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THE APPLICATION OF TUNABLE MONOCHROMATIC SYNCHROTRON RADIATION TO THE QUANTITATIVE DETERMINATION OF TRACE ELEMENTS

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### Authors

Giauque, R.D.

Jaklevic, J.M.

Thompson, A.C.

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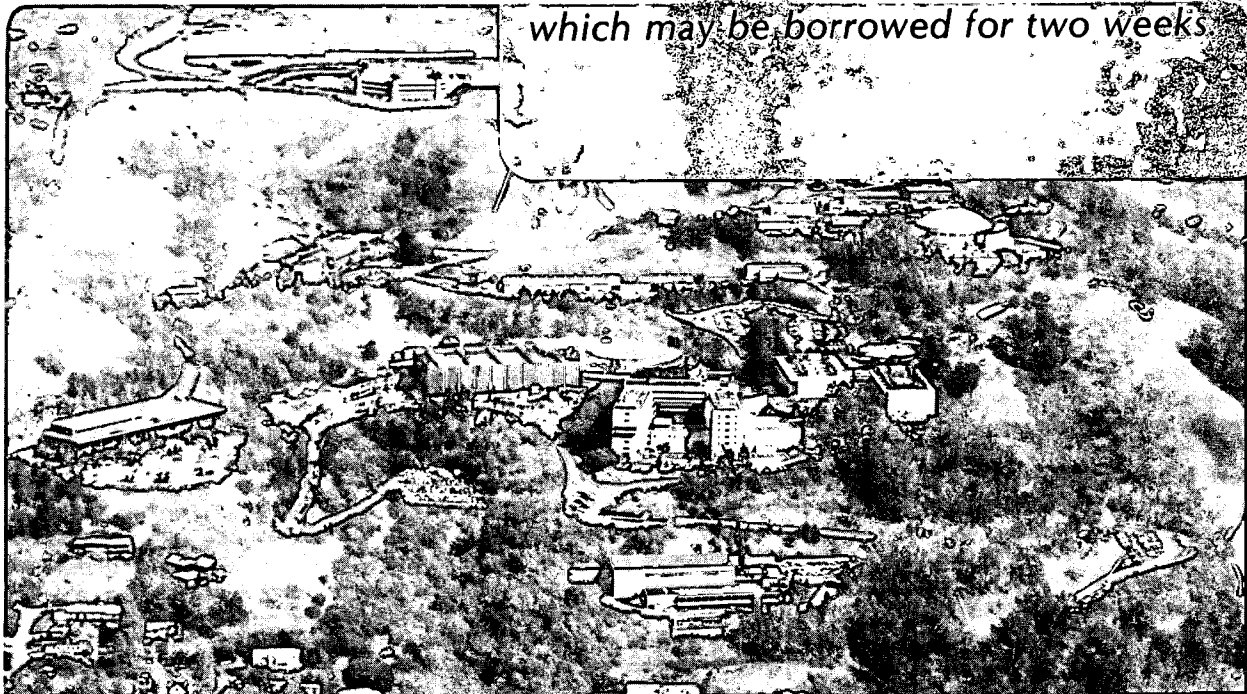
R.D. Giauque, J.M. Jaklevic, and A.C. Thompson

September 1984

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THE APPLICATION OF TUNABLE MONOCHROMATIC SYNCHROTRON  
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R. D. Giaouque, J.M. Jaklevic and A. C. Thompson

