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X-RAY FLUORESCENCE WITH SYNCHROTRON RADIATION

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## X-RAY FLUORESCENCE WITH SYNCHROTRON RADIATION\*

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### Summary

An experimental set-up for x-ray fluorescence analysis with synchrotron radiation was built and installed at the Stanford Synchrotron Radiation Project. X-ray spectra were taken from numerous and varied samples in order to assess the potential of synchrotron radiation as an excitation source for multielement x-ray fluorescence analysis. For many applications, the synchrotron radiation technique is shown to be superior to other x-ray fluorescence methods, especially those employing electrons and protons as excitation sources.

### Introduction

Improved analytical methods for the detection of trace elements are urgently needed to satisfy many demands resulting from advanced technologies. Electron microprobes have received wide usage in the past because of their focusing properties. Compared to electrons, proton-induced fluorescence excitation results in improved signal to noise ratio. At the Stanford Synchrotron Radiation Project (SSRP), we have built and installed an experimental set-up for x-ray fluorescence analysis with synchrotron radiation as the excitation source. The limited experience we have gained at SSRP augurs well for this exciting new technique. Since synchrotron radiation facilities are remote to most users, in order to become viable, these facilities must offer special advantages (improved detection limits, reduction in the heating of samples, accuracy and ease in quantitative analysis, etc.) over conventional analytical methods. These aspects are considered in this paper.

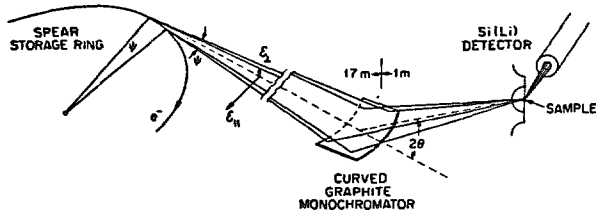


Fig. 1. Schematic layout (not to scale) of the present experiment [see Phys. Rev. Lett. **40**, 507 (1978) for additional details].

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### Experimental Arrangement

Our basic experimental arrangement is shown in Fig. 1. Electrons circulating in the storage ring SPEAR provided an intense flux of photons in a continuous energy range extending into the x-ray region (see Fig. 2). We employed a hot-pressed pyrolytic graphite monochromator to collect and focus the photon beam into a 0.45 mm<sup>2</sup> spot. For 37 keV photons, the energy spread in the focused beam was 460 eV (full width at half maximum) and the flux was  $\approx 15 \times 10^{10}$  photons/sec mm<sup>2</sup>. The fluorescence x-rays were detected with a Si(Li) or a Ge(Li) detector. Additional experimental details are given in Refs. 1 and 2.

Our original motivation for developing the above set-up was provided by reports of the possible discovery of superheavy elements in giant-halo monazite inclusions based on proton-induced x-ray emission (PIXE) studies.<sup>3</sup> From spectra similar to that shown in Fig. 3, we concluded<sup>1,2</sup> that superheavy elements are not present in giant-halo inclusions at detection levels  $\approx 10$ -50 times lower than those reported in Ref. 3. After completing these studies, spectra were also taken from many different samples in order to assess, in a broad and general way, the potential of synchrotron radiation for trace element analysis. These samples included NBS standards of coal, orchard leaves and bovine liver. Detailed analyses of these results will be presented elsewhere.<sup>4</sup> A fluorescence spectrum from a 0.45 mm human hair sample is shown in Fig. 4 to illustrate the quality of the data.

