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Publication Date

1985-07-01

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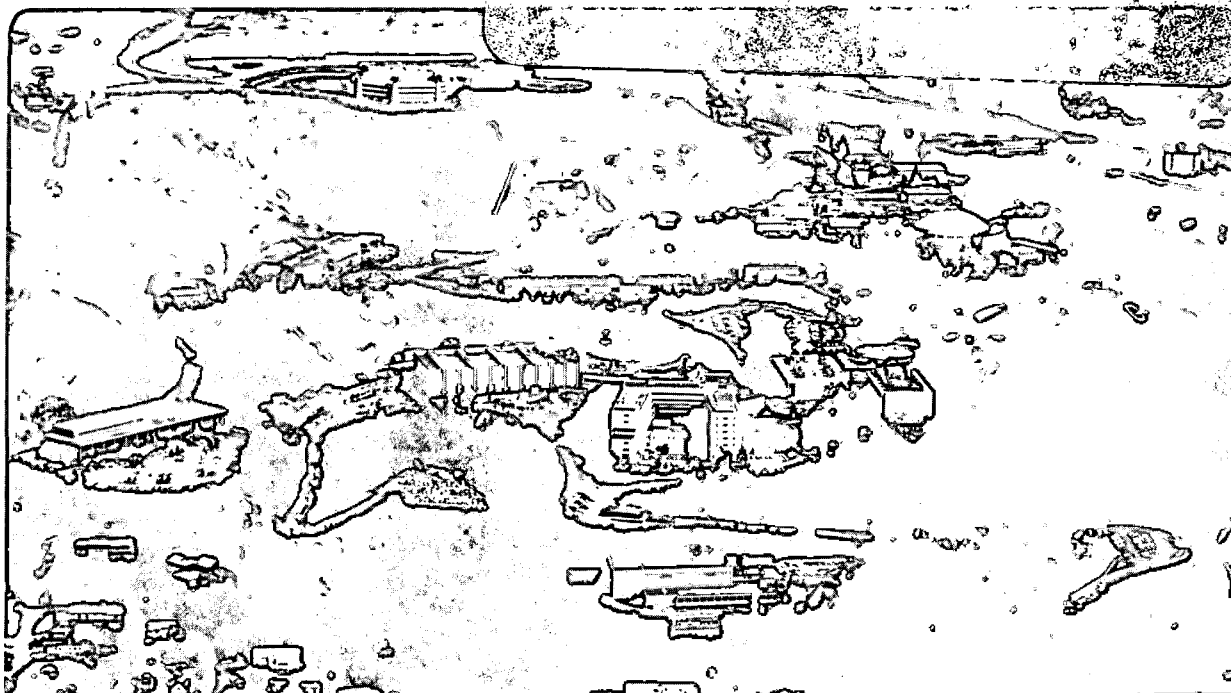
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R.D. Giauque, J.M. Jaklevic and A.C. Thompson

July 1985

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ABSTRACT

The use of synchrotron radiation for high sensitivity trace multielement x-ray fluorescence determinations is demonstrated. Experimental conditions which yield optimum sensitivity are described. Emphasis was placed on establishing calibration techniques and procedures that would yield accurate results with high precision for elements present at concentration levels less than 1 ppm. Comparison of determined and listed elemental concentration values for five standard reference materials are given. Using optimum conditions, minimum detectable limits of 20 ppb were ascertained for most elements. The results clearly illustrate the possibility for high sensitivity trace element determinations of extremely small samples.

This work was supported by the Director's Office of Energy Research, Office of Health and Environmental Research, U.S. Department of Energy Contract No. DE-AC03-76SF00098. The experiment was carried out at SSRL which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences; and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources.

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INTRODUCTION

The development of intense, linearly polarized synchrotron radiation beams has led to significant interest in their application for x-ray fluorescence trace element determinations (1-7). The high intensity of these beams permits the use of tunable crystal monochromators which provide variable energy, narrow bandwidth excitation radiation. Since synchrotron radiation is linearly polarized, the background due to Compton and Raleigh scattering in the specimen can be substantially reduced if the fluorescence detector is placed at 90° to the path of the incidence beam and in the plane of polarization. Although these properties of x-ray fluorescence analysis using monochromatic synchrotron radiation have been demonstrated, very little quantitative trace element data have been reported or procedures verified through the use of Standard Reference Materials. In most cases, one or more Standard Reference Materials has been used to generate x-ray spectra and to calculate minimum detectable limits. In this paper, emphasis was directed towards attaining accuracy for high sensitivity trace element determinations for standard samples which represent the class of materials typically encountered on biological analyses. Quantitative comparisons with standard values are given. Additionally, minimum detectable limits were ascertained and optimum excitation conditions were determined.

EXPERIMENTAL PROCEDURES

Our measurements were carried out using radiation from the LBL/Exxon 54-pole wiggler (8) beam line at the Stanford Synchrotron Radiation Laboratory (SSRL). Radiation from the beam line was focused using an x-ray mirror. A silicon <220> double crystal monochromator was used to select a narrow portion ($\Delta E/E \sim 10^{-4}$) of the continuous radiation spectrum; the maximum energy employed for the present measurements was 20 keV. The experimental geometry is shown in Figure 1. Although the area of the incident beam was set to a 3 x 3 mm cross section using variable horizontal and vertical slits, the intense region of the beam spot was only 1 mm high. The specimens were placed at an angle of 45° to the incident radiation and were continuously scanned across a 4 x 17 mm area during the data acquisition in order to average out sample or beam inhomogeneities. A 5 mm thick, 80 mm² Si(Li) detector was carefully aligned so that it was at the beam height and at 90° to the path of the incidence radiation. This position minimizes scattered radiation into the detector since the beam from the wiggler is about 94% linearly polarized. A pair of 6 mm diameter collimators shielded the periphery region of the detector. An effective solid angle $\Omega/4\pi = 3.5 \times 10^{-4}$ was viewed by the detector. The synchrotron was operated at 3.0 GeV with a maximum current of 100 mA. Maximum incident fluxes of 3×10^{12} and 1.6×10^{13} photons/sec/mm² were obtained at 18 and 10 keV, respectively, for the intense region of the beam spot. A pair of ionization chambers was used to monitor the beam flux a) incident to and b) transmitted by the specimen. For our measurements, the second monochromator crystal was detuned to reduce higher order harmonics and maintain the input count rate seen by the semiconductor detection system at approximately 10,000 counts/sec. The total x-ray flux was measured over the preset counting intervals utilized. Corrections for detector system dead time were made using an empirical curve relating detector throughput to input rate.

