BNL 33371
Conf-830791--1

The Utilization of Synchrotron Radiation for Trace-Element Analyses in Toxicology of Metals

A. L. Hanson, K. W. Jones, H. W. Kraner, and B. M. Gordon

Brookhaven National Laboratory

Upton, New York 11973, USA

BNL--33371

and

DE83 016374

J. R. Chen

State University College of Arts and Sciences

Geneseo, New York 14454, USA

Presented at

Second International Conference on the Clinical Chemistry and Chemical Toxicology of Metals

Montreal, Canada

July 19-22, 1983

The submitted manuscript has been authored under Contract DE-AC02-76CH00016 with the Division of Basic Energy Sciences, US Department of Energy. Accordingly, the US Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

THE UTILIZATION OF SYNCHROTRON RADIATION FOR TRACE ELEMENT ANALYSES IN TOXICOLOGY OF METALS

A. L. Hanson, K. W. Jones, H. W. Kraner, B. M. Gordon, and J. R. Chen*

Brookhaven National Laboratory, Upton, NY 11973 U.S.A.
*State University College of Arts and Sciences, Geneseo, NY 14454 U.S.A.

INTRODUCTION

The utilization of x-ray fluorescence (XRF) for trace element analysis has long been recognized in the biomedical community as an attractive technique for trace element analysis. Electron synchrotron-excited x-ray fluorescence (SXRF) provides several major improvements over conventional tube-excited fluorescence. Some of the improvements include: (1) higher brightness, several orders of magnitude improvement, resulting in the availability of monochromated photons with shorter analysis times; (2) high polarization of the photon beam so that scattering from the target can be reduced; (3) better sensitivities; calculations show sensitivities in the low ppb range for thin carbon matrices with short run times (Gordon (1982), Grodzins (1983)); (4) the photons have low divergence in both the horizontal and vertical direction so the beam can be focussed to a small spot, probably at least 1 μm. (The proposed design for the BNL x-ray microprobe has been given previously by Jones, et al. (1983).); (5) with monoergic beams, elements can be selectively fluoresced and chemical states can be determined.

The National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory is a large facility dedicated only to the production of high intensity photon beams. When fully operational it will be able to support over 100 simultaneous experiments. In preparation for operation of the NSLS we have carried out several experiments at the CHESS facility at Cornell University. Initially, radiation damage to the structure of human blood and tissue samples was investigated with "white" (unfiltered) radiation. Subsequently, we studied sensitivities for trace element analyses and investigated several materials.

Radiation Damage to Human Blood Cells and Tissues

This experiment was to study the radiation damage resistance of certain types of cells on a gross basis, as it would relate to trace elemental analyses of entire cells and portions of tissue. Several samples of K_3EDTA-anticoagulated human blood were spun to a monolayer on a glass microscope slide and then air-dried (Slatkin, et al.(1983)). The slides were then irradiated in white radiation for 10-33000 seconds to fluences of 7×10^{15} to 2.4×10^{19} photons/cm^2. The average photon energy was 15 keV. Light microscope and SEM investigations showed no mass loss from either erythrocytes or leukocytes with fluences below 6×10^{18} photons/cm^2. Obvious mass loss from the leukocytes occurred at 1.6×10^{19} photons/cm^2, and destruction of the leukocytes occurred at 2.0×10^{19} photons/cm^2. Figure 1a shows a sample of cells outside the zone of radiation on one of the slides, and Figure 1b shows cells irradiated with 1.6×10^{19} photons/cm^2. This level of dose corresponds to 1.7×10^4 seconds radiation at the NSLS assuming a high bandpass (2%) monochromator at 10 keV with the machine operating at its full design specification of 2.5 GeV at 500 mA. Even though the samples irradiated with lower fluences showed no structural damage, they did show a resistance to staining. Samples of 8 µm human renal tissue were also irradiated for 1×10^4 to 2×10^4 seconds. These tissue samples also showed no apparent structural damage but stained poorly.

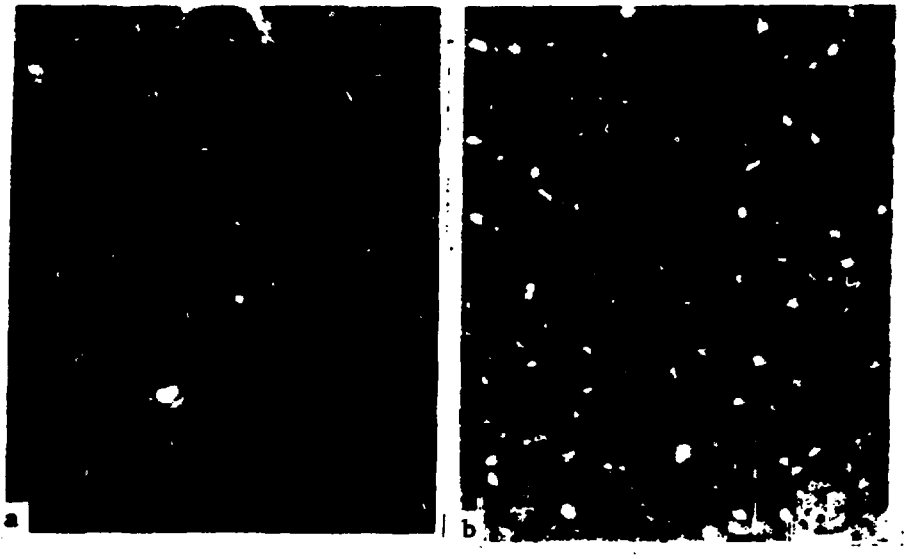

Figure 1. Air-dried K_3EDTA-anticoagulated human blood a) unirradiated, and b)irradiated with 1.6×10^{19} photons/cm^2.

