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Determination of Forty Elements
in Geochemical Samples and Coal Fly
Ash by X-ray Fluorescence Spectrometry

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

February 1977

Lawrence Berkeley Laboratory University of California/Berkeley

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BRIEF

Using two 25-minute analysis periods, results attained are accurate typically to within $\pm 5\%$ when x-ray counting statistics are not the limiting factor.

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ABSTRACT

A method for the determination of forty elements in geochemical samples and coal fly ash is described. Pulverized samples are mixed with sulfur powder and specimens are prepared in the form of pressed disks. In addition to acting as a binder, the sulfur matrix dominates the absorption properties of the specimen disks. Thus, matrix absorption corrections can be determined for a single specimen and applied to the analysis of a wide class of samples. Standardization is achieved using nebulized multielement solution deposits, as well as two single element vacuum vapor deposited thin-film standards. Utilizing two 25-minute analysis periods, results achieved are typically accurate to within $\pm 5\%$ when x-ray counting statistics are not the limiting factor.

INTRODUCTION

Energy dispersive x-ray fluorescence analysis (XRFA) easily permits semi-quantitative determination of a number of elements in a wide range of samples. However, to obtain quantitative data, appropriate means for handling matrix effects must be established. We describe a method in which we stabilize matrix effects for a certain class of samples. The method is applicable for the determination of forty elements of atomic number 22 (Ti) and higher in geochemical and solid waste management samples (e.g., coal fly ash and sludge pond residues).

Claisse (1), Luke (2), Rose, Elder, and Flanagan (3) have reported that fusing certain classes of samples with a flux containing a strongly x-ray absorbing substance such as BaO or La_2O_3 , will yield specimens with essentially equal matrix absorption properties and also eliminate particle size effects. Since matrix effects are stabilized, analytical curves, relating fluorescent x-ray line intensity to concentration, are usually linear. This, in turn, permits accurate results to be realized. However, there is a sacrifice in sensitivities obtainable due to sample dilution and increased matrix absorption.

In this paper a similar technique is reported and applied to the analysis of geochemical and coal fly ash samples. Finely pulverized samples are mixed with sulfur powder and disks are pressed. This yields specimens which have relatively equal matrix absorption properties for x-rays of energies greater than 4.5 keV and also permits corrections for matrix absorption to be determined using thin specimen techniques. Standardization is

achieved using thin-film techniques. Results reported in this paper suggest the method is accurate to within $\pm 5\%$ when x-ray counting statistics are not the limiting factor.

DISCUSSION OF METHOD

To obtain accurate XRFA results, appropriate considerations must be undertaken to ascertain corrections for matrix absorption effects. The absorption correction for a homogeneous sample integrated over a mass thickness, m (g/cm^2), may be expressed

$$Ab_{\text{corr.}} = \frac{\mu m}{1 - e^{-\mu m}} \quad (1)$$

The mass absorption coefficient term, μ (cm^2/g), is determined by summing the contribution of each element and is correctly expressed

$$\mu = \sum_{i=1}^n (\mu_i^e \csc\phi_1 + \mu_i^f \csc\phi_2) w_i \quad (2)$$

where μ^e and μ^f are the total mass absorption coefficients of element i for the exciting and fluorescent radiation, respectively; w_i is the weight fraction of element i ; and ϕ_1 and ϕ_2 are the angles formed by the exciting and fluorescent radiation with the surface of the sample.

In practice, only values of w_i for major constituent elements need be known to calculate μ . However, these values are seldom known. For certain classes of samples, values of μ and, consequently, the absorption correction may be made essentially equal from one specimen to the next by diluting the samples with a highly x-ray

absorbing substance. That is, the contribution of $\mu_i w_i$ for the diluting substance is made large enough so that fluctuations in the weight fractions of the major constituent elements have little effect in the resulting values for μ . Using this procedure, matrix absorption effects are stabilized.

If specimens are prepared of equal mass thickness, individual element standard curves, relating fluorescent line intensity to concentration, are linear. Additionally, matrix enhancement effects are minimized. However, in the interest of stabilizing matrix effects, there is a trade off in sensitivities obtainable, since the sample is diluted and there is an increase in matrix absorption.

In energy dispersive XRFA, all radiations are detected simultaneously. Spectrum background, in most cases, is primarily related to scattered excitation radiation which, for thick specimens, originates from a comparatively larger mass thickness than the fluorescent x-rays. Additionally, for many specimens, system count rate limitations (10-40 K counts/sec) are easily realized, even when the output of a low power x-ray tube (tens of watts) is modified to provide secondary exciting radiation.

For the method, a strongly absorbing substance which was obtainable in the form of a pure fine powder was required. The substance chosen should not yield x-rays in the energy range of interest (4.5-35 keV), nor give rise to x-rays of sufficient intensity to impose significantly on the count rate limitations of the system. Furthermore, it would be desirable if the substance were self-binding so that disks,

which were relatively thin for some of the radiations of interest, could be prepared. Sulfur powder fits the above criteria and was selected as the substance to be mixed with the pulverized materials to be analyzed. Sulfur has a low photoelectric cross section for the excitation radiations (Mo K and Tb K x-rays).

