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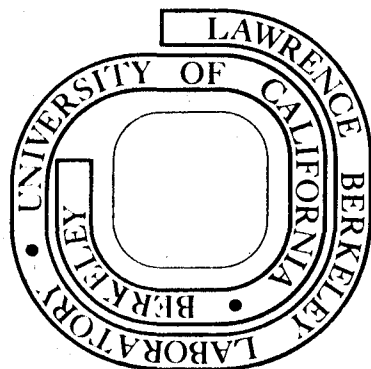
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BRIEF

The concentrations of twenty-eight elements in pulverized geochemical specimens are determined with apparent accuracies of 5% or better within twenty minutes. The intensity of the Compton scattered excitation radiation serves as an internal standard and is used to ascertain corrections required to compensate for matrix absorption effects. Calibration is achieved using geochemical reference standards.

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ABSTRACT

A method for analyzing geochemical specimens by energy dispersive x-ray fluorescence is described. Our approach is an extension of methods used in wavelength dispersive x-ray spectrometry. Advantage is taken of the fact that the Compton scattered excitation radiation can serve as an internal standard since the intensity varies linearly with the reciprocal of the mass absorption coefficient between adjacent major element absorption edges. Furthermore, the method makes use of the fact that the intensity of the spectral background at any given energy is proportional to the intensity of the Compton scattered excitation radiation. For x-ray lines between 4.5 and 7.1 keV, first order corrections are made for the change in the mass absorption curve due to a drop at the Fe K absorption edge. Also, first order corrections are made to compensate for matrix enhancement by Fe K x-rays. Several pure compounds, for which the x-ray cross sections vary over a wide range, are used to develop individual x-ray line spectral background curves. Calibration is achieved utilizing geochemical reference standards. Apparent accuracies typically obtained are 5% or better using twenty minute analysis periods.

INTRODUCTION

In the field of geochemistry, a technique which permits rapid and accurate multielement analysis with a minimum of cost and sample preparation effort is often desired. In this paper we demonstrate that x-ray induced energy dispersive x-ray fluorescence analysis (XRFA) easily lends itself to the determination of twenty-six trace and two major elements in geochemical specimens. Approximately 2 gm of powdered specimen pressed into a cylinder is required for analysis. Apparent accuracies of 5% or better are obtained using twenty minute analysis periods.

The XRFA technique requires the excitation and detection of characteristic K or L x-ray lines from the individual specimen elements that are to be determined. For very thin specimens, x-ray line intensities, counts/sec, vary linearly with elemental concentration. For thick specimens, corrections must be applied to compensate for the attenuation of x-rays due to matrix absorption effects. Determination of elements which have K or L absorption edges of energies less than that of an x-ray line from a major constituent (e.g., Fe) requires corrections to compensate for matrix enhancement effects. That is, x-rays excited from a major constituent can interact with other specimen elements and enhance the production of lower energy x-rays. Some of the methods which have been used to minimize and compensate for matrix absorption and enhancement effects are discussed elsewhere in the literature (1-2).

Reynolds (3-4) has shown that the Compton scattered excitation radiation peak intensity and the mass absorption coefficient are inversely related for infinitely thick specimens. Both Reynolds (3) and Feather and Willis (5) have used this fact to compensate for matrix absorption

effects for the determination of the elements Ni (Z=28) through Zr (Z=40) in geochemical specimens. In each case wavelength dispersive XRFA was the technique used.

In this paper we demonstrate that the approach used by both Reynolds (3) and Feather and Willis (5) is applicable to energy dispersive XRFA and can easily be extended to include the determination of the elements Ti (Z=22) through Fe (Z=26) and Pd (Z=46) through Ba (Z=56). Furthermore, we illustrate that truly infinitely thick specimens are not required if the maximum depth analyzed is restricted by the design of the excitation radiation-specimen-detector geometry.