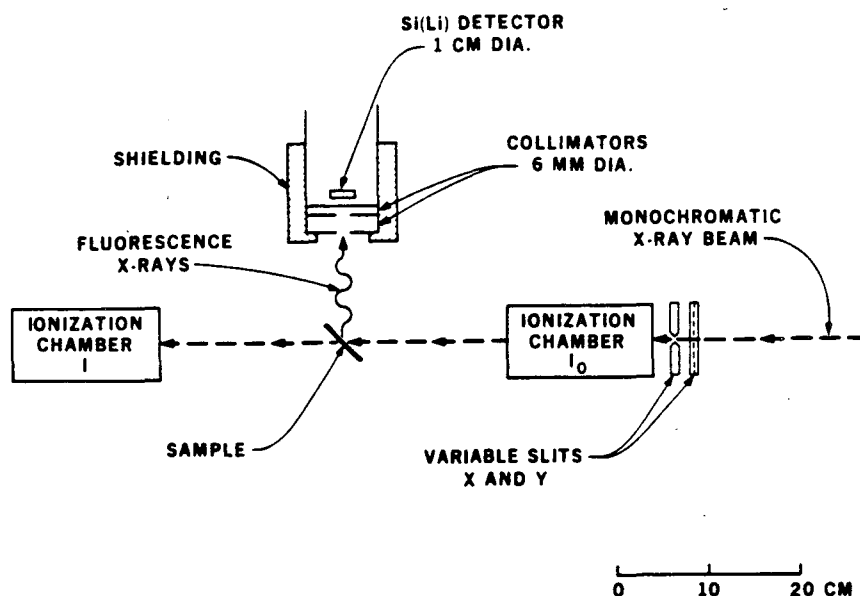
Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720 U.S.A.

INTRODUCTION

The potential advantages of synchrotron sources for x-ray fluorescence analysis have been discussed by several authors<sup>1-7</sup>. These advantages include high incident flux, tunable excitation energies using crystal monochromators, and reduction of scattered background due to polarization effects. Minimum detectable limits have both been calculated and measured, and have demonstrated the improvements that can be achieved using synchrotron sources. In this paper we present results obtained using tunable, monochromatic excitation and a high resolution lithium-drifted silicon, Si(Li), spectrometer for the quantitative analysis of a variety of sample types. Our experiments were designed to investigate the advantages and limitations of tunable monochromatic excitation with respect to optimum sensitivity, accuracy, and elemental selectivity in energy dispersive x-ray fluorescence analysis.

EXPERIMENTAL PROCEDURES

The measurements were performed using the new LBL/Exxon 54-pole wiggler beam line at the Stanford Synchrotron Radiation Laboratory. A double crystal Si<220> monochromator was used to select a narrow ( $\Delta E/E \sim 10^{-4}$ ) portion of the continuous output spectrum. The experimental geometry was adapted from the standard procedures used for performing extended x-ray absorption fine structure studies and is shown in Figure 1. The area of the incident beam is controlled by use of variable horizontal and vertical slits. A pair of ionization chambers are used to monitor the beam flux before and after incidence on the samples. The sample was placed at a 45° angle to the beam in the field of view of a 5 mm thick, 80 mm<sup>2</sup> Si(Li) detector. The detector was carefully aligned at 90° with respect to the incident beam. A pair of 6 mm diameter collimators shielded the periphery of the detector from x-rays originating at the sample and resulted in an effective solid angle  $\Omega/4\pi = 1 \times 10^{-4}$ . In the majority of measurements reported here, the beam profile was a 2 x 2 mm square cross section with a maximum measurement incident flux of  $5 \times 10^{12}$  x-rays/cm<sup>2</sup>/sec at 17.0 keV.



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Fig. 1. Schematic diagram of experimental setup. The monochromatic X-ray beam is incident from the right. The detector is placed at  $90^\circ$  with respect to the incident beam.

The detector-to-sample geometry was chosen to restrict the counting rate to less than  $10^4$  cts/sec. Quantitative analytical results were obtained by normalizing the x-ray spectra to an equivalent amount of incident photon flux using the integrated output from the ionization chamber labeled  $I_0$ .

## RESULTS

### Sensitivity and Detectability

The x-ray geometry was calibrated using a multielement, thin film aerosol particle standard which was generated from a solution containing a quantitative mixture of known elements. The aerosol particles were collected on a thin, teflon filter using an impactor stage to limit the particle size to less than  $2.5 \mu\text{m}$  aerodynamic diameter. Subsequent measurements of individual element mass loadings using a carefully calibrated x-ray spectrometer in our laboratory served to establish the concentration of the multielement standard to an accuracy of 3% or better.

