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The Use of a Synchrotron Radiation X-Ray Microprobe for Elemental Analysis at the National Synchrotron Light Source*

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Abstract

The National Synchrotron Light Source (NSLS), due for completion at Brookhaven National Laboratory by the end of 1981, is a facility consisting of a 700 MeV and a 2.5 GeV electron storage ring and dedicated to providing synchrotron radiation in the energy range from the vacuum ultraviolet to high energy x rays. Some of the properties of synchrotron radiation that contribute to its usefulness for x-ray fluorescence are: a continuous, tunable energy spectrum, strong collimation in the horizontal plane, high polarization in the storage ring plane, and relatively low energy deposition. The highest priority is for the development of an x-ray microprobe beam line capable of trace analysis in the parts per million range with spatial resolution as low as one micrometer. An eventual capability for bulk sample analysis is also planned with sensitivities in the more favorable cases being as low as 50 parts per billion in dry biological tissue. The microprobe technique has application to a variety of fields including the geological, medical, materials and environmental sciences. Examples of investigations include multielemental trace analysis across grain boundaries for the study of diffusion and cooling processes in geological and materials sciences samples; in leukocytes and other types of individual cells for studying the relationship between trace element concentrations and disease or nutrition; and in individual particles in air pollution samples.

Introduction

X-ray fluorescence has long been used as a technique for elemental analysis. Within the past decade technological advances in both detectors and excitation sources brought about the ability to perform trace element analyses in bulk samples. Furthermore, the ability to focus charged particle beams led to the development of microprobes for major and minor elemental analyses with spatial resolution in the submicrometer region. In a pioneering effort, Horowitz (1) constructed a low energy (1 to 5 KeV x rays) synchrotron radiation microprobe at the Cambridge Electron Accelerator. Sparks, et al. (2) used a focussed x-ray beam at the Stanford Synchrotron Radiation Laboratory in an effort to verify claims of the existence of superheavy elements in monazite giant halo inclusions. The construction of high energy electron storage rings as dedicated synchrotron radiation sources will allow the development and use of more efficient x-ray excited microprobes with considerable advantages over other microprobe techniques for applications at one micrometer spatial resolution. Thus it will be a complementary technique to those charged particle microprobes with higher spatial resolution.

The National Synchrotron Light Source (NSLS) will include a 2.5 GeV electron storage ring which will provide a continuous spectrum of radiation up to 30 KeV and, with a wiggler, up to 100 KeV. The NSLS is being built as a

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national users' facility and as such will be available to the general scientific community. The x-ray ring will have twenty-eight beam ports and the provision of two beam lines per port. The NSLS will provide a number of general usage beam lines for users. Most beam lines, however, will be constructed and operated by Participating Research Teams (PRT), which are consortia of users with common interests.

Properties of Synchrotron Radiation

Synchrotron radiation is emitted by electrons as their paths are bent in the orbit of the storage ring. The properties of synchrotron radiation make possible the practical use of an x-ray microprobe with some advantages over other types of microprobes. These properties, and their consequences, include:

1) A broad and continuous energy spectrum from which the desired excitation energy may be selected by appropriate monochromators.
2) A stable beam intensity which decays with a half-life of about eight hours.
3) High brightness, or flux, which permits the use of a microprobe. For the NSLS, the electron beam distribution is gaussian and the 4σ size is 0.4 mm high and 1.3 mm wide. The vertical divergence of the photon distribution is about 0.2 mrad.
4) Predominantly linear polarized light in the plane of the electron orbit, thereby reducing scattering backgrounds when observing the target at 90° to the beam in the horizontal plane.
5) 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 bandwidths which allows for chemical speciation by measurement of absorption edge chemical shifts for elements at trace levels.

The NSLS x-ray ring maximum electron current will be 500 mA. The beam is to be bunched with a bunch length of the order of 1 nsec and a maximum of thirty bunches. Table I illustrates the intensities to be expected over an energy range applicable to x-ray fluorescence analysis

Table I. Integrated Photon Intensities for NSLS[a]

Photon Energy (KeV)	Vertical Angle (mrad)	Total Photons	Fraction of (‖) Polarization
6	0.1	5.6×10^{13}	0.987
	0.2	1.1×10^{14}	0.956
	0.4	1.6×10^{14}	0.901
12	0.1	3.0×10^{13}	0.985
	0.2	5.2×10^{13}	0.955
	0.4	6.5×10^{13}	0.924
18	0.1	1.3×10^{13}	0.985
	0.2	2.0×10^{13}	0.958
	0.3	2.3×10^{13}	0.943
28	0.1	2.5×10^{12}	0.985
	0.2	3.6×10^{12}	0.963
	0.25	3.7×10^{12}	0.958

[a] Photons/500 mA/sec/mrad horizontal angle/1% $\Delta E/E$.

