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DETERMINATION OF TRACE ELEMENTS IN LIGHT ELEMENT MATRICES BY X-RAY FLUORESCENCE SPECTROMETRY WITH INCOHERENT SCATTERED RADIATION AS AN INTERNAL STANDARD

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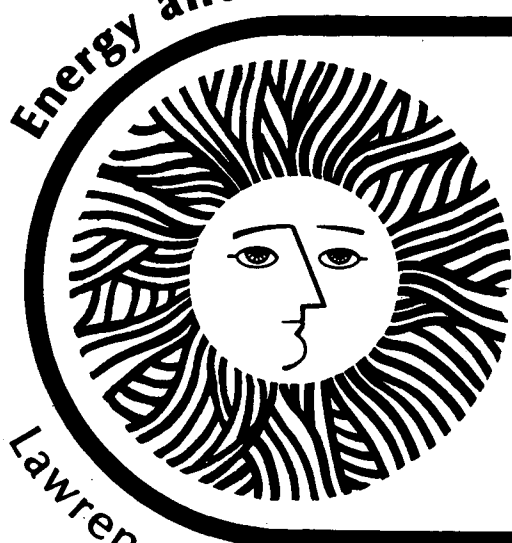
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Determination of Trace Elements in
Light Element Matrices by X-Ray
Fluorescence Spectrometry with
Incoherent Scattered Radiation as
an Internal Standard

*Robert D. Giauque, Roberta B. Garrett,
and Lilly Y. Goda*

December 1978

Lawrence Berkeley Laboratory University of California/Berkeley
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BRIEF

Compton scattered Mo $K\alpha$ excitation radiation, corrected for matrix absorption, serves as an internal standard for the direct determination of trace elements in light element matrices. Analyses of ~ 0.5 g samples, prepared as thin uniform specimens, give results accurate to within $\pm 10\%$, when x-ray counting statistics are not the limiting factor.

*Denotes corresponding author

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ABSTRACT

A method for the direct determination of trace elements in light element matrices is described. It takes advantage of the fact that the incoherent mass scattering coefficient for 17.4 keV Mo $K\alpha$ radiation is relatively constant for the elements Li ($Z=3$) \rightarrow Ca ($Z=20$). Consequently, incoherent scattered Mo $K\alpha$ excitation radiation, corrected for matrix absorption, can serve as an internal standard which compensates for variations in sample mass, x-ray tube output, and sample geometry. Samples of ~ 0.5 g are prepared in the form of thin specimens (~ 0.08 -cm thick) in a cell between two 0.0006-cm thick polypropylene windows. Standardization for most elements is achieved using standard aqueous solutions diluted to ~ 100 ppm. Data obtained from simultaneous transmission measurements for several x-ray energies is used to calculate matrix absorption corrections. For 15-minute analysis periods, results are typically accurate to within $\pm 10\%$ when x-ray counting statistics are not the limiting factor. Sensitivities of 2 ppm or better are realized for 16 of the 22 elements determined (Ti \rightarrow Zr, Hg, Pb, Th, and U).

INTRODUCTION

The determination of trace elements in light element matrices by x-ray fluorescence spectroscopy requires the use of appropriate techniques to compensate for matrix absorption effects. Matrix enhancement effects usually are minor or negligible.

The literature contains a number of methods or approaches to deal with matrix absorption effects. In this paper we will limit our discussion to reported methods which have used scattered x-rays as an internal standard. These methods require minimum sample preparation and do not necessitate prior knowledge of specimen major element concentrations. Andermann and Kemp (1) initially showed that scattered x-rays could serve as internal standards to make matrix absorption corrections. Cullen (2) determined Ni, Cu, and Ag in acid solutions using coherently scattered W L x-rays as an internal standard. Dwiggins (3) has measured both coherent and incoherent scattered W L x-rays to predict spectral background and matrix corrections for the determination of several elements in organic samples. A prerequisite is that the elements have x-rays of energy near those of the scattered x-rays. Reynolds (4) and, more recently, Feather and Willis (5) have used incoherent scattered x-rays to compensate for matrix absorption in analysis of trace elements in thick geochemical specimens. This approach is not applicable to multielement trace analysis of light element matrices due to the amount of material required to attain infinite thickness for all radiations of interest. Furthermore, it is preferable to use thin specimens, because higher peak to background

ratios, and thus, improved sensitivities, are achieved. Nielson (6) has developed a numerical method for computing matrix effects in which the ratio of coherent to incoherent scattered x-rays is used to estimate the light element content in pressed disks of mass 63 mg/cm^2 .

In this paper we describe a method for which the incoherent scattered radiation, corrected for matrix absorption, serves as an internal standard. The method takes advantage of the fact that the incoherent mass scattering coefficient for 17.4 keV Mo $K\alpha$ radiation is relatively constant for most light element matrices. Homogeneous specimens of thin uniform mass thickness are required for analyses.

THEORY

Figure 1 is a plot of the incoherent mass scattering coefficient (7) of the elements H ($Z=1$) through Ca ($Z=20$) for 17.4 keV radiation. Except for hydrogen, the coefficients are relatively constant. The incoherent mass scattering coefficient of a sample, $(\sigma_I/\rho)_{\text{Total}} \text{ cm}^2 \text{ g}^{-1}$, is expressed

$$(\sigma_I/\rho)_{\text{Total}} = \sum_{i=1}^n (\sigma_I/\rho)_i w_i \quad (1)$$

where $(\sigma_I/\rho)_i$ is the incoherent mass scattering coefficient of element i , and w_i is the weight fraction of element i . 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. Table I lists the incoherent

mass scattering coefficients for some light element matrices. The coefficients typically do not vary more than a few percent from that of pure water, with a maximum deviation of 10%. Thus, the intensity of the incoherent scattered radiation, when properly corrected for matrix absorption, can be directly related to the sample mass. However, there are wide variations in the degree to which these matrices attenuate or absorb fluorescent x-rays, as is evident in Table I. For example, the total mass attenuation coefficient, μ/ρ , at 6.40 keV, Fe $K\alpha$ x-ray energy, varies by a factor of 3.

