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TRACE ELEMENT ANALYSIS WITH SEMICONDUCTOR DETECTOR X-RAY SPECTROMETERS *

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BRIEF

The concentrations of more than fifteen trace elements in thin specimens are determined with accuracies of 10% and better in less than one-half hour. A single element thin film is employed for standardization; multielement calibration is accomplished using mass absorption and fluorescent yield data reported in the literature.

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ABSTRACT

A method of obtaining high sensitivity and precision in x-ray fluorescence analysis using semiconductor detector spectrometers is discussed. Mono-energetic exciting radiation is employed to generate characteristic x-rays from trace elements in thin, uniform specimens. Corrections for absorption effects are determined; enhancement effects are omitted as they are negligible for many thin specimens. A single element thin-film standard is used to calibrate for the x-ray geometry, and theoretical cross sections and fluorescent yield data are employed to relate the x-ray yields for a wide range of elements to the thin-film standard. Various corrections which affect the accuracy of the method are discussed including the method for determining x-ray spectral background.

Results obtained in the analyses of biological and geological specimens, and of air particulate filters are reported. Using a single excitation energy, the concentrations of more than fifteen trace elements may be simultaneously determined during a fifteen minute interval for concentrations of 1 ppm or less. This corresponds to less than 10 ng/cm^2 on air particulate filters.

INTRODUCTION

The analytical technique of x-ray emission spectroscopy depends upon the ability to excite and accurately measure characteristic K and L x-rays emanating from the specimen. Prior to 1966, energy separation was usually achieved by using wavelength dispersive spectrometers. Since the first utilization of semiconductor detectors for x-ray spectrometry (1), major advancements have been made. Progress in electronic design over the past several years has significantly improved the energy resolution and count rate performance of semiconductor detector x-ray spectrometers (2,3,4). More recently, the advent of guard-ring detectors (5) has drastically reduced x-ray spectrum background resulting from the degradation of signals due to incomplete charge collection in the detectors. As a result of these improvements, semiconductor detectors are now applicable to many analytical problems, including trace element analyses.

Some of the principal attributes of semiconductor detector spectrometers for energy dispersive analysis are: (1) simultaneous detection of a wide range of energies allowing the intensities of many characteristic x-rays and their respective spectrum backgrounds to be determined together; (2) interelement interference due to overlapping x-ray lines are clearly shown; (3) compact excitation radiation-specimen-detector geometries are permitted, minimizing the required intensity of excitation radiation; (4) high detection efficiencies over a wide energy range; and (5) no requirements for moving parts or mechanical alignments. The energy resolution capabilities of semiconductor detector spectrometers are more than sufficient for most analytical applications, although x-ray spectrometers using crystals for energy dispersion provide somewhat higher

energy resolution for radiation of less than approximately 15 keV. Also, higher individual x-ray intensities can be measured with crystal spectrometers since only a narrow radiation energy is normally imposed on the detection system count rate limitations. However, for most multielement analytical problems, semiconductor x-ray spectrometers now permit analyses to be carried out in much shorter time periods and are less complex to operate than are crystal x-ray spectrometers.

In the first part of this paper factors that affect sensitivities attainable in x-ray fluorescence analysis are discussed. A following section describes the theory of the calibration method employed for multielement analyses. Next, experimental procedures are described and results, including comparisons with results achieved by other methods, are reported. Factors which affect the accuracy of the calibration method are discussed in detail in an appendix.

DISCUSSION OF METHOD

General Technique for Obtaining and Characterizing the X-ray Spectrum. Figure 1 illustrates the technique employed for x-ray fluorescence analysis. Exciting radiation provided by an x-ray tube or radioisotope, either directly or indirectly with secondary targets, impinges upon a specimen. A fraction of these photons, if of sufficient energy, produce vacancies in the inner shells of atoms within the specimen, which in turn can emit characteristic x-rays that are then measured by the detector. In addition to these photoelectric interactions, a portion of the radiation striking the specimen is scattered either coherently (no energy loss) or incoherently (energy loss determined by the Compton process). For many analyses, particularly with low atomic number

matrices, the intensity of scattered x-rays can be quite large compared with that of the characteristic x-rays. Figure 2 shows a generalized energy spectrum obtained from a semiconductor detector in such a situation. The exciting radiation in this case is assumed to be monochromatic. The features of interest in the spectrum are:

- a) The two high-energy peaks produced by coherent and incoherent scattering of the exciting radiation from the specimen.
- b) A low-energy continuum due to specimen scattered x-rays that are in turn scattered out of the detector leaving only a small fraction of the energy in the detector.
- c) A general, rather flat, background which arises partially from incomplete charge collection in the detector.
- d) The characteristic x-rays from the elements in the specimen.

Factors Determining Sensitivity. The main conditions that limit x-ray fluorescence sensitivities are the x-ray peak intensities and their ratios to the background. Some of the principal factors affecting sensitivities are the selection of the exciting radiation, the geometry employed, and the form of the specimen.

Selection of the exciting radiation.

Since the ratio of fluorescent to scattered x-ray intensities is often very small, the energy of the scattered x-rays should be sufficiently high that the scattered x-rays will not cause substantial interference with the characteristic x-rays. Because a continuum of such interfering scattered radiation is obtained if conventional x-ray tubes or Bremstrahlung sources are employed

to directly provide the exciting radiation, monochromatic exciting radiation is used. Monochromatic exciting radiation can be obtained by employing characteristic x-ray tubes (6), conventional x-ray tubes and secondary targets, radioisotope source-target assemblies (7), or radioisotopes which decay only by electron capture, i.e., Cd-109 and Fe-55.

The selection of the exciting radiation energy is strongly influenced by the range of elements to be studied. Maximum sensitivity is achieved by employing an exciting radiation energy slightly greater than the K or L absorption edge energies of the elements to be analyzed, but of sufficient energy that the incoherently scattered radiation does not produce significant overlapping background. Figure 3 is a plot of photoelectric cross sections (τ) vs the K absorption edge energy of various elements for two excitation energies. As shown, the elements with K absorption edge energies in the 2-15 keV range photoelectrically absorb 15 keV radiation approximately seven times more efficiently than the 30 keV radiation.

Geometry considerations.

It is important that the excitation-specimen-detector geometry be designed for the maximum practical efficiency so a large number of counts can be acquired in a short time. Furthermore, it is desirable that the energy loss by the incoherent scattering process be a minimum. The minimum energy loss occurs when the exciting x-rays are scattered at small angles, and the energy loss which is defined by the Compton scattering process increases slightly for $\theta = 90^\circ$ as can be seen from Equation 1

$$E_{\text{incoherent}} = E_{\text{exciting}} / [1 + .001957(1 - \cos\theta)E_{\text{exciting}}] \quad (1)$$

where the x-ray energies are expressed in keV. However, minimum intensity of the scattered radiation relative to the fluorescent radiation intensities occurs when $\theta = 90^\circ$ -- a factor of two less than at 180° . Thus, it is desirable to maintain an angle near 90° between the exciting and detected radiation to yield the highest peak to background ratios.

Form of specimen.

Absorption effects increase more rapidly for the fluorescent x-rays than for the scattered exciting radiation, hence, sensitivity decreases as the specimen thickness approaches the critical thickness (i.e., the thickness beyond which an increase in thickness does not measurably increase a fluorescent x-ray intensity). Thus, high sensitivity is obtained by using relatively thin specimens. For example, Figure 4 shows the spectra obtained from NBS SRM 1571 orchard leaves specimen prepared in the form of pellets, 30 and 300 mg/cm² thick. The spectra were obtained in equal times with identical counting rates. The improvement in sensitivity for lower energy x-rays with the thin specimen is obvious. For most applications, the reduced counting rates realized with thinner specimens can be compensated by employing a more intense exciting radiation.

Equipment and Characteristics. For the experiments discussed in this paper, a guard-ring detector (5) with pulsed light feedback electronics (4) and a multichannel pulse height analyzer were employed. The total resolution of the system, FWHM, was 225 eV at 6.4 keV (FeK α x-ray energy) at 5,000 counts/sec using a 8 μ sec pulse peaking time. Excitation was provided by a molybdenum transmission x-ray tube (6) with a combined anode plus window thickness of

.010 cm. The x-ray tube was operated at 42 kV with regulated currents varying from 10-400 μ A. The x-ray tube, detector, and specimen changer are shown in Figure 5. The distances between the x-ray tube anode to the specimen, and between the specimen to the detector were approximately 6 and 2.5 cm, respectively. The angles formed by the exciting and the detected emergent radiations with the specimen surface were both near 45° . The total area of the specimens used varied from approximately 2 to 3 cm^2 depending upon the external x-ray tube collimation employed. Corrections for system dead time resulting either through pile-up rejection or analyzer dead time were made using a gated clock that measured the total system live time (8). The maximum total count rates were 10,000 counts/sec. At this count rate, the system dead time was 50%. The high count rate capabilities permitted the use of intense x-ray excitation so that adequate statistical accuracies could be obtained for the measured fluorescent x-ray intensities in relatively short periods of time.

CALIBRATION METHOD

General Considerations. The use of thin specimens minimizes matrix effects in x-ray fluorescence analysis. The preparation of thin uniform specimens usually eliminates the tedious procedure of either preparing sets of standards similar to the specimens to be analyzed, or the addition of internal standards to correct for matrix effects. When employing thin specimens, matrix enhancement effects are normally very small. Matrix absorption effects may be determined if the critical thicknesses for the x-ray energies of interest have not been reached. For most analytical applications, the corrections necessary for matrix absorption effects are one to two orders of magnitude higher than for matrix enhancement effects. The use of monochromatic exciting radiation and a single

element thin film standard for calibration of the x-ray spectrometer, and the employment of theoretical calculations to standardize for the analyses of many elements has previously been reported (9). Factors converting counts/sec to $\mu\text{g}/\text{cm}^2$ for the elements are obtained by calculating the relative probability of fluorescence excitation and detection of x-ray lines as a function of Z. Absolute normalization of the calibration curve to the x-ray tube intensity is accomplished by measuring an x-ray line intensity from the single element thin film standard of known mass. An elaboration of the technique is presented in this section.

Most x-ray fluorescence analysis problems deal with the measurement of characteristic K or L x-rays arising from transitions to the inner atomic shell vacancies. These vacancies are created by photoelectric interactions of the atoms with radiation of sufficient energy. A simplified version of some of the basic atomic processes occurring in x-ray fluorescence analysis is shown in Figure 6. K x-rays are usually employed for the analysis of elements up to atomic numbers in the 55 to 60 range, and L x-rays are used for the elements of higher atomic number. For the development of the method, the specimen will be treated initially as being infinitely thin.

The relative ability of the elements to photoelectrically absorb the exciting radiation is determined by their photoelectric cross sections. To ascertain the contribution of a particular energy level to the total photoelectric cross section at the exciting energy, corrections must be made for the fraction of the cross section arising from interactions involving the other energy levels. The total photoelectric cross section for this individual energy level plus all lower energy levels (τ) is multiplied by the quantity

$\left(1 - \frac{1}{J_{K,L}}\right)$ where $J_{K,L}$ is the ratio (jump ratio) between the photoelectric mass absorption coefficients at the top and bottom of the absorption edge energy. For absorption occurring in the K shell, the value of τ is the total photoelectric mass absorption coefficient for this exciting energy. However, for L energy levels, the value of τ is obtained by extrapolation of the curve for the particular energy level to the exciting energy. This procedure compensates for the contribution of energy levels higher than the level of interest.

Only a fraction of the vacancies created in a particular energy level are filled by transitions which give rise to the direct emission of x-rays. Some vacancies are filled by transitions involving the emission of Auger electrons (10). The fraction of vacancies filled by transitions which directly yield x-rays is known as the fluorescence yield value ($\omega_{K,L}$). Figure 7 shows curves of theoretical fluorescence yield values for a wide range of elements for the K and L_{III} energy levels.

Transitions to a particular energy level give rise to the emission of more than one x-ray line since they can originate from several initial energy states. The fraction emitted of a particular x-ray line with respect to the total is referred to as the fractional value (f).