Preparation of Specimens. It was desirable to have specimens which would exhibit relatively constant matrix absorption effects, be physically strong enough to handle, and also have the advantages of thin specimen characteristics for x-rays from the elements of interest. Since for each sample only one specimen was to be prepared for analysis of elements which had fluorescent x-rays over a broad energy range, a trade off in x-ray line/spectral background ratios to be realized for some of the elements was required. Three-fourths of the elements to be determined have x-rays of energies greater than 10 keV, and most of these elements would usually be present in relatively low concentrations. Hence, it was decided to prepare specimens with an approximate mass of 100 mg/cm^2 . Doing so would yield essentially thick specimens for radiations of energies less than 14 keV in the geometry utilized for analysis. For fluorescent x-rays of energies comparable to that of the excitation radiation, severe losses in x-ray line/spectral background ratios are not obtained for thick specimens.

For any given energy of radiation, sulfur and sample particles have different x-ray mass absorption coefficient values. When x-ray absorption is sufficiently large compared to the particle size, so

that the radiation of interest comes from a depth of only a couple of particle layers or less, the specimen is considered heterogeneous for analysis, and inter-mineral effects exist. Consequently, both the sample and the sulfur powder should be pulverized until the particle diameters are smaller than one-fifth the effective penetration depth for the measured x-ray energy (4). Using sulfur as the matrix, this corresponds to a particle size of approximately 40 microns for 7.5 keV ($\text{NiK}\alpha$) x-rays, and 10 microns for 4.5 keV ($\text{TiK}\alpha$) x-rays.

For analysis, 100 mg of finely pulverized sample is mixed with 400 mg of sulfur powder using an agate mortar and pestle, transferred to a 2.54 cm I.D. die, pressed at 15,000 psi and weighed. This yields a specimen disk of mass 98.7 mg/cm^2 .

Characteristics of Equipment. The x-ray system, shown in Figure 1, was designed and constructed by Jaklevic and co-workers (5). It consists of a low power W-anode x-ray tube, automatic interchangeable secondary targets used to provide nearly monochromatic secondary excitation radiation, a Si guard-ring reject detector, and a 1024 channel pulse-height analyzer. The total resolution of the system, FWHM, was 195 eV at 5.9 keV ($\text{MnK}\alpha$ x-ray energy) at 4,000 counts/sec using a 17 μsec pulse peaking time.

For the determination of elements Ti(Z=22) through Sr(Z=38), as well as heavy elements Ta, W, Hg, Pb, Th, and U, the x-ray tube was operated at 54 kV and 300 μ amps. A Mo secondary target, with a 0.025 cm V prefilter followed by a 0.015 cm Al filter, was used to provide the excitation radiation. For the determination of elements Y(Z=39) through Ce(Z=58), a Tb secondary target with a 0.010 cm Ta prefilter was utilized. The x-ray tube was operated at 80 kV and 200 μ amps.

Correction for system dead time, resulting from either pile-up rejection or analyzer dead time, was made using a gated clock that measured total system live time. Spectral data acquired were recorded on magnetic tape. Computations were made using a Control Data 6600 computer. The program required approximately 40 K of core space.

CALIBRATION METHOD

Standardization. Relative excitation-detection efficiencies of the x-ray system for x-ray lines from twenty-eight of the forty elements determined were ascertained using nebulized multielement solution deposits on thin substrata (6). One of the elements in each of the multielement standard solutions served as an internal standard. Actual standardization of the system was achieved using two single element thin-film standards, one for each excitation condition. The standards were prepared by vacuum vapor deposition of the elements onto thin substrata. Relative response of the system to x-ray lines from the other twelve elements was achieved by interpolation.

Table I lists the individual elements or compounds used to prepare standard solutions and the solvent used. (Note: Solutions containing Th were nebulized in a box designed to contain radioactivity.) To obtain maximum characteristic x-ray line to spectral plus overlapping x-ray background ratios for the class of specimens to be analyzed, the following x-ray lines were chosen: Ti → Ce ($K\alpha$) except for Co ($K\beta$); Hg, Th, and U ($L\alpha$); Ta, W and Pb ($L\beta$).

Determination of Absorption Corrections. Giaouque et al., (7) have previously shown that by using nearly monochromatic excitation radiation, matrix absorption effects for thin uniform specimens may be determined experimentally. In the method, relative x-ray intensity is measured, with and without the thin specimen, from a target located at a position adjacent to the back of the specimen. The combined attenuations, A , of the exciting and the fluorescent radiations in the total specimen thickness, m (g/cm^2), is expressed

$$A = \frac{I_T' - I_S}{I_T} = e^{-\mu m} \quad (3)$$

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 plus the target, respectively.

As mentioned in the section "Preparation of Specimens", sulfur disks of mass $100 \text{ mg}/\text{cm}^2$ are thick specimens in the system for radiations of energies less than 14 keV. To determine x-ray absorption corrections

to be applied for analysis for these radiations, a thin pure sulfur disk of mass 29.6 mg/cm^2 was prepared. Using Mo excitation radiation, relative x-ray line intensities, with and without the thin sulfur disk, were measured for Fe, Ni, Cu, Zn, Ga, Se, Br, Rb, Sr, and Pb x-rays simultaneously from a multielement target.

Experimental cross section values determined, $\mu_S^{\text{expt.}}$, were plotted versus x-ray energy, as shown in Figure 2. These values include the cross-sections for both the excitation and the fluorescent radiations as well as the geometry factors. Also shown is the cross section curve, $\mu_S^{\text{f}} \text{ csc}\phi_2^{\text{expt.}}$, established for the fluorescent radiation only. Using mass absorption coefficient data reported by McMaster et al., (8), a cross section curve, $\mu_S^{\text{f}} \text{ lit.}$, for pure sulfur was also plotted. The difference between the experimental and the literature cross sections is that the literature values do not include the geometry factor for the fluorescent radiation, nor the contribution of the excitation radiation.