Giauque et al. (8) have previously shown that matrix absorption effects can be determined experimentally for thin uniform samples. Relative x-ray intensities are measured from a target located at a position adjacent to the back of the sample, with and without the sample, as illustrated in Figure 2. The combined fraction of the exciting and fluorescent radiations transmitted in the total sample thickness, m (g cm^{-2}), is expressed

$$e^{-(\mu_e/\rho + \mu_f/\rho)m} = \frac{I_{T'} - I_S}{I_T} \quad (2)$$

where I_S , I_T , and $I_{T'}$ are the intensities of the x-ray plus background from the sample alone, the target alone, and the sample plus the target, respectively. The values μ_e/ρ and μ_f/ρ are the total mass attenuation coefficients of the sample for the excitation and the fluorescent radiations, respectively.

Integration of the x-ray absorption over the thickness of the sample

yields the absorption correction which is expressed

$$Ab_{\text{corr.}} = \frac{(\mu_e/\rho + \mu_f/\rho)m}{1 - e^{-(\mu_e/\rho + \mu_f/\rho)m}} \quad (3)$$

If values of $(\mu_e/\rho + \mu_f/\rho)$ are experimentally determined for several x-ray energies and plotted versus the fluorescence x-ray energy on a log-log scale, an approximate value for $(\mu_e/\rho)m$ can be obtained by extrapolation of the curve to the excitation radiation energy. By difference, values for $(\mu_f/\rho)m$ can be calculated, a curve for $(\mu_f/\rho)m$ values drawn, and a new value for $(\mu_e/\rho)m$ established. This procedure can be iterated several times. Using data from the latter curve, absorption corrections for all radiations of interest can be calculated from equation 3.

EXPERIMENTAL

Equipment and Characteristics. The x-ray system, shown in Figure 3, was designed by Jaklevic and co-workers. It consists of a guard-ring detector with pulsed light feedback electronics and 512-channel pulse-height analyzer. The resolution of the system, FWHM, is 200 eV at 6.4 keV (Fe $K\alpha$ x-ray energy) at 8000 counts/s using an 18 μ s pulse peaking time.

A low power Mo-anode x-ray tube followed by a 0.010-cm Mo filter was used to provide the Mo K excitation radiation. The x-ray tube was operated at 45 kV. The regulated x-ray tube current was adjusted between 50 and 300 μ A for each sample to obtain a count rate of approximately 8000 counts/s. This eliminated or minimized potential spectral zero level

or gain shifts, which would have produced errors in our peak unfolding routine.

Correction for system dead time, resulting either from pile-up rejection or analyzer dead time, was made using a gated clock that measured total system live time. Spectral data were recorded on magnetic tape. Computations were made using a Control Data 7600 computer. Our program required approximately 50K of core space.

Preparation of Specimens. The sample cell is illustrated in Figure 4. The cell is composed of two sections - each consisting of two rings which snap together to hold a 0.0006-cm thick polypropylene window. A spacer ring, 0.08-cm thick, is placed in the bottom section of the cell. Liquid to be analyzed (~ 0.5 ml) is pipetted into this section, after which the top section is inserted against the spacer ring. Any excess liquid is dispersed to the perimeter of the spacer ring. Viscous oils require slight heating prior to pipetting to reduce the viscosity, which usually permits specimens of uniform mass thickness to be prepared.

In the preparation of self-binding material, 250 to 350 mg of finely pulverized sample is placed in a die and a 2.5-cm o.d. disk is pressed at 15000 psi. This sample is then placed in the cell without the spacer ring for analysis.

For a non self-binding material such as coal, 200 to 250 mg of pulverized powder is distributed in the bottom of the cell within the spacer ring. The top section of the cell is inserted and a disk is

pressed at 2000 psi.

CALIBRATION METHOD

Standardization. Standards for the elements are prepared by dissolving pure metals or standard weighing forms as reported elsewhere (9).

Portions of these solutions are diluted to produce element standards in the 100 to 500 ppm range. The diluted standards are pipetted into the sample cell and used to calibrate the x-ray system. Attenuation measurements are made on each of the standards to determine matrix absorption corrections. For each standard a sensitivity factor, K_i , is determined and expressed

$$K_i = \frac{I_i}{I_{\text{Incoh.}}} \times \frac{(Ab_{\text{corr.}})_i}{(Ab_{\text{corr.}})_{\text{Incoh.}}} \times \frac{1}{\text{ppm}_i} \quad (4)$$

where I_i and $I_{\text{Incoh.}}$ are the x-ray intensities from the standard element and the incoherent scattered Mo $K\alpha$ radiation, respectively; $(Ab_{\text{corr.}})_i$ and $(Ab_{\text{corr.}})_{\text{Incoh.}}$ are the absorption corrections for these same radiations; and ppm_i is the concentration of the standard.

Corrections for Absorption Effects. The degree to which the specimen attenuates the incident and fluorescent x-rays in the total specimen thickness is measured experimentally. Relative x-ray intensity is measured at five x-ray energies, with and without the specimen, from a target located at a position adjacent to the back of the specimen, as shown in Figure 2. The target, shown in Figure 4, is contained in a holder which seats over and within the sample cell. The composition

of the target and the x-ray energies for which attenuation measurements are determined are listed in Table II.

