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QUANTITATIVE X-RAY FLUORESCENCE ANALYSIS USING MONOCHROMATIC SYNCHROTRON RADIATION

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Abstract

The use of high-intensity, tunable monochromatic x-rays for the quantitative analysis of biological and geochemical specimens at the 10^{-8} g level is described. Incident x-rays were obtained from the new LBL-EXXON permanent magnet wiggler beamline at the Stanford Synchrotron Radiation Laboratory. The sample detector geometry was designed to make optimal use of polarization advantages for background reduction. Questions regarding the sensitivity and accuracy of the measurements were studied with particular emphasis on the advantages of tuning the x-ray energies for optimum excitation for specific elements. The implications of these measurements with respect to the use of x-ray microprobe beams will be discussed.

1. Introduction

The unique properties of synchrotron radiation are ideally suited for use as an excitation source in x-ray fluorescence analysis. The high intensity exceeds the flux available from conventional x-ray tubes by several orders of magnitude. The narrow divergence angle facilitates the design of efficient monochromators and other x-ray optical devices. Finally, the high degree of linear polarization inherent in the beam can be exploited to reduce scattered background. This is particularly important for energy dispersive measurements where the sensitivity is often limited by the amount of background viewed by the detector.

Although these advantages can benefit all types of analysis, it is most interesting to consider those cases in which the use of synchrotron radiation facilitates analytical measurement which might otherwise not be possible. Areas of current interest include the use of intense beams for the analysis of minute specimens[1] or the use of focused microprobe beams for scanning samples with high spatial resolution[2,3]. The potential advantages of x-ray fluorescence over charged particle beams in such applications include better analytical sensitivity and the possibility of obtaining chemical information from x-ray absorption fine structure.

A number of authors have discussed the minimum detectable limits which might be achieved under various assumed excitation and detection conditions. Experimental studies have explored the use of both monochromatic and continuous excitation[3-6]. The present paper presents some recent results obtained using high-intensity, tunable monochromatic excitation for the quantitative analysis of a variety of specimen types with energy dispersive x-ray fluorescence analysis. Emphasis was placed on quantitative analysis and the intercomparison of results with other measurements both in terms of sensitivity and accuracy.

2. Experimental

The measurements were performed at the Stanford Synchrotron Radiation Laboratory using the LBL/EXXON wiggler beam line. The unique feature of this line is the 52-pole permanent magnet wiggler which produces x-ray fluxes in the energy region of interest (5 - 20 keV) which are greatly increased over conventional synchrotron sources[7]. The continuous x-ray spectrum was incident on a Si<220> double crystal monochromator which selected a narrow ($\Delta E/E = 10^{-4}$) energy band which could be tuned.

The experimental geometry was adapted from the standard configuration 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 is 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 mm² 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 and restricted the field of view to the region of the sample. The effective solid angle was $\Omega/4\pi = 1 \times 10^{-4}$. In the majority of measurements reported here, the beam profile was a 2 x 2 mm square cross section with a maximum measured incident flux of 5×10^{12} x-rays/cm²/sec at 17.0 keV.

The detector-to-sample geometry was adjusted to restrict the counting rate to 10^4 counts/sec or less which is a reasonable upper limit for Si(Li) semiconductor detector x-ray spectrometers. X-ray intensities from successive measurements were normalized to a fixed x-ray fluence using the integrated output from the ionization chamber labeled I_0 in Figure 1. Counting loss from electronic dead time was corrected using an empirical curve determined at the beginning of the experiment.

Calibration of the system was achieved using a multielement standard prepared by generating an aerosol from a solution containing a quantitative mixture of known elements. The selection of elements was dictated by the requirement that the resulting x-ray spectrum should not exhibit major line overlaps. The aerosol particles were collected on a thin, teflon filter using an impactor stage to limit the particle size to less than 2.5 μm aerodynamic diameter. Particle loadings on the resultant thin film standard were kept below the concentration where layer absorption corrections were required. Subsequent measurements of individual element mass loadings using a carefully calibrated x-ray spectrometer in our laboratory established the concentrations of the multielement standard to an accuracy of 3% or better.

3. Experimental Results

Spectra were obtained from a number of sample types under varying excitation conditions. Minimum detectable limits (MDL) were calculated by integrating the background region beneath a given peak and using the definition $\text{MDL} = 3\sqrt{\sigma}$ where σ is the root mean square statistical variation in the background count[8]. Measurements were made for both a thin film substrate ($\sim 0.4 \text{ mg/cm}^2$) such as one might encounter in atmospheric aerosol analysis and an intermediate thickness ($\sim 25 \text{ mg/cm}^2$) corresponding to typical biological specimens as prepared in our laboratory. Table 1 is a summary of results obtained for 17 keV excitation energy. This energy is approximately equal to the Mo K_{α} excitation energy used in many conventional spectrometers. Comparison of these values with those obtained in an equivalent tube excited configuration shows that the results are typically a factor of 10 to 15 lower[10]. This reduction can be attributed primarily to the polarization advantage of synchrotron radiation.