In this paper all specimens are treated as having a cross section equivalent to that of a mixture composed of 20% USGS AGV-1 Andesite and 80% sulfur. Using major element data reported by Flanagan (9) and mass absorption coefficient data from the literature (8), x-ray cross section curves were calculated for pure Andesite, $\mu_{\text{AGV-1}}^{\text{f}} \text{ calc.}$, as well as for the above mixture, $\mu_{\text{mix}}^{\text{f}} \text{ calc.}$ These curves are also shown in Figure 2.

Over the energy range of most of the elements to be determined, the cross section for Andesite is equal to 0.592 times the cross section for pure sulfur. Hence, for analysis the disks are treated as having cross sections equal to 0.918 times that of pure sulfur:

$$(0.20 \times 0.592 (\mu_S) + 0.80 \times 1.00 (\mu_S)) = 0.918 (\mu_S).$$

Thus, these values, along with a mass thickness of 0.0987 g/cm^2 , were used in equation 1 to calculate the absorption correction factors.

Values of μ_m for x-ray lines from the elements determined with Tb excitation radiation ($Y \rightarrow Ce$) were ascertained experimentally on a pure 500 mg sulfur disk, as this was a thin specimen for these radiations. Determined values for μ_m were also multiplied by 0.918 before calculating the absorption corrections to be applied for analysis.

Determination of Overlapping X-ray Background. The analysis program uses a fixed number of channels to measure characteristic x-ray line intensities for each element to be determined. Peak overlaps were initially established from x-ray spectra generated from thin deposits of each element. The deposits were prepared by nebulization of solutions of individual elements onto Nuclepore polycarbonate filters, or by dusting the element or appropriate compound onto tape.

Characteristic x-ray line ratios (e.g., $K\beta/K\alpha$) realized in analysis deviate from the ratios ascertained using thin deposits, since x-ray absorption increases with decreasing x-ray energy. Absorption corrections were calculated for fluorescent x-ray lines using experimental cross section values, $\mu_f \text{ csc } \theta_2$, determined for 98.7 mg/cm^2 disks composed of 20% Andesite and 80% sulfur. Table II lists the corrections for six pairs of x-ray lines and corrections calculated for a pure sulfur disk of mass 98.7 mg/cm^2 . As shown, the ratios of the corrections, $K\alpha/K\beta$, for any one element deviate by less than 2%. Accordingly, the peak overlaps established from thin deposits are adjusted by these ratios.

A small amount of additional overlapping x-ray background, due to fluorescent radiation scattered from within the disk, resulted from high intensity x-ray peaks. Overlapping x-ray backgrounds from Fe, Se, and Ba K x-rays were established from 98.7 mg/cm² disks composed of approximately 0.2% of the element, 10% LiBO₂, and 90% sulfur.

Spectrum Background. The background under each of the x-ray lines used for analysis is referred to as the spectral background. In most cases, it is principally related to Compton and coherent scattered excitation radiation. Curves which related the intensity of spectral background to the intensities of both Compton and coherent scattered excitation radiation were established from spectra acquired on three 500 mg disks of varying x-ray cross sections: 20% Na₂CO₃, 80% sulfur; 10% Na₂CO₃, 90% sulfur; 100% sulfur. For each element, spectral background was plotted versus the ratio of the coherent to the Compton plus coherent scattered excitation radiation intensity.

Individual x-ray line spectral background curves for each element were expressed by the equation for a straight line

$$\text{Bkg}_i = (C(1) + C(2)) \times \left[\left(\frac{C(1)}{C(1) + C(2)} \right) \times S_i + R_i \right] \quad (4)$$

where C(1) and C(2) are the total counts for two regions of scattered excitation radiation; S_i is the slope of the spectral background curve for the x-ray line from element i; and R_i is the intercept at C(1) = 0. With the Mo secondary target, the two regions for C(1) and C(2) were

the coherent and Compton scattered $\text{MoK}\alpha$ radiations, respectively. In the Tb secondary target mode, the first region was the coherent scattered $\text{TbK}\alpha$ radiation plus the overlapping Compton scattered $\text{TbK}\beta$ radiation and the second region was the Compton scattered $\text{TbK}\alpha$ radiation.

RESULTS

To demonstrate the capability of the method, four standard materials of varying x-ray cross sections were chosen for analysis and prepared in quintuplicate. Specimens were prepared from three USGS International Geochemical Standards: USGS-AGV-1 Andesite, USGS-BCR-1 Basalt, USGS-G-2 Granite, and from NBS SRM 1633 Trace Elements in Coal Fly Ash. The concentrations of the elements were calculated using equation 5

$$\text{ppm}(i) = \frac{C_i}{C_s} \times \text{Ab}_{\text{corr}(i)} \times \frac{m_s}{0.0987} \times \frac{1}{K_i} \times 10^6 \quad (5)$$

where C_i and C_s are the characteristic x-ray count rates from element i and the standard; $\text{Ab}_{\text{corr}(i)}$ is defined by equation 1; m_s is the mass of the standard (g/cm^2); and K_i is the relative excitation-detection efficiency of the x-ray system for a x-ray line from element i compared with that of the standard element x-ray line.