Calibration curves were determined for several excitation energies. Results obtained with unknown samples were normalized to the standard calibration curves using an equivalent x-ray flux as measured by the  $I_0$  ionization chamber.

Table 1 lists the minimum detectable limits calculated for the case of 17.0 keV excitation, 100 second counting interval with  $10^4$  counts/sec, and using two separate substrates corresponding to a typical biological specimen of  $30 \text{ mg/cm}^2$  and a thin membrane of  $0.4 \text{ mg/cm}^2$  mass thickness. In the case of the membrane substrate, it is estimated that

Table L. Minimum Detectible Limits

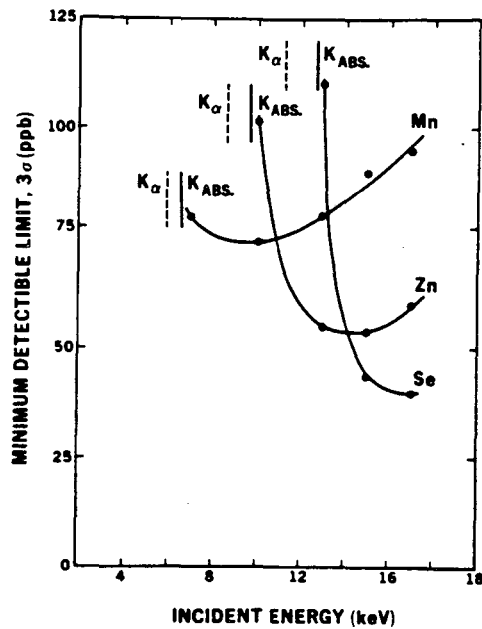
Z	Element	30 mg/cm <sup>2</sup> Cellulose (ppb)	0.4 mg/cm <sup>2</sup> Teflon Membrane (ng/cm <sup>2</sup> )
24	Cr	120	5.0
26	Fe	90	3.5
30	Zn	60	2.0
34	Se	40	2.0
38	Sr	90	4.0

60% of the scattered background is due to the air surrounding the sample--a helium atmosphere or vacuum environment would reduce the background accordingly.

The observed minimum detectable limits are approximately four to six times lower than the best results achieved by conventional, x-ray tube excited x-ray fluorescence analysis. This is the direct result of the reduction in scattered x-ray background due to the minimum cross section at 90° associated with a linearly polarized x-ray beam. Calculations for the geometry indicate a 10<sup>-3</sup> reduction in background for a perfectly polarized beam. The fact that the average polarization of the beam from the wiggler magnet at SSRL over the 2 mm x 2 mm area is approximately 95% accounts for the observed background reduction factor of 20. These measured minimum detectable limits are consistent with earlier measurements and calculations when appropriate adjustments are made to account for the varying beam fluxes and counting times<sup>1-4</sup>. The improvement in detectable limits relative to a conventional source is greater for the 30 mg/cm<sup>2</sup> sample reflecting the dominant effect of scattering from the substrate.