Although the 17 keV excitation energy was chosen as a convenient basis for comparison with other methods, it is well known that more optimum excitation

can be achieved for specific elements by adjusting the incident energy to a value near the maximum x-ray absorption cross section. Figure 2 summarizes the results of such an attempt at optimization for the case of three elements. These plots show that a minimum in the MDL is achieved for excitation energies which are significantly greater than the K absorption edges for the respective elements as indicated.

The fact that optimum excitation does not occur near the peak of the photoelectric cross section is explained by reference to Fig. 3. This shows a spectrum of background in the region near the coherent and incoherent scattered peaks for 17 keV radiation incident on a 30 mg/cm² cellulose pellet.

The observed structure in the inelastic platter peak can be interpreted as corresponding to multiple scattering events which occur with maximum cross sections. These involve 180° scattering angles which return the photons back along the direction of the beam where they can scatter at 90° from the sample to the detector. This phenomenon is exaggerated with synchrotron radiation since the polarization effects favor 180° events. It is possible that the multiple scattering could be reduced by more effective collimation and shielding in the experimental geometry, however, it is unlikely that the results of Fig. 2 would be dramatically changed.

Another area where the tunability of excitation can be used to advantage is in the selective elimination of certain elements in the spectrum. The accuracy of x-ray fluorescence analysis of complex samples is often limited by the presence of overlapping emission lines from two or more elements. This effect is particularly significant in the case of energy dispersive analysis when the spectrometer energy resolution is of the order of 175 eV. Although peak fitting algorithms can be used, they are of limited use in cases where a minute quantity of an element is to be detected in the presence of a major concentration of another.

An example where the selection of an incident x-ray energy below a major absorption edge can discriminate against a given element is shown in Figs. 4(a) and (b). The two spectra represent data obtained above and below the Pb L_{III} edge and illustrate the measurement of 2 ng/cm² As concentration in the presence of 460 ng/cm² Pb. The As K_α (10543 eV) Pb L_α (10549 eV) interference is one of the most troublesome overlaps occurring in x-ray fluorescence and is unresolved even at resolution achieved by wavelength dispersion.

A second example involves a case where small changes in excitation energy which will result in minor changes in excitation for all elements except the one whose absorption edge has been bracketed. Figure 5 is an example of spectra obtained on an NBS SRM Bovine Liver sample acquired with x-ray excitation above and below the Se K edge.

Quantitative results were obtained for a number of NBS biological and geochemical reference materials. Typical intercomparison results are shown in Table 2 for the case of a 40 mg/cm² pellet of NBS SRM 1632 Coal. Matrix absorption corrections were made using the experimental K_α, K_β x-ray line intensity ratio for iron compared to that obtained for a thin sample. The total sample mass involved in the present determination was approximately 16 mg which is significantly less than the 250 mg minimum recommended by NBS in order to avoid inhomogeneity problems. Nevertheless, the agreement between the present results and the reference values is quite good.

4. Polarization Calculation

As noted earlier, the measured MDL for 17 keV excitation was significantly lower than can be achieved by conventional excitation under equivalent counting rate conditions. This reduction can be attributed primarily to the scattered background reduction at 90° due to the beam polarization. We have performed calculations of the scattered intensity for polarized excitation under various

conditions in order to examine the improvement one might expect in specialized applications such as microprobe beams.

The benefits which derive from polarization can be best described with reference to Fig. 6. Here we show the dependence on detector acceptance angle ($\tan \theta = r/d$ where r = radius and d = distance) of two efficiency functions, $\epsilon_1(\theta)$ and $\epsilon_2(\theta)$. These describe the fraction of total flux which will be detected at 90° for a variable solid angle for the case of isotopically distributed radiation emitted from the source, $\epsilon_1(\theta)$; and radiation with a $\sin^2\theta$ crosssectional dependence, $\epsilon_2(\theta)$. The function $\epsilon_1(\theta)$ corresponds to fluorescence radiation; $\epsilon_2(\theta)$ describes the dependence of linearly polarized radiation scattered at 90° . It is the reduction in scattered background relative to fluorescence signal at small solid angles which produces the polarization advantages.

For the case of 100% beam polarization, these calculations can be summarized as follows[11]:

$$\text{MDL} = \frac{C}{\sqrt{I_0 T}} \frac{\sqrt{\epsilon_2}}{\epsilon_1}$$

where C is a constant for any specific element, I_0 is the x-ray flux, and T is the measurement interval. Some insight into the behavior of this function can be gained by considering that for small solid angles $\epsilon_2 \propto (r/d)^4$ and $\epsilon_1 \propto (r/d)^2$. For cases where I_0 is fixed, the MDL is unchanged as the solid angle is reduced and no improvement due to polarization is achieved. One would then operate the system in a configuration where the counting rate was low enough that good spectrometer resolution could be achieved. On the other hand, if I_0 can be adjusted to always maintain the maximum possible count rate allowed by the spectrometer, reductions in the MDL can be realized. If we assume that the counting rate is dominated by scattered background, then, for constant counting rate as a function of θ , $I_0 \propto (r/d)^{-4}$ and $\text{MDL} \propto (r/d)^2$.