Analyses were accomplished using two 25-minute counting periods for each specimen. Data obtained by XRFA are listed in Tables III and IV. The geochemical reference values are from tables compiled by Flanagan (9). NBS certified values and results (mostly obtained by instrumental neutron activation analysis) reported by four laboratories (10) are listed for NBS SRM 1633. Proposed values are shown

in parenthesis. Errors listed are two standard deviations. Figures 3 and 4 are spectra obtained on a NBS SRM 1633 specimen using each of the excitation conditions for analysis.

DISCUSSION OF ERRORS

Errors caused by non-uniform distribution of the samples with the sulfur are estimated to be 2% (2σ). Relative x-ray excitation-detection efficiencies determined using multielement solution deposits are accurate typically to within 1%. Listed in Table V are calculated errors that could be expected for the three USGS International Geochemical Standards, presuming that all specimens are homogeneous, with cross-sections equivalent to those of the USGS-AGV-1 specimens which do not include corrections for change in the cross section curve at the FeK absorption edge, 7.1 keV. These values were calculated using major element concentration data reported by Flanagan (9) and cross section plus fluorescence yield data from the literature (8,11).

As shown, the errors for the Ti determination far exceed the calculated errors listed in Table V. This is attributed to inter-mineral effects (4) which most likely were also prevalent for the determination of V and Cr, but were not apparent due to the relatively poor x-ray counting statistics realized for these elements. Nevertheless, excellent results were obtained for most of the elements determined, as shown in Tables III and IV.

Errors in the absorption correction values applied for analysis could be minimized by using ratios of the intensities from the two regions of

scattered excitation radiation as a measure of the specimen cross section. Using this information, the correction for the change in the cross section curve at the FeK absorption edge, and for matrix enhancement effects could be calculated as reported elsewhere (12). However, for simplicity, these corrections are not included in this paper.

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CREDIT

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Table I. Compounds for Standard Solutions

Element	Compound	Solvent
Ti	Ti	HF + HNO ₃
V	-	-
Cr	K ₂ Cr ₂ O ₇	H ₂ O
Mn	Mn	dil. HNO ₃
Fe	Fe	dil. HCl + HNO ₃
Co	Co	dil. HNO ₃
Ni	Ni	dil. HNO ₃
Cu	Cu	dil. HNO ₃
Zn	Zn	dil. HNO ₃
Ga	-	-
Ge	-	-
As	As ₂ O ₃	dil. NH ₄ OH
Se	-	-
Br	KBrO ₃	H ₂ O
Rb	RbCl	H ₂ O
Sr	SrCO ₃	dil. HNO ₃
Y	Y ₂ O ₃	dil. HNO ₃
Zr	Zr	HF + HNO ₃
Nb	-	-
Mo	Mo	HNO ₃
Ru	-	-
Rh	-	-
Pd	-	-
Ag	AgNO ₃	H ₂ O
Cd	Cd	dil. HNO ₃
In	In	dil. HNO ₃
Sn	Sn	HCl + H ₂ O ₂

Table I (continued)

Element	Compound	Solvent
Sb	Sb	HF + HNO ₃
Tc	-	-
I	KIO ₃	H ₂ O
Cs	Cs ₂ SO ₄	H ₂ O
Ba	BaCO ₃	dil. HNO ₃
La	La ₂ O ₃	dil. HNO ₃
Ce	Ce ₂ O ₃	dil. HNO ₃
Ta	-	-
W	Na ₂ WO ₄ · 2H ₂ O	dil. NH ₄ OH
Hg	-	-
Pb	Pb	dil. HNO ₃
Th	Th	HNO ₃ + H ₂ O ₂
U	-	-

Table II. Absorption Corrections for Fluorescent X-rays only (98.7 mg/cm² Disks).

X-ray line	20% andesite 80% sulfur	100% sulfur
CrK α	29.32	31.95
CrK β	22.58	24.60
Ratio	1.298	1.299
FeK α	18.43	20.08
FeK β	14.05	15.31
Ratio	1.312	1.312
ZnK α	8.05	8.77
ZnK β	6.05	6.59
Ratio	1.331	1.331
ZrK α	1.835	1.929
ZrK β	1.582	1.629
Ratio	1.160	1.184
CdK α	1.243	1.267
CdK β	1.166	1.183
Ratio	1.066	1.071
IK α	1.128	1.141
IK β	1.087	1.096
Ratio	1.038	1.041

Table III. Comparison of XRFA Results for USGS International Geochemical Standards (F.J. Flanagan 1973)
($\mu\text{g/g} \pm 2\sigma$ unless otherwise indicated)