DISCUSSION OF METHOD

Background of Method. Andermann and Kemp (6) were the first to show that scattered x-rays could be used as an internal standard in XRFA. Reynolds (3) and, more recently, Feather and Willis (5) have used the intensity of the Compton scattered excitation radiation to correct for matrix absorption effects in analysis of trace amounts of the elements Ni (Z=28) through Zr (Z=40) in geochemical specimens. In their method, advantage is taken of the fact that the intensity of the Compton scattered radiation varies linearly with the reciprocal of the mass absorption coefficient between adjacent major element absorption edges. Since Fe is typically the highest atomic number major constituent present in geochemical specimens, individual specimen mass absorption coefficient curves vary smoothly above the Fe K absorption edge. These same investigators have also shown that the intensity of the spectral background, for each of the element characteristic x-ray lines within this range, varies linearly with the

intensity of the Compton scattered excitation radiation. They used infinitely thick pure materials, for which the x-ray mass absorption coefficient varied over a wide range, to relate spectral background to Compton scattered radiation intensity. Using this procedure, individual element spectral background curves were established. Hence, the Compton scattered excitation radiation serves a dual role, (1) as an internal standard to compensate for matrix absorption effects and (2) to ascertain the intensities of the spectral background for individual elements to be determined.

Reynolds (4) has also reported using a series of simultaneous equations to calculate mass absorption coefficients for some of the elements, Ti (Z=22) through Fe (Z=26), which have x-ray lines of energies below the Fe K absorption edge. However, in his analytical approach, matrix enhancement effects are neglected.

General Technique for Obtaining X-ray Spectra. Figure 1 illustrates the technique employed for energy dispersive XRFA. Radiation provided by an x-ray tube is used to excite characteristic x-rays from elements within the specimen. These x-rays along with scattered excitation radiation are simultaneously measured by the detector. Since detection system count rate limitations, generally around 10,000 counts/sec, are often easily attained, near monochromatic excitation radiation is frequently utilized to achieve high peak to background ratios for x-rays excited from a given range of elements.

Preparation of Specimen. Specimens initially should be pulverized until the particle diameters are smaller than one-fifth the effective penetration depth for the measured x-ray energy to minimize the possibility of

mineralogical effects (7). For many geochemical specimens this corresponds to a size of 50-100 microns when analyzing for elements down to Ti ($Z=22$). Approximately 2 gm of powder is pressed at a pressure of 8,000 psi into a lucite cylinder, 2.5 cm O.D., 1.27 cm I.D., and 1.3 cm high, as shown in Figure 2. The specimen is contained by Scotch tape (No. 302) on the bottom. The amount of powder required for analysis is defined by the maximum specimen thickness which is in direct line with both the excitation and the detection radiations. In our geometry, this corresponds to a specimen thickness of 7 mm as shown in Figure 1.

Equipment and Characteristics. A guard-ring detector with pulsed light feedback electronics and a 512 channel pulse height analyzer were used for the analytical determinations. The total resolution of the system, FWHM, was 225 eV at 6.4 keV (Fe $K\alpha$ x-ray energy) at 5,000 counts/sec using an 8 μ sec pulse peaking time. Excitation was provided by a Mo transmission x-ray tube with a combined anode plus window thickness of 0.010 cm. The x-ray tube was operated at 42 kV with regulated currents varying from 100-300 μ A when analyzing for the elements Ti-Zr. For the determination of the elements Pd-Ba, the x-ray tube was operated at 48 kV and a 0.010 cm Mo filter was inserted externally to the x-ray tube. Using this procedure higher sensitivities were obtained since the exciting Bremsstrahlung radiation was shifted to higher energies with a maximum intensity at 38 keV. The distances between the x-ray tube anode and the specimen and between the specimen and 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 specimen volume that is in direct line with both the excitation and detection radiation beams is shown in Figure 1. For analysis the spectral data acquired were recorded on magnetic tape. Computations were made using a Control Data 6600 computer. Our program requires less than 50 K of core space.

CALIBRATION METHOD

Spectrum Background. The background under each of the x-ray lines that are used for analysis is referred to as the spectral background. Spectral background curves which related the intensity of the spectral background to the intensity of the Compton scattered excitation radiation were established for x-ray lines from each of the elements to be determined using five powdered materials, MgO, Al₂O₃, NaSCN, KH₂PO₄, and S. These were chosen since they have mass absorption coefficients which cover the range of most geochemical specimens. Additionally, they were, in most cases, free of measurable impurities. Figure 3 shows the spectral background curve established for nickel. This curve illustrates the relationship between the intensity of the Compton scattered excitation radiation, the reciprocal of the mass absorption coefficient of the specimen for Ni K α x-rays, and the intensity of the spectral background. Similar background curves were established for each of the elements determined. The background counts obtained from each material were all normalized to the same counting period and x-ray tube current. (Backgrounds were determined using essentially constant data acquisition rates by varying the x-ray tube current. This was done to minimize the possibility of a minor base line or gain shift.