Thus the MDL will continue to improve as the solid angle is reduced while maintaining maximum counting rate.

Figure 7 shows the results of more detailed calculations in which the effects of a partial degree of linear polarization are included. The MDL has been calculated for the element Zn in a 1 mg/cm^2 carbon matrix under the assumption that I_0 is maintained at a level corresponding to 10^4 cts/sec in the x-ray spectrometer. The curves are labeled according to the degree of polarization. A small admixture of elliptical polarization limits the improvement in MDL for the case of extremely small acceptance angles. In the present study, a MDL of 60 ppb was measured for Zn at an acceptance angle corresponding to $r/d = 2.0 \times 10^{-2}$. This corresponds to approximately 90% polarization according to Fig. 7. Although this is consistent with estimates for the degree of polarization from other sources[7], it is likely that the agreement is fortuitous since the idealized model used in the calculations would tend to underestimate the calculated MDL.

Since the polarization advantage is achieved only under conditions of maximum counting rate, it is informative to estimate the effects of reducing the beam size to smaller dimensions. If we form a $2 \text{ }\mu\text{m}$ square beam spot, the reduction in flux would be 10^{-4} . Assuming that it would be possible to increase the flux by 10^2 using focusing mirrors or other x-ray optical devices, then the reduction in counting rate would be 10^{-2} . Thus, although the restricted beam size in the vertical direction would improve the degree of polarization, the necessity for increasing the solid angle would result in an overall loss in the polarization improvements.

4. Summary

Numerous advantages to the use of monochromatic synchrotron radiation for energy dispersive x-ray fluorescence analysis have been demonstrated. Reduction in the minimum detectable limits have been shown to be consistent with

calculations for background reduction due to linear polarization effects. The advantages of tunability for the efficient excitation of specific elements and the discrimination against others have been demonstrated and the limitations noted. Calculations of the variability of the minimum detectable limit with detector geometry have illustrated the limitations which can apply for small area beams.

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Table 1. Minimum Detectible Limits

| Z | Element | 30 mg/cm ² Cellulose (ppb) | 0.4 mg/cm ² Teflon Membrane (ng/cm ²) |
|----|---------|--|---|
| 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 |

Table 2. Measured Concentrations for NBS SRM 1632 Coal

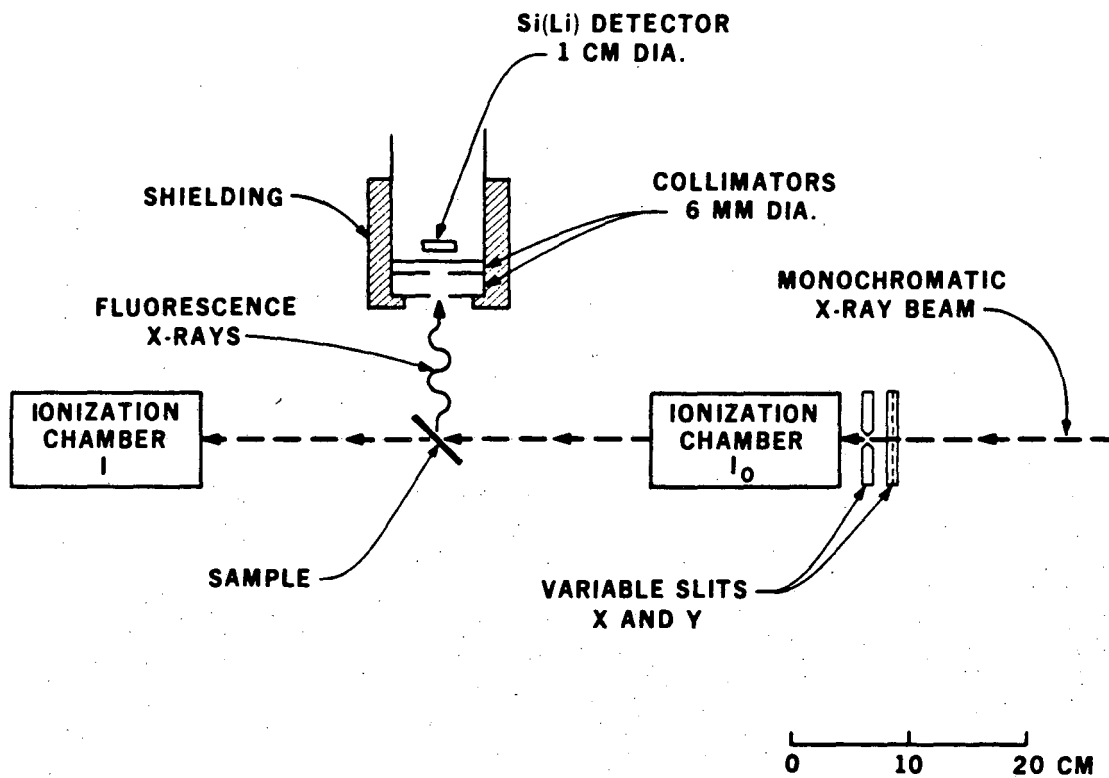
| | This work* | Reference ⁹ | NBS** |
|----|------------|------------------------|------------|
| Fe | 7200 ± 700 | 8500 ± 700 | 8700 ± 300 |
| Ni | 15 ± 3 | 15 ± 2 | 15 ± 1 |
| Cu | 17 ± 2 | 17 ± 2 | 18 ± 2 |
| Zn | 17 ± 2 | 36 ± 3 | 37 ± 4 |
| Ga | 6 ± 1 | 6.0 ± 1.4 | - |
| Ge | 2.1 ± 0.4 | - | - |
| 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 16 mg.

