white light

excitation modes, the use of crystal spectrometers for detection will increase the signal to background ratios for improved sensitivity as long as the excitation photon fluence is great enough to provide a usable signal.

One of the major assets for using synchrotron radiation is the natural high degree of linear polarization, which is utilized to reduce the background from scattered radiation. This effect is particularly useful using solid state detectors which become saturated at high count rates. The angular distribution of scattered radiation for linearly polarized light is minimized at  $90^\circ$  to the beam direction in the plane of the electric vector. For a small, but finite sized Si(Li) detector, the scattered radiation from the horizontally polarized light is held to a minimum and the sensitivity is limited by the small component of vertically polarized light. The use of monochromatic radiation reduces the background under the fluorescence peaks to bremsstrahlung originating from energetic electrons produced in the target. Although Compton and Rayleigh scattering still take place, it is limited to that of the excitation photons. Photon beams used for bulk analysis are about 95% linearly polarized and provide much improved signal-to-background ratios. For those situations where the sensitivity is limited by the detector saturation, the polarization of the beam can be improved to the order of 99% by appropriate collimation for acceptance of low angle photons from the source. Sensitivities may improve by as much as a factor of five.<sup>3</sup>

Detection limits at the NSLS for trace elements in thin carbon matrices were calculated<sup>2</sup> to be of the order of 60 ppb for one-minute irradiations using a solid state detector. Extrapolation of experimental results using less than optimum conditions of fluence and detectors indicates the calculated detection limits are reasonable goals. Chen, et al.<sup>5</sup> studied elemental concentrations in coal. Recently Giauque, et al.<sup>6</sup> using a solid state detector system and a narrow bandwidth monochromator were able to achieve detection levels of 20 ppb for bulk analysis using a "wiggler" beam line at the Stanford Synchrotron Radiation Laboratory (SSRL). They used a  $3 \times 3$  mm beam and continuously scanned a  $4 \times 17$  mm area to average out sample and beam inhomogeneities. The counting interval was 300 s.

Iida, et al.<sup>7,8</sup> have reported detection limits for a milliprobe system at the Photon Factory, Tsukuba, Japan. Using white light excitation of an organic matrix and 100 s intervals, detection limits of 400-500 ppb were achieved for a beam spot of  $3.5 \times 10^{-3}$  mm<sup>2</sup>. For zinc this is equivalent to 0.13 pg. Using a thick Al absorber on the excitation beam, sensitivities for first-row transition elements ranged from 170 ppb to about 400 ppb. Narrow bandwidth monochromatic radiation yielded detection limits of about 70 ppb for a 1.1 mm<sup>2</sup> beam. A reflection/transmission wide bandpass monochromator provided for detection levels of 0.1 ppm in a  $4.2 \times 10^{-3}$  mm<sup>2</sup> area corresponding to 0.03 pg Zn.<sup>8</sup>

The x-ray fluorescence facility at the NSLS is distinguished by being dedicated full time to x-ray fluorescence analysis and the development of microbeams for microprobe analysis. This facility takes advantage of the design of the NSLS as the most brilliant and brightest (photons-s-source area-solid angle) synchrotron radiation source yet built. The current excitation mode is white light without focussing of the light. Figure 1 shows photon intensities from an assumed point source at the X-26 bending magnet port in units of photons-s-mA-eV-mm<sup>2</sup>. The vertical and horizontal acceptance angles are 0.05 mrad giving a one mm<sup>2</sup> beam at 20 m from the source. The intensities are corrected for absorption by Be windows and Ar in the air path near the target. The family of curves are for the indicated Al absorbers on the primary beam and indicate the use of filters to reduce scattering of the primary beam at spectrum energies corresponding to the fluorescence peaks of elements being measured. The current experimental arrangement is pictured in Figure 2, which is a view looking upstream towards the source. The beam, after passing through a series of Be windows and masks, is defined by four remotely-controlled tantalum plates at component A. This slit system can produce reproducible beam sizes down to 20  $\mu$ m. The beam then passes through a gas ionization chamber (B) which monitors the excitation beam. The sample holder, shown at  $45^\circ$  to both the beam and detector (D), is positioned by an X-Y-Z translational stage (C) whose position is reproducible to 1  $\mu$ m. The target is viewed by a microscope (E) with the image transferred through a video camera to a monitor at the control panel. Figure 3 shows a spectrum taken in 600 s for a thick IAEA Animal Muscle standard. The beam,  $50 \times 50$   $\mu$ m<sup>2</sup>, was filtered by 400  $\mu$ m Al, and the detector had a Kapton filter to reduce the response of the abundant lower Z elements. As shown, the minimum detection limits for Fe and Zn are 0.30 ppm and 0.20 ppm respectively and correspond to 0.5 pg Zn being detected. Figure 4 shows a spectrum for a more dense matrix, the NBS glass standard for 1 ppm nominal concentrations. In this case the beam size was  $100 \times 100$   $\mu$ m and the count time was 300 s. The detection limits for the observed trace elements are Fe: 2.4 ppm; Cu: 0.37 ppm; Pb: 0.33 ppm; Rb: 0.47 ppm; and Sr: 0.35 ppm.

