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MAPPING OF TRACE ELEMENTS WITH PHOTON MICROPROBES: X-RAY FLUORESCENCE WITH FOCUSSED SYNCHROTRON RADIATION

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and George Schidlovsky

High energy electron synchrotron storage rings provide copious quantities of polarized photons that make possible the mapping of many trace elements with sensitivities at the parts per billion (ppb) level with spatial resolutions in the micrometer range. The brightness of the x-ray ring of the National Synchrotron Light Source (NSLS), presently being commissioned, will be five orders of magnitude larger than that of the bremsstrahlung spectrum of state-of-the-art rotating anode tubes. We will discuss mapping trace elements with a photon microprobe presently being constructed for use at the NSLS. This microprobe will have micrometer spatial resolution.

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Brookhaven National Laboratory is presently commissioning the NSLS, an electron synchrotron storage ring dedicated only to the production of high intensity x rays. This facility consists of two storage rings that will separately cover the vacuum ultraviolet (vuv) and x-ray regions of the electromagnetic spectrum. The larger, 2.5 GeV storage ring will provide a continuous spectrum of x rays with useful intensities up to an energy of approximately 20 keV. This storage ring is a high current machine (500 mA design current) with bending magnets of 6.875m radii.

Figure 1 represents the energy spectrum of photons available on the high energy ring. The typical beam line is positioned on a bending magnet and is labelled "arc source" in the figure. This curve is for the design electron current of 500 mA and a 1% energy bandwidth (through a monochromator). The other curves show spectra for the special cases in which multipole magnetic devices (wigglers) are inserted into straight sections of the storage ring to provide oscillations which enhance certain properties. For example, the high magnetic field of the superconducting wiggler will harden the x-ray spectrum to provide usable flux to 100 keV. The 24-pole REC wiggler using permanent magnet structures simply increases the flux by a factor of twenty-four over that of the arc source using a comparable magnetic field.

When used for x-ray fluorescence, synchrotron radiation provides a number of advantages over other fluorescence techniques utilizing charged particles and x-ray tubes. The broad and continuous spectrum of photons has sufficient intensity that a band of energies about a desired excitation energy may be selected with a monochromator. The combination of high brightness and polarization of the photons results in sensitivities in the 1-100 ppb range for many elements with analysis times of one minute or less.

Elemental mapping is made possible due to the low divergence of the photon beam which allows for x-ray focussing with mirrors at grazing angles.

Sensitivities for elemental analysis with x-ray fluorescence have been calculated[1] for focussed x-ray beams assuming a 30-μm beam spot and intensities available from the NSLS. The calculations are shown in Figures 2 and 3. The calculations were for trace elements in thin biological matrices (2 mg/cm^2 carbon) and thin geological matrices (3 mg/cm^2 USGS BCR-1), respectively. The calculations were based on the expected output from a scanning crystal spectrometer with 5-sec irradiating time. The discontinuity in the curves represents the required change of analyzing crystal. Sensitivities using a Si(Li) detector and 60-sec irradiation times are about a factor of ten poorer due to inherently higher backgrounds.

Several experiments have been carried out at the Cornell High Energy Synchrotron Source (CHESS). The results of measurements of minimum detectable limits (MDLs) for thick biological samples in ambient air using the arc source (<20mA current) and a low bandpass monochromator have been reported elsewhere.[2,3,4] The MDLs, measured with a Si(Li) detector were on the order of 200 ppb. These measurements scale within an order of magnitude with the calculations of Gordon.[1] More recent measurements with 30-43 keV x rays from the wiggler at CHESS will be presented. These measurements emphasized analyses of geological samples with monochromated (low bandpass) x rays. Sufficient fluences of x rays were available for analyses with beam spots apertured to 100x100 μm^2.

The X-Ray Microprobe

One beam line on the x-ray ring at the NSLS is dedicated to development and use of an x-ray microprobe for x-ray fluorescence analysis of trace elements. The design of the x-ray microprobe will utilize mirrors at grazing angles to the beam to demagnify the x rays ultimately to a 1-10 μm diameter beam spot. The present design of this microprobe includes a monochromator and a focussing platinum-coated ellipsoidal mirror. This mirror will provide an eightfold demagnification with an energy limit of 17 keV. The final beam spot will be 20- to 30-μm diameter. The final design of the beam line will use the focussed 30-μm beam spot as the source image for further demagnification to 1-10 μm. With a source-defining pinhole at the second phase focal point, no pinhole would be required at the third phase focal point. Ray tracing studies to determine fluxes transmitted through this system are in progress to determine the optimum optics and the available sensitivities.