For a particular excitation radiation, x-ray excitation curves may be established for x-ray lines from individual energy levels by multiplying the values of the terms τ , $\left(1 - \frac{1}{J_{K,L}}\right)$, $\omega_{K,L}$, and f . The values of each of these terms are reported in the literature (11-15). Figure 8 shows some calculated curves for the excitation of characteristic $K\alpha$ and $L\alpha$ x-rays with molybdenum exciting radiation (71% $MoK\alpha$ and 29% $MoK\beta$ radiation). Such curves

can be easily determined for any monochromatic exciting radiation. As shown, the relative ability to excite characteristic x-rays with a specific excitation radiation energy drops off rapidly with decreasing absorption edge energy. Even though sensitivity for lower atomic number elements can be enhanced by selecting an excitation radiation of lower energy, sensitivities attainable are less than for elements near the middle of the periodic table as a result of low fluorescence yield values, and in most cases, high absorption effects.

Due to geometry considerations, only a small fraction of the x-ray lines emitted may be detected. A small proportion of the x-rays may be attenuated by the air or helium path, if present, and by the detector window. Also, for higher energy x-rays the efficiency (ϵ) of the detector may be less than unity. For any specific energy, the fraction transmitted (T) by the media between the specimen and the detector, and the efficiency of the detector may be calculated with relative ease using mass absorption coefficients listed in the literature. For any given geometry and for constant exciting radiation intensity, the relative ability to excite and detect various x-ray lines from "infinitely" thin specimens may be determined from the ratios of the product:

$$K_j = \tau \left(1 - \frac{1}{J_{K,L}} \right) \omega_{K,L} f T \epsilon \quad (2)$$

where the subscript j refers to the specific element.

Table I lists a comparison of calculated and experimental values of relative excitation and detection efficiencies, K_j , for the system employed, for seven x-ray lines normalized to the $\text{CuK}\alpha$ values. Theoretical fluorescence yield values (12,13) were used to determine the calculated values. The

experimental values were determined from the average value obtained from three thin film standards of masses varying from 50 to 150 $\mu\text{g}/\text{cm}^2$. The standards were prepared by evaporation of the elements onto thin aluminum backings of mass 800 $\mu\text{g}/\text{cm}^2$. The precisions listed are for one standard deviation. Although the accuracy of the calculations depends on the selection of theoretical values, the actual calibration could be done by using experimental data such as shown in the table, thereby avoiding possible errors.

Since the intensity of an x-ray line from an "infinitely" thin specimen is directly proportional to the concentration, $m_j(\text{g}/\text{cm}^2)$ of the element, the intensities and elemental concentrations may be expressed as:

$$I = I_0 G K_j m_j \quad (3)$$

where I_0 is the exciting radiation intensity and G is a geometry factor.

For constant exciting radiation intensity and for constant geometry, the value of $I_0 G$ can be determined from a single element thin film standard for which the absorption effects are negligible. In effect, theoretical values of relative excitation and detection efficiencies are calculated. The values are calibrated in units of cm^2/g using a convenient element for which a thin-film standard is available.

Corrections for Absorption Effects. Since specimens prepared for analyses are not infinitely thin, corrections must be applied for matrix absorption effects. Two processes of absorption by the specimen occur, one for the exciting radiation, the other for the x-rays from elements within the specimen. The net absorption equals the product of these two absorption effects in the total

specimen mass. Integrating these effects over the thickness of the uniform specimen, the correction may be written:

$$\text{Absorption correction} = \frac{1 - e^{-(\mu_1 \csc\phi_1 + \mu_2 \csc\phi_2)m}}{(\mu_1 \csc\phi_1 + \mu_2 \csc\phi_2)m} \quad (4)$$

where

μ_1 and μ_2 are the total mass absorption coefficients (cm^2/g) of the specimen for the exciting and the characteristic radiation, respectively.

ϕ_1 and ϕ_2 are the angles formed by the exciting and characteristic radiation with the specimen surface.

m is the mass (g/cm^2) of the specimen.

Applying this correction for absorption effects to Equation 3 gives

$$I = I_o G K_j m_j \frac{1 - e^{-(\mu_1 \csc\phi_1 + \mu_2 \csc\phi_2)m}}{(\mu_1 \csc\phi_1 + \mu_2 \csc\phi_2)m} \quad (5)$$

If the critical thickness for the x-ray energy of interest is not attained, the individual values of μ_1 , μ_2 , ϕ_1 , ϕ_2 , and m need not be known for the determination of this correction because the quantity $e^{-(\mu_1 \csc\phi_1 + \mu_2 \csc\phi_2)m}$ may be measured directly since it represents the combined attenuations of the incident and fluorescent x-rays in the total specimen thickness. This is done by measuring the relative x-ray intensity with and without the specimen from a target located at a position adjacent to the back of the specimen as shown in Figure 9. The calculation is expressed:

$$A \equiv \frac{I'_T - I_S}{I_T} = e^{-(\mu_1 \csc\phi_1 + \mu_2 \csc\phi_2)m} \quad (6)$$

where

I_S , I_T , and $I_{T'}$ are the intensities of the x-ray plus background from the specimen alone, the target alone, and the specimen with the target, respectively.

The target should be at least of critical thickness for the x-ray energy of interest. To minimize possible absorption correction errors arising from enhancement of the specimen radiation by scattered target radiation, targets that yield a high ratio of scattered to fluorescent radiation should not be used.

Figure 5 shows the assembly employed to make absorption measurements. Many absorption correction measurements may be easily made by positioning the absorption slide bar containing the targets. With this assembly, the targets are located less than 0.15 cm from the specimen. Simultaneous absorption measurements for many x-rays can often be made by using a multielement uniform target. However, to use this procedure, the contribution of enhancement effects between the specimen and the target must be negligible. Conversely, enhancement effects between the specimen and the target may exist for low trace element concentrations and still have a negligible effect on the results since the value of I_S is low compared to the value of $I_{T'}$. For thin specimens with similar element concentrations, repetitive absorption measurements often need not be made if the specimens are prepared of approximately equal total mass concentrations (g/cm^2). For some thin specimens, particularly when higher energy x-rays are employed for analyses, absorption effects are negligible.

Preparation of Thin Standards and Specimens.

Preparation of standards.

Thin-film standards are prepared by evaporation of the elements onto thin aluminum films. The standards are made thin enough that self-absorption

effects are negligible, generally around $100 \mu\text{g}/\text{cm}^2$. Thin standards can also be prepared by absorbing known amounts of the elements in solution on cellulose powder, drying at approximately 80°C , weighing, pulverizing, and using a fraction of the mixture to press a thin pellet which is then weighed. Absorption correction measurements must be made on cellulose standards.

Preparation of specimens.

The principal considerations dictating the desired specimen thickness are the matrix effects that will be prevalent and the characteristics of the x-ray spectrometer employed. Specimens should be prepared thin enough that:

- a) The critical thicknesses for the x-ray energies of interest are not attained.
- b) Matrix enhancement effects are quite small for the analyses to be performed.
- c) Count rate limitations are not imposed upon the x-ray detection system when near maximum excitation intensity is employed.
- d) Total system geometries do not significantly vary with respect to the standard employed for analysis.

Nevertheless, specimens should be prepared thick enough that favorable statistics in analysis are obtained in relatively short periods of time.

Biological specimens.

Specimens consisting of biological material such as tissue, blood, plants, etc. are either freeze-dried or oven-dried, pulverized, and subsequently 2.54 cm diameter pellets are pressed at $15,000 \text{ psi}$ and weighed. The pellets typically are of mass $30 \text{ mg}/\text{cm}^2$ and are approximately $.03 \text{ cm}$ thick. The

freeze-drying process not only allows the preparation of thin uniform specimens, but also permits higher trace element sensitivity due to the concentration factor of up to ten and more which can often be obtained.

Rock, glass, and pottery specimens.

Finely pulverized rock, glass, or pottery specimens are collected on thin filters using the apparatus shown in Figure 10. While maintaining a vacuum behind a filter on a glass frit, short blasts of air are let into the glass vessel by quick manipulation of the stopcock. This procedure converts the specimen into a fine dust which is collected on a 0.8 μ Millipore filter 2.5 cm in diameter and of mass 5 mg/cm². Deposits prepared cover an area of 3 cm² and are of approximate mass 5 mg/cm². Specimens must be pulverized fine enough that particle size will neither effect the deposit nor the analysis. Grinding the specimens to pass through a 325 mesh screen (< 44 microns) is sufficient for many analyses.

This preparation procedure has worked well in some cases and been entirely unsatisfactory in other cases. Some of the finely pulverized specimens have fine particles which selectively stick to the side of the vessel, and consequently, unrepresentative specimens are prepared. To overcome this problem, some specimens may be fused with lithium metaborate to form a homogeneous mixture which is then finely pulverized.

Elements in solution.

Elements in solution may be absorbed on cellulose powder, dried at approximately 80°C, pulverized, and pressed into 2.54 cm diameter pellets. Trace ionic impurities often may be collected on ion-exchange resin-loaded

papers (16), but care must be taken to correct for uneven distributions between the front and the back of the papers when lower energy x-rays are employed for analysis. Trace amounts of many elements may be precipitated with a carrier and collected on a filter paper (17).

Air particulate filters.

The concentrations of many elements present in air collection specimens on filter papers are simply determined by measuring the intensities of the characteristic x-rays since absorption effects can be considered negligible. Absorption by the filter of lower energy x-rays (around 4 keV and less) from particles impacted within the pores of the filter can become important for some analyses. A procedure to compensate for this effect is not known. To obtain high sensitivity in analysis on air pollution specimens, filters of low mass should be used to minimize scattered excitation radiation background.

RESULTS

The following results were obtained with the previously described equipment. Standardization was accomplished in 100 sec using a 101 $\mu\text{g Cu/cm}^2$ evaporated thin-film standard. Calculated values for relative excitation and detection efficiencies (K_j) were employed for analyses. Absorption correction measurements were made when necessary and the concentrations of the elements were calculated using Equation 7.

$$\text{ppm}(j) = \frac{c_j}{c_s} \times \frac{i_s}{i} \times \frac{\ln A}{1 - A} \times \frac{m_s}{m} \times \frac{1}{K_j} \times 10^6 \quad (7)$$

where

c_j and c_s are the characteristic x-ray count rates from element j and the standard.

i and i_s are the x-ray tube currents employed for the specimen and the standard.

A is defined by Equation 6.

m and m_s are the specimen and the standard masses (g/cm^2).

Due to detection system count rate limitations, absorption correction measurements were usually made at lower tube currents than those employed for obtaining the specimen spectrum.

Biological Specimens. Table II shows the results of the analyses from five separately prepared specimens of standard NBS SRM 1571 orchard leaves. Pellets 2.54 cm in diameter and of mass $30 \text{ mg}/\text{cm}^2$ were prepared. To determine the correction for the moisture content, a weighed amount of the orchard leaves was dried for 24 hours at 90°C and weighed. Total analysis time, including absorption measurements, was thirty minutes for each specimen. The errors listed are for two standard deviations.

Figure 11 shows the spectrum and results obtained in thirty minutes from a freeze-dried human serum specimen which was pulverized, and pressed into a 2.54 cm diameter pellet of mass $30 \text{ mg}/\text{cm}^2$. Since the concentration factor obtained by freeze-drying the specimen was ten, the concentrations of the elements in the original specimen are one-tenth the values listed.

Pottery and Rock Specimens. Table III illustrates a comparison of the results obtained by x-ray fluorescence and LBL neutron activation on a pottery specimen.

Thin specimens of mass 5 mg/cm^2 were prepared on 0.8μ Millipore filter of mass 5 mg/cm^2 , employing the apparatus shown in Figure 10. The errors listed are for one standard deviation for five separately prepared specimens. The Ti, V, Cr, and Mn results have been corrected for x-ray background from BaL x-rays. For these corrections, the barium concentration of 712 ppm determined by neutron activation was chosen to calculate the interfering x-ray correction. The barium concentration could be determined by employing exciting radiation of sufficiently high energy to produce BaK x-rays from the specimen. Figure 12 shows a spectrum obtained from one of the specimens. Forty minutes were required to analyze each specimen.

A comparison of the x-ray fluorescence and LBL neutron activation results in the analysis of U. S. Geological Survey Andesite is shown in Table IV. Again, the errors tabulated are for one standard deviation for five separately prepared specimens of mass 5 mg/cm^2 . Total analysis time for each specimen was forty minutes. The neutron activation result of 1210 ppm Ba was used to correct for BaL x-ray line interferences.

The x-ray fluorescence potassium and calcium results are probably low because of absorption by the filter of lower energy x-rays from particles collected within the pores of the filter rather than on the surface. For these analyses, the specimens are assumed to have been collected entirely on the surface of the filter. Also, particle size effects can increase rapidly with decreasing x-ray energy (18,19), and slight nonuniformities in the thickness of the specimens when large absorption correction measurements are necessary would both yield low results.