Calibration

Two multielement thin standards were used to calibrate the system. The first standard contained Ca, Ti, Mn, Cu, and Ge and the second contained V, Fe, Ni, Zn, Rb, Sr, and Pb. These elements were chosen because their characteristic x-rays span the fluorescence x-ray energy range of interest. The standards were prepared by aspirating dilute solutions containing the elements into a large chamber connected to the intake line of a dichotomous aerosol sampler. Stretched polytetrafluoroethylene (PTFE) filters, 37 mm in diameter, mounted into plastic slide frames were used to collect the aerosols. The standards were collected from the fine stage which limited the particle size to less than 2.5 micron diameter. The deposits were made thin enough that x-ray absorption due to mass loading was not of consideration. Individual mass loadings were designed to yield similar response for all elements on the standard when excited by monochromatic radiation.

The actual mass loadings of the individual elements on the two standards were determined at our laboratory using a calibrated x-ray spectrometer. Absolute calibration of this spectrometer for a single element, Cu, was achieved using several evaporated gravimetric thin film standards prepared at LBL. Calibration for nearly all other elements was realized from multielement standard solution deposits collected from the fine stage of the dichotomous sampler. The multielement solutions were prepared from aliquots of individual element standard solutions, most of which were prepared by dissolving weighed amounts of high purity elements in acidic solutions and making up to volume. In some cases, dried high purity compounds were used when the pure elements were not appropriate weighing forms (e.g., As, Br, Rb, and Sr). The actual amount of multielement standard solutions collected on individual filters was unknown. However, in most cases, Cu served as the internal standard in the multielement

standard solutions which were used to determine the absolute response of the spectrometer system for various elements.

Figure 2 illustrates spectra obtained at SSRL for our standards using 18 keV excitation radiation. Individual element concentration values in $\mu\text{g}/\text{cm}^2$ are listed above each element. It should be noted that the two spectra shown were collected over 200 sec intervals using radiation fluxes which differed by a factor of 1.62. The two standards were run before and after each of the five standard reference materials which were analyzed. Absolute response for each element using 18 keV excitation radiation is shown in Fig. 3. Actual x-ray flux utilized was determined from clock-gated values for the flux in the incidence ionization chamber. Total count rates were corrected for the detection system dead time. Very high precision was realized for the system calibration using the two standards and is reflected by an overall 2σ deviation of 1.9% for the 12 elements.

Peak Shapes

Spectral analysis of the data were performed using empirical characteristic x-ray peak shapes and background distributions. Element x-ray peak shapes were obtained from spectra of single element deposits, typically of mass loadings of 20 to 40 $\mu\text{g}/\text{cm}^2$. All peak shapes were measured at a 10 K counts/sec input rate, equivalent to the rate utilized for our determinations. This procedure minimized any potential x-ray spectral variations associated with input rate. For our determinations, fixed channel windows which contained more than 94% of the major x-ray line from each element were utilized.

Spectral Background

Spectra were acquired on three blank disks which were used to simulate x-ray spectral background due to scattered excitation radiation. The disks,

of mass thickness 50 mg/cm^2 , were composed of microcrystalline cellulose and sulfur powder, with the sulfur content varying from 0 to 10%. These disks yielded varying ratios of Raleigh to Compton scattering due to the different effective Z of the matrices. Relationships between Raleigh and Compton scattering intensities and the spectral background in specific energy regions of interest were established. Similar procedures have been reported elsewhere (9). It should be noted that very low concentration levels of several elements including Fe, Cu, Zn, Br, and Pb were detected as impurities in the blanks. The relatively weak x-ray lines from these elements were not considered as a part of the scattered radiation background.

Sample Preparation

For our experiments five trace element Standard Reference Materials, SRMs, were utilized. Included were three from the National Bureau of Standards—SRM 1549 Non-Fat Milk Powder, SRM 1567 Rice Flour, SRM 1568 Wheat Flour, and two from the National Institute for Environmental Studies in Japan—NIES-4 Freeze Dried Serum, and NIES-5 Hair. Weighed standard reference materials were compressed into 2.54 cm disks at a pressure of 700 kg/cm^2 . No binder material was used. All reference materials were prepared in triplicate. Disk mass thicknesses were in the range of 40 to 60 mg/cm^2 .

Matrix Corrections

The specimens were assumed to have a mass absorption coefficient curve of the same slope as that of a typical hydrocarbon matrix with a hydrogen/carbon atomic weight ratio of 2. One point on the curve, at 10 keV, was determined experimentally using transmission data for 10 keV excitation radiation. For each SRM, transmission measurements were made on only one disk, and the results determined were applied to all three disks since they were of very similar mass

thicknesses. These measurements were achieved using 100 sec count intervals and using ionization chamber I/I_0 ratio values, with and without the specimen, to calculate the value of μ_m for the specimen at 10 keV.

Minimum Detectable Limits

To establish minimum detectable limit (MDL) curves, excitation radiation for energies varying from 6.6 to 20 keV was used to acquire spectra for a blank microcrystalline cellulose disk of mass thickness 40 mg/cm^2 . Additional spectra were acquired for one of the multielement standards at each of the excitation radiation energies utilized. MDL curves established for four elements Mn, Zn, Se, and Rb are shown in Fig. 4. These curves are for 300 sec count intervals. The MDLs include matrix absorption corrections. Comparable MDLs could have been realized for thinner specimens since in most cases the double crystal monochromator was detuned to reduce the incident photon flux by as much as a factor of 5 in order to maintain a 10 K counts/sec input rate to our detector system.