Mapping trace elements with the microprobe will be performed by scanning a sample through the focussed beam spot. Distributional maps of the trace elements in the samples can be made with minimum detectable limits on the order of those shown in figures 2 and 3. As stated before, the beam line will be equipped with a monochromator to select a specific energy band from the incident x-ray beam. For x-ray fluorescence, monochromators with the largest available band passes will be implemented to maximize the photon flux. However, if a low band pass monochromator is used, with a sacrifice in sensitivity, the chemical states of the elements can be studied by measuring the fine structure of the absorption or fluorescence around the elements' absorption edges.

X rays in the energy region available with the NSLS have a depth of penetration large enough for tomography, so the microprobe will permit the development of microtomography. The monochromatic x rays that will be available should improve the resolution obtainable with normal tomography. By measuring the fluoresced x rays, it will be possible to perform depth profiling of the trace elements. Similarly, the tomographic technique can be used in a transmission mode just above and below an absorption edge to provide a depth pr ile of the major and minor elements.

References

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4. K. W. Jones et al., Nucl. Instrum. Methods B3 (1984) 225-231.
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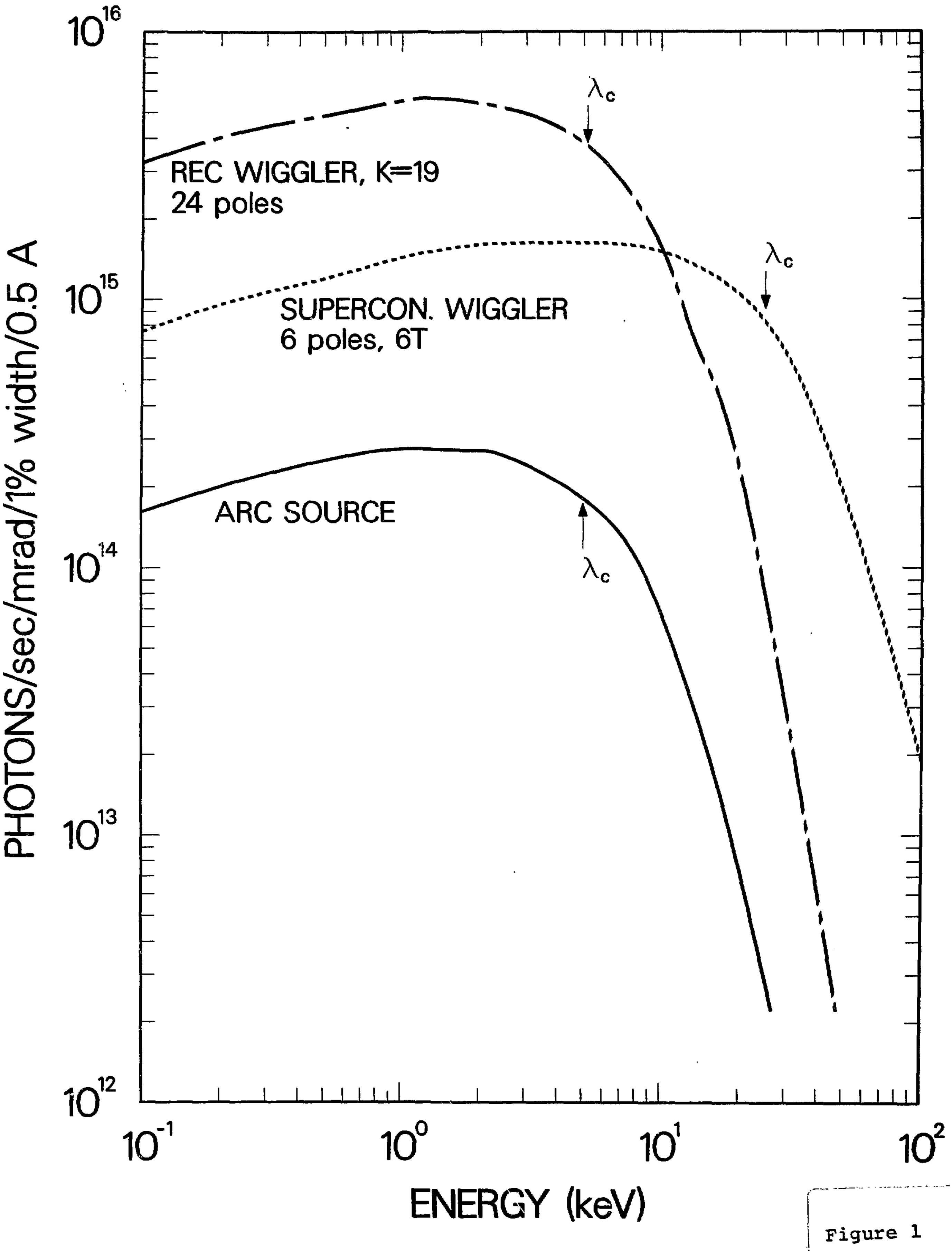
Figure Captions

Figure 1. Photon energy spectrum for NSLS x-ray ring operating at 2.5 GeV. X-ray microprobe will be situated on arc source.