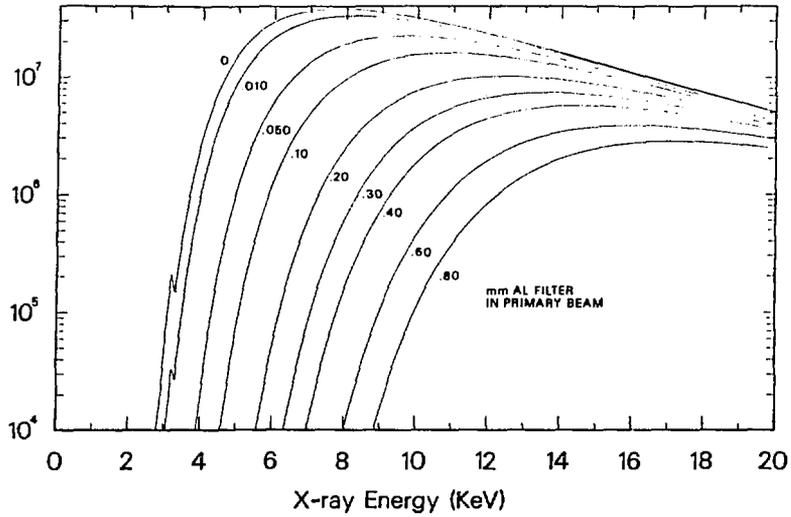


Figure 1. Photon beam intensities after passing indicated thicknesses of Al filters. In units of  $\text{ph}/(\text{s-mA-eV-mm}^2)$ .

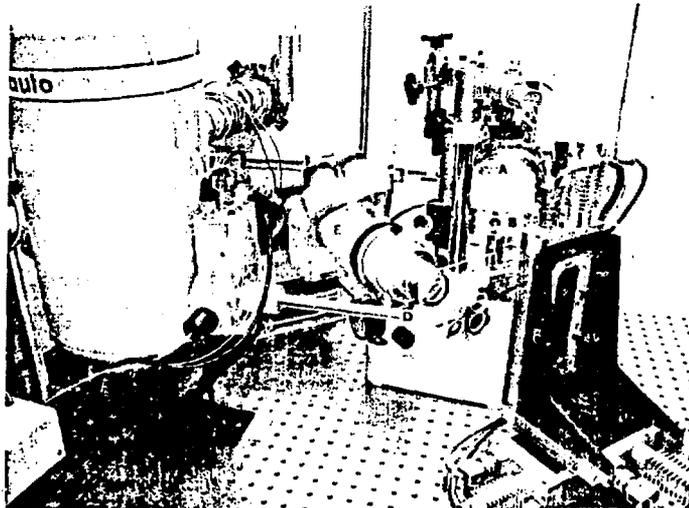


Figure 2. Upstream view of detection system. A: remotely-controlled slit system, B: ionization chamber, C: X-Y-Z translational stage, D: Si(Li) detector, E: microscope and video camera.