The range of energies available can be increased considerably through use of a wiggler, which consists of a series of superconducting magnets installed in a straight section of the storage ring. The wiggler bends the beam out of its normal path with a small radius of curvature and then bends it back to its original path. By this process, the energy spectrum of photons emitted at the wiggler station is shifted to higher energies by a factor equal to the ratio of magnetic field strengths for the wiggler and ring magnets. At NSLS this ratio will be four, thereby providing useful intensities as high as 100 KeV.

X-Ray Fluorescence Analysis

Sparks (3) has analyzed the parameters that affect the sensitivity of microprobes using a variety of excitation methods. The results are summarized in Figure 1. The sensitivities were calculated for electrons whose energies are three times the absorption edge energies of the respective elements and for x rays at absorption edge energies. The continuum and filtered x-ray fluxes are those from the Stanford Synchrotron Radiation Laboratory. Intensities at NSLS will be greater at energies up to 12 KeV and fluxes probably will be greater even above 12 KeV because of a smaller source size. The power depositions, illustrated in Figure 1 for the different excitation methods under the conditions cited, indicate the relative amounts of radiation damage to be expected. Electron microprobes will perform best under those conditions of high spatial resolution and very thin targets, in which case the electrons are transmitted with a minimum of energy deposition and the scattering is held to a minimum in order to preserve spatial resolution.

Ray tracing calculations (4) are now being performed to obtain the optimum conditions for the NSLS microprobe. Consideration is being given to a tuneable monochromator and mirror system as well as to a series of doubly bent crystals for discrete energy selection over the entire energy spectrum. Collimation to the desired spatial resolution will be by passage of the focussed beam through a pinhole in an appropriate absorber foil. Samples will be held on a X-Y translational stage and will be viewed by a Si(Li) solid state detector at 90° to the beam. The sample will also be viewed by an arrangement of fixed or scanning crystal spectrometers.

There is considerable interest in a bulk analysis capability at the NSLS. Although the primary interest of the PRT is the x-ray microprobe, consideration is being given to a bulk analysis beam line. An existing eighty sample automated chamber, based on a Carousel projector, could be used on a monochromated or a filtered continuum beam line. Figure 2 summarizes sensitivities for bulk analysis using monochromatic radiation of 6, 15, and 30 KeV x rays at the NSLS. The results are compared with sensitivities for 3.5 MeV proton excitation. The target is 2 mg/cm^2 thick dry biological tissue on a 1 mg/cm^2 Millipore Filter backing. The time of analysis is 1 min for the photons and an integrated beam of 3μC for the protons. The solid angle included by the 30 mm^2 detector of 155 eV resolution at 5.9 KeV was 2.4×10^{-4} of the total solid angle. The background was calculated using the analysis of Goulding and Jaklevic (5) and the vertical angle acceptance was limited to that which gave 8000 counts/sec of scattered radiation. With the assumed geometry of the detector at 90° to the beam, the scattered count rate was primarily due to the presence of vertically polarized x rays. Analysis using synchrotron radiation is particularly advantageous for geological samples where the elements of highest abundance exhibit the lowest x-ray production cross sections, thereby tending to equalize the detector response of elements throughout the periodic table. In the case of charged particle excitation, the highest abundance elements exhibit the highest cross sections and tend to mask the response of higher Z trace elements.

Another important aspect of a trace element analysis program made possible by synchrotron radiation excitation is the ability to study chemical speciation of trace elements. This would be accomplished by the determination of the absorption edge position for an element by scanning through the absorption edge with a narrow energy bandwidth, typically 1 eV. The energy position of the edge can be compared with those of model compounds of that element covering the range of known oxidation states. This type of experiment would use an EXAFS beam line in a fluorescence mode. Using this technique, Cramer, et al. (6). studied the chemical environment of molybdenum in nitrogenase.