Element	Andesite USGS-AGV-1		Basalt USGS-BCR-1		Granite USGS-G-2	
	XRFA	Ref.	XRFA	Ref.	XRFA	Ref.
Ti	$0.77\% \pm .03$	(0.62%)	$1.67\% \pm .14$	(1.28%)	$0.36\% \pm .03$	(0.28%)
V	<270	(125)	414 ± 96	(399)	<225	(35.4)
Cr	<140	(12.2)	<175	(17.6)	<115	(7)
Mn	779 ± 58	(763)	1423 ± 96	(1406)	263 ± 32	(260)
Fe	$4.84\% \pm .14$	4.75%	$9.22\% \pm .45$	9.41%	$1.92\% \pm .06$	1.88%
Co	<115	(14.1)	<120	(38)	<108	(5.5)
Ni	16 ± 6	(18.5)	17 ± 6	(15.8)	<16	(5.1)
Cu	58 ± 12	(59.7)	23 ± 11	(18.4)	8 ± 7	(11.7)
Zn	84 ± 4	84	116 ± 3	120	94 ± 9	85
Ga	18 ± 4	20.5	20 ± 5	(20)	20 ± 5	22.9
Ge	<6	(1.3)	<6	(1.54)	<6	(1.15)
As	<5	(0.8)	<5	(0.70)	<5	(0.25)
Se	<3	<0.14	<3	(0.10)	<3	<0.7
Br	<3	(0.5)	<3	(0.15)	<3	(0.3)
Rb	64 ± 2	67	42 ± 2	46.6	168 ± 5	168
Sr	657 ± 15	657	317 ± 12	330	487 ± 11	479
Y	17 ± 2	(21.3)	33 ± 19	(37.1)	9 ± 6	12
Zr	229 ± 11	225	181 ± 10	(190)	332 ± 27	300
Nb	15 ± 3	15	13 ± 2	13.5	15 ± 3	13.5
Mo	<6	(2.3)	<6	(1.1)	<6	(0.36)
Ru	<4	-	<4	(0.001)	<4	-
Rh	<4	-	<4	(0.0002)	<4	-
Pd	<4	<0.005	<4	(0.012)	<4	<0.0005
Ag	<4	0.11	<4	(0.036)	<4	(0.049)

Table III (continued).

Element	Andesite USGS-AGV-1		Basalt USGS-BCR-1		Granite USGS-G-2	
	XRFA	Ref.	XRFA	Ref.	XRFA	Ref.
Cd	<4	(0.09)	<4	(0.12)	<4	(0.039)
In	<4	(0.04)	<4	(0.095)	<4	(0.034)
Sn	3 ± 2	(4.2)	<4	(2.6)	<4	(1.5)
Sb	<5	(4.5)	<5	(0.69)	<5	(0.1)
Te	<5	<1	<5	<1	<5	<1
I	<6	-	<6	<1	<6	-
Cs	<9	(1.4)	<9	0.95	<10	(1.4)
Ba	1239 ± 36	1208	680 ± 44	(675)	1908 ± 113	1870
La	33 ± 18	(35)	<36	(26)	99 ± 12	(96)
Ce	65 ± 40	(63)	<70	53.9	176 ± 24	(150)
Ta	<19	0.9	<19	0.91	<20	0.91
W	<16	(0.55)	<16	(0.40)	<16	(0.1)
Hg	<11	(0.015)	<11	(0.011)	<11	(0.039)
Pb	33 ± 7	(35.1)	10 ± 2	(17.6)	31 ± 6	(31.2)
Th	6 ± 3	6.41	<8	6.0	22 ± 4	24.2
U	<10	(1.88)	<10	(1.74)	<11	(2.0)

Table IV. Comparison of XRFA Results for NBS SRM 1633, Trace Elements in Coal Fly Ash ($\mu\text{g/g} \pm 2\sigma$ unless otherwise indicated)

Element	XRFA	NBS	Ref. (10)
Ti	$0.86\% \pm .11$	-	$0.74\% \pm .03$
V	295 ± 156	214 ± 8	235 ± 15
Cr	159 ± 115	131 ± 2	127 ± 6
Mn	528 ± 104	493 ± 7	496 ± 19
Fe	$6.22\% \pm .48$	-	$6.2\% \pm 0.3$
Co	<130	(38)	41.5 ± 1.2
Ni	101 ± 7	98 ± 3	98 ± 9
Cu	133 ± 4	128 ± 5	-
Zn	216 ± 14	210 ± 20	216 ± 25
Ga	41 ± 7	-	-
Ge	26 ± 5	-	-
As	63 ± 7	61 ± 6	58 ± 4
Se	11 ± 1	9.4 ± 0.5	10.2 ± 1.4
Br	6 ± 2	-	12 ± 4
Rb	108 ± 4	(112)	125 ± 10
Sr	1342 ± 20	(1380)	1700 ± 300
Y	60 ± 5	-	62 ± 10
Zr	290 ± 7	-	301 ± 20
Nb	28 ± 2	-	-
Mo	25 ± 5	-	-
Ru	3 ± 2	-	-
Rh	<4	-	-
Pd	<4	-	-
Ag	<4	-	-

Table IV (continued)