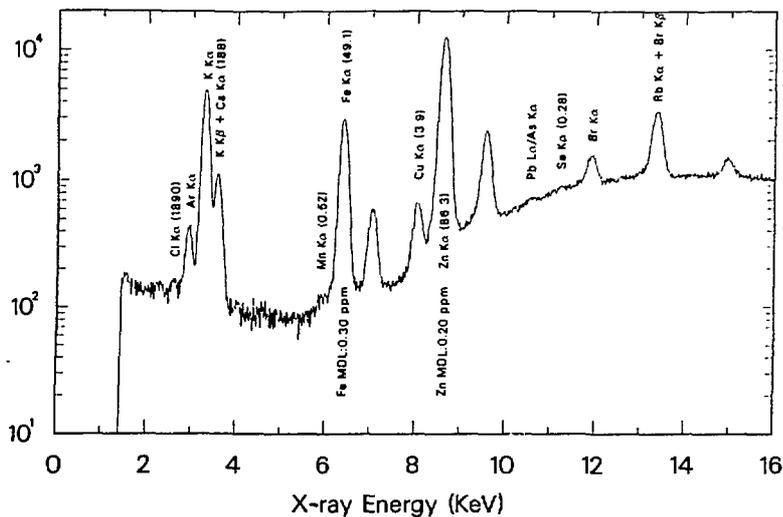


Figure 3. XRF spectrum of IAEA H-4 Animal Tissue Standard. Excitation was by 0.4 mm Al filtered white light. Units are counts/channel.

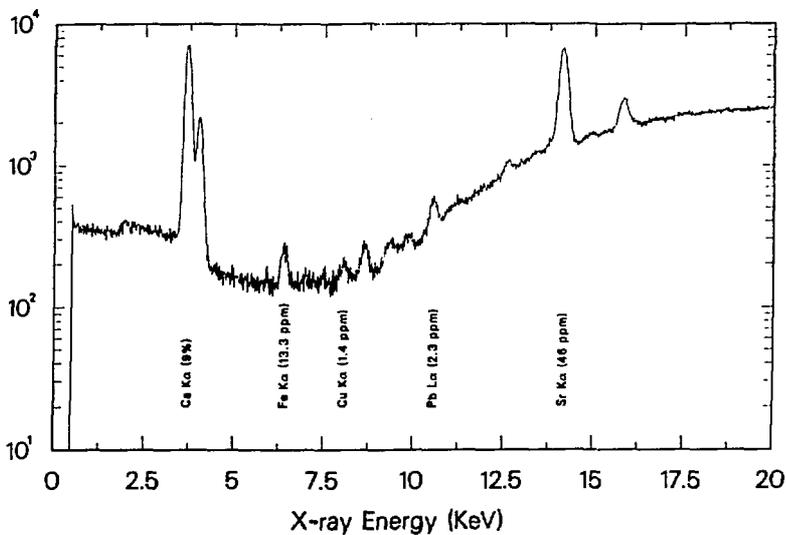


Figure 4. XRF spectrum of NBS 614 Glass Standard. Excitation was by 0.4 mm Al filtered white light. Units are counts/channel.

NSLS XRF facility

Current development work is directed toward a microprobe facility using photon beams on the order of one micrometer in size. The first step is to obtain a focussed 30- $\mu\text{m}$  beam spot and is schematically illustrated in Figure 5. The beam source assumed for ray tracing studies was  $1.5 \times 1.5 \text{ mm}^2$  as shown. It should be noted, however, that the NSLS has now achieved its design value for the electron beam size of 0.5 mm high and 1.5 mm wide, 4 $\sigma$ . Fabrication of an 8:1 demagnification ellipsoidal mirror is being attempted. It will focus the center 240  $\mu\text{m}$  of the source through the 30  $\mu\text{m}$  pinhole to be placed about 4 mm in front of the target. The 30- $\mu\text{m}$  pinhole can be the source for further demagnification to the 1- to 5- $\mu\text{m}$  range with a Kirkpatrick-Baez system. Sensitivity calculations<sup>4</sup> predict detection in the 50- to 100-ppb range for 60-s counting times using a solid state detector. However, using a wavelength dispersive crystal spectrometer, detection levels are reduced to below 10 ppb for 5-s runs, which simulates the counting times for an energy scanning spectrometer. The detection level for Zn of 4 ppb corresponds to the measurement of  $7 \times 10^{-17} \text{ g}$ , or  $7 \times 10^5$  atoms. Figure 6 illustrates detection and quantitation limits<sup>4</sup> (QL) for a geological matrix using a wavelength dispersive detector. The discontinuities in curves representing K-shell excitation are due to different analyzing crystals using for different energy ranges. The detection limits are higher than those for a carbon matrix because of higher bremsstrahlung count rates produced in the target of higher average Z.