The intensity of the spectral background at the intercept which corresponds to zero Compton scattered excitation radiation intensity is referred to as the residual background and, most likely, is due to system scattering (e.g., scattering from air and the Scotch tape window). The portion of the spectral background which is above the residual background is the true background as described by Feather and Willis (5). It is this portion of the spectral background which is proportional both to the intensity of the Compton scattered excitation radiation and to the reciprocal of the mass absorption coefficient. This is the key to the entire analytical method and it is the information which, in effect, is used to compensate for matrix absorption effects.

For the elements Ti-Zr, Compton scattered Mo $K\alpha$ radiation was used to establish the background curves. The Bremstrahlung scattered radiation between 26 and 30 keV was utilized to establish background curves for the elements Pd-Ba. This energy range of Bremstrahlung scattered radiation contained a minor fraction of coherent scattered radiation. In the geometry employed for analysis, between 1.5 and 2.0 keV is lost by the Compton scattering process in the energy range of Bremstrahlung used. Consequently, this minimizes the contribution of coherent scattered radiation to the energy range utilized.

Overlapping X-ray Background. Our analysis program uses windows of fixed width for each element to be determined. Peak overlaps are initially established 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. Corrections for differences of characteristic x-ray line ratios (e.g., $K\beta/K\alpha$) to be realized from thick specimens were calculated for USGS geochemical reference standards which are used for standardization. Figure 4 illustrates mass absorption coefficient curves for three standards. Mass absorption coefficient data reported by McMaster et al. (8) and major element concentration data reported by Flanagan (9) and Perlman and Asaro (10) are used for the calculations. For the different matrices, calculated mass absorption coefficient ratios for characteristic x-ray lines (e.g., $K\beta/K\alpha$) from any one element were found to be constant to within $\pm 0.5\%$. These calculated ratios were applied directly to adjust relative characteristic x-ray line intensity ratios ascertained from thin deposits of each of the elements. Additional minor corrections were made to these ratios to compensate for the absorption by the Scotch tape window. These corrections were established by making transmission measurements using the Scotch tape as an absorber for the excitation and fluorescent radiations. Absolute calibration for overlap of L with K x-ray lines (e.g., Ba L x-rays with Ti, V, Cr, and Mn K x-rays) was ascertained using nebulized standard solution deposits (11).

Standardization. Elements with Characteristic X-rays of Energy above the Fe K Absorption Edge. Calibration for the analysis of the elements Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Ba, and Pb was accomplished using five USGS geochemical reference standards, AGV-1, BCR-1, DTS-1, PCC-1, and G-2 (9) and Standard Pottery (10). The procedure used has been described by Feather and Willis (5). In effect, linear calibration curves, some of which are illustrated in Figure 5, were established for each element by

plotting the ratio of the spectral peak intensity to the true background versus concentration. Again, the determination of the true background is the key to the method used to compensate for matrix absorption effects. Calibration for Cd, Sn, Sb, and Cs was achieved using a French multielement synthetic glass standard, VS-N (12). Calibration for Ge, Se, Br, Pd, Ag, In, Te, and I was accomplished by interpolation of the response of the x-ray system to the analysis of nearby elements.

Standardization. Elements with Characteristic X-rays of Energies below the Fe K Absorption Edge. Calibration for the elements Ti-Fe requires first order corrections to compensate for the change in the total mass absorption coefficient curve due to the drop at the Fe K absorption edge as illustrated in Figure 4. Linear curves which related apparent total mass absorption coefficient, μ_{app} , with experimentally determined spectrum background data were established. This was possible since the value of μ_{app} varies linearly with the ratio of the total (true + residual) to the true spectrum background. In effect, μ_{app} is not corrected for the change in the cross section curve. Its value is determined by extrapolation of the mass absorption coefficient curve which exists above the Fe K absorption edge. Apparent mass absorption coefficient curves were established for x-ray lines from the elements Ti-Fe using the geochemical reference standards and total mass absorption coefficient data reported in the literature (8). For these calculations, the mass absorption coefficients used for Fe were the values ascertained by extrapolation of the total cross section curve that exists above the Fe K absorption edge. Figure 6 illustrates the apparent mass absorption coefficient curve we established for Fe K α x-rays.