MDLs approximately 20 ppb were measured for most of the elements that we determined. However, since only one energy of excitation radiation is normally utilized for analysis, MDLs actually realized for some elements can increase by as much as a factor of 5. It should be noted that the curves in Fig. 4 illustrate that the optimum MDL for any given element was achieved when the excitation radiation is of energy substantially above the K shell absorption edge energy. In our experiments we determined that the optimum excitation radiation energy corresponds to that energy which could not yield spectral background in the region of interest due to five Compton scattering events.

In some cases, sensitivity for a given element can be substantially enhanced relative to other elements present in the specimen by optimization of the excitation radiation energy. The ability to precisely tune the incident

beam energy over a wide energy range enables one to fully exploit monochromatic excitation. In one of our earlier experiments (10), we were able to measure the concentration of As at the 2 ng/cm^2 level in an atmospheric aerosol specimen which contained 460 ng/cm^2 Pb by selecting an excitation radiation of energy 12.900 keV, which is below the Pb_{III} L absorption edge yet above the As K absorption edge.

RESULTS

Except for NBS SRM 1549 Non-Fat Milk Powder, our trace element determinations for the SRMs were carried out using an excitation radiation energy of 18.00 keV. For this former SRM, excitation energies of 10.00 keV and 18.00 keV were employed. Figure 5 clearly illustrates that the sensitivities realized for the determination of the elements Mn and Ni were substantially enhanced by using 10.00 keV photons. Figure 6 is a spectrum acquired for NBS SRM 1568 Rice Flour. The elements Ni, As, Se, and Sr are all present at concentration levels less than 500 ppb and significant x-ray line intensities were realized. Counting intervals of 300 sec were utilized for our determinations. The mean results for the triplicate determinations for the three NBS and the two NIES SRMs are listed in Tables 1 and 2. The errors shown for the XRF determinations are 2σ values for calibration and counting errors. In nearly all cases, excellent results were achieved. Also shown are results ascertained for some elements not reported by NBS, Sr for all three SRMs and Ni for SRM 1549.

The following example is used to illustrate that synchrotron radiation is easily adaptable to the analysis of small biological specimens. Figure 7 is a spectrum obtained on a $2 \mu\text{l}$ droplet of whole blood (air dried). The concentrations listed are in $\mu\text{g/g}$. Since air drying concentrated the whole blood by a factor of 5, the concentrations of the listed elements in the original whole blood were a factor of 5 lower. A beam spot size of $2 \times 2 \text{ mm}$ was utilized

for 17 keV excitation radiation and counts were acquired over a 400 sec interval. The Compton scattered radiation intensity served as a measure of sample mass. Except for hydrogen, the incoherent mass scattering coefficients (11) are relatively constant for the elements H(Z=1) through Ca(Z=20). The weight fraction of hydrogen in most light element matrices varies between 0 and 14%. The major fraction of the light atomic number matrices are made up of other elements. Thus, the incoherent mass scattering coefficient is relatively constant for most light element matrices. If the specimens are relatively thin--on the order of several mg/cm^2 --matrix absorption effects are essentially negligible for all the elements that we determined except for K and Ca. The results ascertained for the above specimen could easily have been achieved using a much smaller specimen or a reduced beam spot size.

These results demonstrate the feasibility of performing trace element determinations on biological specimens with minimum detectable limits substantially below the ppm level. The fact that the beam intensity is restricted to a small area opens up the possibility of analysis of extremely small samples such as might be obtained for tissue biopsy.

ACKNOWLEDGMENTS

The authors especially thank W.L. Searles for his technical contribution in the design of the equipment, and A.L. Catalano for his support and untiring efforts in carrying out the experiments. The authors also thank L. Sindelar for her efforts. The authors are grateful to Dr. K. Okamoto of the NIES, Japan Environmental Agency, for providing us with the two NIES SRMs.

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FIGURE CAPTIONS

- Fig. 1. Schematic of x-ray fluorescence analysis technique.
- Fig. 2. Spectra acquired for the two multielement thin standards using 18 keV excitation radiation.
- Fig. 3. Calibration curve established for 18 keV excitation radiation.
- Fig. 4. Minimum detectable limit curves established for microcrystalline cellulose disk of mass thickness 40 mg/cm^2 .
- Fig. 5. Spectra obtained for NBS SRM 1549 Non-Fat Milk Powder using 10 and 18 keV excitation radiation.
- Fig. 6. Spectrum acquired for NBS SRM 1568 Rice Flour using 18 keV excitation radiation.
- Fig. 7. Spectrum of $2 \text{ }\mu\text{l}$ droplet of whole blood air dried.