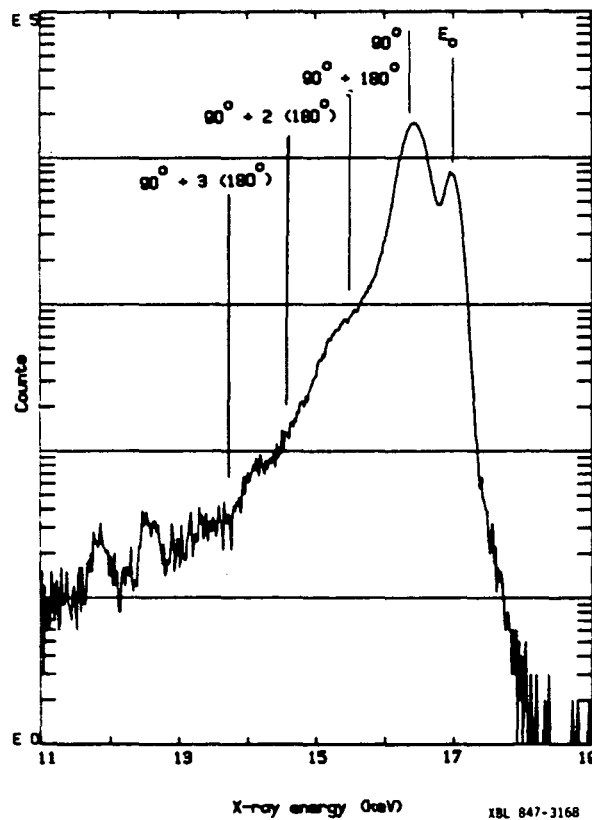
#### Optimization of Excitation Energy

The ability to precisely tune the incident beam energy over a wide range should enable one to exploit monochromatic excitation to the fullest extent for the analysis of specific elements. Simple consideration of the energy dependence of photoelectric cross sections would indicate that optimum sensitivity is achieved for excitation energies at the peak of the photoelectric cross section immediately above a major absorption edge. Figure 2 shows how these considerations are modified for realistic situations in which the elements are measured in the presence of a scattered background arising from a 30 mg/cm<sup>2</sup> cellulose substrate. The minimum detectability is achieved at energies several keV above the absorption edge of interest. Figure 3 is a background spectrum which illustrates the reason for these differences. The multiple scattering cross sections are still large enough to produce significant background even at energies corresponding to four or five inelastic scattering events. It is interesting to point out that with the well-collimated, polarized synchrotron sources, one is able to observe structures in the scattered background corresponding to the lower-order multiple scattering events labeled.



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Fig. 2. Experimental minimum detectable limits as a function of incident photon energy for Mn, Zn and Se. The  $K_{\alpha}$  x-ray energies and K absorption edges are indicated for each element.



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Fig. 3. Scattered background resulting from a 17 keV monochromatic beam incident on a 30 mg/cm<sup>2</sup> cellulose pellet. The energies of probable multiple scattering events are indicated.

## Selectivity of Elements

The broad-range, continuous tunability of a high-intensity source opens up the possibility of precisely choosing the incident energy to selectively discriminate against certain elements present in the sample. This feature is illustrated in Fig. 4 which shows the high energy portion of two spectra obtained from a NBS Standard Reference Material 1577 Bovine Liver Sample. Figure 4a shows the spectrum obtained with an excitation energy of 12650 eV immediately below the Se K absorption edge, and Fig. 4b shows the spectrum obtained with 12900 eV, above the edge. The Se  $K_{\alpha}$  peak corresponding to 1.1 ppm is clearly visible in the latter spectrum.

A more practical example of the advantages of tunability was demonstrated in the case of an atmospheric aerosol sample containing 2 ng/cm<sup>2</sup> As in the presence of 460 ng/cm<sup>2</sup> Pb. For a typical excitation energy of 17000 eV, the Pb L x-rays were dominant in the spectrum and the As  $K_{\alpha}$ , Pb  $L_{\alpha}$  interference precluded any measurement of the As concentration. However, at an excitation energy of 12900 eV, below the Pb  $L_{III}$  edge and above the As K edge, the As  $K_{\alpha}$  peak could be clearly resolved and the concentration determined.