For analysis, the initial weight fraction results determined for Fe were adjusted by iteration ten times using Equation 1.

$$W_k = \left(\frac{\mu_{\text{app}} - \Delta\mu \cdot W_j}{\mu_{\text{app}}} \right) W_o \quad (1)$$

where

W_k , W_j , and W_o are the new, present, and initial weight fractions, respectively.

$\Delta\mu$ is the difference between the extrapolated and the true cross section for pure Fe at the Fe $K\alpha$ x-ray energy.

For the elements Ti-Mn, the values ascertained for W_o were adjusted once using Equation 1. For these calculations the determined weight fraction of Fe, corrected for matrix absorption effects, was used for W_j and the value assigned for $\Delta\mu$ was the difference between the extrapolated and the true cross section for pure Fe at the $K\alpha$ x-ray energy of the individual element.

Additional first order corrections were made for the elements Ti-Mn to compensate for matrix enhancement by the Fe K x-rays. The cross section of the geochemical specimens for the exciting Mo K radiation was a magnitude less than that for the Fe K x-rays. Hence, the intensity of the Fe K radiation was treated as being essentially constant across the specimen depth from which Ti-Mn K x-rays were measured. Utilizing physical data reported in the literature (8, 13-14), corrections for matrix enhancement by Fe K x-rays were made using Equation 2.

$$W'_k = W_k \left[1 - \left(\frac{\tau_i \cdot W_k}{\mu_{app} - \Delta\mu \cdot W_{Fe}} \right) \omega_i \cdot f_i \cdot \frac{I_{Fe \text{ K}\alpha}}{I_{i \text{ K}\alpha}} \cdot R \right] \quad (2)$$

where

W_k and W'_k are the weight fraction of element i corrected for matrix absorption and for matrix absorption plus enhancement, respectively.

W_{Fe} is the weight fraction of Fe corrected for matrix absorption.

τ_i is the photoelectric mass absorption coefficient of element i for Fe $K\alpha$ x-rays.

ω_i is the K fluorescence yield for element i .

f_i is the fraction of $K\alpha$ to total K x-rays emitted from element i .

$\Delta\mu$ is the difference between the extrapolated and the true Fe cross section at energy $i \text{ K}\alpha$.

$I_{Fe \text{ K}\alpha}$ and $I_{i \text{ K}\alpha}$ are the spectral $K\alpha$ line intensities determined for Fe and element i .

R is a constant which accounts for enhancement by both Fe $K\alpha$ and $K\beta$ x-rays and also corrects for the differences in their cross sections.

For the elements Ti-Cr, R has a value of 1.10. For Mn, R has a value of 0.10 since only Fe $K\beta$ x-rays will cause enhancement effects.

RESULTS

To illustrate the capability of the method, four French geochemical reference standards were analyzed using the previously described equipment. Each of the standards was prepared in quintuplicate. Corrections for any slight deviation in the x-ray tube output or the excitation radiation-specimen-detector geometry were established daily using a $227 \mu\text{g}/\text{cm}^2$ thin-film copper standard. Such deviations could have a small effect upon the residual background fraction of the total spectrum background ascertained for the individual spectral lines. Concentrations were calculated using Equation 3.

$$\text{ppm}(i) = \frac{I_i}{\text{tbkg}_i} \cdot \text{slope}(i) \quad (3)$$

where

I_i is the spectral x-ray intensity from element i .

tbkg_i is the true background intensity determined for element i .

$\text{slope}(i)$ is the slope of the standard curve for element i .

The results are shown in Tables I-IV. Total analysis time for each specimen was twenty minutes. The errors listed are two standard deviations. For the elements which were determined to be below our detection limits, three standard deviations for counting statistics are reported. The neutron activation values listed were determined by F. Asaro and co-workers at this laboratory. The reported values are from the literature (15,16). Proposed values are listed in brackets.

Figures 7 and 8 show the spectra obtained on Granite GA. Spectral background for the elements with K x-rays in the range of 31 to 32 keV

(Cs, Ba) contain a fraction of coherent scattered excitation radiation, which causes larger errors in the determination of these elements. These errors could essentially be eliminated and much higher sensitivities realized for these elements by operating the x-ray tube at approximately 60 kV and inserting a thicker external Mo filter. However, our excitation system is limited to a maximum voltage of 50 kV.