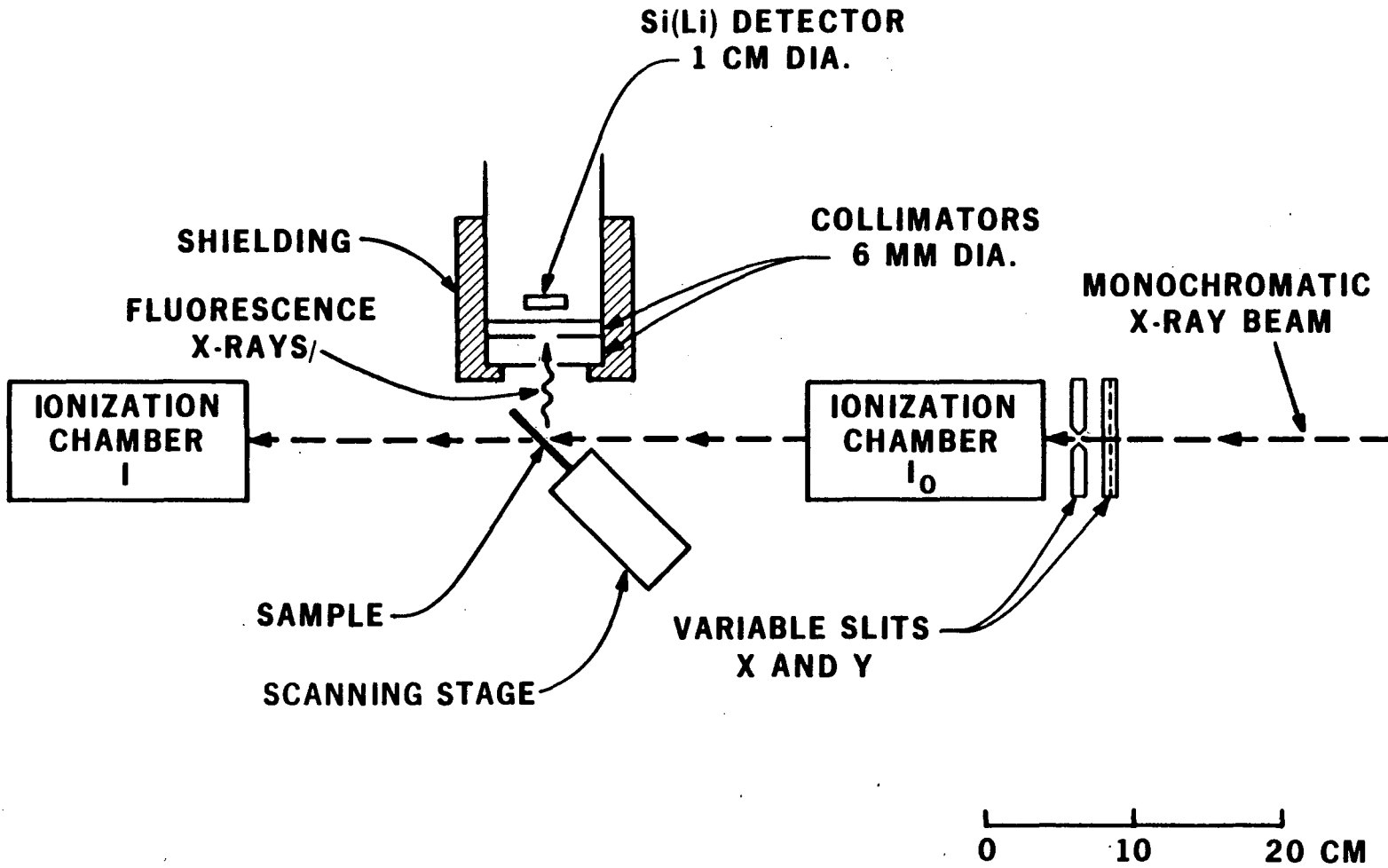
Table 1. Results Determined for Three NBS Standard Reference Materials

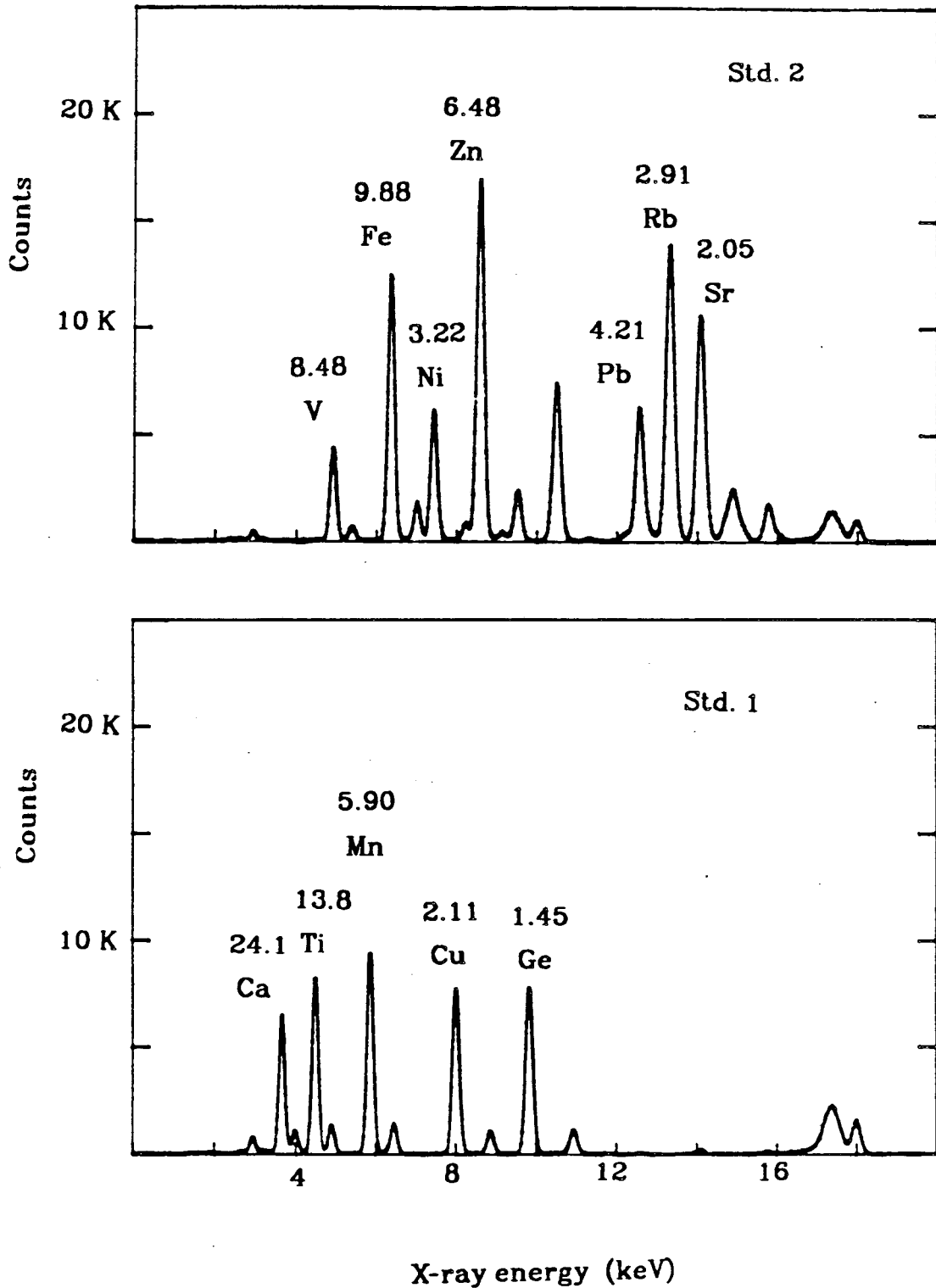
Mass Thickness of Disks Wt. of Area Scanned Recommended Sample Wt.	Non-Fat Milk Powder SRM 1549		Wheat Flour SRM 1567		Rice Flour SRM 1568	
	51 mg/cm ² 37 mg 500 mg		60 mg/cm ² 43 mg 400 mg		60 mg/cm ² 43 mg 400 mg	
Element	NBS	XRF	NBS	XRF	NBS	XRF
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
K	16900 ± 300	17800 ± 2000	1360 ± 40	1220 ± 130	1120 ± 20	1360 ± 160
Ca	13000 ± 500	12000 ± 800	190 ± 10	174 ± 10	140 ± 20	158 ± 14
Cr	0.0026 ± 0.0007	< 0.6	-	< 0.3	-	< 0.4
Mn	0.26 ± 0.06	0.33 ± 0.12	8.5 ± 0.5	8.2 ± 1.8	20.1 ± 0.4	22.1 ± 2.8
Fe	(2.1)	2.30 ± 0.16	18.3 ± 1.0	17.1 ± 4.8	8.7 ± 0.6	9.1 ± 1.2
Ni	-	0.24 ± 0.06	(0.18)	0.11 ± 0.06	(0.16)	0.18 ± 0.06
Cu	0.7 ± 0.1	0.65 ± 0.04	2.0 ± 0.3	1.88 ± 0.12	2.2 ± 0.3	2.21 ± 0.22
Zn	46.1 ± 2.2	46.9 ± 0.9	10.6 ± 1.0	10.3 ± 0.4	19.4 ± 1.0	21.9 ± 1.8
As	(0.0019)	< 0.05	(0.006)	< 0.03	0.41 ± 0.05	0.42 ± 0.09
Se	0.11 ± 0.01	0.09 ± 0.04	1.1 ± 0.2	0.92 ± 0.06	0.4 ± 0.1	0.38 ± 0.04
Br	(12)	12.1 ± 0.2	(9)	8.5 ± 1.4	(1)	1.19 ± 0.17
Rb	(11)	13.1 ± 0.2	(1)	0.94 ± 0.06	(7)	8.4 ± 0.9
Sr	-	3.69 ± 0.10	-	0.82 ± 0.04	-	0.19 ± 0.04
Hg	0.0003 ± 0.0002	< 0.1	0.001 ± 0.0008	< 0.06	0.0060 ± 0.0007	< 0.08
Pb	0.019 ± 0.003	< 0.1	0.020 ± 0.010	< 0.1	0.045 ± 0.010	0.10 ± 0.09