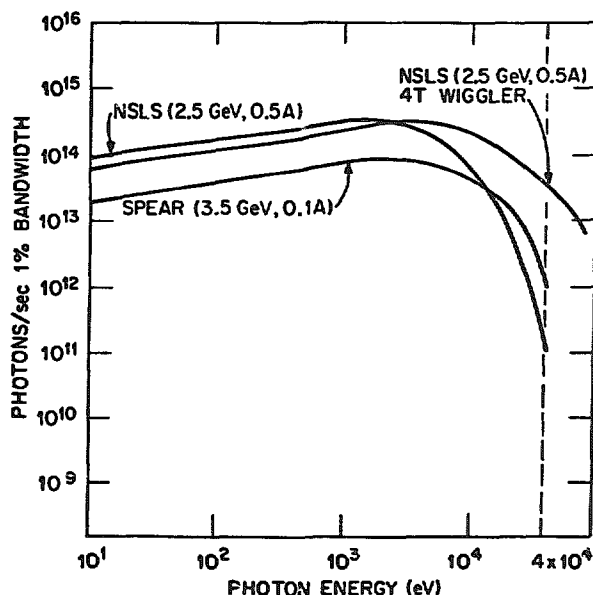


Fig. 2. Spectral distribution of synchrotron radiation at the Stanford Positron Electron Asymmetric Ring (SPEAR) and at the Brookhaven National Synchrotron Light Source (NSLS).

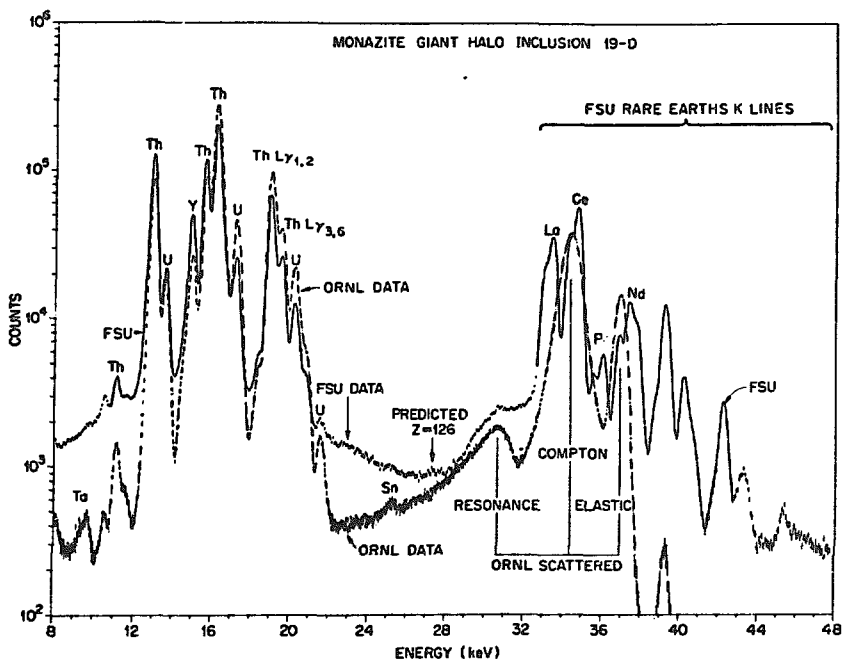


Fig. 3. Comparison of our photon-induced x-ray fluorescence data (ORNL) on 19D with proton-induced data (FSU) reported in Ref. 3 [see Phys. Rev. Lett. **40**, 507 (1978) for additional details].

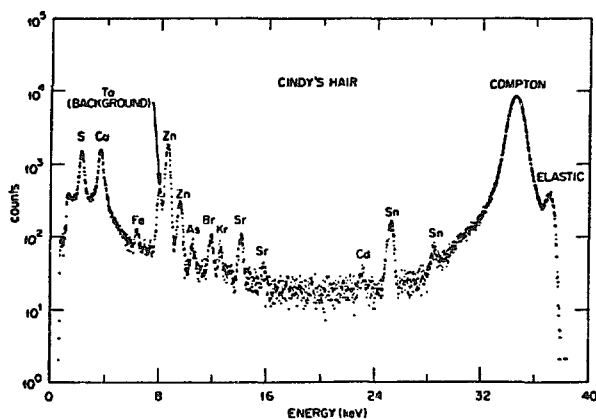


Fig. 4. X-ray fluorescence spectrum of a 0.45 mm human hair sample excited by 37 keV synchrotron radiation.