**Certified values based on at least 250 mg.

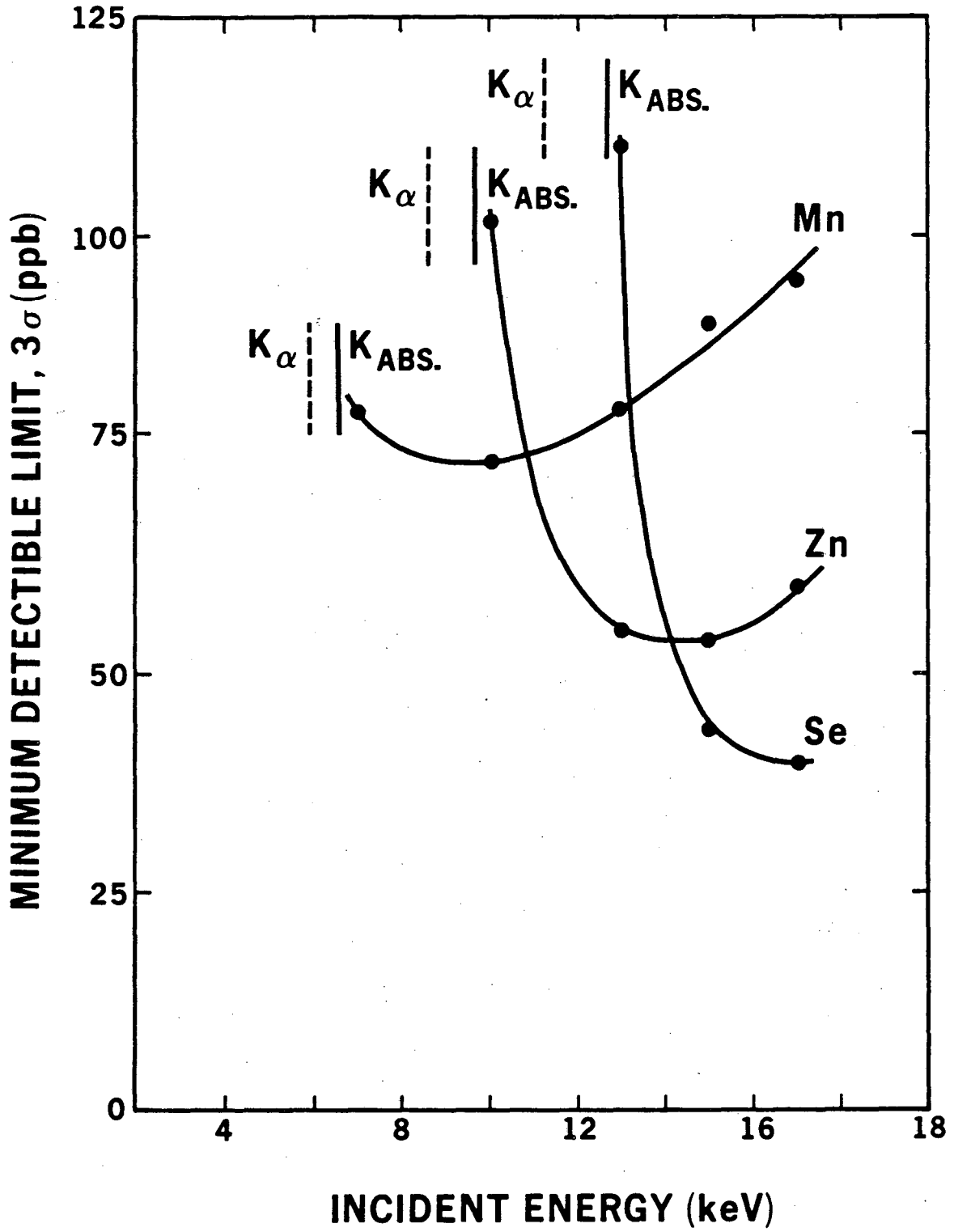
FIGURE CAPTIONS

- Fig. 1. Schematic diagram of experimental setup. The monochromatic x-ray beam is incident from the right.
- Fig. 2. Experimental minimum detectable limits as a function of incident photon energy for Mn, Zn and Se. The K_{α} x-ray energies and K absorption edges are indicated for each element.
- Fig. 3. Scattered background resulting from a 17 keV monochromatic beam incident on a 30 mg/cm² cellulose pellet. The energies of probable multiple scattering events are indicated.
- Fig. 4. Spectra of atmospheric aerosol sample obtained at a) 17.0 keV excitation and b) 12.9 keV. Numbers in parentheses are concentrations in ng/cm².
- Fig. 5. 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).
- Fig. 6. Relative efficiency at a function of detector acceptance angle for isotropic source (ϵ_1) and scattered linearly polarized x-rays (ϵ_2); r = detector radius, d = source-to-detector distance.
- Fig. 7. Calculated minimum detectable limit as a function of detector acceptance angle for the case of Zn in a 1 mg/cm² carbon matrix. A constant detector counting rate of 10^4 events/second is assumed.