Using data from the attenuation measurements and equation 2, values of $(\mu_e/\rho + \mu_f/\rho)_m$ are calculated for the five x-ray energies listed in Table II. These values are plotted versus fluorescence x-ray energy on a log-log diagram. The value of $(\mu_e/\rho)_m$ is estimated by extrapolation of the curve to 17.4 keV, the energy of the excitation radiation. In turn, values for $(\mu_f/\rho)_m$ are calculated, a curve for these values is drawn, and a new value for $(\mu_e/\rho)_m$ is ascertained by extrapolation of this curve to 17.4 keV. This last step is iterated several times. Finally, three separate curves for $(\mu_f/\rho)_m$ values are plotted between 4.50 and 7.11 keV; 7.12 and 10.54 keV; and 10.55 and 17.4 keV, using $(\mu_f/\rho)_m$ values determined for Cr $K\alpha$ and Fe $K\alpha$; Zn $K\alpha$ and Pb $L\alpha$; and Pb $L\alpha$ and Pb $L\beta$ x-rays, respectively. From these curves, values of $(\mu_f/\rho)_m$ and, in turn, values of $(\mu_e/\rho + \mu_f/\rho)_m$ are determined for all x-ray energies in our program. These values are used in equation 3 to calculate the absorption corrections. The above steps are shown in the Appendix.

Corrections for Overlapping X-rays. Our analysis program uses a fixed number of channels as a measure of x-ray intensity for each element determined. Peak overlap factors are initially established from x-ray spectra generated from thin deposits of individual element solutions nebulized onto Nuclepore polycarbonate filters.

Characteristic x-ray line ratios (e.g., $K\beta/K\alpha$) obtained in analysis deviate from the ratios ascertained using thin deposits, since x-ray absorption increases with decreasing x-ray energy. The deviations in

these ratios are determined experimentally using data from the attenuation measurements for the five x-ray lines listed in Table II. The following elements and corresponding x-ray lines are selected for analysis: Ti→Fe, Ni→Zr(K α); Co (K β); Hg, Th, U (L α); and Pb (L β).

Spectral Background. Spectral background under each of the x-ray lines is principally related to incoherent and coherent scattered excitation radiation intensities. Curves which relate the intensity of the spectral background to the intensities of both incoherent and coherent scattered Mo K α radiation are established from spectra acquired on three 300-mg disks (60 mg/cm²) of varying x-ray mass scattering cross sections. These disks, prepared from cellulose and sulfur powders, are composed of 100% cellulose; 90% cellulose, 10% sulfur; and 80% cellulose, 20% sulfur. Figure 5 illustrates four x-ray line spectral background curves. All spectral background curves are expressed by the equation for a straight line

$$\text{Bkg}_i = \left[C_i + S_i \times \left(\frac{I_{\text{Coh.}}}{I_{\text{Coh.}} + I_{\text{Incoh.}}} \right) \right] \times (I_{\text{Coh.}} + I_{\text{Incoh.}}) \quad (5)$$

where S_i is the slope of the spectral background curve for element i and C_i is the intercept at $I_{\text{Coh.}} = 0$.

RESULTS

To demonstrate the capability of the method, four National Bureau of Standards trace element standard reference materials and a shale oil

sample were analyzed. A flowchart illustrating the steps undertaken to calculate element concentrations is listed in the Appendix.

Ten samples (~ 200 to 250 mg) of SRM 1632 Coal were pulverized using an agate mortar and pestle. The powders were distributed within the sample cell spacer ring, and disks were pressed with both sample cell windows in place. Analysis periods, live time, were 1000 sec for the disks alone and 100 sec for the attenuation measurements. Figure 6 is a spectrum obtained on the coal.

Curves of $(\mu_e/\rho + \mu_f/\rho)m$ and $(\mu_f/\rho)m$ values determined for one specimen are shown in Figure 7. There is a minor drop in these curves at 7.11 keV, the Fe K absorption edge energy, since Fe is a minor constituent (0.8%) and not a trace element. Table III lists the results determined for 24 elements. The Ti-Mn values were corrected for overlapping Ba, La, and Ce L x-rays, using concentration values published by Ondov et al. (10). Most of the referenced values (10) were determined by instrumental neutron activation analysis at four laboratories. All results have been corrected for moisture content. We have reported results for four elements (Ga, Ge, Y, and Zr) that are not included in the NBS or referenced values. NBS values listed in brackets are not certified.

The XRF values are generally in good agreement with the NBS and referenced values. The coal was found to be inhomogeneous with respect to Zn and Pb in that the deviation in the results were substantially larger than the precision of the XRF method. The coal has also been reported to be inhomogeneous for Sb (10). The XRF results for V are quite

likely low. Six spectral lines overlap at 4.95 keV: Ti $K\beta$, V $K\alpha$, Fe $K\beta$ escape peak, Ba $L\beta$, La $L\beta$, and Ce $L\alpha$. Using NAA results (10) for Ba, La, and Ce, the calculated intensity of the three L x-ray lines is 2.5 times that of V $K\alpha$. If the samples are not ground sufficiently fine to eliminate particle size effects (11), an overcorrection for the L x-ray lines would be calculated and, in turn, a low result determined for V. However, our Pb result suggests that the certified value is in error for the batch of coal we purchased from NBS. Our Pb result has been substantiated by another analytical technique, Zeeman atomic absorption spectroscopy (12).

Ten samples (~ 250 to 350 mg) of both SRM 1571 Orchard Leaves and SRM 1577 Bovine Liver were pressed into 2.5-cm o.d. disks and analyzed. Tables IV and V list the results. In both cases, the XRF values are in excellent agreement with the certified values.