Applications

The capability of obtaining in situ, high spatial resolution, non-destructive analysis of major, minor, and trace elements in mineralogical systems has been a major objective of geochemists. The development of an x-ray fluorescence microprobe technique, although not without its own special types of problems, will open the door to many petrological problems unsolvable by other techniques. Examples of such studies are: 1) The measurement of trace element mineral/mineral and mineral/melt distribution coefficients in experimental systems as a function of pressure, temperature, oxygen pressure, major elemental composition, etc. The results are to be applied to understanding the petrogenesis of naturally occurring igneous and metamorphic assemblages on the earth and the moon. 2) The analysis of trace and major element variations at grain boundary interfaces to study diffusion rates in both experimental and natural systems. 3) The identification of unaltered magmas produced by melting of lunar interior for the study of petrogenesis of lunar mare basalts. 4) The study of abundance patterns in iron meteorites which is made more complex by possible competition of other phases such as silicates, oxides, sulfides, etc., for the elements of interest. Because iron meteorites are malleable, they cannot be crushed to permit mineral separation by normal techniques. High spatial resolution analysis of individual minerals may provide the only means by which ambiguities may be resolved. 5) The study of siting of parent radionuclides in meteorite age determinations. 6) The use of trace elements as meteoritic cosmothermometers. The interpretation of experimental indium contents rests on the proposition that the reaction $In_2S(g) + FeS = 2InS + Fe$ effectively describes the behavior of indium during condensation from the solar nebula. (7) Photon microprobe and chemical speciation experiments could help determine the distribution of indium between sulfide phases and oxidation states. 7) The study of ratios of oxidation states of some trace elements and how they reflect on the redox conditions at the time of condensation from the solar nebula.

The importance of a number of trace elements in the proper functioning of living systems has been evident for many years. More recently, the number of trace elements shown to be important, either as beneficial or as toxic agents, has increased to include most of the common elements. Also, the interrelationships among trace elements have been shown to be important in living systems. X-ray fluorescence analysis has been applied to multielemental analysis of a great variety of sample types. The scanning electron microprobe has been most successfully employed as a tool for elemental analysis on a sub-cellular level in biomedical systems. The photon microprobe can complement these studies to include trace elemental analyses on a cellular level with the advantage of reducing the radiation damage in the target samples. Some areas of study are: 1) Human nutrition. Chemical speciation of trace elements and the relation of chemical state to uptake is of great importance in the establishment of recommended human requirements. 2) The study of trace element levels in components of blood, namely, lymphocytes, monocytes, and polymorphonuclear leukocytes. Trace elements in these components exchange rapidly with some body organs and may indicate trace element concentrations existing in those organs. Bulk determinations in whole blood or plasma may not provide accurate information. 3) The study of the relationship between trace element levels and carcinogenicity. 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. (8) It is clear that the chemical form of the element is important as is the method of uptake. Some non-carcinogenic elements are important in that their deficiency can contribute to development of neoplasms. Trace element microanalysis of biopsy tissue and correlation with pathological observation should be an important aspect of such a study. 4) The study of environmental interactions of trace elements in communities near industries processing those elements.

In the material sciences, the x-ray microprobe will advance our scientific understanding in areas such as: 1) Inhomogeneities in metals and ceramics and their relationship to chemical and physical properties. 2) Interfaces, as illustrated by grain boundaries, cracks and pores. A critical area in ceramic science is the relationship between properties and microstructure. The x-ray microprobe will improve our capability to determine the elemental and phase distributions and stress levels of these microstructures. 3) The effect of trace impurities on physical and chemical processes in materials. Radiation effects, mechanical properties, crystal growth, annealing behavior and recrystallization, chemical reactions, catalysts, and colloid chemistry can be drastically altered by trace impurities. The improved sensitivity of the x-ray microprobe can provide new insights into the effect of trace impurities on these processes.

PRT Organization

The x-ray microprobe is scheduled to begin operation in the latter half of 1982. The line will be established and operated by a PRT whose membership consists of those national users who are able to contribute to the effort. The PRT term will be for a maximum of three years and will be renewable upon review of the scientific program. The NSLS is responsible for design, construction and installation of the front ends, for which the respective PRTs will be billed. The PRT is responsible for scheduling the usage of its beam line by its own members. The x-ray fluorescence analysis PRT, as other PRTs at the NSLS, must provide at least 25% of its total operational time to users outside PRT membership. Non-PRT users will not be required to enter into a scientific collaboration as a condition for using the PRT beam line. Proposals of non-PRT users will be subject to review by the NSLS. There will be no charge for the use of the facility provided that the research is of documented programmatic interest to the DOE and the user agrees to publish the results of the research in the scientific or technical literature. If the user performs proprietary research, a full cost recovery fee will be charged for the amount of beam time utilized.