XBL 847-3174

Figure 1.



XBL 847-3176

Figure 2.

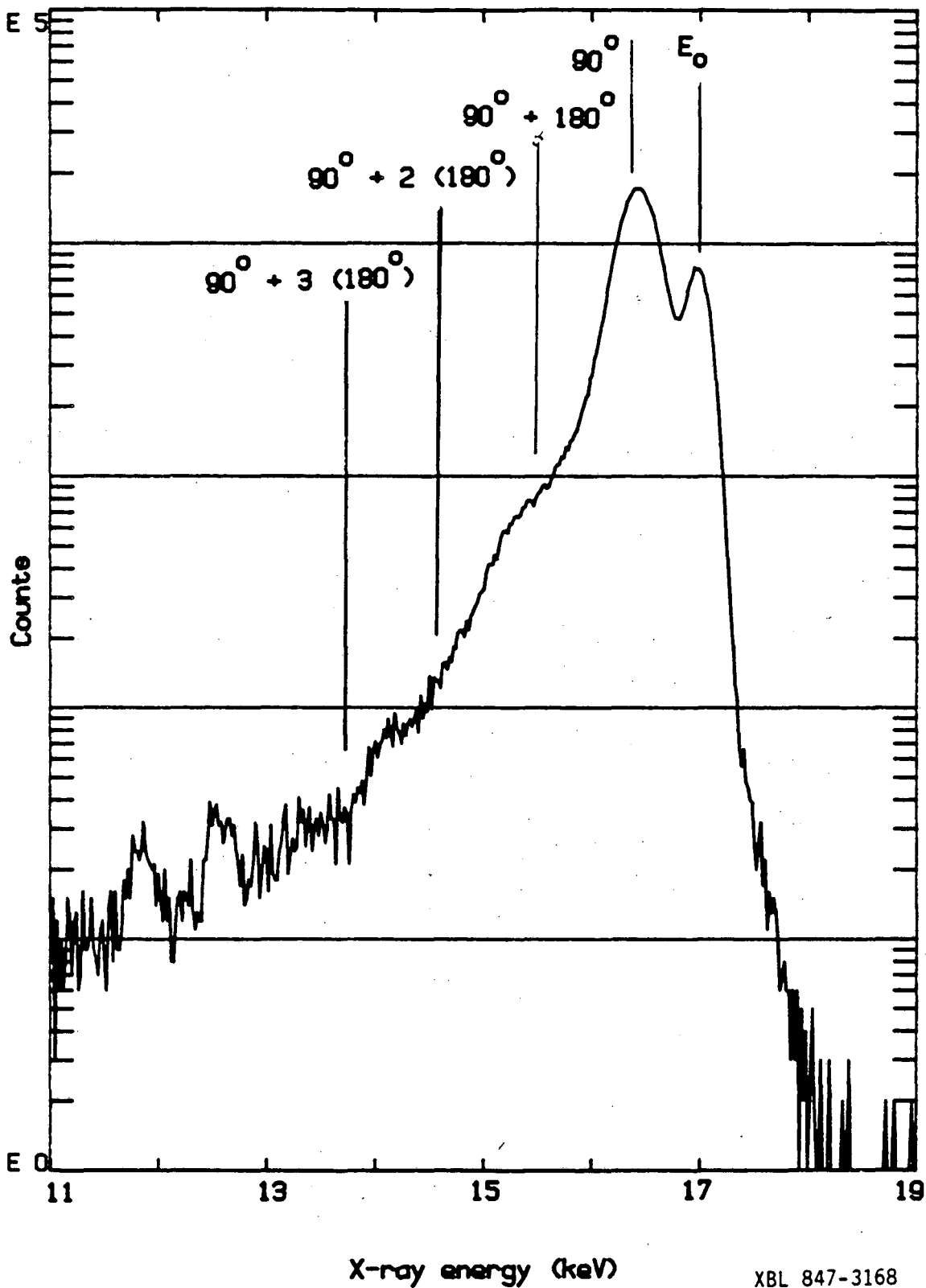
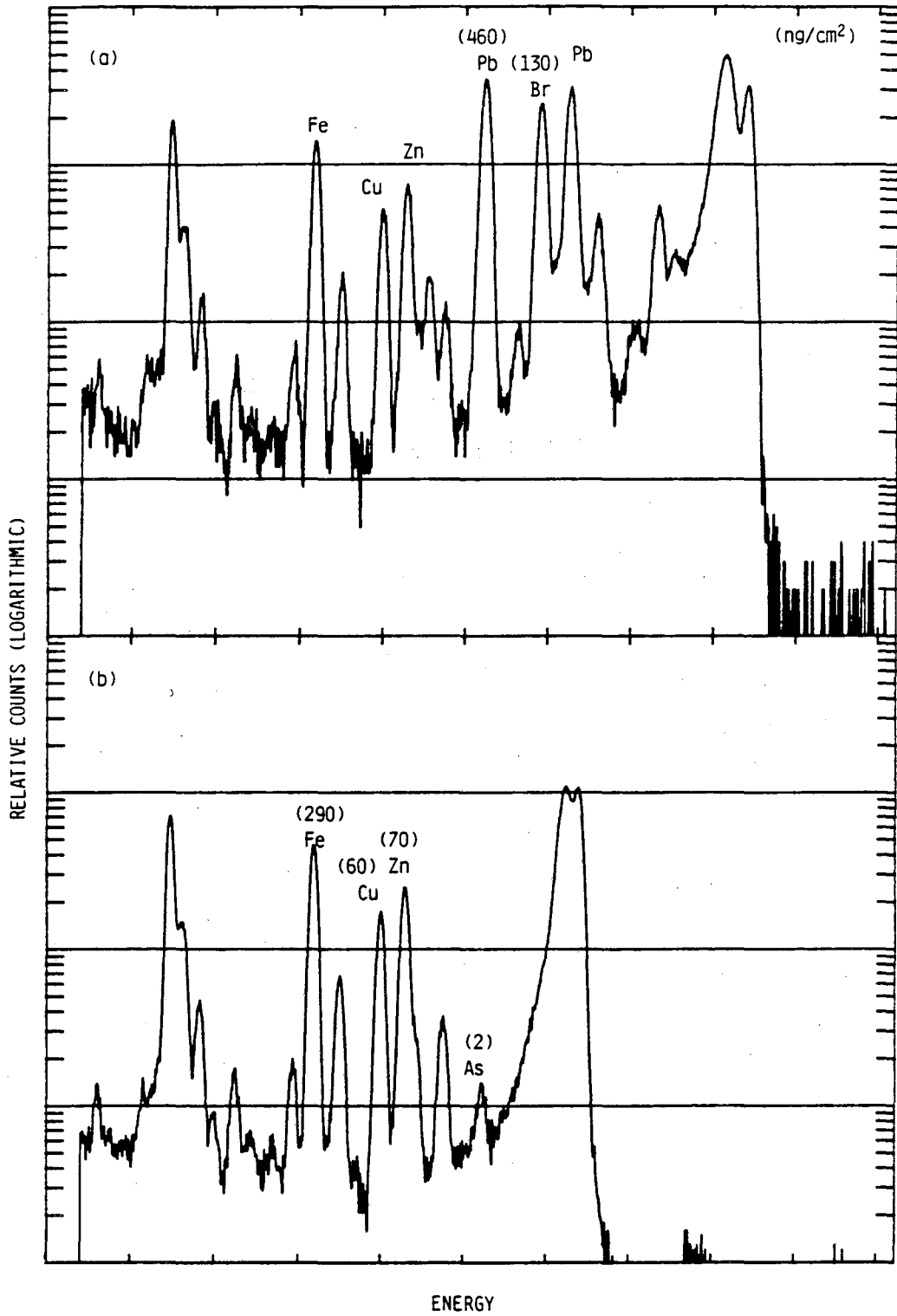