Table 2. Results Determined for Two NIES Standard Reference Materials

Mass Thickness of Disks Wt. of Area Scanned Recommended Sample Wt.	Freeze-Dried Serum NIES-4		Hair NIES-5	
	40 mg/cm ² 29 mg -		40 mg/cm ² 29 mg 200 mg	
Element	NIES	XRF	NIES	XRF
	µg/g	µg/g	µg/g	µg/g
K	2140 ± 140	2360 ± 260	34 ± 3	56 ± 16
Ca	970 ± 120	970 ± 130	728 ± 30	904 ± 55
Ti	-	-	(22)	29 ± 4
Cr	0.04 ± 0.03	< 0.5	1.4 ± 0.2	1.8 ± 0.7
Mn	-	< 0.4	5.2 ± 0.3	5.6 ± 0.3
Fe	13.3 ± 0.9	15.2 ± 3.4	225 ± 9	241 ± 17
Ni	-	< 0.2	1.8 ± 0.1	1.8 ± 0.3
Cu	12.7 ± 1.3	12.8 ± 1.0	16.3 ± 1.2	16.9 ± 1.3
Zn	10.8 ± 1.6	11.5 ± 0.9	169 ± 10	178 ± 16
Ga	-	< 0.07	-	0.3 ± 0.2
As	-	< 0.05	-	< 0.2
Se	(1.6)	1.47 ± 0.07	(1.4)	1.6 ± 0.2
Br	78 ± 47	97 ± 8	(90)	102 ± 13
Rb	2.8 ± 1.0	2.42 ± 0.25	(0.19)	0.3 ± 0.2
Sr	(0.6)	0.62 ± 0.06	2.3 ± 0.2	2.4 ± 0.3
Ba	-	-	(3.2)	-
Hg	-	< 0.1	4.4 ± 0.4	4.8 ± 0.5
Pb	-	0.20 ± 0.14	(6.0)	6.4 ± 0.8