Twelve samples (~ 0.5 ml) of SRM 1634 Fuel Oil were analyzed using 400 sec counting periods for the oil specimens, and 40 sec for the attenuation measurements. The XRF results, listed in Table VI, are low for V and Ni. The oil was found to contain 11.5% hydrogen and 85.7% carbon by combustion analysis. Thus, the incoherent mass scattering coefficient of this oil is most likely about 4% higher than that of water or a pure hydrocarbon with a 1:1 hydrogen to carbon atomic weight ratio as shown in Table I. Even if an adjustment was made for this difference, the XRF result for V would still be low. The low V result can be attributed to the preparation of specimens of non-uniform mass thickness due to the relatively high viscosity of the oil. With non-uniform specimens,

absorption corrections determined are smaller than expected. This discrepancy becomes larger at lower x-ray energies.

Table VII lists the results for a shale oil sample. Five determinations were made by XRF and two by NAA (neutron activation analysis). The NAA results were obtained by Jon Fruchter, Battelle Pacific Northwest Laboratories. Again, very good agreement has been achieved by these two instrumental analytical techniques.

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Table I. INCOHERENT MASS SCATTERING and TOTAL MASS
ATTENUATION COEFFICIENTS (cm^2/g)

Coefficient	σ_1/ρ	μ/ρ
Radiation	Mo $K\alpha$	Fe $K\alpha$
Energy	17.4 keV	6.40 keV
Matrix		
CH	0.172	7.9
CH with 2% S	0.171	11.3
CH with 2% Ca	0.171	14.1
CH ₂	0.186	7.4
C	0.156	8.6
H ₂ O	0.173	19.8
Sea Water	0.172	23.9
H ₂ O with 2% Ca	0.172	25.8

Table II. TARGET for ABSORPTION MEASUREMENTS

Element or Compound	Weight (mg)	X-ray Lines	Energy (keV)
Cr	600	Cr $K\alpha$	5.41
Fe_2O_3	1000	Fe $K\alpha$	6.40
Zn	200	Zn $K\alpha$	8.63
Pb_3O_4	150	Pb $L\alpha$	10.54
--	--	Pb $L\beta$	12.61
Cellulose	200	--	--

Table III. ELEMENTAL CONCENTRATIONS IN NBS SRM 1632 COAL

 $(\mu\text{g/g} \pm 2\sigma)$

Element	XRF	NBS	NAA (10)
Ti	951±53	(800)	1040±110
V	24±8	35±3	36±3
Cr	22±8	20.2±0.5	19.7±0.9
Mn	39±3	40±3	43±4
Fe	7790±360	8700±300	8400±400
Co	8.5±4.2	(6)	5.7±0.4
Ni	14.5±1.2	15±1	--
Cu	17.7±1.5	18±2	--
Zn	35.7±9.9	37±4	30±10
Ga	6.1±0.3	--	--
Ge	2.9±0.2	--	--
As	4.7±1.0	5.9±0.6	6.5±1.4
Se	3.1±0.2	2.9±0.3	3.4±0.2
Br	17.5±0.3	--	19.3±1.9
Rb	20.1±0.6	--	21±2
Sr	151±4	--	161±16
Y	7.9±0.6	--	--
Zr	33±4	--	--
Hg	<1.1	0.12±0.02	--
Pb	13.6±6.5	30±9	--
Th	2.7±0.7	(3.0)	3.2±0.2
U	<2.3	1.4±0.1	1.41±0.07

Table IV. ELEMENTAL CONCENTRATIONS in NBS SRM 1571 ORCHARD
LEAVES ($\mu\text{g/g} \pm 2\sigma$)

Element	XRF	NBS
Ti	18.0±8.5	--
V	<8	--
Cr	<5	2.6±0.3
Mn	86.5±4.9	91±4
Fe	274±19	300±20
Co	<6	(0.2)
Ni	1.2±0.5	1.3±0.2
Cu	11.5±1.0	12±1
Zn	25.3±2.1	25±3
Ga	<0.5	(0.08)
Ge	<0.4	--
As	10.1±0.8	10±2
Se	<0.3	0.08±0.01
Br	9.0±0.5	(10)
Rb	11.5±0.6	12±1
Sr	36.3±1.3	(37)
Y	<1	--
Zr	<3	--
Hg	<1	0.155±0.015
Pb	40.7±3.0	45±3
Th	<1	--
U	<2	0.029±0.005

Table V. ELEMENTAL CONCENTRATIONS IN NBS SRM 1577
BOVINE LIVER ($\mu\text{g/g} \pm 2\sigma$)

Element	XRF	NBS
Ti	<11	--
V	<6	--
Cr	<4	--
Mn	9.4 \pm 1.1	10.3 \pm 1.0
Fe	267 \pm 5	270 \pm 20
Co	<6	(0.18)
Ni	<0.8	--
Cu	192 \pm 4	193 \pm 10
Zn	134 \pm 2	130 \pm 10
Ga	<0.5	--
Ge	<0.4	--
As	<0.3	(0.055)
Se	1.1 \pm 0.2	1.1 \pm 0.1
Br	8.8 \pm 0.4	--
Rb	18.4 \pm 0.4	18.3 \pm 1.0
Sr	<1	(0.14)
Y	<1	--
Zr	<3	--
Hg	<0.8	0.016 \pm 0.002
Pb	<1	0.34 \pm 0.08
Th	<1	--
U	<2	(0.0008)

Table VI. ELEMENTAL CONCENTRATIONS in NBS SRM
1634 FUEL OIL ($\mu\text{g/g} \pm 2\sigma$)

Element	XRF	NBS
V	283±12	320±15
Cr	<6	(0.09)
Mn	<3	(0.12)
Fe	14.0±1.5	13.5±1.0
Ni	32.0±1.6	36±4
Cu	<0.8	--
Zn	<0.6	0.23±0.05
As	<0.4	(0.095)
Pb	<1.5	0.041±0.005

Table VII. COMPARISON of XRF and NAA ELEMENTAL
RESULTS for SHALE OIL, S-09 ($\mu\text{g/g} \pm 2\sigma$)