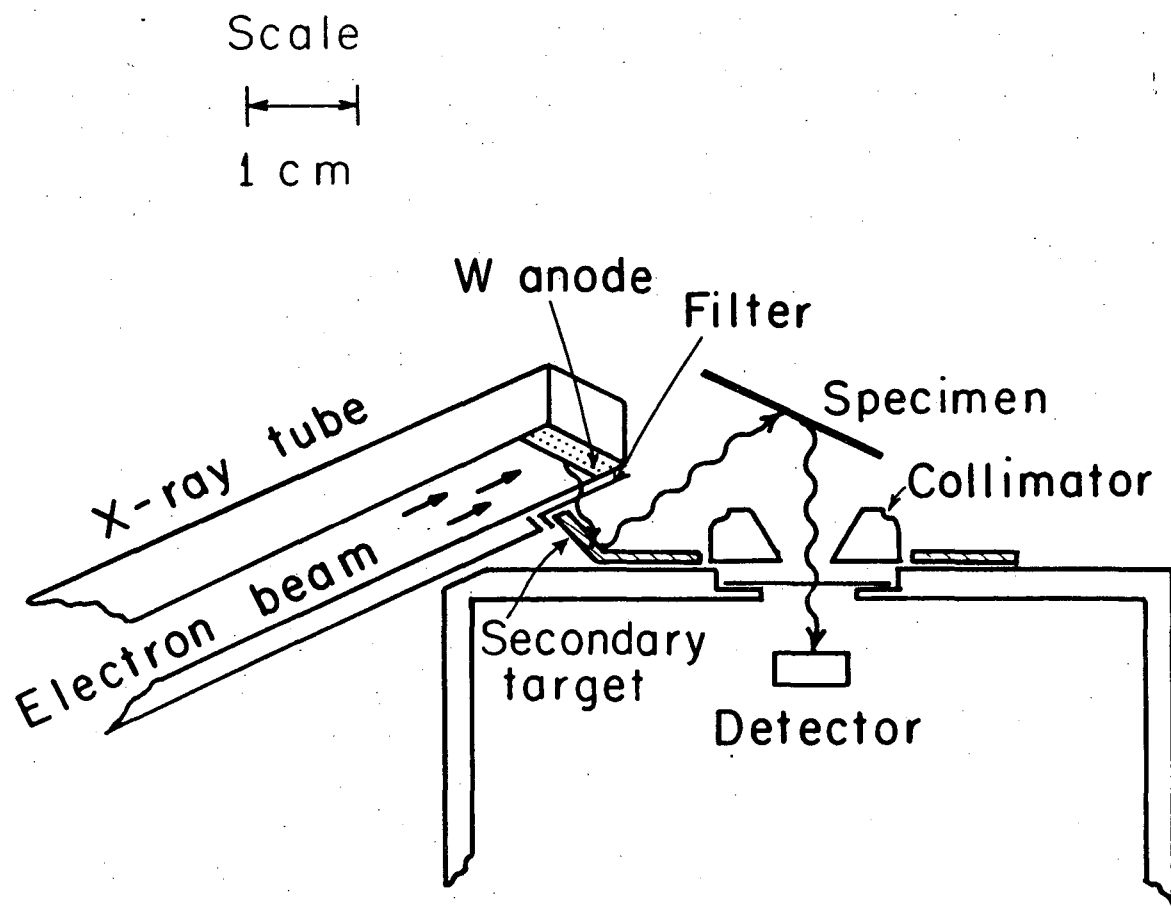
Element	XRFA	NBS	Ref. (10)
Cd	<4	1.45 ± .06	-
In	3 ± 2	-	0.32 ± .10
Sn	5 ± 2	-	-
Sb	4 ± 3	-	6.9 ± 0.6
Te	<5	-	-
I	<6	-	2.9 ± 1.2
Cs	<10	-	8.6 ± 1.1
Ba	2670 ± 85	-	2700 ± 200
La	82 ± 20	-	82 ± 2
Ce	160 ± 23	-	146 ± 15
Ta	<22	-	1.8 ± 0.3
W	<19	-	4.6 ± 1.6
Hg	<12	0.14 ± .01	-
Pb	72 ± 5	70 ± 4	75 ± 5
Th	21 ± 3	(24)	24.8 ± 2.2
U	9 ± 6	11.6 ± 0.2	12.0 ± 0.5

Table V. Calculated XRFA Errors (%) for USGS
International Geochemical Standards.

Source of Error	Specimen	Ti	Fe	Co + Sr	Zr	Ba
Assume constant cross section based on 20% USGS-AGV-1, 80% sulfur specimen with no correction for change in cross section curve at FeK absorption edge.	USGS-AGV-1	+3.8	+3.2	0.0	0.0	0.0
	USGS-BCR-1	+3.7	+2.8	-3.3	-2.1	-0.4
	USGS-G-2	+3.8	+3.4	+2.1	+1.1	+0.2
Enhancement by FeK fluorescent radiation	USGS-AGV-1	+1.3	-	-	-	-
	USGS-BCR-1	+2.5	-	-	-	-
	USGS-G-2	+0.5	-	-	-	-
Total calculated errors	USGS-AGV-1	+5.1	+3.2	0.0	0.0	0.0
	USGS-BCR-1	+6.2	+2.8	-3.3	-2.1	-0.4
	USGS-G-2	+4.3	+3.4	+2.1	+1.1	+0.2