### Discussion

We have made a preliminary evaluation of synchrotron radiation as a unique analytical tool by comparing our results with those obtained by electron and proton excitations. Parameters important for this evaluation include: fluorescence cross sections; spectral backgrounds; specimen damage; spatial resolution; and available intensities.

### Fluorescence Cross Sections

The fluorescence cross section  $\sigma_{ij}$  is the product of the subshell ionization cross section  $\sigma_i$ , the probability that this vacancy results in a fluorescence event  $\omega_i$  (fluorescence yield), the fraction of these events  $F_{ij}$  (fractional radiative rate) belonging to the particular line of interest, and the electron-hole transfer factor  $T_{i,k}$  to account for the transfer of holes from deeper vacancies by Auger, Coster-Kronig and radiative transitions.

$$\sigma_{ij} = (\sigma_i \omega_i F_{ij} T_{i,k})$$

The subscript  $i$  denotes the subshell ionized,  $j$  identifies the final state of an x-ray transition, and  $k$  the subshell to which a vacancy has been shifted.

A comparison of the ionization cross section for x-rays, electrons and protons is shown in Fig. 5. Data for the x-ray cross sections were taken from Krause et al.,<sup>5</sup> electron values from Refs. 6-13, and proton values from Refs. 9, 14-19. The uppermost curves (labelled  $L_3$  edge and K edge) were obtained with x-ray excitation energies that were 1.007 times the  $L_3$  or K binding energies. The curves labelled 2, 4, 10, 18 and 40 keV reveal how rapidly the cross sections decrease with decreasing  $Z$  values. The above five x-ray energies were chosen in order to assure the excitation of every element above  $Z = 10$  in the periodic table. With a monochromator, it would be possible, of course, to select a bombarding energy such that the detection sensitivity is maximized for a particular element. In Fig. 5, we have also indicated the electron energies (20, 50 and 100 keV) and proton energies (2 and 5 MeV) chosen for this type of comparison of different techniques. It is clear from

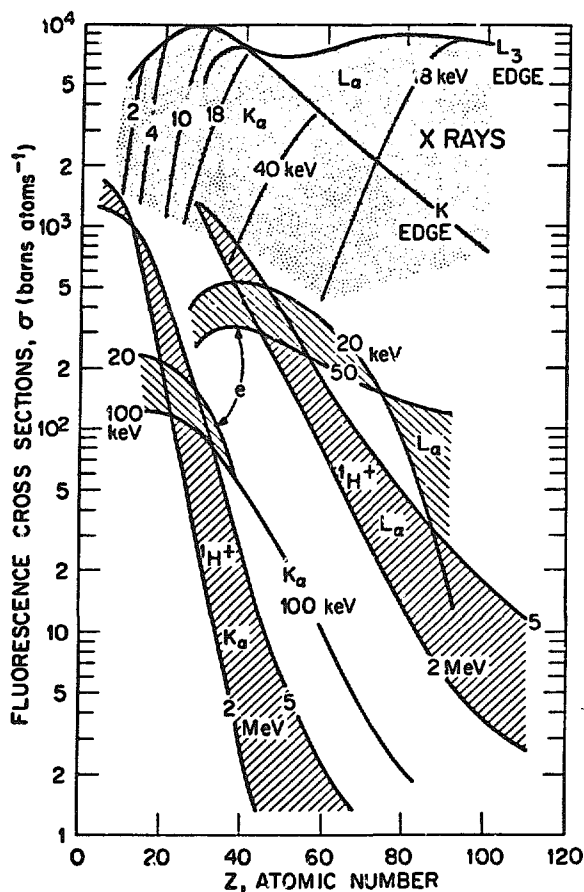


Fig. 5. Relative x-ray fluorescence cross sections for synchrotron radiation (x-rays), electrons (e) and protons ( $^1\text{H}^+$ ).

this figure that the cross sections favor x-ray excitation. This is especially important because, other things being equal, the intensity of the excitation source required to achieve a desirable minimum detection limit varies inversely as the square of these cross sections (see below).