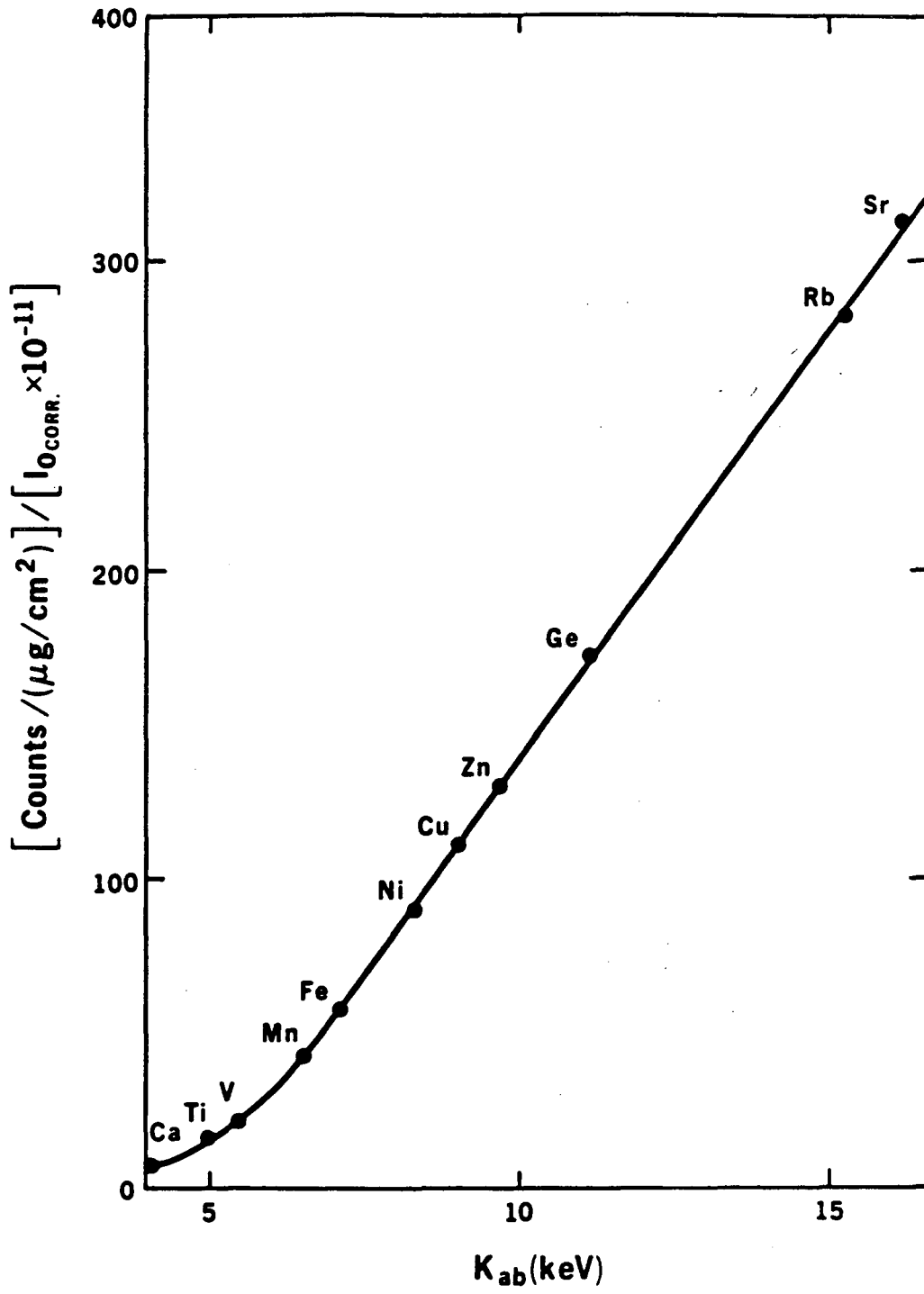
Figure 1.





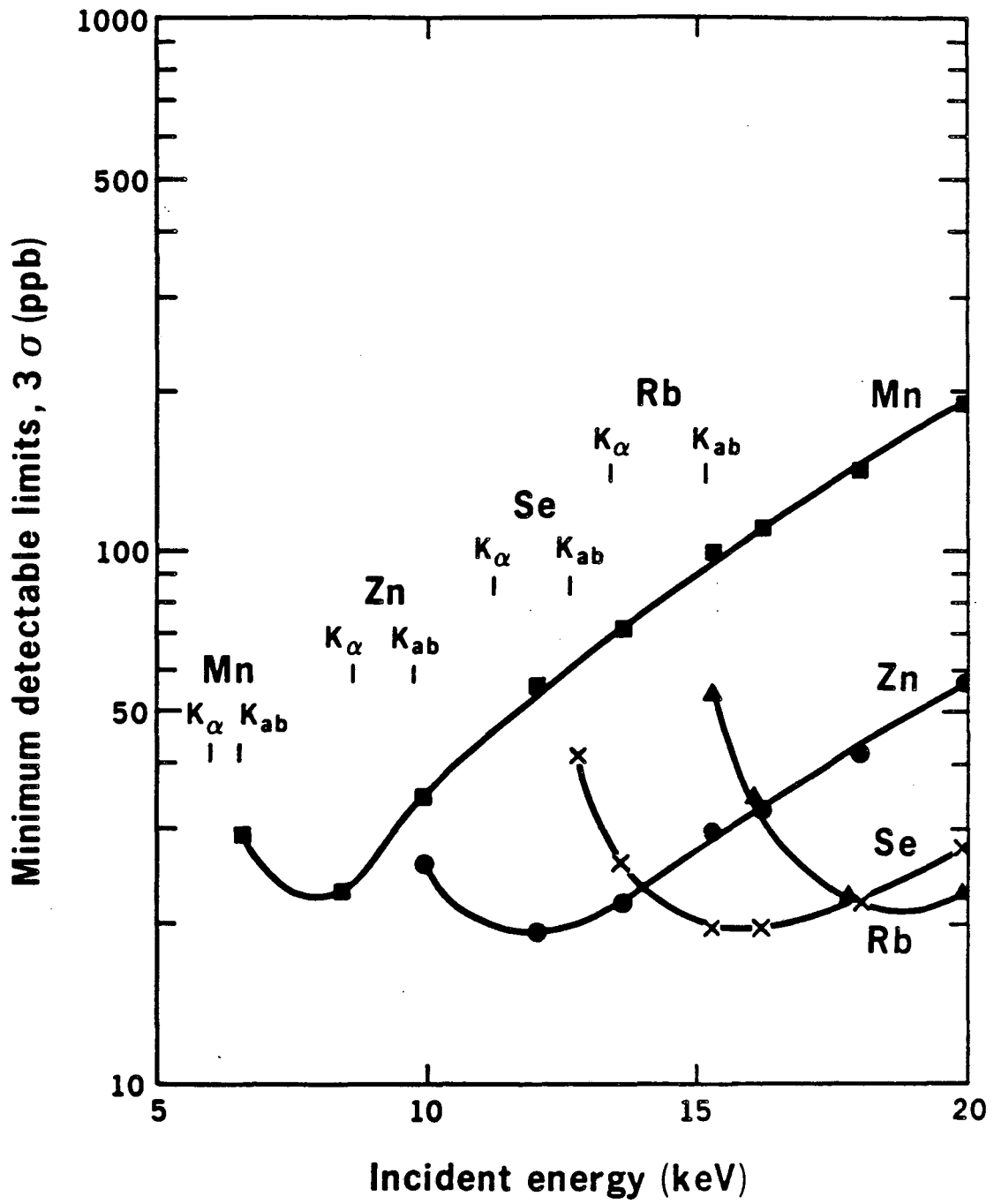
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Figure 2.