Air Particulate Filters. Figure 13 shows the spectrum and results obtained on an air pollution filter of mass 5 mg/cm^2 . This specimen represents three cubic meters of air passed through a filter area of 4 cm^2 in one hour. The spectrum was taken in 800 seconds and the concentrations listed are in nanograms/ cm^2 .

Theoretical Limits of Detection. Theoretical limits of detection with the equipment used are shown in Table V for three separate types of specimens. In this paper the minimum detectable amount is defined as that concentration or quantity which gives a line intensity above background equal to three times the square root of the background for counting times not to exceed 1000 sec (including total system dead time). This criterion gives a confidence level of 95%. Higher sensitivity for many of these elements can be obtained by employing different characteristic x-ray tubes (6). Detection limits can be further improved by approximately a factor of four if both a double guard-ring detector (5) and a pulsed x-ray tube (20) are employed.

CONCLUSION

The use of monoenergetic exciting radiation and a semiconductor detector, and the preparation of thin specimens permits many trace element analyses to be performed with relative ease, in shorter time intervals, and often with higher sensitivity than other analytical techniques such as neutron activation and atomic absorption. The ability to use a single element thin film standard to accurately calibrate for the analyses of many elements is unique for instrumental methods of analysis.

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Table I. Relative Excitation and Detection Efficiencies (K_j)

Line	Calculated	Determined
CrK α	.381	.370 $\pm$.011
MnK α	.450	.435 $\pm$.003
FeK α	.587	.559 $\pm$.003
NiK α	.884	.882 $\pm$.007
CuK α	1.000	1.000 $\pm$.015
AsK α	1.653	1.660 $\pm$.083
SeK α	1.776	1.753 $\pm$.057
PbL α	.804	.774 $\pm$.019

Table II. Analysis of NBS SRM 1571 Orchard Leaves

X-ray Fluorescence		NBS
Cr	2.5ppm±1.6	2.3ppm
Mn	88.6ppm±2.2	91ppm±4
Fe	276ppm±8	300ppm±20
Ni	1.3ppm±0.4	1.3ppm±0.2
Cu	12.6ppm±0.6	12ppm±1
Zn	23.7ppm±0.8	25ppm±3
As	10.6ppm±0.8	14ppm±2
Br	9.3ppm±0.6	10ppm
Rb	11.0ppm±0.8	12ppm±1
Sr	36.6ppm±1.2	37ppm
Pb	45.4ppm±2.0	45ppm±3

Table III. Analysis of Pottery Specimen

X-ray Fluorescence		Neutron Activation
K	0.95%±.02	1.35%±.04
Ca	0.28%±.01	<1.0%
Ti	0.77%±.01	0.78%±.03
V	176ppm±16	176ppm±16
Cr	107ppm±5	115ppm±4
Mn	31ppm±4	40.9ppm±0.5
Fe	1.05%±.01	1.017%±.012
Ni	277ppm±4	279ppm±20
Cu	56ppm±2	59ppm±8
Zn	61ppm±1	59ppm±8
Ga	46ppm±1	44ppm±5
As	32ppm±1	30.8ppm±2.2
Se	<2ppm	—
Br	<3ppm	2.3ppm±0.9
Rb	70ppm±2	70.0ppm±6.3
Sr	145ppm±2	145ppm±22
Pb	35ppm±3	—

Table IV. Analysis of Andesite

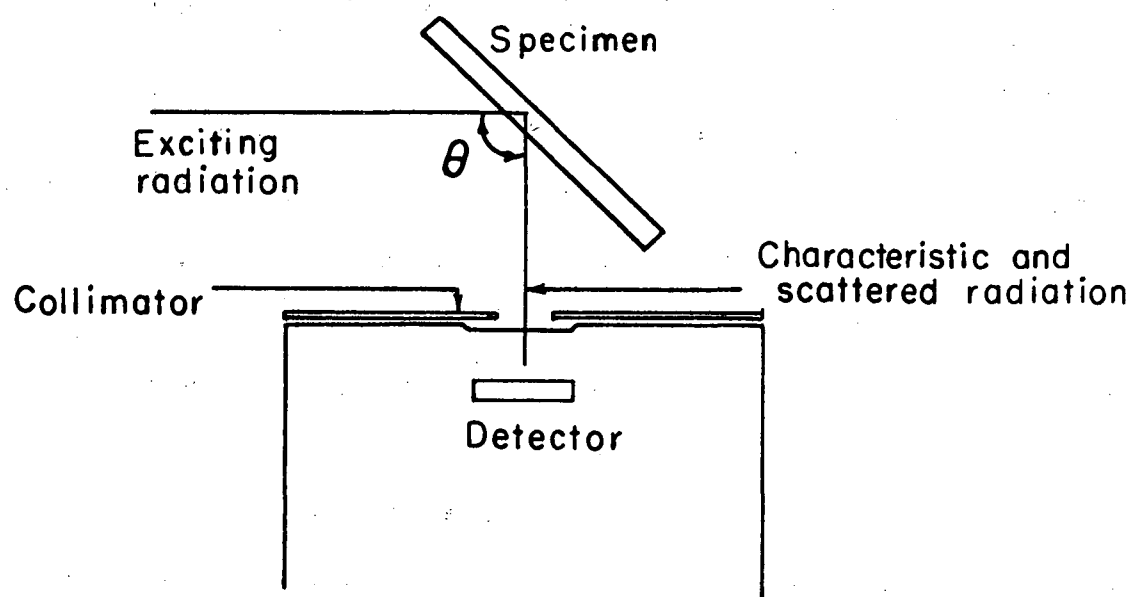
X-ray Fluorescence		Neutron Activation
K	1.79%±.02	2.6%±.3
Ca	3.17%±.04	3.9%±.5
Ti	0.61%±.01	0.59%±.04
V	125ppm±16	157ppm±28
Cr	<20ppm	8.5ppm±4
Mn	734ppm±11	736ppm±12
Fe	4.61%±.06	4.88%±.06
Ni	20ppm±2	—
Cu	69ppm±2	—
Zn	87ppm±2	104ppm±9
Ga	23ppm±1	—
As	3ppm±1	—
Se	<2ppm	—
Br	<2ppm	—
Rb	69ppm±2	91ppm±12
Sr	755ppm±8	1021ppm±276
Pb	38ppm±3	—

Table V. Theoretical Limits of Detection

Specimen	Biological	SiO ₂ on filter of mass 5 mg/cm ²	Air particulate on filter of mass 5 mg/cm ²
Mass (mg/cm ²)	30	5	—
Tube current (μ amps)	250	400	400
Area analyzed (cm ²)	3	2	3
Element and spectral line			
TiKα	3 ppm	10 ppm	15 ng/cm ²
CrKα	1	4	9
FeKα	0.6	3	5
CuKα	0.3	1	3
HgLα	0.4	2	5
PbLα	0.4	2	5
BrKα	0.3	1	3
RbKα	0.4	2	6

FIGURE CAPTIONS

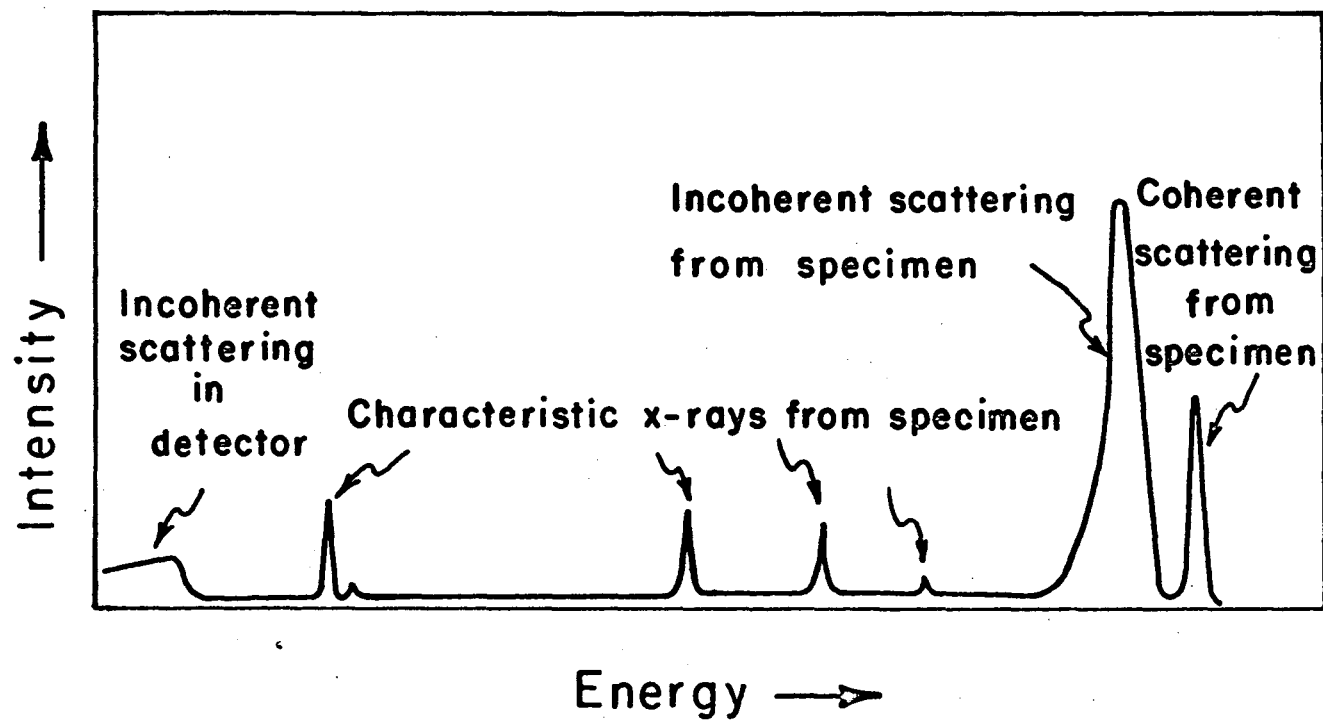
- Fig. 1. Schematic of x-ray fluorescence analysis technique.
- Fig. 2. Generalized energy spectrum obtained from a low atomic number matrix with a semiconductor detector. The exciting radiation is assumed to be monochromatic.
- Fig. 3. Photoelectric cross section curves for 15 and 30 keV photons.
- Fig. 4. Spectra from NBS orchard leaves specimens of masses 30 and 300 mg/cm².
- Fig. 5. Photograph of x-ray tube, detector, specimen changer, and built-in absorption measurement capabilities.
- Fig. 6. Simplified version of some of the basic atomic processes that can occur in x-ray fluorescence analysis.
- Fig. 7. Theoretical fluorescence yield curves for the K and L_{III} energy levels.
- Fig. 8. X-ray excitation curves for molybdenum exciting radiation.
- Fig. 9. Schematic of method for absorption correction measurements.
- Fig. 10. Apparatus for preparation of thin rock, glass, and pottery specimens.
- Fig. 11. Spectrum from freeze-dried serum specimen. Concentrations listed are for freeze-dried specimen. This preparation gave a concentration factor of ten.
- Fig. 12. Spectrum from pottery specimen of mass 5 mg/cm².
- Fig. 13. Spectrum from air filter of mass 5 mg/cm². Concentrations listed in nanograms/cm².