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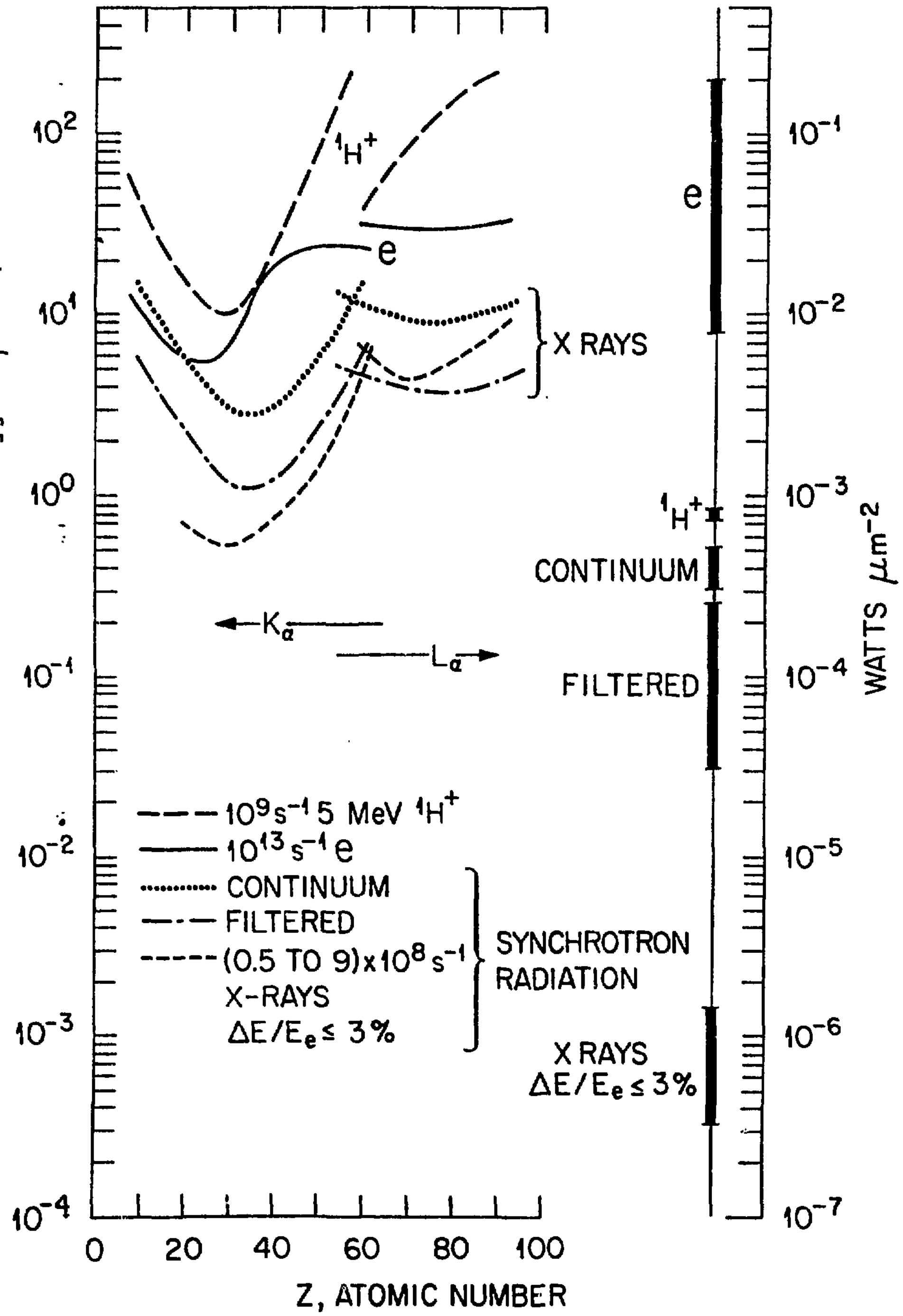
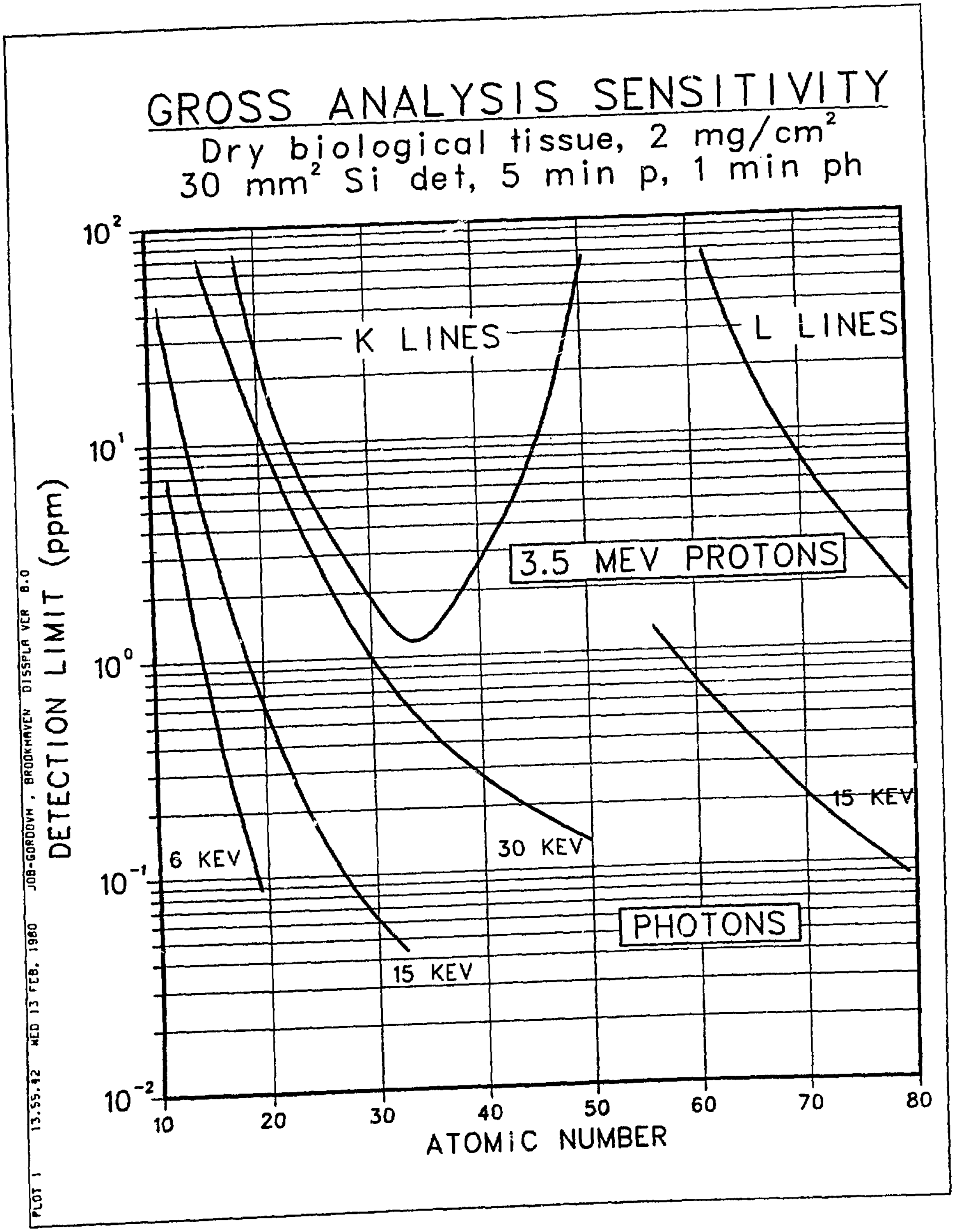
Figure 1