CONCLUSION

X-ray induced energy dispersive x-ray fluorescence analysis easily lends itself to the rapid and accurate determination of twenty-six trace and two major elements in geochemical specimens. Corrections for matrix absorption effects can be ascertained from the intensity of the Compton scattered excitation radiation. This radiation serves as an internal standard for individual element x-ray lines which lie between adjacent major element absorption edges. Additionally, the intensity of the spectral background for individual elements to be determined can be calculated from linear background curves which relate spectral background to the intensity of the Compton scattered excitation radiation. Corrections for enhancement by FeK x-rays are easily calculated. Truly infinitely thick specimens are not required if the maximum depth analyzed is restricted by the design of the excitation radiation-specimen-detector geometry.

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Table I. Analysis of Granite GA

	X-ray Fluorescence	Neutron Activation	Reported
Ti	0.226%±.014	0.174%±.042	0.228%
V	<160ppm	—	36ppm
Cr	<51ppm	7.4ppm±2.6	(10)ppm
Mn	712ppm±33	631ppm±16	665ppm
Fe	1.94%±.08	1.95%±.06	1.98%
Ni	<8ppm	<26ppm	7ppm
Cu	20ppm±8	—	14ppm
Zn	72ppm±7	76ppm±8	75ppm
Ga	15ppm±2	—	16ppm
Ge	<2ppm	—	(1.5)ppm
As	<3ppm	<4ppm	—
Se	<3ppm	—	—
Br	<3ppm	—	—
Pb	32ppm±2	—	—
Rb	180ppm±2	175ppm±12	175ppm
Sr	313ppm±4	—	305ppm
Y	21ppm±2	—	(18)ppm
Zr	123ppm±11	—	140ppm
Pd	<5ppm	—	—
Ag	<5ppm	—	—
Cd	<4ppm	—	—
In	<5ppm	—	—
Sn	<6ppm	—	(4)ppm
Sb	<7ppm	<0.20ppm	—
Te	<9ppm	—	—
I	<11ppm	—	—
Cs	19ppm±15	6.6ppm±0.4	(5)ppm
Ba	840ppm±37	816ppm±36	850ppm

Table II. Analysis of Basalt BR

	X-ray Fluorescence	Neutron Activation	Reported
Ti	1.57%±.04	1.64%±.05	1.57%
V	175ppm±86	—	240ppm
Cr	310ppm±44	379ppm±10	420ppm
Mn	1587ppm±36	1521ppm±36	1600ppm
Fe	9.13%±.09	9.10%±.22	9.01%
Ni	232ppm±12	281ppm±41	270ppm
Cu	80ppm±11	—	70ppm
Zn	151ppm±12	171ppm±16	160ppm
Ga	17ppm±3	—	(20)ppm
Ge	<3ppm	—	—
As	<3ppm	5.5ppm±3.2	—
Se	<3ppm	—	—
Br	<3ppm	—	—
Pb	6ppm±4	—	(16)ppm
Rb	43ppm±2	36ppm±25	45ppm
Sr	1326ppm±9	—	1350ppm
Y	35ppm±2	—	(27)ppm
Zr	259ppm±25	—	240ppm
Pd	<7ppm	—	—
Ag	<6ppm	—	—
Cd	<6ppm	—	—
In	<6ppm	—	—
Sn	<7ppm	—	(8)ppm
Sb	<8ppm	0.28ppm±.26	—
Te	<11ppm	—	—
I	<14ppm	—	—
Cs	<30ppm	0.65ppm±.50	—
Ba	1288ppm±84	1095ppm±50	1050ppm