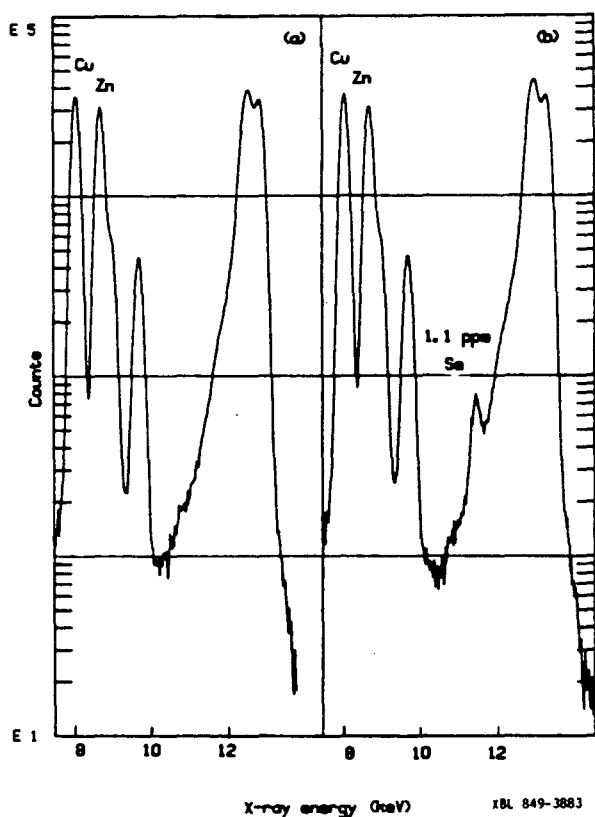
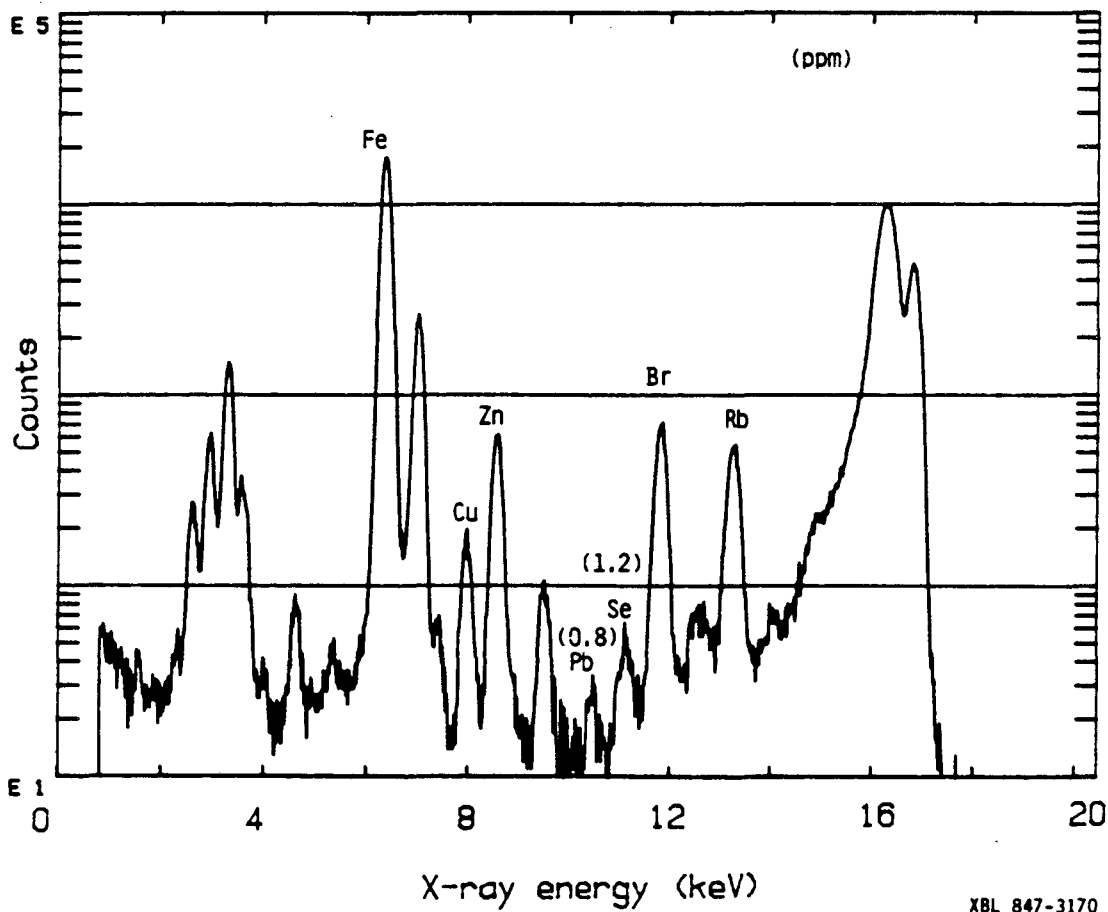


Fig. 4. Pulse height spectra obtained on a NBS SRM 1577 Bovine Liver specimen for excitation energies a) below the Se K edge (12.5 keV) and b) above the Se K edge (12.9 keV).