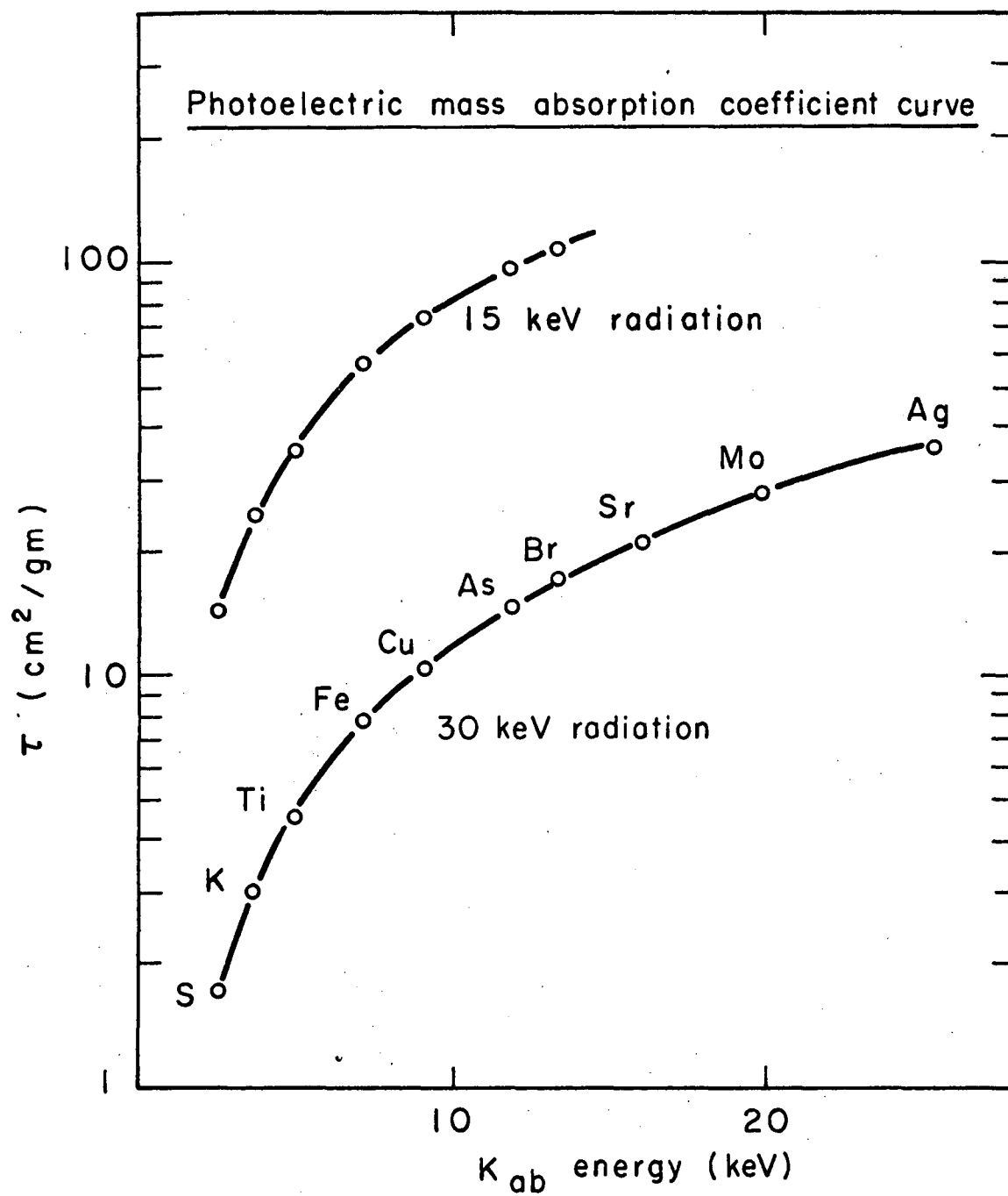
XBL725-2937

Fig. 1

Fig. 2

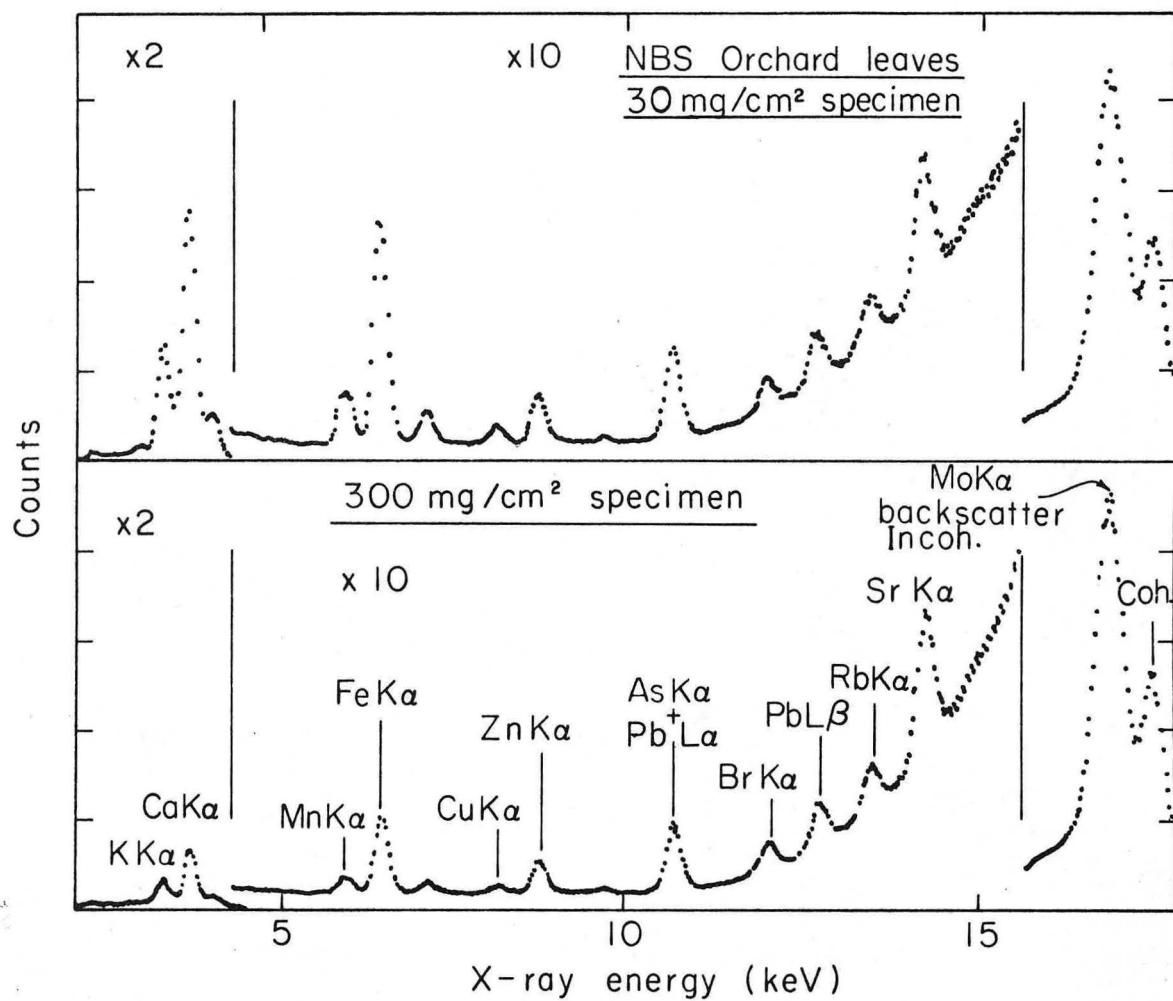


XBL725 -2938



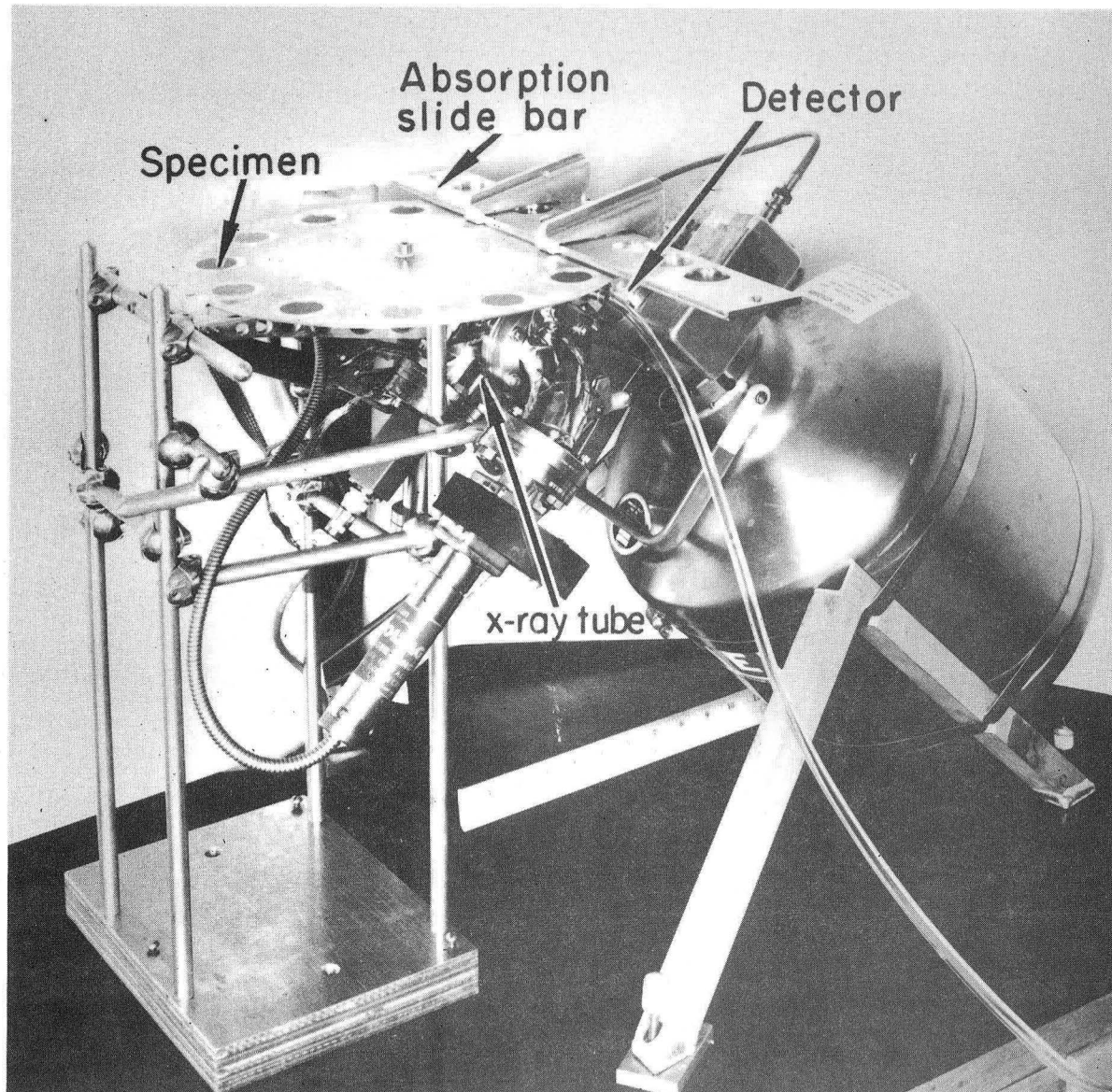
XBL725-2950

Fig. 3



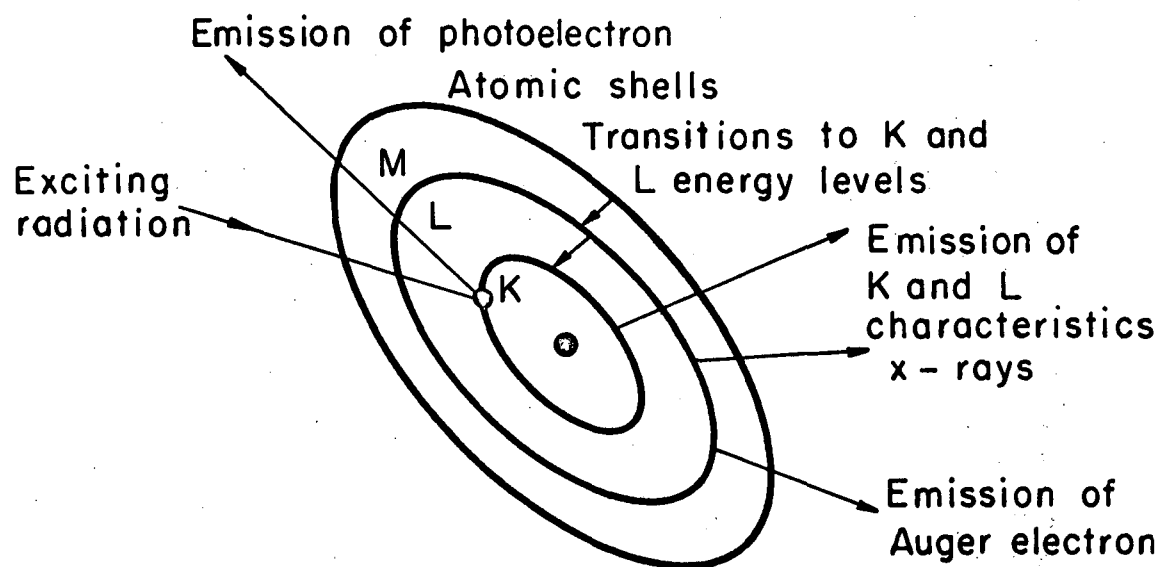
XBL725-2932

Fig. 4



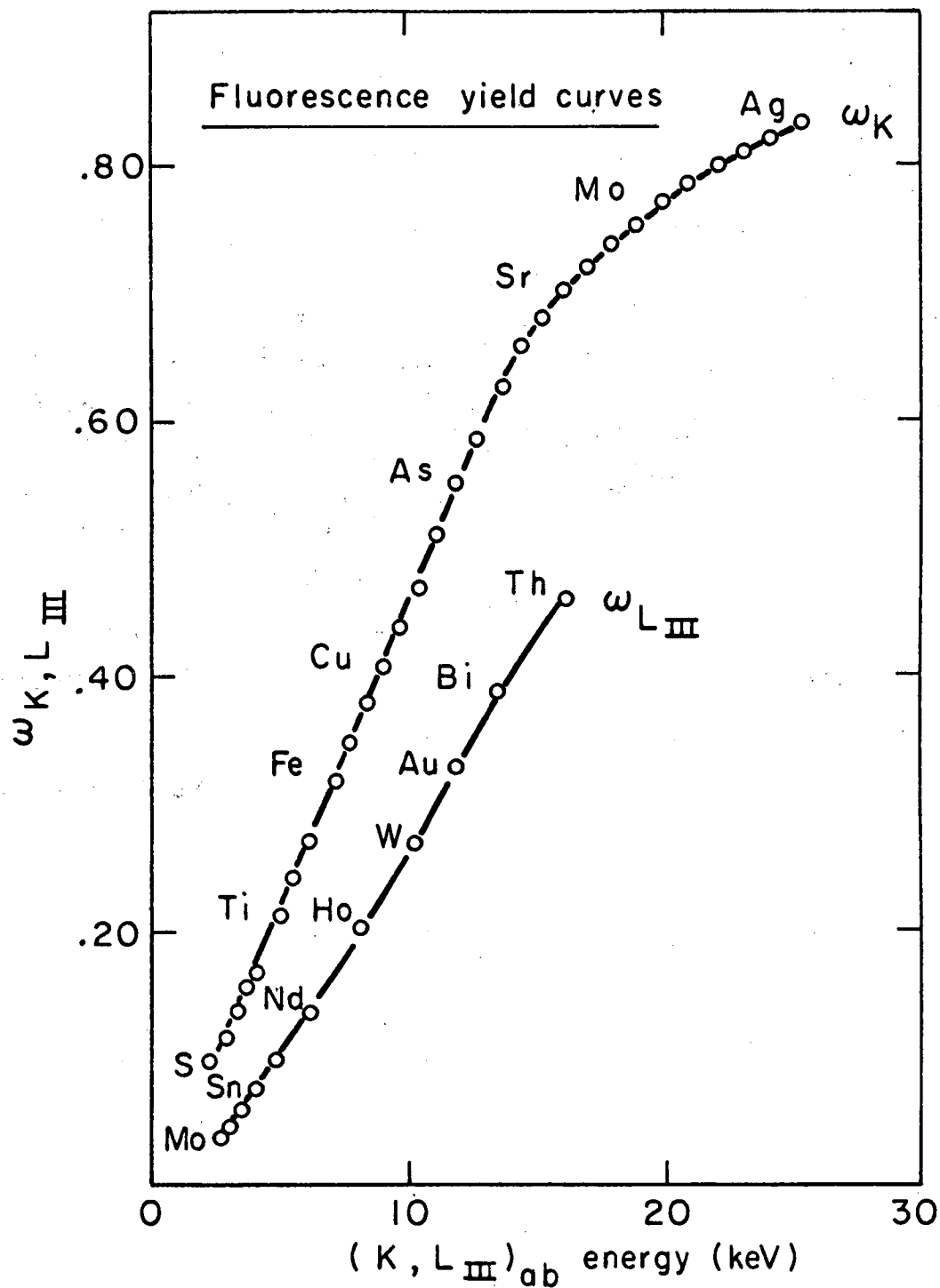
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Fig. 5