#### Minimum Detectable Limit

For 95% confidence in detection, the minimum detectable limit (MDL) is defined as  $MDL = 3.29 \sqrt{N_b/N_s}$ , where  $N_s$  is the number of signal counts and  $N_b$  the background counts. We let  $x$ ,  $e$  and  $p$  denote x-rays (synchrotron radiation), electrons, and protons, respectively, as the excitation source. Since the number of fluorescence events  $N_s$  is proportional to the number of incident x-rays,  $N_x$ , times the corresponding cross section,  $\sigma_x$ , we can write

$$MDL_x = 3.29 \sqrt{N_b \sigma_{bx} / N_x \sigma_{sx}}$$

$$MDL_e = 3.29 \sqrt{N_b \sigma_{be} / N_e \sigma_{se}}$$

$$MDL_p = 3.29 \sqrt{N_b \sigma_{bp} / N_p \sigma_{sp}}$$

Comparing x-rays and electrons, for the same MDL

$$N_x/N_e = (\sigma_{se})^2 \sigma_{bx} / (\sigma_{sx})^2 \sigma_{be}$$

and for x-rays and protons

$$N_x/N_p = (\sigma_{sp})^2 \sigma_{bx} / (\sigma_{sx})^2 \sigma_{bp}$$

Since it is simpler to work with signal to background ratios, we rewrite the above equations as

$$N_x/N_e = \sigma_{se}(N_s/N_b)_e / \sigma_{sx}(N_s/N_b)_x$$

$$N_x/N_p = \sigma_{sp}(N_s/N_b)_p / \sigma_{sx}(N_s/N_b)_x$$

Data were taken from Refs. 21-24 in order to determine the relative merit of x-rays over electrons and protons for the same MDL. The conclusions are given in Table I. The required beam intensities in order to achieve comparable detection limits are much lower in the case of synchrotron radiation.

#### Energy Deposited in the Sample

In many applications, it is extremely important that the energy dissipation in the sample should be kept to a minimum. Otherwise, volatile compounds may be evaporated; redistribution of elements may occur; and chemical bonding may be affected. Organic and biological materials are especially vulnerable to both heat and radiation damage.

An estimate of the energy deposited in thick samples by 5-40 keV monochromatic x-rays to that deposited by 20-100 keV electrons is readily obtained from the number of x-rays to the number of electrons ( $N_x/N_e$ ) required to produce the same MDL (see Table I). Moreover, for optimum results, the x-ray energy chosen would be just above the binding energy of the appropriate electron shell, whereas the electron bombarding energy would be typically three times the binding energy. It can be shown, in a straightforward manner, that the energy deposited by an x-ray beam is  $2 \times 10^{-3}$  to  $10^{-5}$  times smaller than that deposited by an electron beam for the same MDL. Similar considerations show that, in thick samples, a 2 MeV proton beam will deposit >100 times as much energy as an equivalent 20 keV x-ray beam.

#### Spatial Resolution and Available-Intensities

Even though electron and proton microprobes have excellent spatial resolution, their usable intensities will be limited by the volatility of the sample. For practical purposes, we consider beam spots of  $1 \mu\text{m}$  diameter. As shown in Table I, an x-ray beam of this size, but  $\sim 10^{-4}$  times weaker than a charged particle beam, will yield similar MDL values. Photon intensities of  $\sim 2 \times 10^5$  photons/sec in a  $1 \mu\text{m}$  spot, already achievable at SSRP, will, therefore, compete favorably with an  $\sim 1 \text{ nA}$  ( $\sim 6 \times 10^9$  protons/sec) beam of 3 MeV protons, also focused to a  $1 \mu\text{m}$  spot. With x-ray optics designed to intercept the maximum amount of the available synchrotron radiation and to produce the minimum focus, intensities 100 times greater than those obtained in the earlier SSRP experiments are feasible. As shown in Fig. 2, the addition of a wiggler magnet will produce a further improvement factor of 10 to 100.