## Sensitivity

The extremely high flux density of the synchrotron source enables one to efficiently excite small area samples. In the case of the present beam line, it was possible to obtain reasonable counting rates even with a solid angle  $10^{-4}$  steradians using the  $.04 \text{ cm}^2$  beam area. Figure 5 illustrates an example in which this capability is used to perform an elemental analysis on an extremely small sample of human blood. The original sample consisted of a  $3 \mu\text{l}$  droplet which was evaporated to dryness and analyzed using  $17000 \text{ eV}$  monochromatic radiation. The concentration of  $0.8 \text{ ppm}$  Pb and  $1.2 \text{ ppm}$  Se correspond to the values measured in the sample as presented to the beam--the concentrations referred to the original whole blood would be approximately a factor of 4 lower.



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Fig. 5. Pulse height spectrum of  $3 \mu\text{l}$  whole blood sample. Concentrations indicated on plot represent those measured in the dry sample. Values referred to original sample are a factor of 4 lower.

This ability to analyze small samples is important in cases where the original material is difficult to obtain in significant quantities such as biological samples and valuable artifacts. A further extension of the small sample capability can be implemented with the use of smaller collimators and focusing optical elements which can be used to produce x-ray microprobe beams of a few microns.

### Quantitative Results

The accuracy of quantitative measurements performed in the present experiment is influenced by several factors not normally encountered in x-ray fluorescence measurements. The excitation flux is calibrated by means of the ionization chamber in the incident beam path. The small area of the beam and low divergence can emphasize sample inhomogeneity and particle size effects. The presence of higher order beam reflections from the monochromator can modify the energy spectrum of the incident beam in unpredictable ways.

The result of a quantitative measurement of a number of elements in a NBS SRM 1632 coal sample are given in Table 2. The sample was in the form of a 40 mg/cm<sup>2</sup> pellet. Matrix absorption corrections were made using the experimental relative  $K_{\alpha}$ ,  $K_{\beta}$  x-ray line intensity ratio for iron compared to that obtained from a thin sample. The total sample mass involved in the present determination was approximately 2.2 mg which is significantly less than the 250 mg minimum recommended by NBS to avoid inhomogeneity problems. Nevertheless, the agreement between the present results and the reference values is quite good. However, the potential sample inhomogeneity problem does point out the necessity for revising methods of standardization for the analysis of extremely small samples.

Table 2. Measured Concentrations for NBS SRM 1632 Coal

	This work*	Reference <sup>8</sup>	NBS**
Fe	7200 ± 700	8500 ± 700	8700 ± 300
Ni	15 ± 3	15 ± 2	15 ± 1
Cu	17 ± 2	17 ± 2	18 ± 2
Zn	17 ± 2	36 ± 3	37 ± 4
Ga	6 ± 1	6.0 ± 1.4	-
Ge	2.1 ± 0.4	-	-
As	4.5 ± 1.0	5.8 ± 0.6	5.9 ± 0.6
Se	2.6 ± 0.3	3.0 ± 0.3	2.9 ± 0.3
Br	17 ± 1	18.2 ± 2.1	-
Rb	20 ± 1	21 ± 3	-
Sr	145 ± 8	145 ± 22	-
Y	9 ± 2	(7.8)	-
Pb	9 ± 1	28 ± 5	30 ± 9

\*This work was performed using an effective sample mass of 2.2 mg.

\*\*Certified values based on at least 250 mg.

## SUMMARY

The advantages of using monochromatic polarized synchrotron radiation sources for energy dispersive x-ray fluorescence analysis have been demonstrated in terms of reduced scattering, better selectivity for specific elements, and sensitivity for the analysis of small samples. The importance of the kinematic behavior of matrix scattered radiation on the sensitivity for specific elements has been emphasized. Accurate calibration curves have been developed and the quantitative analysis of standard samples has been demonstrated.

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