MINIMUM DETECTABLE LIMIT (10^{-6} gg^{-1}s^{-1}μm^{-2})
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0
20
40
60
80
100
Z, ATOMIC NUMBER
^{1}H$^+$
e
X RAYS
K$_\alpha$
L$_\alpha$
10^9s^{-1} 5 MeV ^{1}H$^+$
10^{13} s^{-1} e
CONTINUUM
FILTERED
(0.5 TO 9)x10^8 s^{-1}
X-RAYS
$\Delta E/E_e \leq$ 3%
SYNCHROTRON RADIATION
e
^{1}H$^+$
CONTINUUM
FILTERED
X RAYS
$\Delta E/E_e \leq$ 3%
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
WATTS μm^{-2}

Figure 1. Comparisons of minimum detectable limits for thick samples and power dissipated among charged-particle and synchrotron radiation fluorescence microprobes (after Sparks (3)).

Figure 2


GROSS ANALYSIS SENSITIVITY
Dry biological tissue, 2 mg/cm²
30 mm² Si det, 5 min p, 1 min ph
DETECTION LIMIT (ppm)
ATOMIC NUMBER
K LINES
L LINES
3.5 MEV PROTONS
PHOTONS
6 KEV
15 KEV
30 KEV
15 KEV
10²
10¹
10⁰
10⁻¹
10⁻²
10
20
30
40
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60
70
80
PLOT 1 13.55.42 WED 13 FEB, 1980 JOB-GORDOVM, BROOKHAVEN DISSPLA VER 8.0

Figure 2. Comparison of bulk analysis sensitivities in biological material between proton-induced and monochromatized synchrotron radiation induced fluorescence techniques.