Element	XRF	NAA
Fe	40.3 \pm 2.0	38 \pm 3
Ni	4.5 \pm 0.6	4.2 \pm 0.2
Cu	4.9 \pm 0.6	4.6 \pm 1.8
Zn	3.3 \pm 0.3	2.4 \pm 0.4
As	18.2 \pm 1.0	18.2 \pm 1.0
Se	0.8 \pm 0.3	0.7 \pm 0.1

FIGURE CAPTIONS

- Fig. 1 Incoherent mass scattering coefficients of the elements H through Ca for 17.4 keV radiation.
- Fig. 2 Schematic of experimental procedure used to determine matrix absorption effects.
- Fig. 3 Schematic of x-ray fluorescence analysis system.
- Fig. 4 Sample cell and target for x-ray absorption measurements.
- Fig. 5 Spectral background curves for As, Se, Br, and Pb.
- Fig. 6 X-ray spectrum obtained on NBS SRM 1632 Coal.
- Fig. 7 Curves of $(\mu_e/\rho + \mu_f/\rho)_m$ and $(\mu_f/\rho)_m$ values determined for a NBS SRM 1632 Coal specimen.

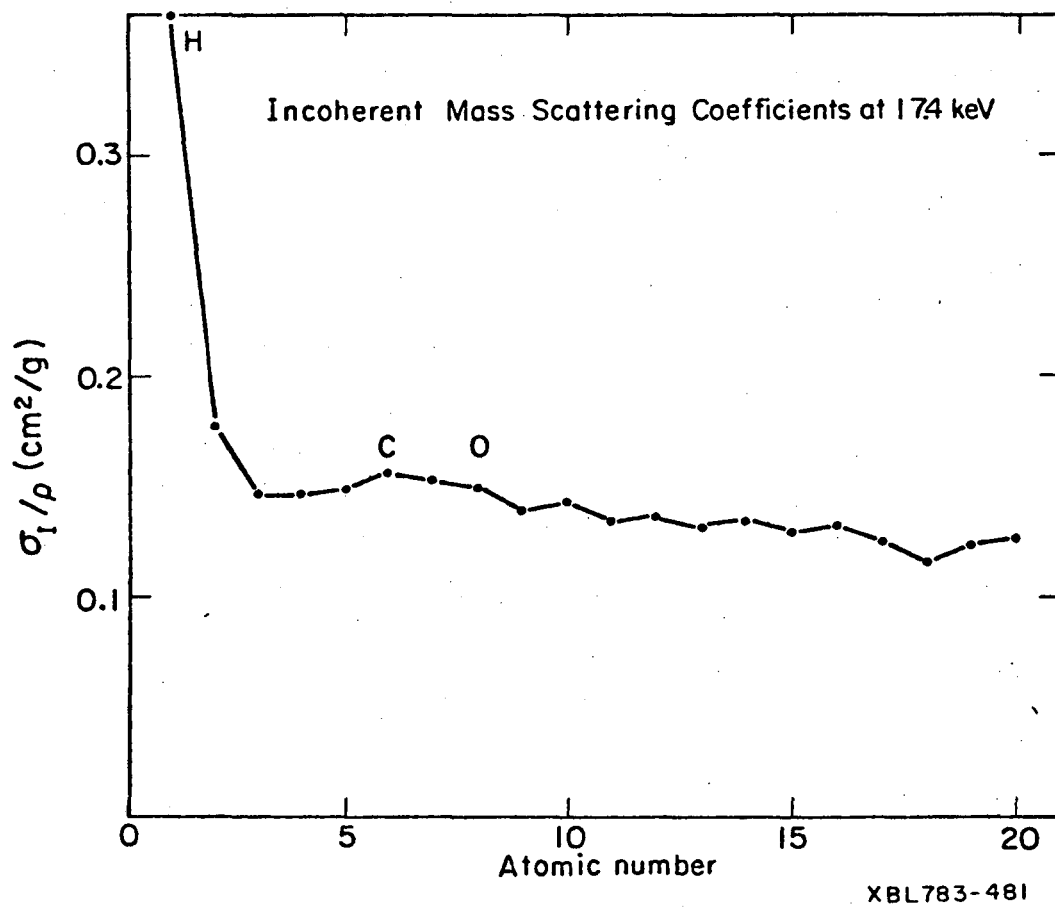
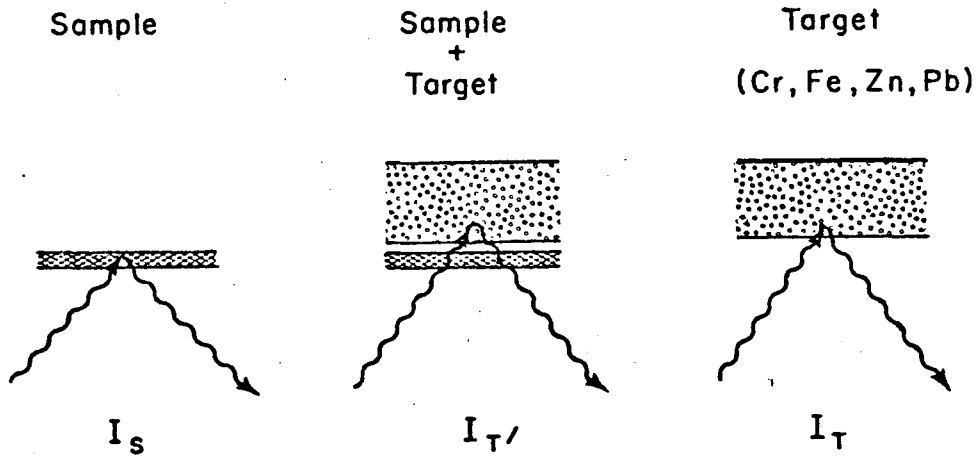
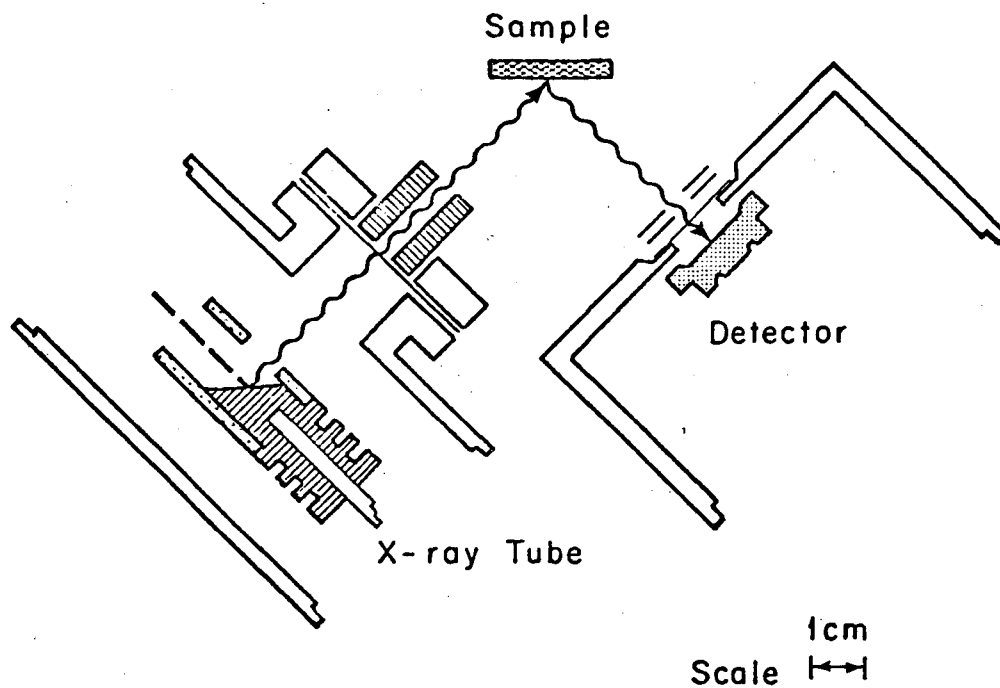