Figure 3.

XBL 847-3168



XBL 849-4051

Figure 4.

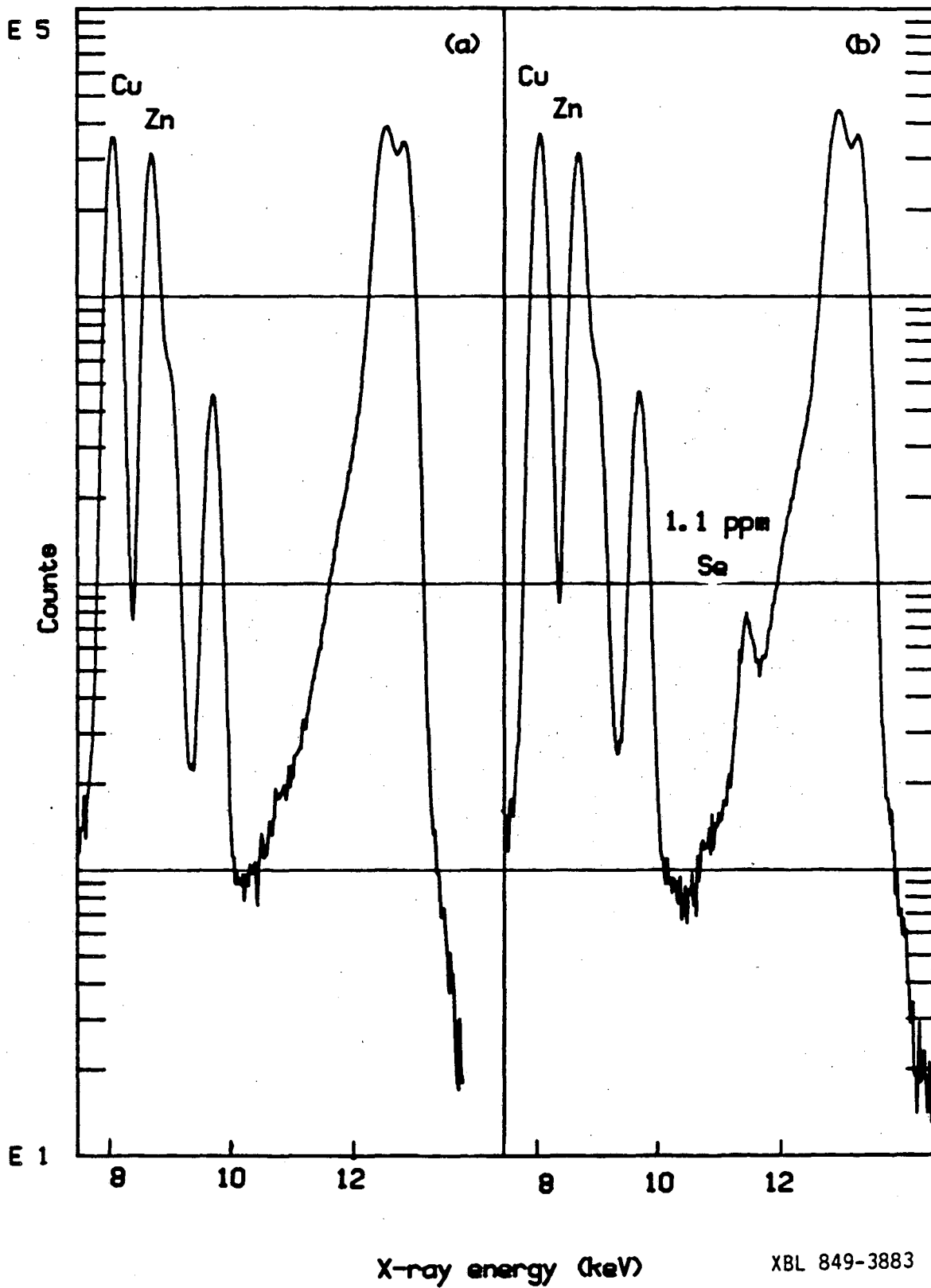
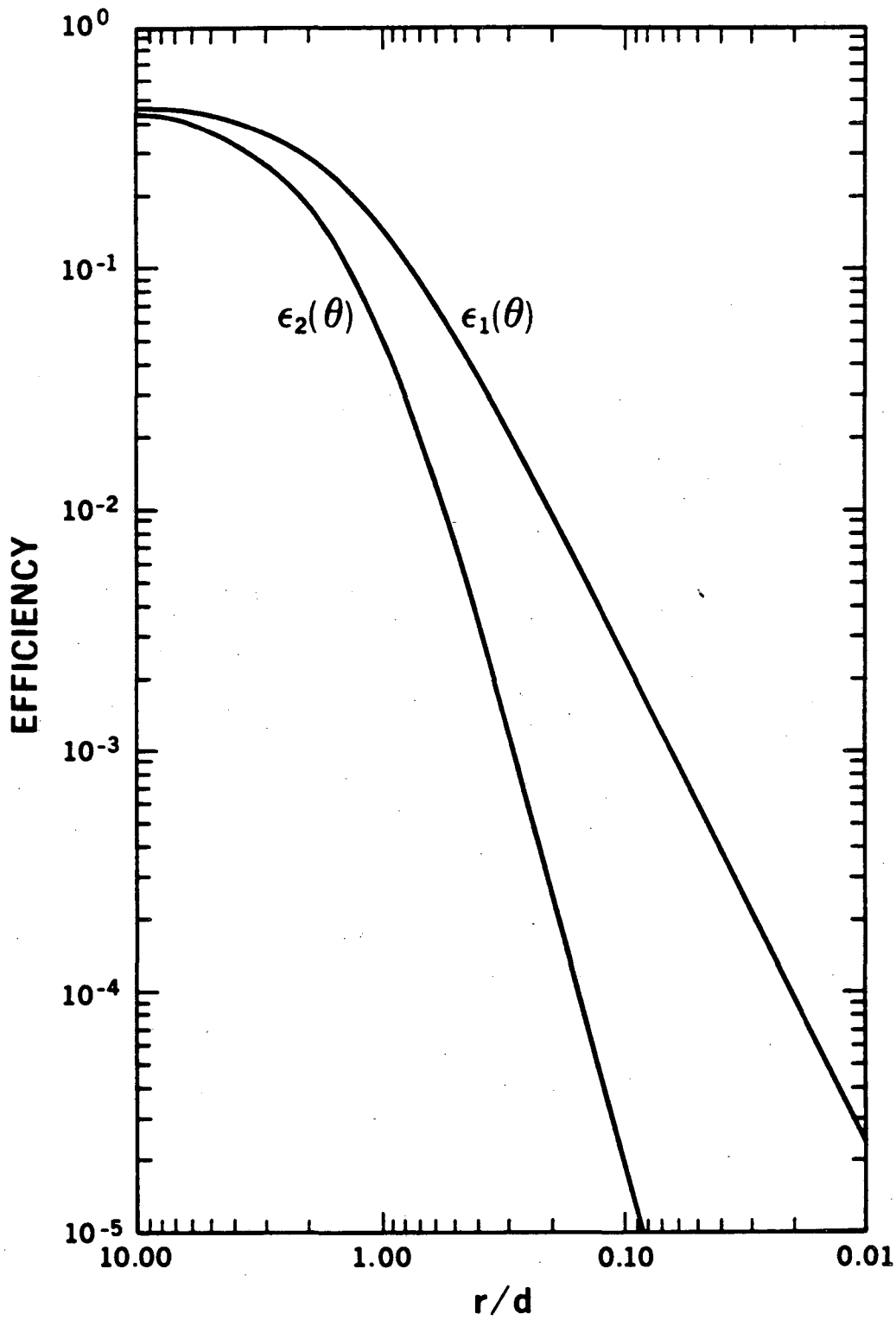