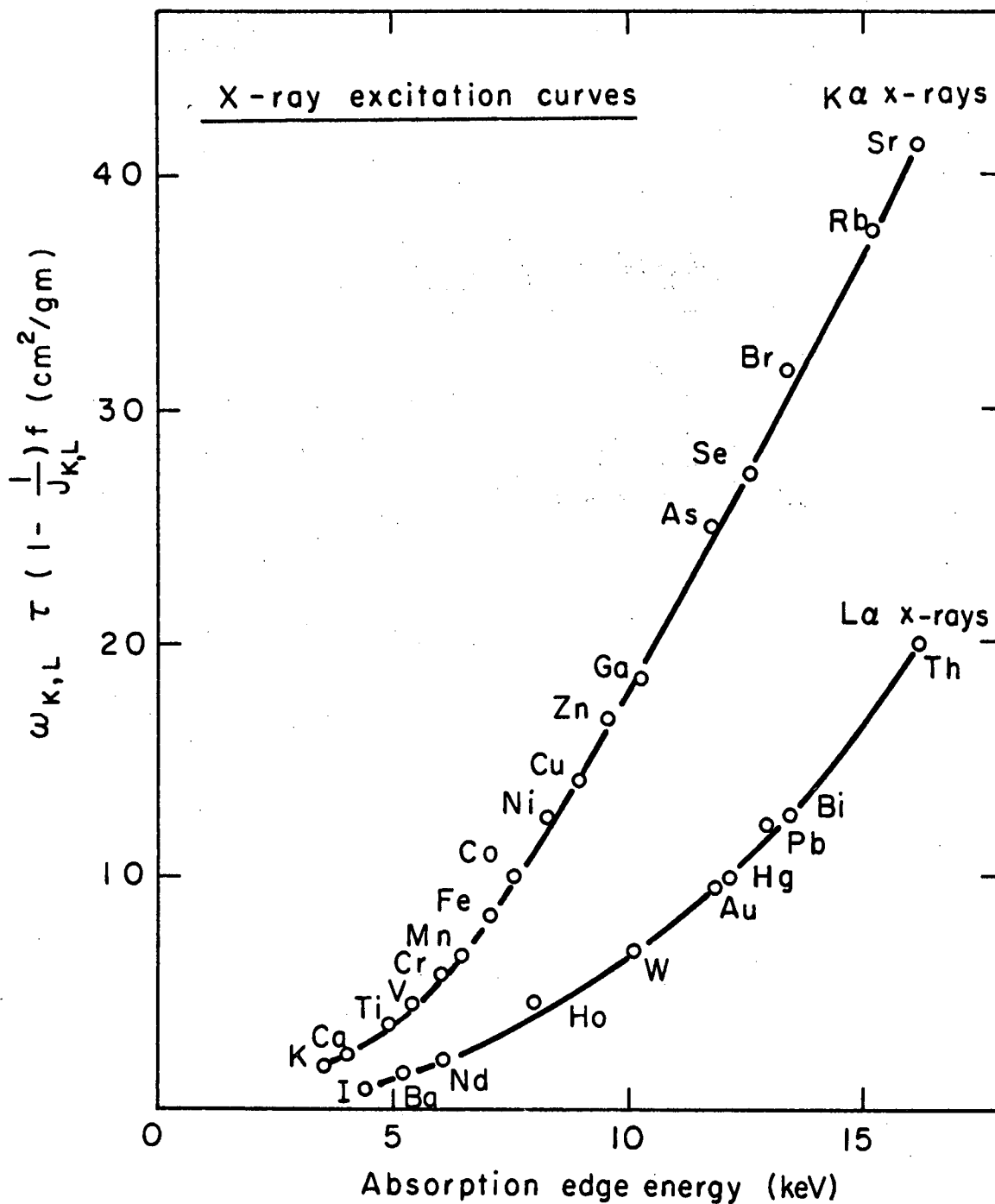
XBL725-2943

Fig. 6



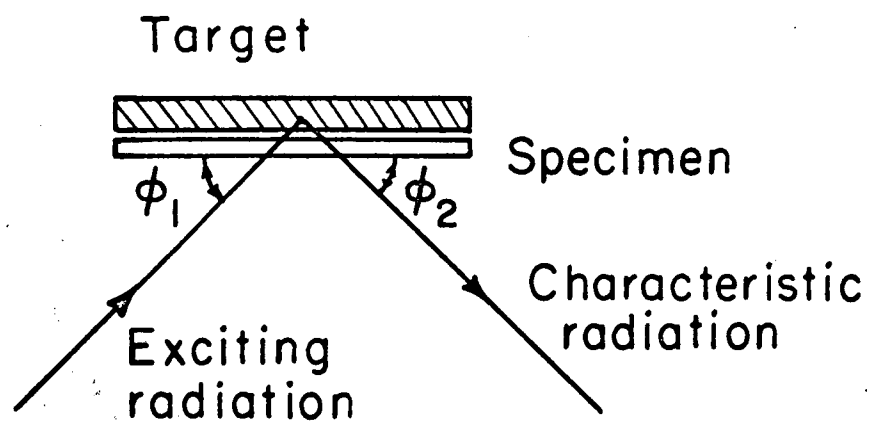
XBL725-2949

Fig. 7



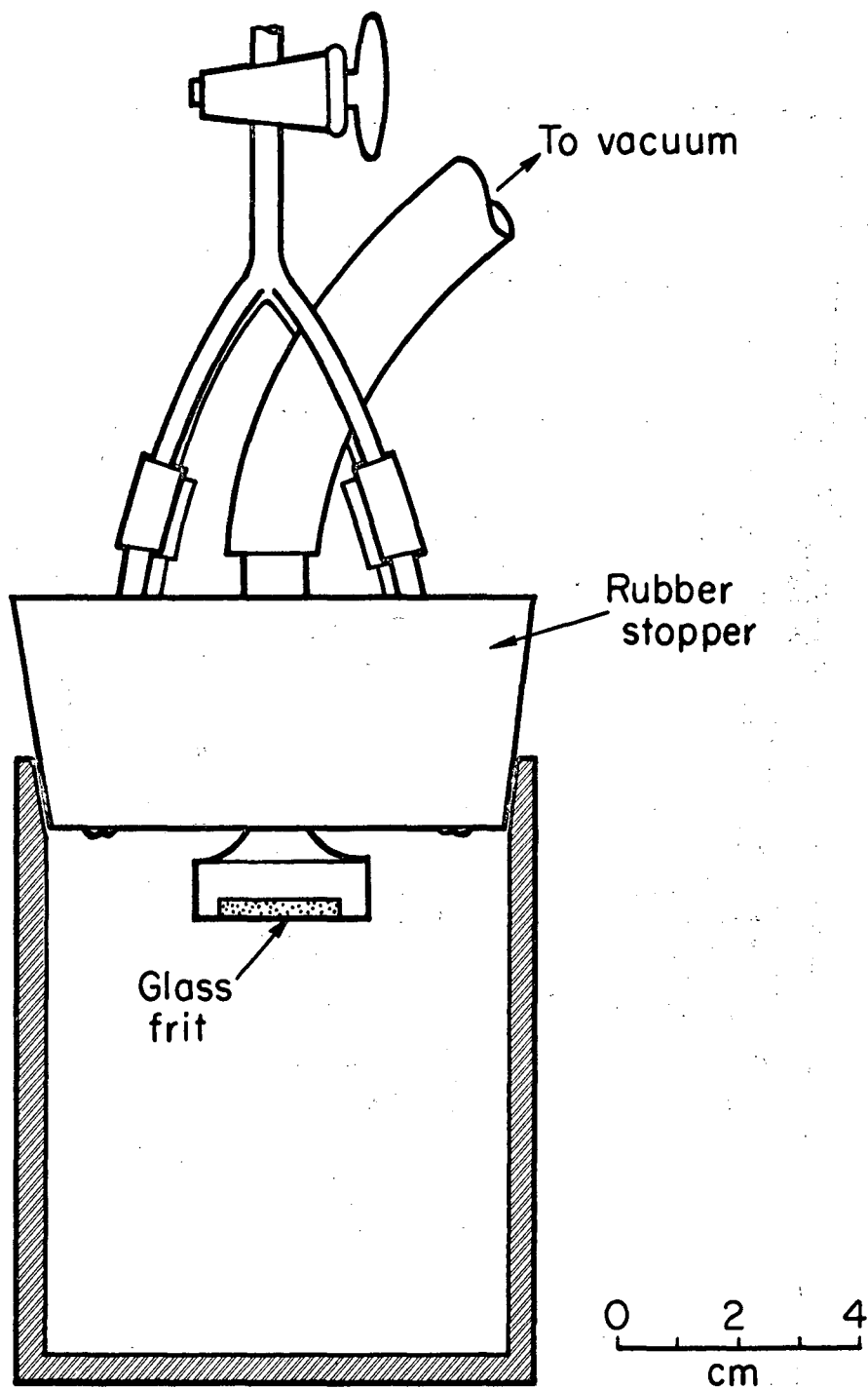
XBL725-2948

Fig. 8



XBL725 - 2941

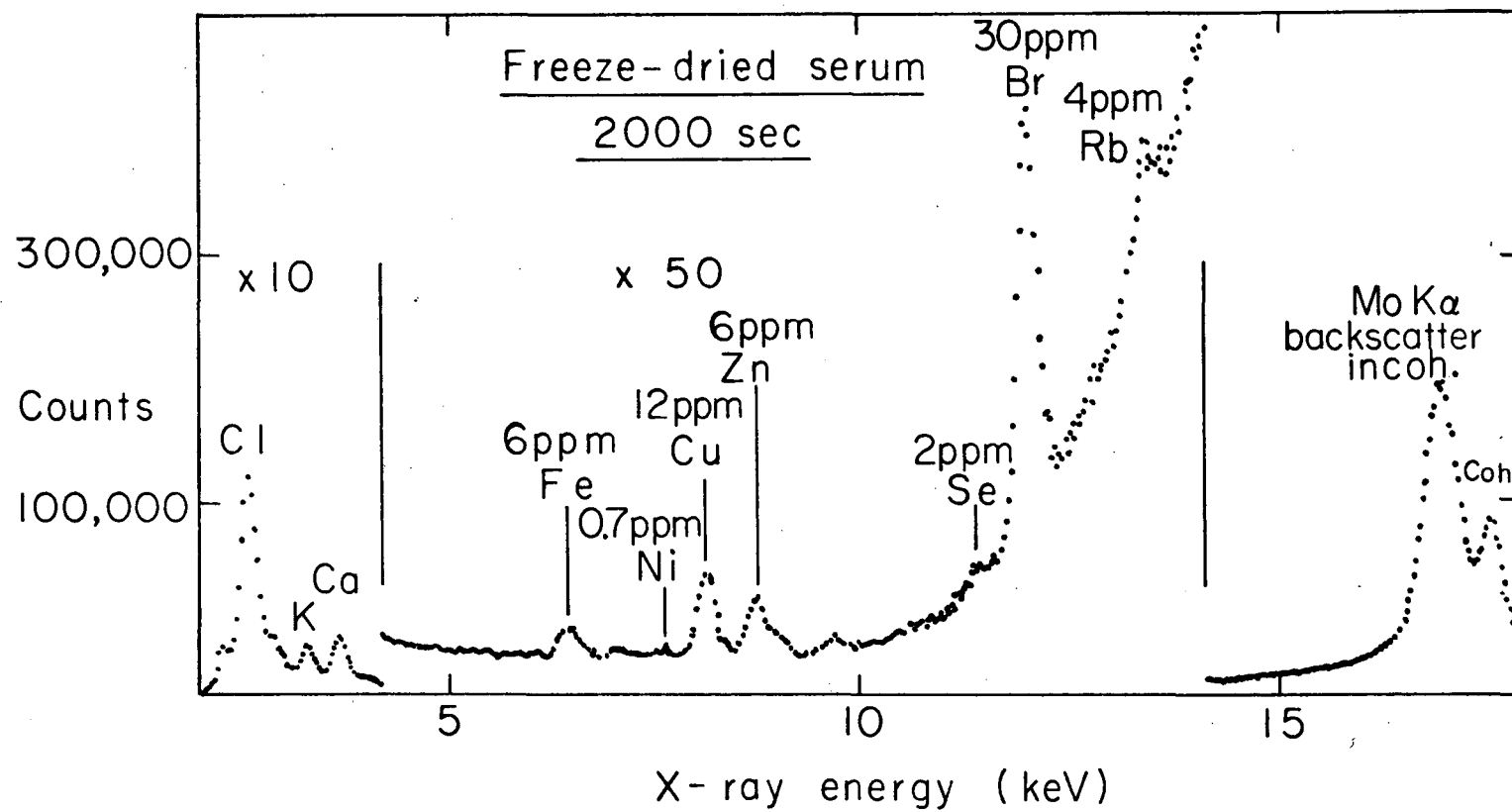
Fig. 9



XBL 726-3204

Fig. 10

Fig. 11



XBL725-2935

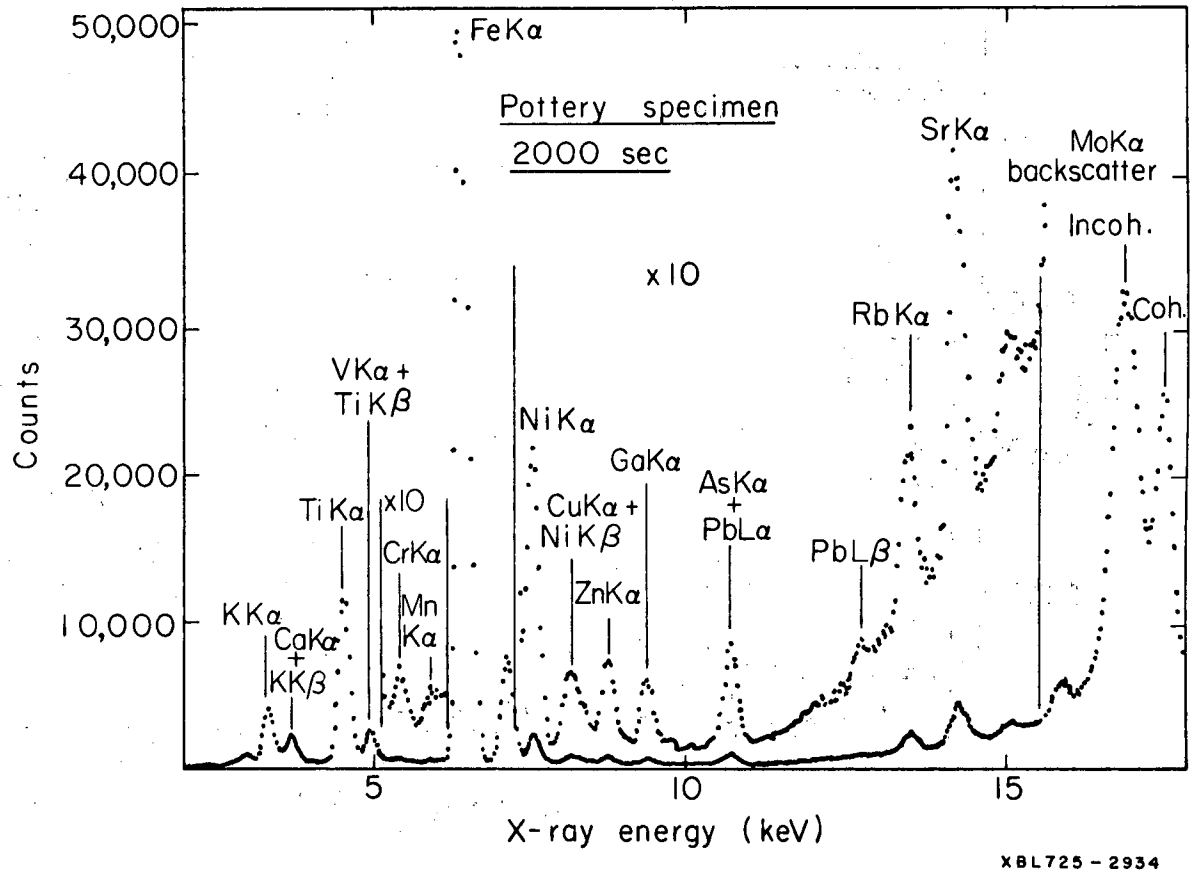
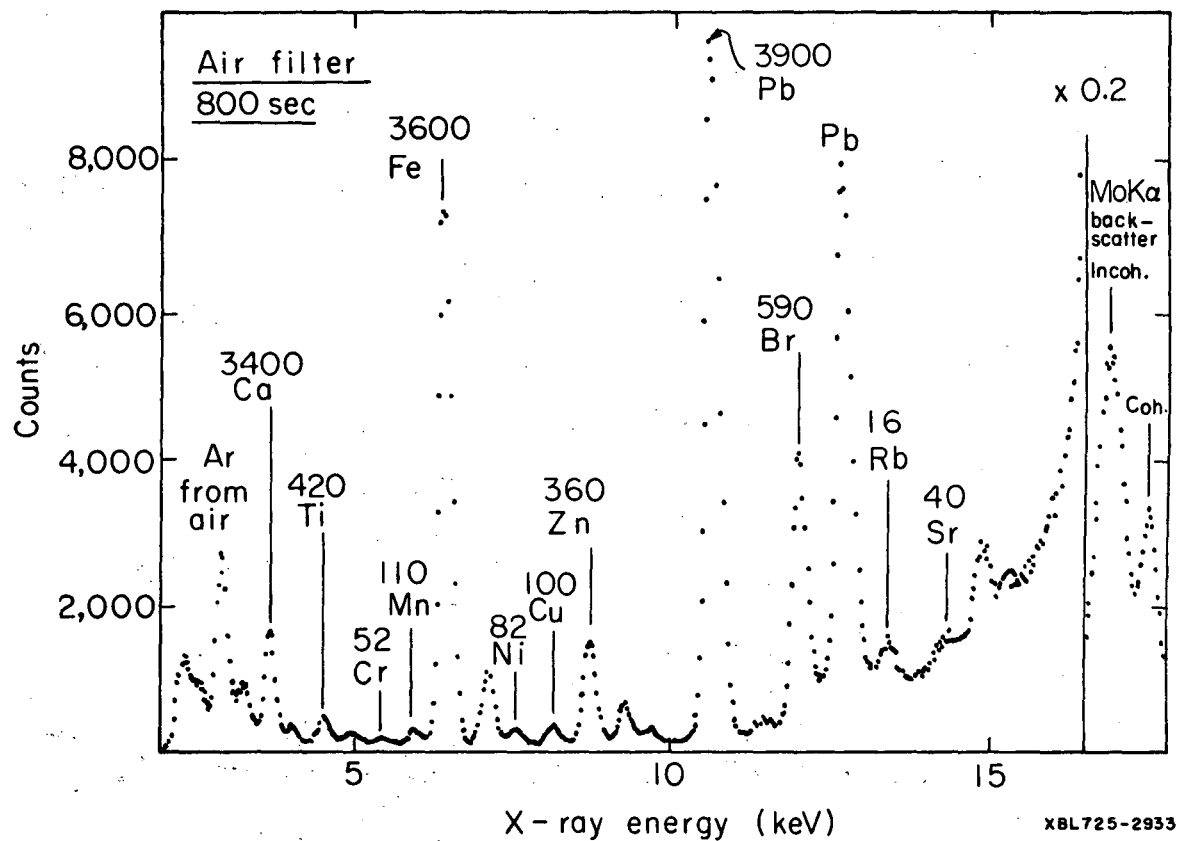


Fig. 12



Concentration in nanograms/cm²

Fig. 13

APPENDIX

In this section, factors which affect the accuracy of the method are discussed. Included are considerations for some of the individual terms used to calculate the relative excitation and detection efficiencies for various x-ray lines with the system employed. Also, methods for the accurate determination of x-ray spectra background and for the compensation of overlapping x-rays are described.

Determination of the Values for the Terms $\omega_{K,L}$, τ_j , $J_{K,L}$, ϵ , and f .

Fluorescence yield, $\omega_{K,L}$.

Theoretical fluorescent yield values (12,13) are used in the calculation. L x-rays originate from transitions to three separate energy levels. Since possible errors exist in the reported fluorescence yield values for x-rays from transitions to the L_{II} and L_I energy levels due to considerations for Coster-Kronig transitions, an x-ray resulting from a transition to the L_{III} energy level is selected for the calculations; hence, the $\omega_{L_{III}}$ values are used. There is generally several percent disagreement between the theoretical and the experimental fluorescent yield values reported in the literature. As previously shown in Table I, the experimental data obtained were consistent with the use of theoretical values in the calculations.

Photoelectric mass absorption coefficient, τ_j .