Figure 1.



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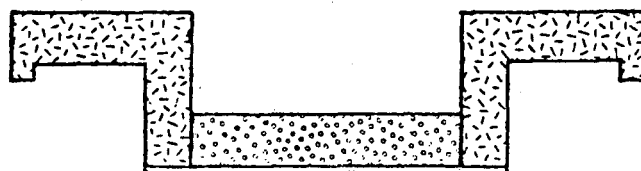
Figure 2.



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Figure 3.

TARGET FOR ABSORPTION MEASUREMENTS



SAMPLE CELL



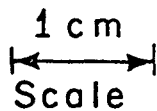
TOP



SPACER

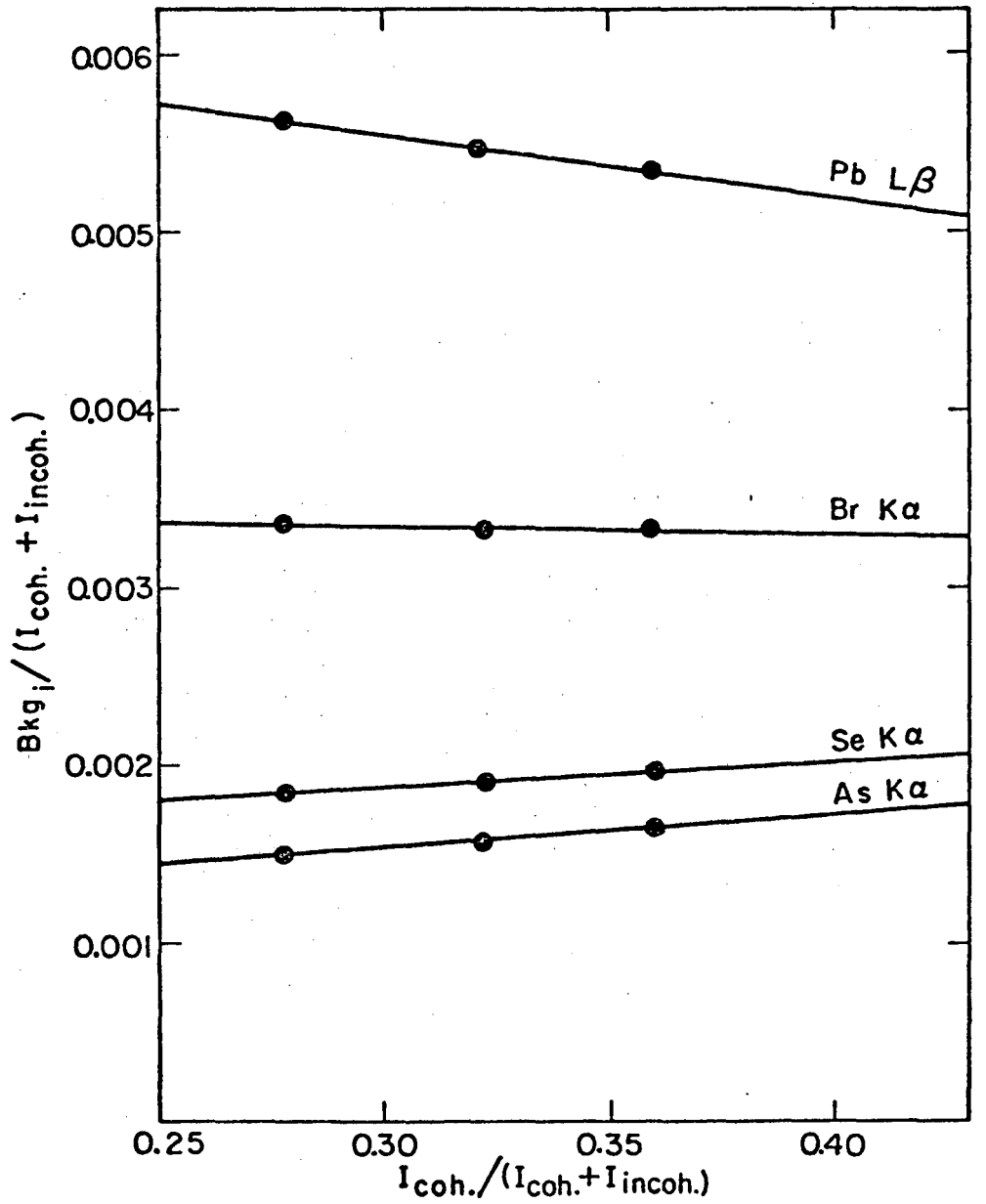


BOTTOM



XBL787-1233-A

Figure 4.



XBL788-1666

Figure 5.

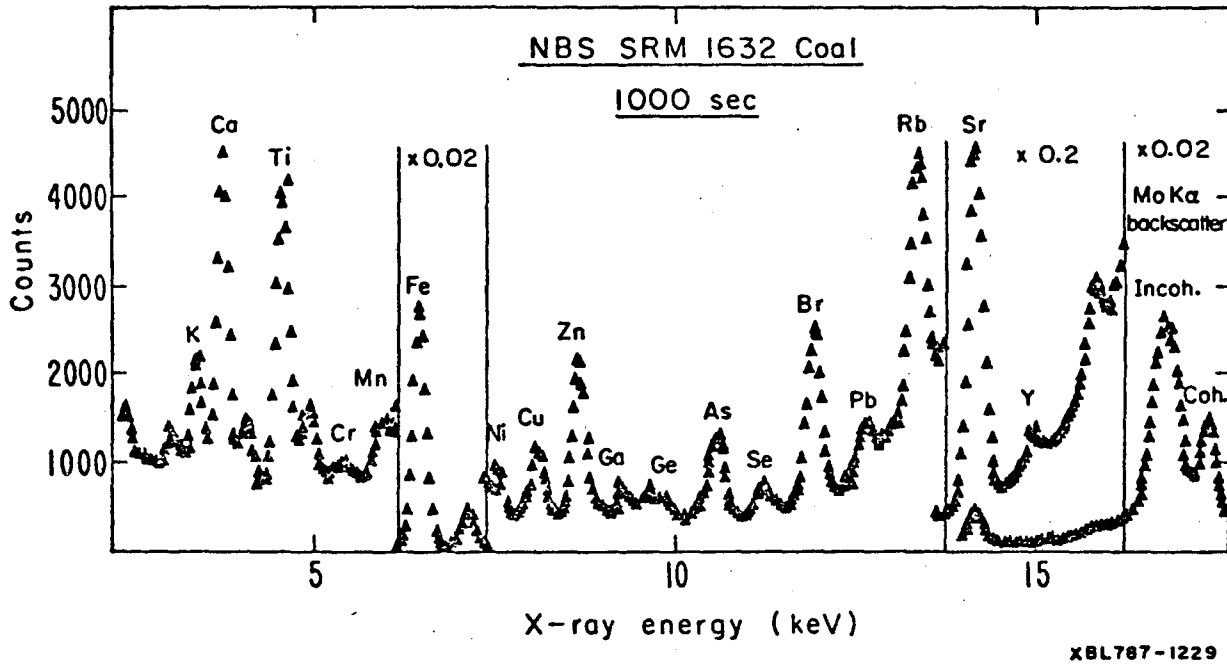
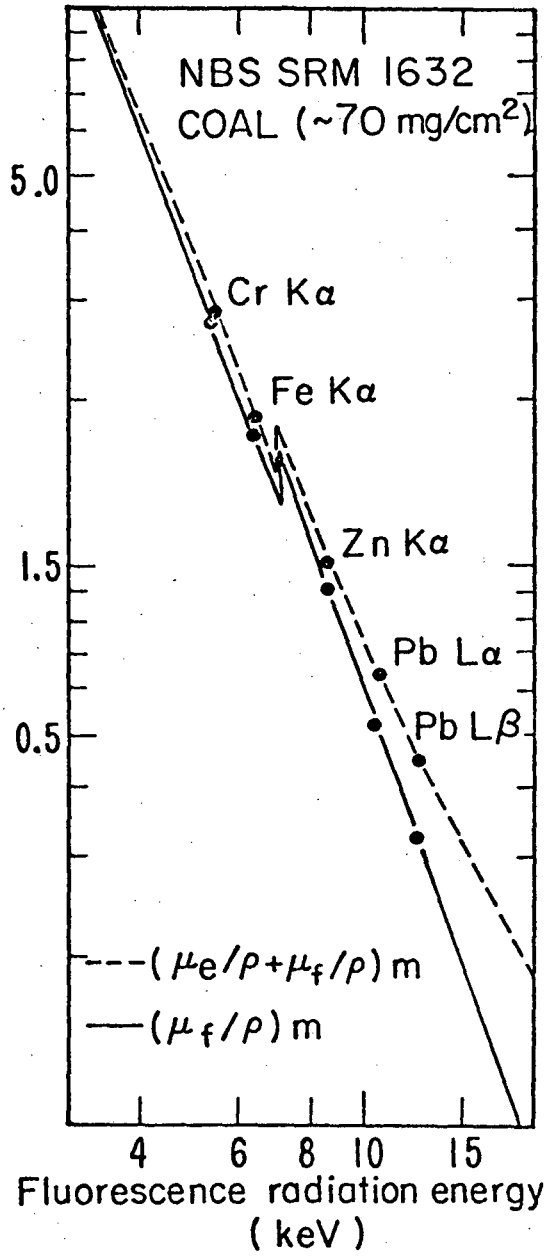


Figure 6.