TABLE I. Comparison of different excitation sources (synchrotron radiation x-rays, electrons and protons)

Properties Compared <sup>a</sup>	Range of Values	Z Ranges	
<b>(i) Fluorescence Cross Sections</b>			
$K_{\alpha}$ , x-rays/electrons, $\sigma_{SX}/\sigma_{Se}$	30 - 200	15 - 50	
$L_{\alpha}$ , x-rays/electrons, $\sigma_{SX}/\sigma_{Se}$	12 - 60	40 - 92	
$K_{\alpha}$ , x-rays/protons, $\sigma_{SX}/\sigma_{Sp}$	6 - 800	15 - 50	
$L_{\alpha}$ , x-rays/protons, $\sigma_{SX}/\sigma_{Sp}$	10 - 350	40 - 92	
<b>(ii) Thick Target Fluorescence Yields</b>			
$K_{\alpha}$ , x-rays/electrons	5 - 150	15 - 50	
$L_{\alpha}$ , x-rays/electrons	10 - 50	40 - 92	
$K_{\alpha}$ , x-rays/protons	1 - > 1000	15 - 50	
$L_{\alpha}$ , x-rays/protons	3 - 1000	40 - 92	
<b>(iii) Signal to Background</b>			
x-rays/electrons	100 - 1000	$\geq 10$	
x-rays/protons	$10^b$	$Z \leq 25, Z \geq 35$	
<b>(iv) Background Cross Sections</b>			
x-rays/electrons, $\sigma_{bX}/\sigma_{be}$	$\leq 1$	$\geq 10$	
x-rays/protons, $\sigma_{bX}/\sigma_{bp}$	$10^c$	$Z \leq 25, Z \geq 35$	
<b>(v) Projectile Intensity Required to Produce Same Minimum Detectable Limit</b>			
x-rays/electrons, $N_x/N_e$	$(700 - 3) \times 10^{-5}$	15 - 92	
x-rays/protons, $N_x/N_p$	$(1 - 2) \times 10^{-5}$	15 - 92	
<b>(vi) Energy Deposited for Same Minimum Detectable Limit</b>			
x-rays/electrons	$(200 - 1) \times 10^{-5}$	15 - 92	
x-rays/protons	$10^{-2} - 10^{-7}$	15 - 92	
<b>(vii) Accuracy of Concentration</b>			
Determinations	<u>x-rays</u>	<u>electrons</u>	<u>protons</u>
similar standards <sup>d</sup>	1%	6%	5-10%
pure element standards	5%	>10%	>10%

<sup>a</sup>x-ray energies are 1.007 times the energy of the absorption edge; electron energies are 20-100 keV; and proton energies are 2-5 MeV.

<sup>b</sup>Lower values in the  $25 < Z < 35$  region.

<sup>c</sup>Higher values in the  $25 < Z < 35$  region.

<sup>d</sup>Prepared standards similar in composition to the sample under study.

### Conclusions

Synchrotron radiation has several advantages over other excitation sources for x-ray fluorescence analysis. Some of these are as follows: (1) The continuous photon energy spectrum from a storage ring permits selection by monochromatization of photons in a narrow energy band. By choice of bombarding energy close to the absorption edge, the photoionization cross section for a particular element can be enhanced over those for lower Z elements. (2) The energy of the absorption edge can be correlated with the fluorescence x-rays, providing a unique Z identification. (3) Since synchrotron radiation is highly polarized, the unwanted scattered radiation (Rayleigh and Compton) reaching the detector can be greatly reduced. (4) Overheating of the sample can be avoided. Because of these and other advantages, it is our opinion that x-ray analysis employing synchrotron radiation will emerge in the near future as the method *par excellence* for microprobe analyses of a variety of samples.

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