Photoelectric mass absorption coefficients are reported in the literature (11). Figure 14 shows the output of the molybdenum transmission x-ray tube operated at 42 kV. As illustrated, the exciting radiation is treated as two monochromatic x-ray beams corresponding to the $MoK\alpha$ and $MoK\beta$ x-ray

energies. The net effective photoelectric mass absorption coefficient is determined by multiplying the fraction of each radiation times the photoelectric mass absorption coefficient for each radiation and summing them. As shown, there is a radiation continuum in the range of 25 to 40 keV. The continuum accounts for about 10% of the total exciting radiation. The photoelectric mass absorption coefficients for this continuum are approximately a factor of five less than for the MoK radiation. The net effect on the photoelectric mass absorption coefficients for elements with absorption edge energies below the MoK α energy would be only 2% and essentially would be proportionally the same for all of these elements. Thus, the contribution from this continuum is ignored in the calculations. In addition, a small fraction of the exciting radiation consists of energies just below that of the MoK α x-ray energy. The molybdenum anode and window are poor absorbers of radiation of these energies since they are barely below the MoK absorption edge energy. As illustrated, this radiation is treated as part of the MoK α radiation for analysis. Thus, the photoelectric mass absorption coefficient is appropriately reduced for those elements that have absorption edge energies above part of this radiation which corrects for the ineffective portion of the exciting radiation. To illustrate the magnitude of those corrections, the total photoelectric mass absorption coefficients for strontium and bromine are reduced by 9.7 and 1.8%, respectively. If the exciting radiation had consisted of only MoK α and MoK β x-rays, and if only the photoelectric mass absorption coefficients for MoK α radiation were used for elements with characteristic x-rays in the 3 to 14 keV range (potassium to strontium K x-rays, and cadmium to bismuth L x-rays), the relative error introduced over this range would have been only 1%.

For L x-rays, the photoelectric mass absorption coefficient for the production of x-rays from transitions to the L_{III} energy level are used in the calculations. Figure 15 shows a plot of the total mass absorption coefficient for lead. The photoelectric cross section due to the L_{III} energy level is determined by extrapolation, as illustrated.

Photoelectric mass absorption coefficient jump ratio, $J_{K,L}$.

Photoelectric mass absorption coefficient jump ratios are reported in the literature (11). For L x-rays, the J_L values corresponding to the L_{III} energy level are employed in the calculations.

Detector efficiency, ϵ .

The detector efficiency for radiation striking the detector at an angle of 90° near the center of the sensitive region of the detector can be calculated from the detector mass and the photoelectric mass absorption coefficient of the detector as written:

$$\text{Detector Efficiency} = 1 - e^{-\tau \rho t} \quad (8)$$

where

τ is the photoelectric mass absorption coefficient (cm^2/g) of the detector for the energy of interest.

ρ is the density (g/cm^3) of the detector.

t is the thickness (cm) of the detector.

For radiation between 4 and 15 keV striking a 5 mm thick silicon detector in the described manner, the efficiency is unity. However, with geometries employed for analyses, a fraction of the radiation strikes the detector at

angles of less than 90° and impinges upon the detector near the periphery of the sensitive region. Figure 16 shows the total system geometry employed. The approximate sensitive region of the detector is shaded. To determine the effect of geometry on the detector efficiency, the intensities of characteristic x-rays from reference specimens were measured (1) using the geometry employed for analysis, and (2) with the fine collimator set in place of the exterior of the two detector collimators such that x-rays detected approached the detector in the center of the sensitive region at an angle close to 90° . The reference specimens were prepared of infinite thickness for the radiation of interest so that the geometry would not effect the apparent reference specimen thickness.

Detector efficiency was assumed to be unity for both geometries for lower energy x-rays (around 4 keV), and thus, the effect of the geometry employed on the detector efficiency was determined from the ratio of the intensities with and without the fine collimation. This geometry was found to reduce the detector efficiency to 0.79, 0.90, and 0.98 for $\text{SrK}\alpha$ (14.14 keV), $\text{AsK}\alpha$ (10.53 keV) and $\text{CuK}\alpha$ (8.04 keV) x-rays, respectively.

Fraction of x-rays of interest with respect to total x-rays emitted from transitions to a particular energy level, f.

Figure 17 presents the most prominent K and L transitions leading to K and L x-ray series lines. All K x-rays originate from transitions to a single energy level. Accurate relative x-ray transition probabilities to the K shell are reported in the literature (14). The L x-ray series is more complex and originates from transitions to three energy levels as shown. The literature (15) cites approximate relative probabilities for these transitions. Sometimes more than one of the L x-rays from transitions to the L_{III} energy level are not

resolved from x-rays originating from transitions to other L energy levels (such as the β_2 and β_1 x-rays from lead). This, in turn, requires approximation as to the fraction of the unresolved x-rays that originate from transitions to the L_{III} energy level. The percentage errors arising from these approximations is small when the most intense L x-ray lines ($L\alpha$) are employed for the calculations.

Determination of X-ray Spectra Background from Scattered Exciting Radiation.

The use of monochromatic exciting radiation permits the development of accurate background curves which are related to the ratio of the intensities of the coherent and the incoherent scattered radiation. These curves are established from reference specimens of varying effective atomic number. The reference specimens are prepared of mass similar to the specimens to be analyzed, and should not contain elements which have x-rays in the energy range of interest. Using these curves, the total spectrum backgrounds due to scattered exciting radiation can be determined from the intensities of the coherent and incoherent scattered exciting radiation.

As an illustration, five reference specimens of varying cellulose and sulfur contents were prepared to simulate scattered exciting radiation backgrounds that would be obtained with biological specimens. All reference specimens were of mass 30 mg/cm^2 ; the sulfur contents varied from 0 to 40%. Since the respective ratios of the coherent and incoherent scattering cross sections (for $\text{MoK}\alpha$ and $\text{MoK}\beta$ radiation) from low atomic number matrices such as these are nearly constant, and since the relative difference in the absorption effects of the scattered radiation is small for similar specimens to be analyzed, only the intensities of the scattered $\text{MoK}\alpha$ x-rays were employed to determine spectral

line background contributions from the scattered exciting radiation. To further simplify the determination of the background contributions of the coherent and the incoherent scattered radiation, all reference specimens were run to yield approximately equal total scattered radiation. Although the coherent and incoherent scattered MoK α x-rays were not completely resolved, fixed energy ranges centered on the peaks were selected that gave approximately the same total net counts for the two peaks from all five reference specimens. Even though the ratio of the intensities of the coherent to the incoherent scattered radiation varied by a factor of two, accurate background curves were established for the individual x-ray lines and were expressed by the equation for a straight line as written:

$$\text{Bkg}_j = (\text{Bkg}_{\text{coh.}} + \text{Bkg}_{\text{incoh.}}) \times \left[\left(\frac{\text{Bkg}_{\text{coh.}}}{\text{Bkg}_{\text{coh.}} + \text{Bkg}_{\text{incoh.}}} \right) \times S_j + B_j \right] \quad (9)$$

where

$\text{Bkg}_{\text{coh.}}$ and $\text{Bkg}_{\text{incoh.}}$ are the total counts for the fixed energy ranges for the coherent and incoherent peaks, respectively.

S_j is the slope of the background curve for the x-ray line from element j .

B_j is the intercept at $\text{Bkg}_{\text{coh.}} = 0$

Typically, the standard deviations for the points forming the individual curves were in the range of 0.1 to 0.5%. In x-ray fluorescence analysis, the ratio of incoherent to coherent scattered radiation increases as the exciting radiation energy increases, and as the effective atomic number of the matrix decreases.

Determination of Overlapping X-ray Background. Thin-films are prepared to determine overlapping x-ray lines by establishing relationships between individual x-ray peak shapes and relative intensities. These thin-films are prepared either by dusting the finely pulverized material onto mylar tape, or by evaporation onto thin backings, such as aluminum or mylar. The masses of these thin-films are unimportant as long as the relative difference of the absorption of the x-rays is negligible. For analyses, absorption correction measurements are applied to determine the relative effects. Also, from these films relative excitation and detection efficiencies, such as for L x-rays originating from transitions to either the L_{II} or L_I energy levels, are established in relationship to previously calculated values (K_j in Equation 2) for x-rays from transitions to the L_{III} energy level.

X-rays detected by semiconductor detectors often produce peaks that tail on the low energy side. This tailing effect becomes more pronounced with increasing x-ray energy and can cause overlapping of x-ray lines, particularly when trying to discern x-rays of low intensity adjacent to a high-intensity higher energy peak.

When widely differing counting rates are used, a slight base line shift can occur in the energy spectrum. Thus, one or more of the intense x-ray lines in the energy spectrum are used to appropriately adjust for any base line shift that may occur.

Escape peaks and pile-up can be of consideration for trace element analyses when both high and low intensity (differing by more than an order of magnitude) x-rays are present. The energy of escape peaks corresponds to the

original x-ray energy minus the energy of the escaping photons, which in the case of silicon detectors are the SiK x-rays. The intensity of the escape peaks, although energy dependent, are more than two orders of magnitude less than the initial x-ray intensity. At high count rates, pile-up (simultaneous detection of more than one x-ray at a time, hence, sums of the x-rays are recorded) can occur even though pile-up rejection is used. At 10,000 counts/sec, the peak intensity due to pile-up is more than two orders of magnitude less than the intensity of the initial radiation. The minor corrections for overlapping x-ray background due to peak tailing, escape peaks, and pile-up are established with relative ease from the thin-films.

Geometry-Absorption Correction Consideration. Figure 16 illustrates the geometrical relationship between the exciting radiation, the specimen, and the detector. The absorption correction for radiation coming from various parts of the specimen changes with ϕ_2 . The net effective value of ϕ_2 determines the apparent mass of the specimen. To ascertain whether the net effective value of ϕ_2 changes with increasing correction for absorption effects and, in turn, introduces errors in analyses, thin aluminum foils of mass 8.1 mg/cm^2 were successively stacked and the concentrations of iron present were determined. The analysis of iron was selected because the mass absorption of the aluminum for the FeK α x-rays was a factor of twenty more than that of the aluminum for the exciting MoK radiation. Thus, the absorption correction is almost solely dependent on the absorption of FeK α x-rays. The results obtained are shown in Table VI. It is concluded from these results that for absorption corrections up to a factor of five (the value $[\mu_1 \csc\phi_1 + \mu_2 \csc\phi_2]m \cong 5$) errors due to varying effective values of ϕ_2 are negligible.

Table VI. Analysis of Aluminum Foil

mass (mg/cm ²)	Absorption Correction	ppm Fe
8.1	1.61	4,130
16.2	2.45	4,130
24.3	3.38	4,120
32.4	4.35	4,070
40.5	5.30	4,120