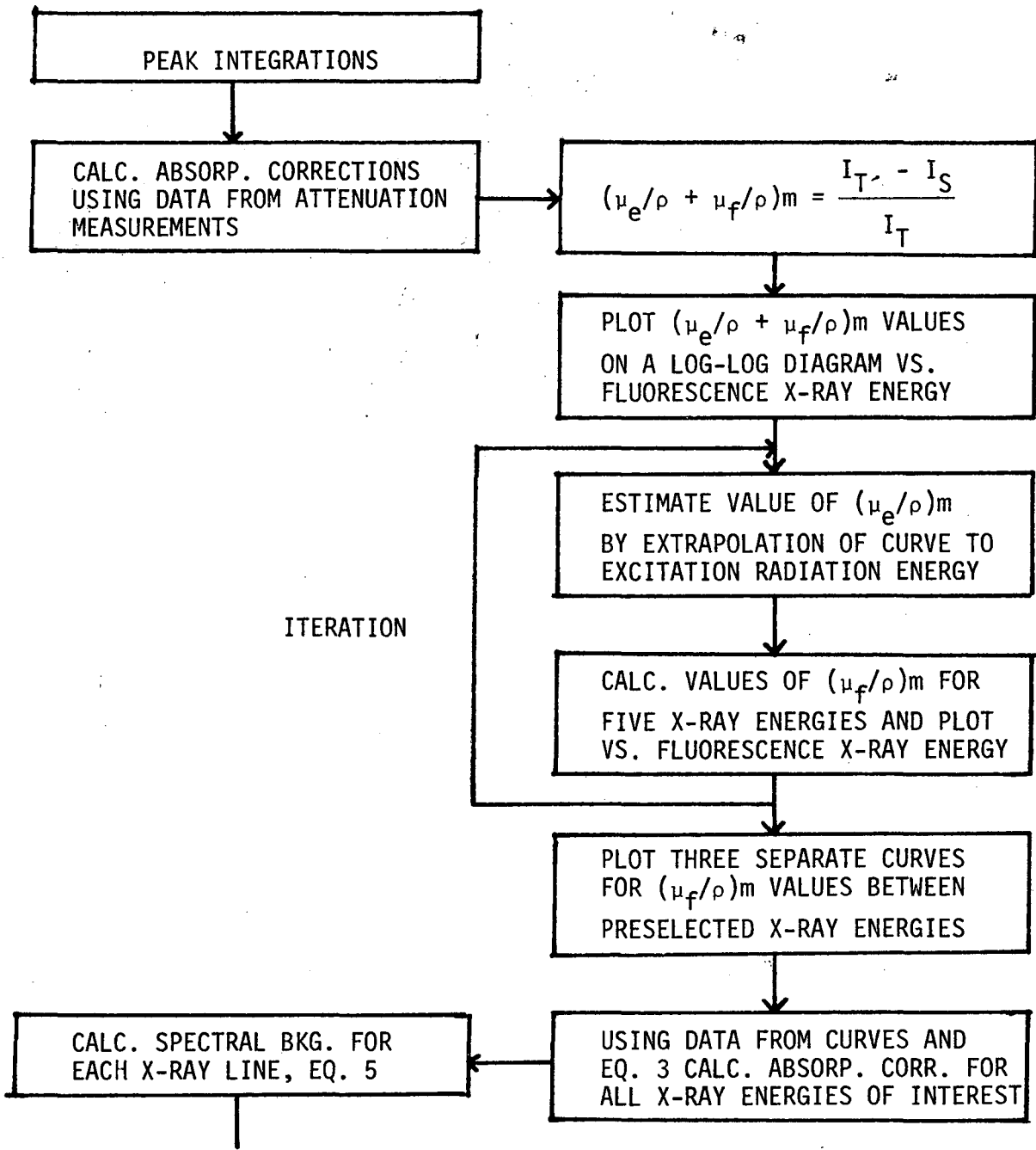
XBL 789-2283

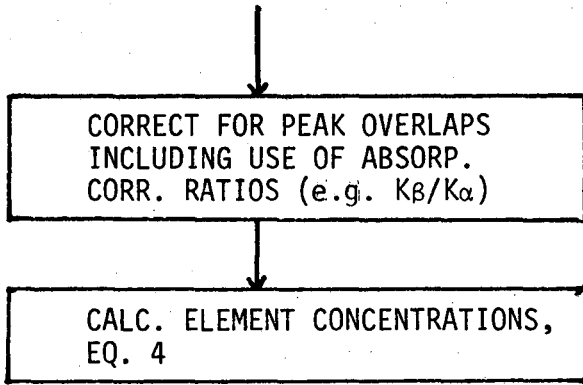
Figure 7.

APPENDIX

In this section a flowchart illustrating the steps undertaken to determine element concentrations is shown. For each sample two spectra are acquired, one for the sample alone, and one with a target located at the back of the sample. Additionally, once each day, a spectrum is acquired on the target only. Using data from the above spectra, matrix absorption corrections are established for all x-ray energies of interest. These corrections are applied to the unfolding of peak overlaps, as well as to compensate for matrix absorption for the individual element determinations. The incoherent scattered radiation intensity, corrected for matrix absorption, serves as the internal standard.

FLOW CHART FOR ANALYSIS PROGRAM





CREDIT

This work was done with support from both the U. S. Department of Energy and the California Department of Public Health. Any conclusions or opinions expressed are solely those of the author(s) and not necessarily those of the Lawrence Berkeley Laboratory, the U. S. Department of Energy, nor of the California Department of Public Health.

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