Figure 5.

XBL 849-3883



XBL 849-4050

Figure 6.

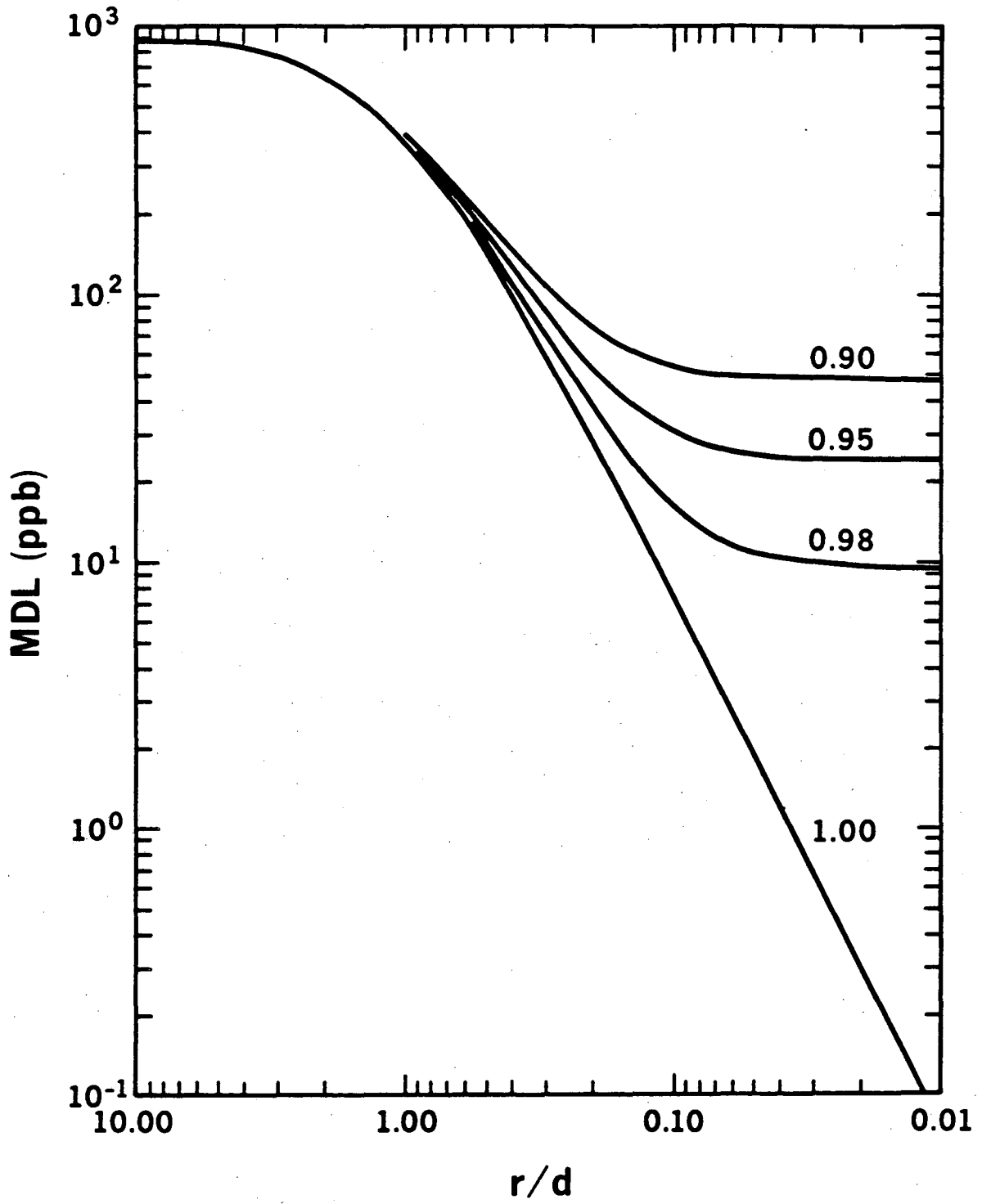


Figure 7.

XBL 849-4049

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