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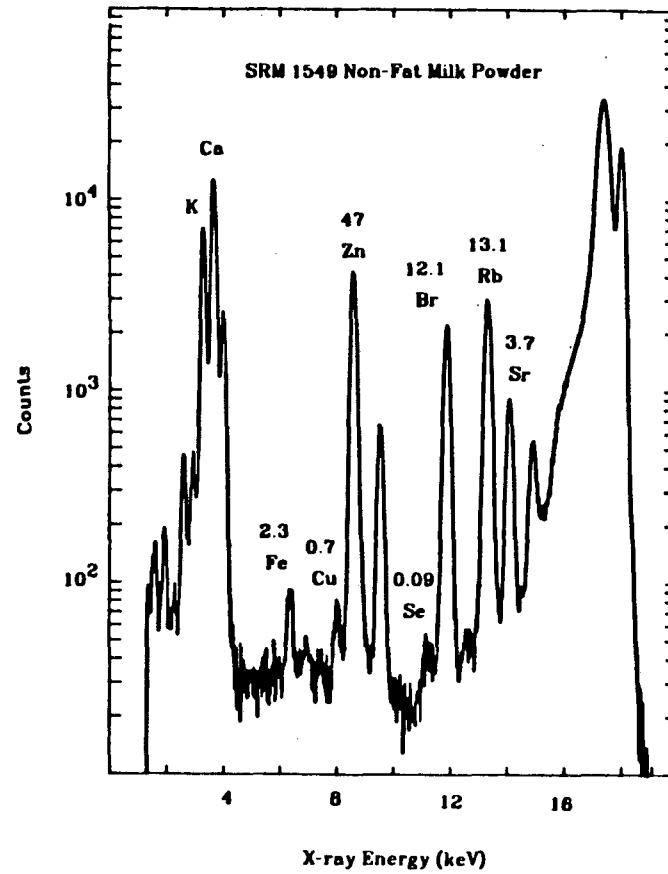
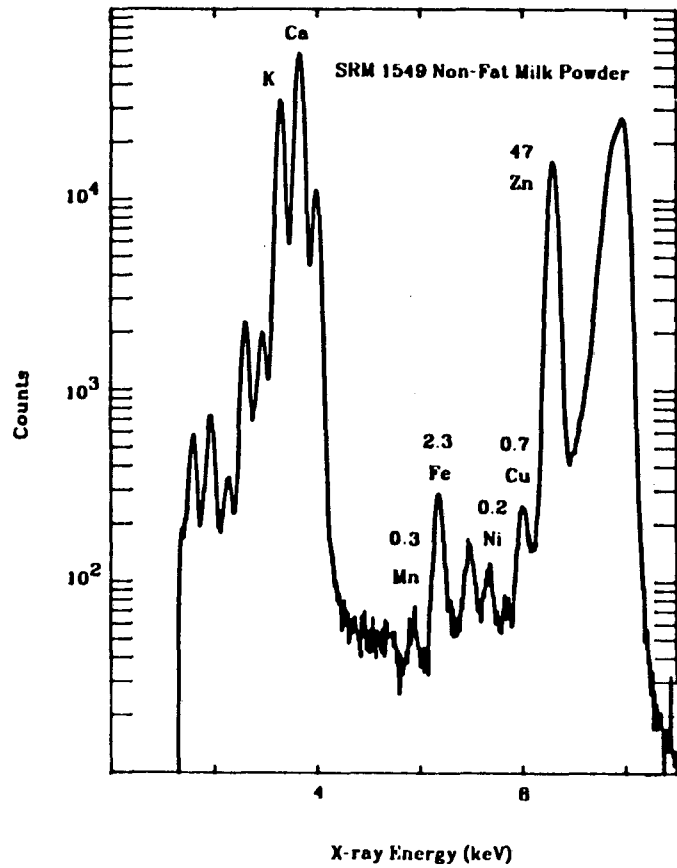
Figure 3.