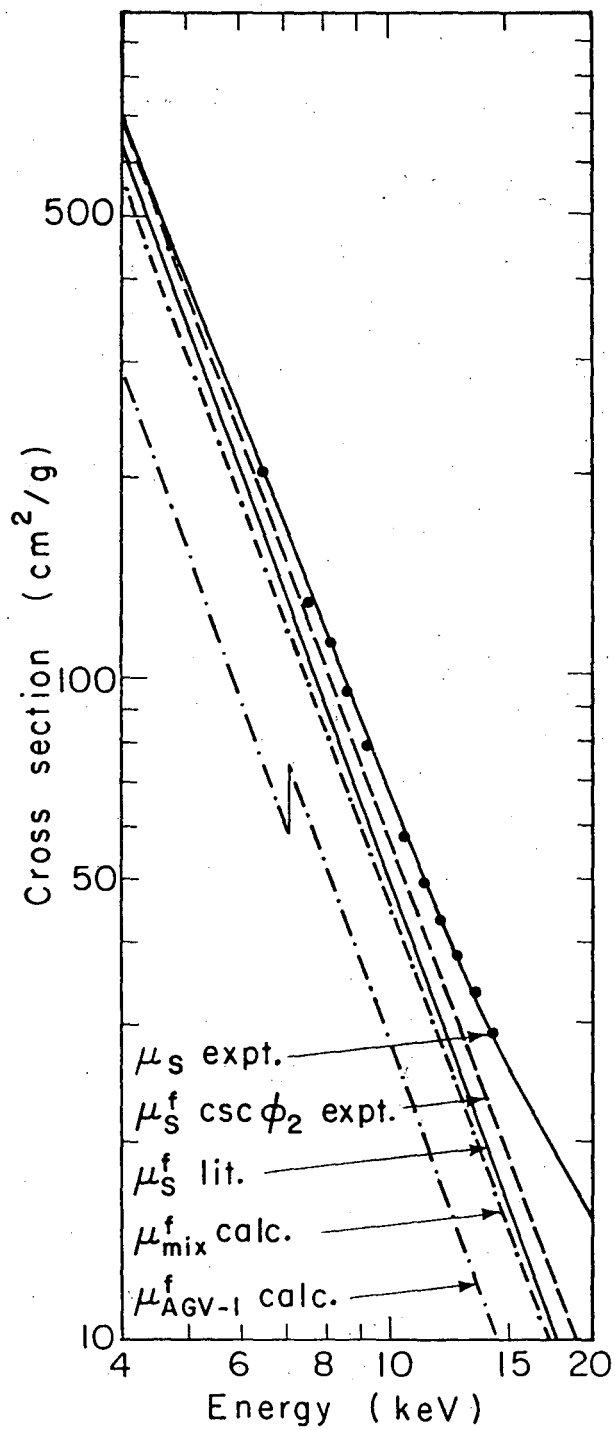
FIGURE CAPTIONS

- Fig. 1 Schematic diagram of x-ray fluorescence system.
- Fig. 2 Experimental and calculated cross section curves. Experimental curve for sulfur, $\mu_S^{\text{expt.}}$, includes the contributions of both the excitation and the fluorescent radiations as well as geometry factors. Curve determined for the fluorescent radiation only, $\mu_S^{\text{f}} \text{csc}\phi_2^{\text{expt.}}$. Curve for sulfur, $\mu_S^{\text{f}} \text{lit.}$, from data reported in the literature. Calculated cross section curves for mixture of 20% USGS-AGV-1 andesite and 80% sulfur, $\mu_{\text{mix}}^{\text{f}} \text{calc.}$; and andesite only, $\mu_{\text{AGV-1}}^{\text{f}} \text{calc.}$.
- Fig. 3 X-ray spectrum obtained on NBS SRM 1633 specimen using Mo excitation radiation for the determination of the elements Ti → Sr, Ta, W, Hg, Pb, Th and U.
- Fig. 4 X-ray spectrum obtained on NBS SRM 1633 specimen using Tb excitation radiation for the determination of the elements Y → Ce.