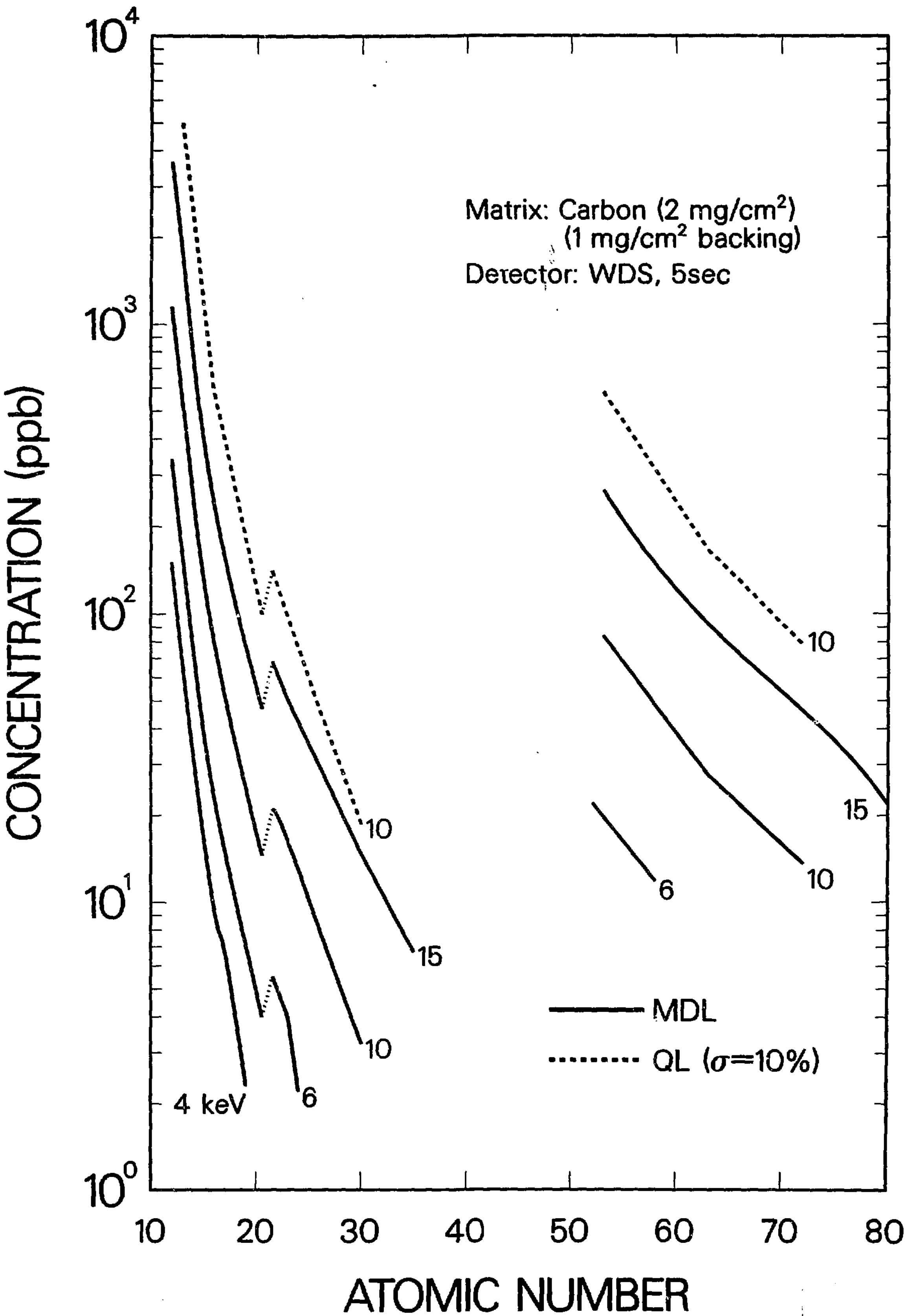
Figure 2. Sensitivity for trace element fluorescence analysis in thin biological matrix using 30-μm beam spot. MDL is minimum detectable limit and QL is quantitation limit (Ref. 5) where standard deviation is 10%. From Ref. 1.

Figure 3. Sensitivity for trace element fluorescence analysis in thin geological matrix using 30-μm beam spot. From Ref. 1.