The availability of small beam spots and the ability to program the remotely-controlled target stages have made possible transmission computerized tomography. A group from Linköping University,<sup>9</sup> Sweden, in collaboration with our group is developing a capability for transmission computerized tomography and has produced a density map of the cross section of a pencil in 40-m with 60- $\mu\text{m}$  pixel resolution. In addition, an image of the head of a freeze-dried caterpillar was produced for a 20- $\mu\text{m}$  thick slice and 30- $\mu\text{m}$  pixels in a  $177 \times 177$  array. The density differences extended over a range of only 2%. The tomography technique will be extended to produce trace element distributions by using x-ray fluorescence measurements. Typical point-by-point scanning for trace elements makes very inefficient use of detectors. Typical tomographic analysis would make far more efficient use of detectors and provide for greater precision of results. Gurker<sup>10</sup> has suggested that detector efficiency can be increased by irradiating targets through a coded aperture and applying image reconstruction algorithms to the data.

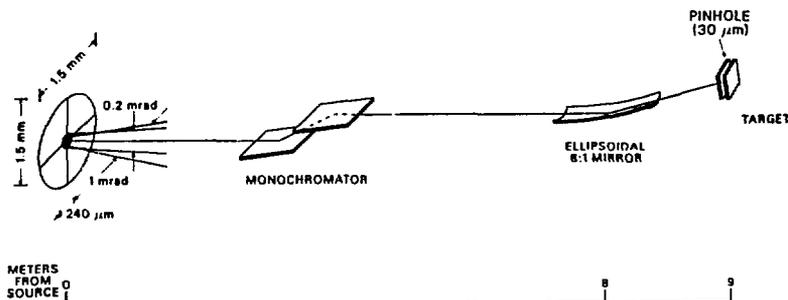


Figure 5. Schematic plan for obtaining 30- $\mu\text{m}$  beam spot using ellipsoidal mirror. All photons passing through pinhole originate in center 240  $\mu\text{m}$  of source. (From ref. 4)

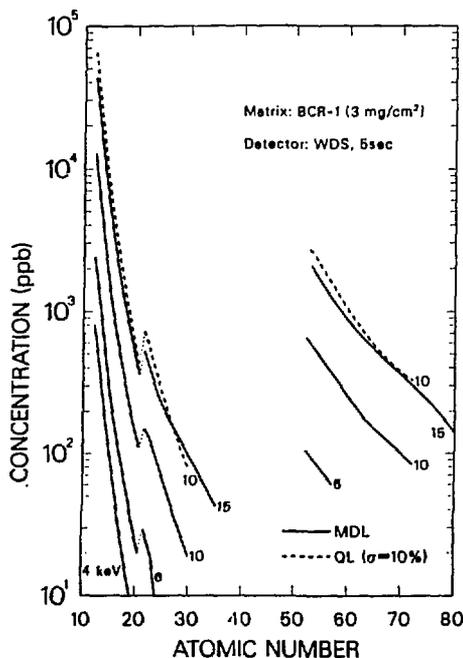


Figure 6. Calculated sensitivity curves for a geological matrix for selected excitation energies. The beam is  $30 \times 30 \mu\text{m}^2$  and the bandwidth is 2%. (From ref. 4)

#### Other applications of synchrotron radiation

A final application of synchrotron radiation to XRF to be noted is the chemical speciation of elements at trace levels. Chemical speciation has been carried out by noting chemical shifts in the fluorescence energies using crystal spectrometer detectors. Synchrotron radiation, being a high brightness source, can be scanned across the absorption edge of an element with a narrow bandwidth and the onset and structure of the absorption edge region observed.<sup>11</sup> The region above the absorption edge is the familiar EXAFS region which yields information on structure of molecular dimensions. The region of the absorption edge can be analyzed for its position as an indicator of the oxidation state of the element. Pre-absorption edge peaks are often indicative of molecular symmetries and unoccupied molecular orbitals. Using a large solid angle crystal analyzer, Hastings, et al.<sup>12</sup> were able to measure the EXAFS spectrum of 75 ppm Fe in copper in an attempt to determine the extent of Fe atom clustering. Maylotte, et al.<sup>13</sup> reported on the chemical states of vanadium found in coal before and after combustion. The determination of chemical state is usually carried out by comparing the spectra obtained with those of known model compounds of the same element.

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