XBL 747-3767A

Figure 1



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Figure 2

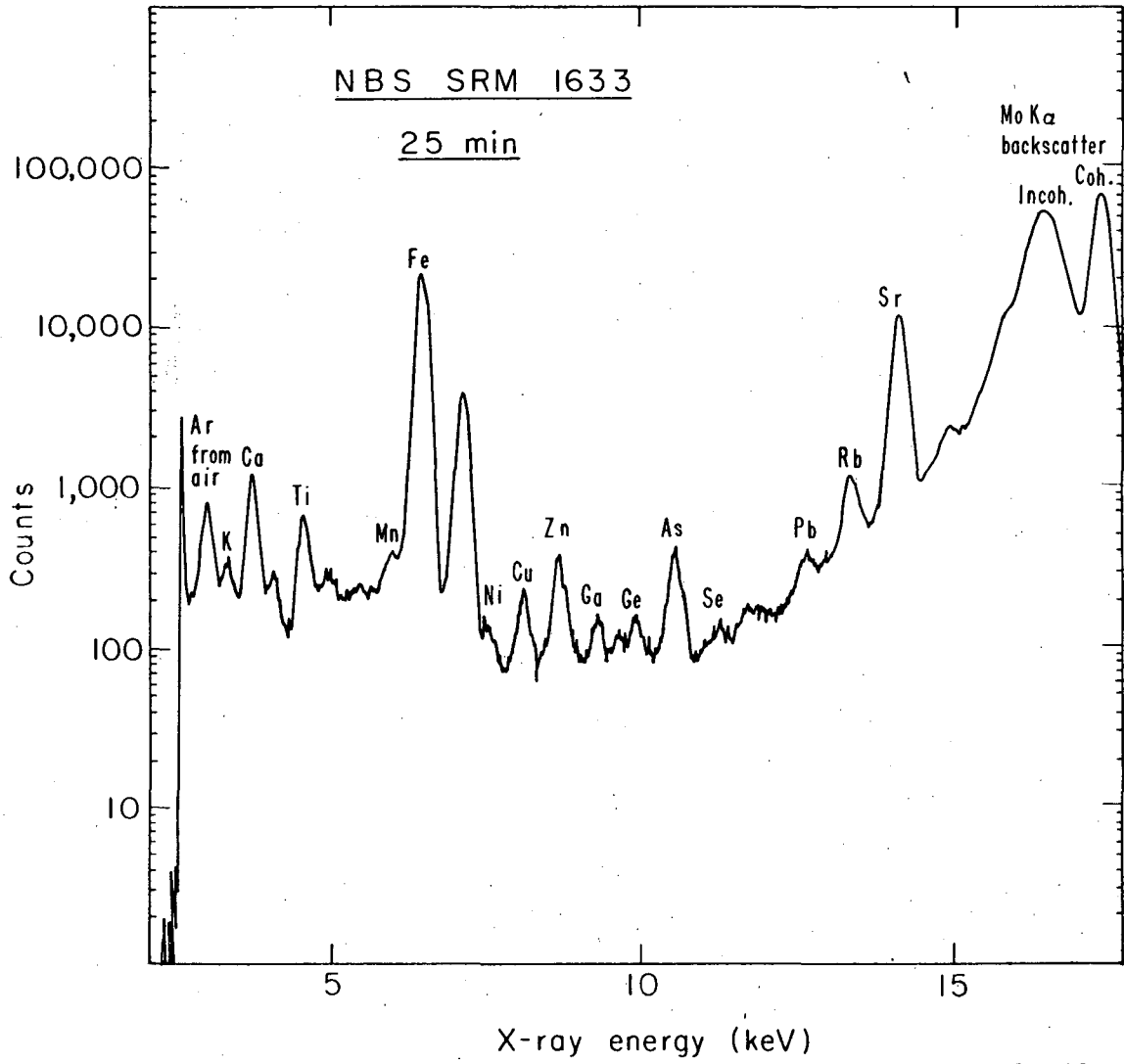
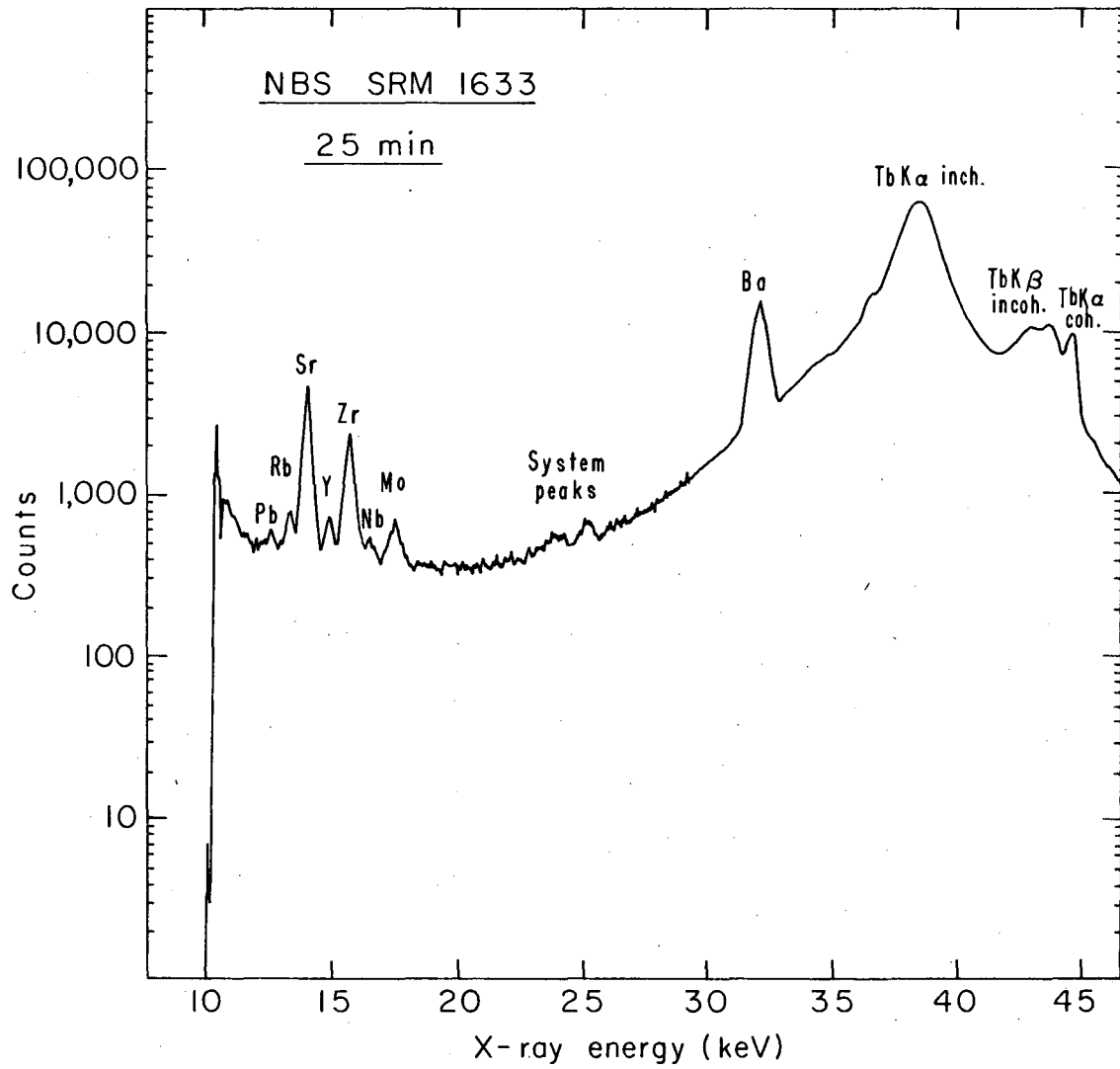


Figure 3



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Figure 4

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

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