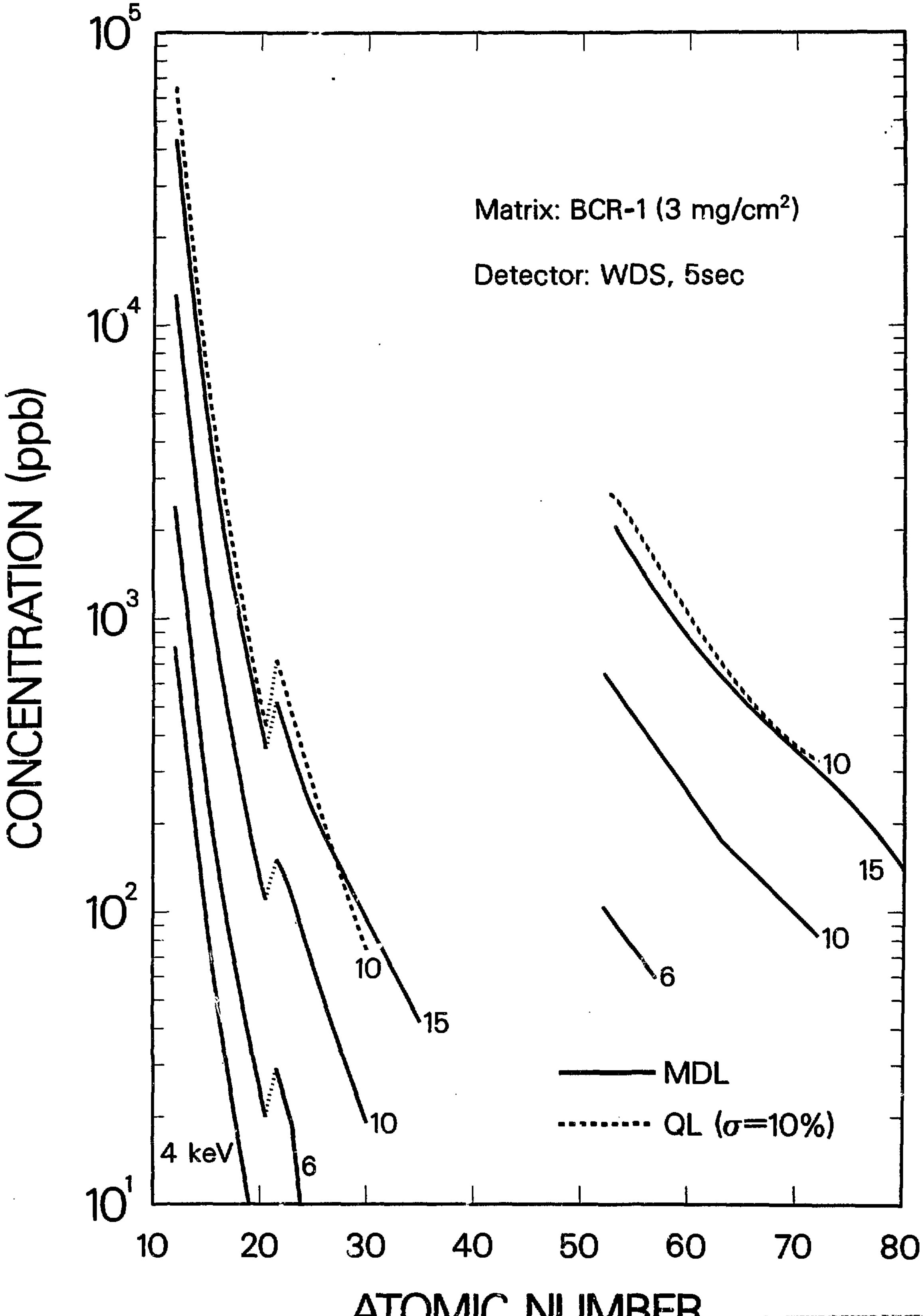
PHOTONS/sec/mrad/1% width/0.5 A
ENERGY (keV)
REC WIGGLER, K=19
24 poles
SUPERCON. WIGGLER
6 poles, 6T
ARC SOURCE
λ_c
λ_c
λ_c
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{-1}
10^{0}
10^{1}
10^{2}

Figure 1



Matrix: Carbon (2 mg/cm²)
(1 mg/cm² backing)
Detector: WDS, 5sec
CONCENTRATION (ppb)
ATOMIC NUMBER
10⁴
10³
10²
10¹
10⁰
10
20
30
40
50
60
70
80
4 keV
6
10
15
10
6
10
15
10
MDL
QL (σ=10%)

Figure 2



Matrix: BCR-1 (3 mg/cm²)
Detector: WDS, 5sec
CONCENTRATION (ppb)
10^5
10^4
10^3
10^2
10^1
ATOMIC NUMBER
10
20
30
40
50
60
70
80
4 keV
6
10
15
10
15
10
6
10
MDL
QL (σ=10%)

Figure 3