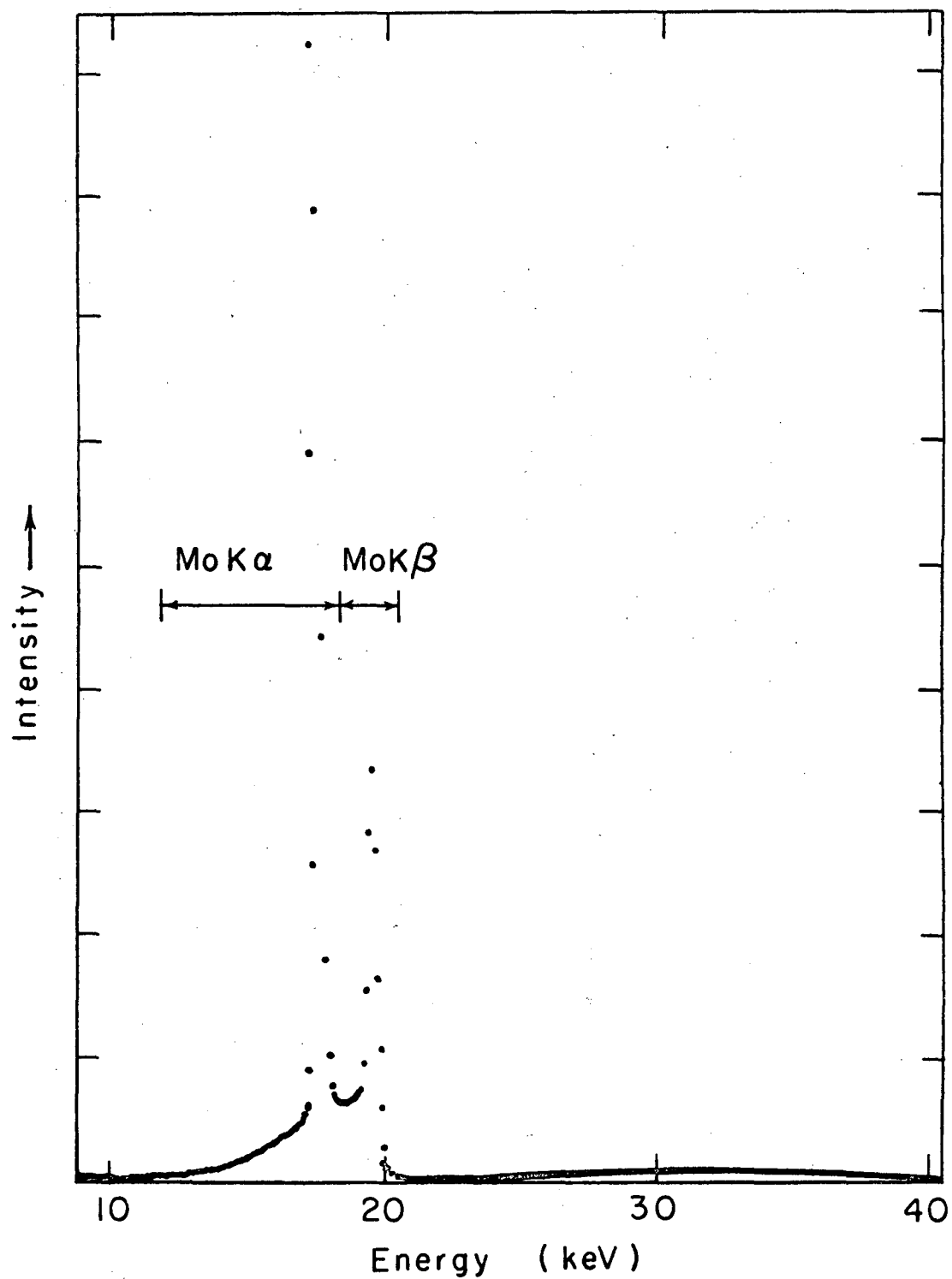
FIGURE CAPTIONS

Fig. 14. Spectral output of molybdenum transmission x-ray tube operated at 42 kV.

Fig. 15. Photoelectric mass absorption coefficient plot for lead.

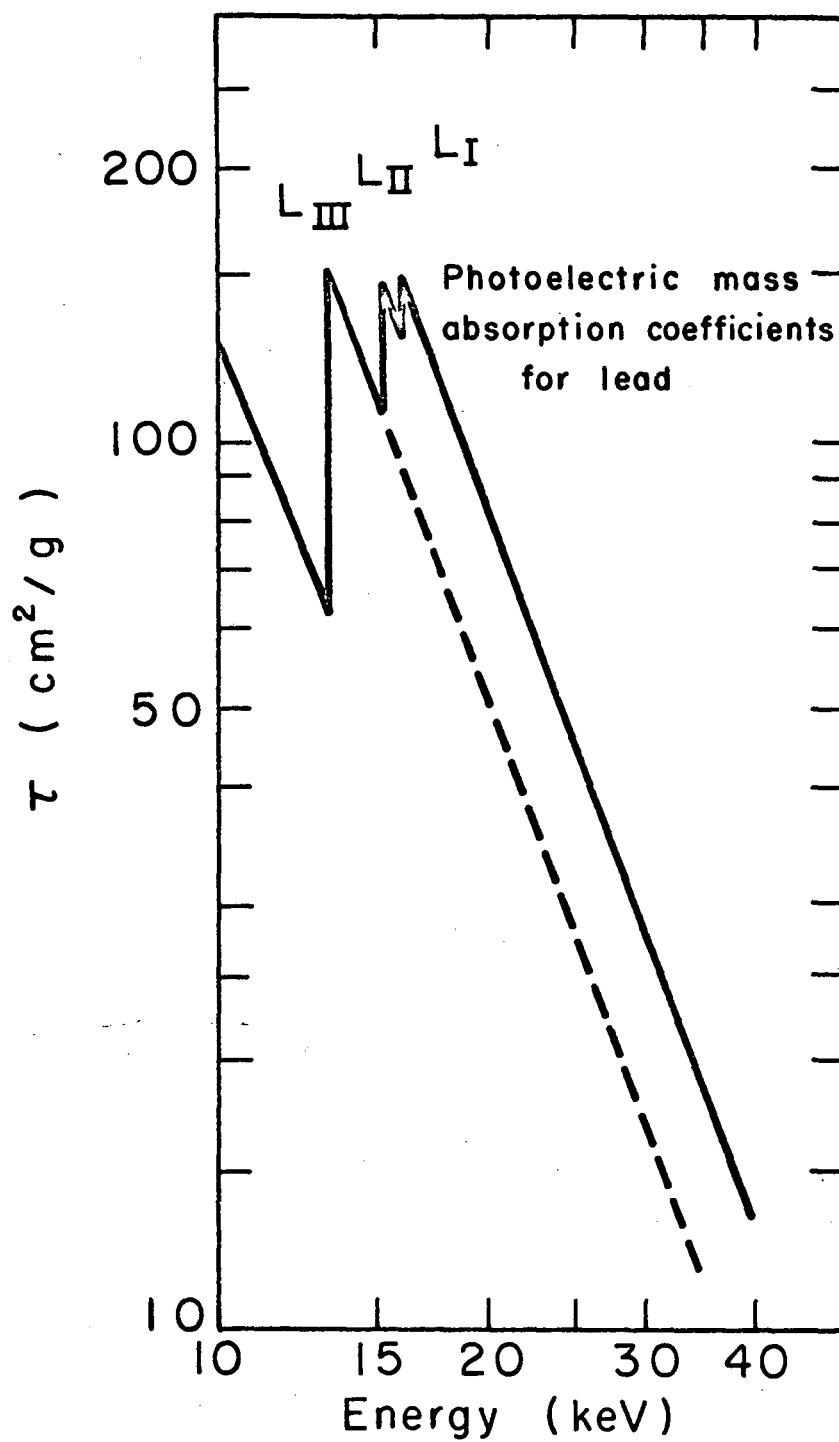
Fig. 16. Schematic diagram for obtaining x-ray spectrum and absorption measurements.

Fig. 17. X-ray energy level diagram.



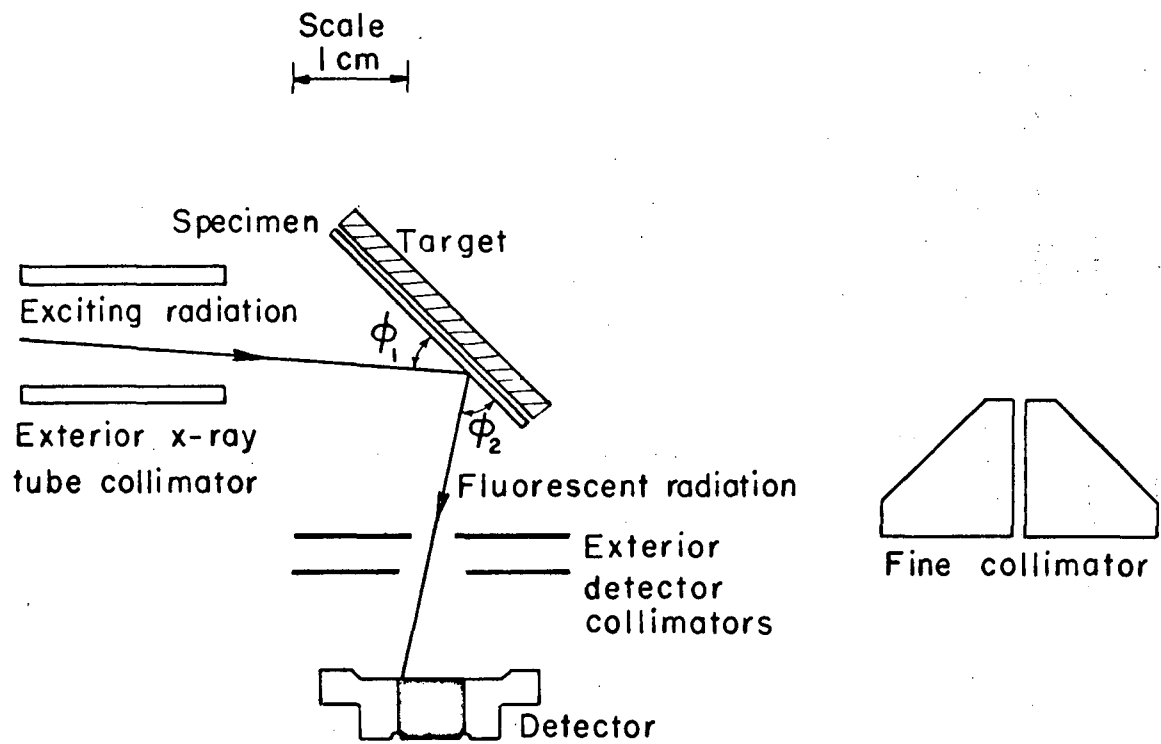
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Fig. 14



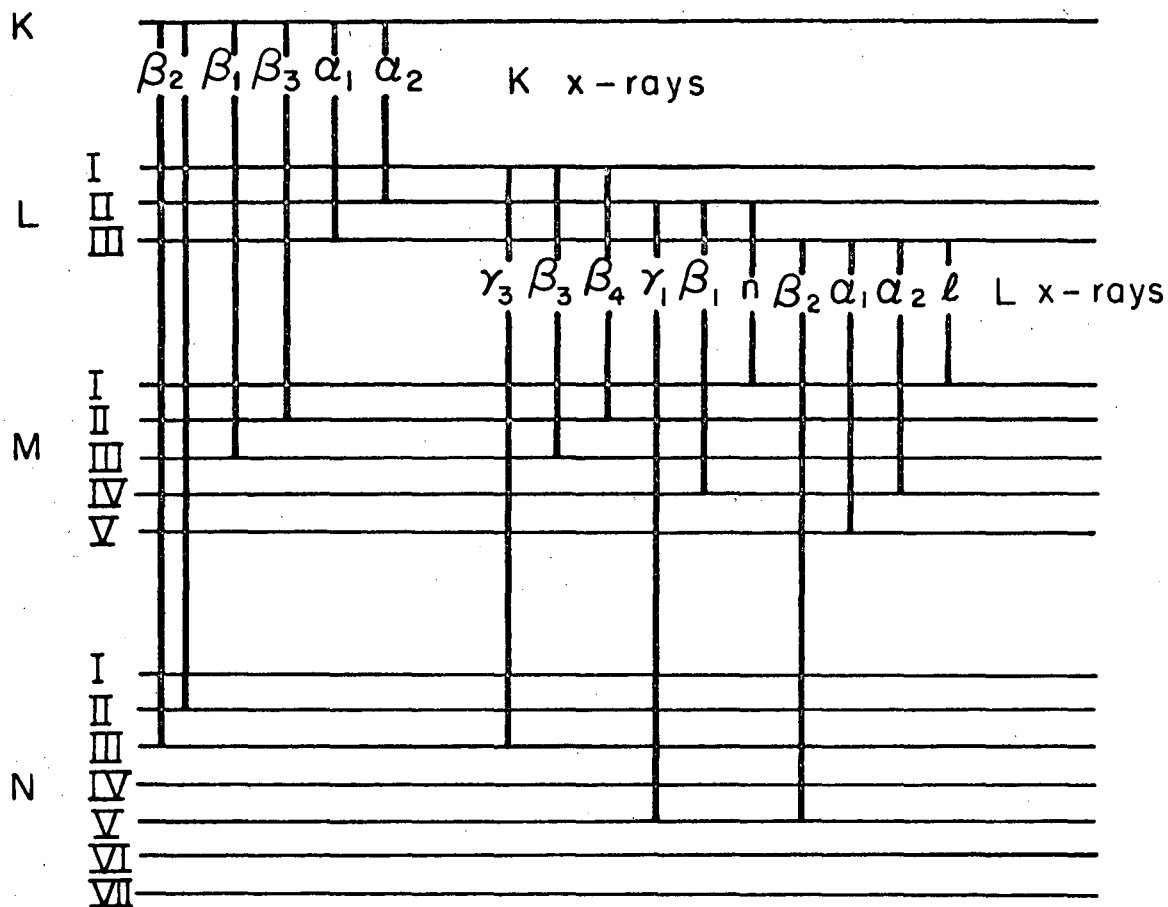
XBL725-2947

Fig. 15



XBL725 - 2944

Fig. 16



XBL725 - 2945

Fig. 17

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