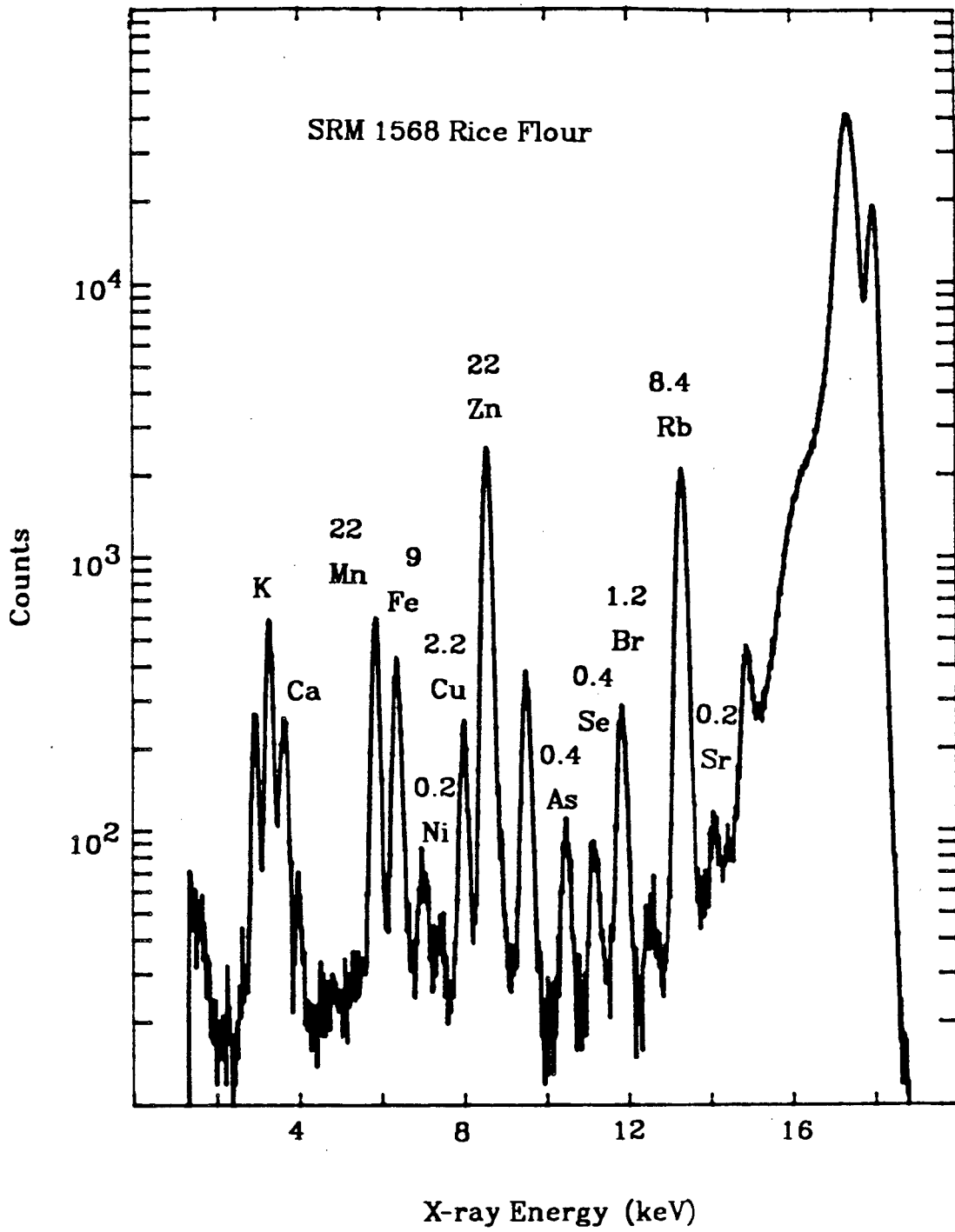
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Figure 4.

Figure 5.

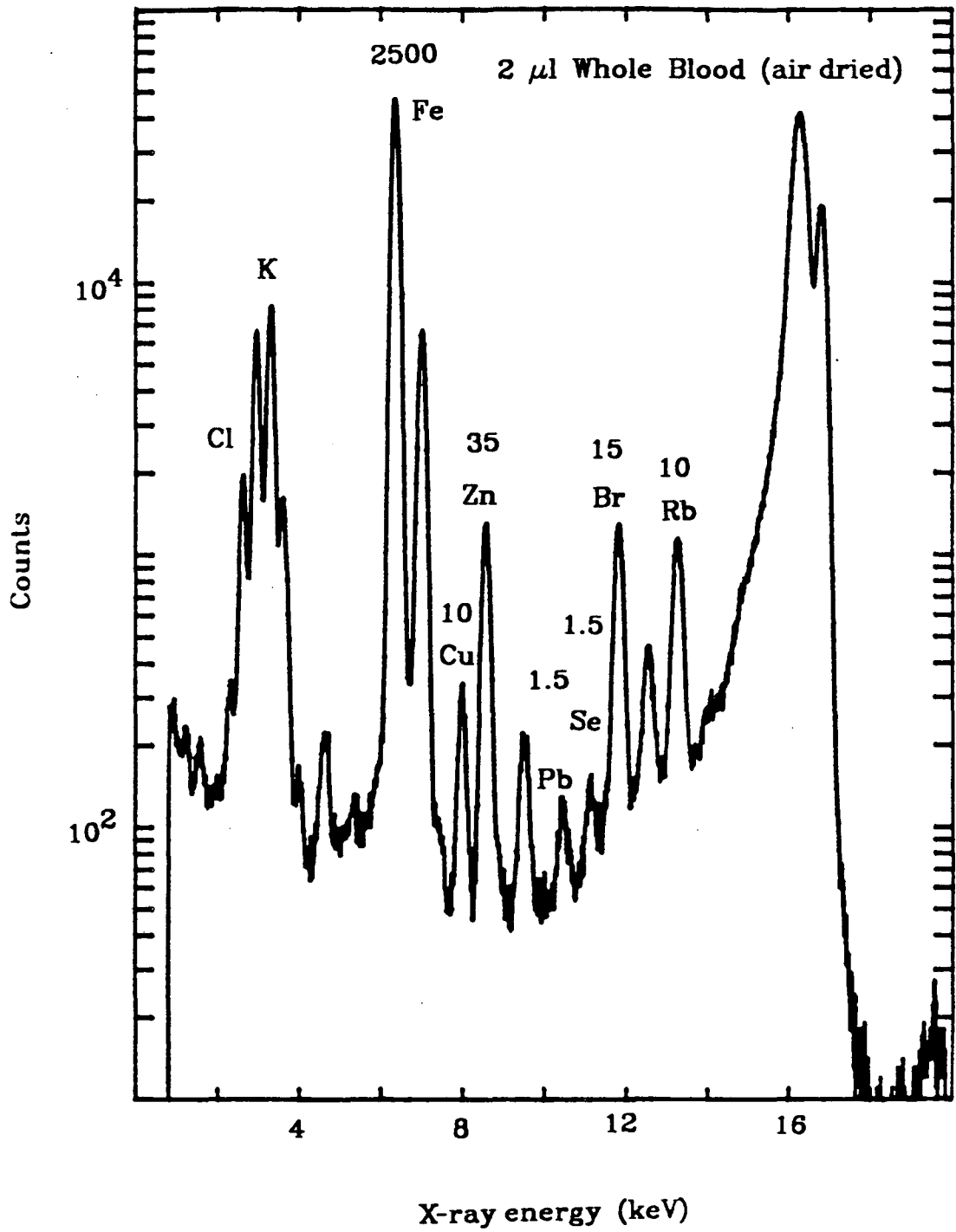


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XBL 857-3084

Figure 6.



XBL 857-3083

Figure 7.

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