Trace Element Analyses with Synchrotron Radiation

Several samples of NBS standard reference materials were analyzed for trace metals. In Hanson (1983) we showed a plot of minimum detectable limits (MDLs), as defined by Currie (1968), for trace elements in 1-mm thick samples of pressed NBS Orchard Leaves at several incident photon energies. All of the analyses were performed with a 30-mm^2 Si(Li) detector 15 cm from the sample. In Jones, et al. (1983) we presented the best MDL for each element analyzed. Between nickel and strontium we were able to obtain 160-290 ppb. The MDLs for elements lighter than nickel were considerably worse; 0.67 ppm for iron, 0.84 ppm for manganese, 14 ppm for calcium, and 23 ppm for potassium. One of the problems with analysis of the lighter elements was poorer transmission of photons through the beam line components at lower, more optimum energies.

Figure 2 shows a fluorescence spectrum of yeast fluoresced with an 8.4-keV monochromated photon beam, the monochromator having a bandpass of 5-10 eV. The sample was several layers of yeast spores sandwiched between two 10 $\mu g/cm^2$ formvar films. The spectrum was accumulated for 600 seconds with a 30-mm^2 Si(Li) detector. The interest in the yeast was in relation to ingestion of chromium and nickel at trace levels. The chromium content was less than 20 $\mu g/cm^2$ for a total of 3 μg of chromium in the beam, and the nickel concentration was 14 $\pm$ 2 $\mu g/cm^2$ for a total of 2 μg. This spectrum is notably

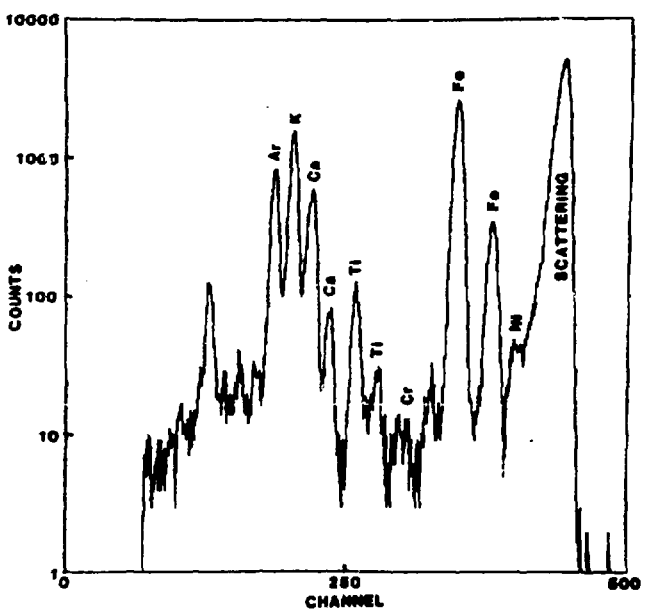

Figure 2. X-ray fluorescence spectrum of yeast fluoresced with an 8.4-keV monochromated photon beam.

cleaner from background (under the photo peaks) radiation than spectra from tube-excited XRF. Since monochromated radiation was used, the scattered radiation is confined to a fairly small energy region just below the incident photon energy. Since energy dispersive (Si(Li)) detectors have problems with incomplete charge collection, 3-5% of the photons at a particular energy will be distributed throughout the spectum at lower energies. Therefore, reducing the scattered radiation will reduce the background. Since the photons are highly polarized, proper placement of the detector can greatly reduce the scattered radiation. It is estimated that less than 10% of the photons were able to scatter in the direction of our detector at 90°.

CONCLUSIONS

The use of SXRF will nicely complement other more widely used analytical techniques for trace elements. The experiments at CHESS showed minimum detectable limits for 1-mm thick organic matrices with monochromated photon beams to be on the order of 160-300 ppb for Ni to Sr with minimal structural damage to the material being irradiated. Extrapolations to operating conditions at the NSLS, with a facility designed for XRF, indicate the MDL limits of 10-100 ppb should be achievable. The utilization of wavelength dispersive detectors should gain an order of magnitude in sensitivity, but with trade-off of some flexibility in multielemental analyses.

ACKNOWLEDGMENTS

This work was sponsored by the Processes and Techniques Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

REFERENCES

L. A. Currie (1968) Anal. Chem, 40, 586.

B. M. Gordon (1982) Nucl. Instrum. Methods, 204, 223-229.

L. Grodzins (1983) Proceedings of Workshop on Uses of Nuclear Analytical Methods in Metal Toxicology, Brookhaven National Laboratory, October 11-12, 1983, Neurotoxicology (to be published).

A. L. Hanson, H. W. Kraner, K. W. Jones, B. M. Gordon, R. E. Mills and J. R. Chen (1983) IEEE Trans. Nucl. Sci. NS-30, 1339-1342.

D. N. Slatkin, G. C. Finkel, A. L. Hanson, K. W. Jones, H. W. Kraner and J. B. Warren (1983) Damage to Air-Dried Human Blood Cells and Tissue Sections by Synchrotron Radiation (to be submitted).