Table III. Analysis of Diorite DR-N

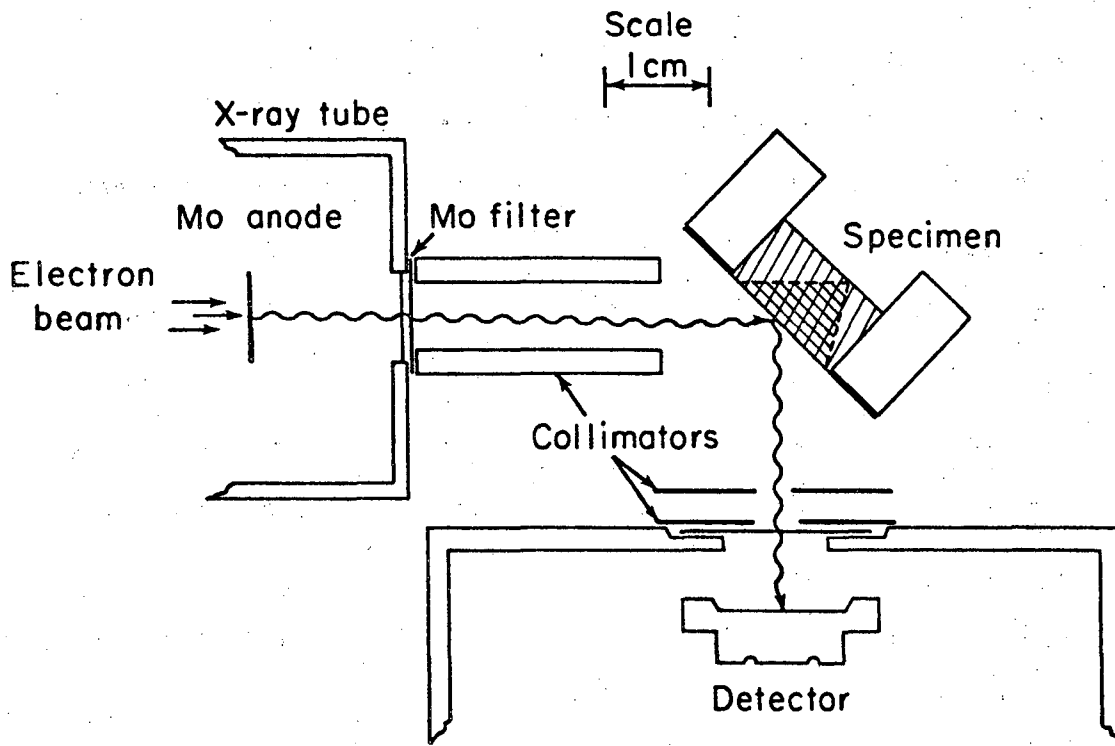
	X-ray Fluorescence	Neutron Activation	Reported
Ti	0.57%±.02	0.62%±.04	0.67%
V	168ppm±126	—	225ppm
Cr	<60ppm	31.8ppm±4.6	45ppm
Mn	1785ppm±51	1640ppm±38	—
Fe	6.95%±.12	6.72%±.16	6.93%
Ni	<20ppm	38ppm±34	16ppm
Cu	44ppm±6	—	52ppm
Zn	144ppm±3	150ppm±14	150ppm
Ga	20ppm±2	—	(25)ppm
W	81ppm±11	—	—
As	3.7ppm±2.0	3.9ppm±2.6	—
Se	<3ppm	—	—
Br	<3ppm	—	—
Pb	55ppm±4	—	(75)ppm
Rb	70ppm±2	63ppm±22	(75)ppm
Sr	393ppm±3	—	400ppm
Y	29ppm±3	—	—
Zr	120ppm±14	—	—
Pd	<6ppm	—	—
Ag	<5ppm	—	—
Cd	4ppm±3	—	—
In	<6ppm	—	—
Sn	<6ppm	—	—
Sb	<8ppm	0.47ppm±.26	—
Te	<10ppm	—	—
I	<13ppm	—	—
Cs	<26ppm	6.2ppm±0.5	—
Ba	470ppm±35	380ppm±30	360ppm

Table IV. Analysis of Serpentine UB-N

	X-ray Fluorescence	Neutron Activation	Reported
Ti	0.035%±.011	0.042%±.015	0.07%
V	<100ppm	—	(100)ppm
Cr	2359ppm±47	2520ppm±60	2200ppm
Mn	1025ppm±24	971ppm±20	—
Fe	6.14%±.06	5.83%±.14	5.96%
Ni	1907ppm±13	2113ppm±146	2000ppm
Cu	18ppm±4	—	(30)ppm
Zn	84ppm±3	107ppm±14	—
Ga	3.0ppm±1.1	—	—
Ge	2.1ppm±1.3	—	—
As	11ppm±2	12.4ppm±1.8	—
Se	<3ppm	—	—
Br	5ppm±2	—	—
Pb	11ppm±3	—	—
Rb	<3ppm	<24ppm	—
Sr	3ppm±2	—	(10)ppm
Y	<4ppm	—	—
Zr	<9ppm	—	—
Pd	<5ppm	—	—
Ag	<5ppm	—	—
Cd	<5ppm	—	—
In	<5ppm	—	—
Sn	<6ppm	—	—
Sb	<7ppm	0.28ppm±.24	—
Te	<9ppm	—	—
I	<12ppm	—	—
Cs	25ppm±15	11.3ppm±0.6	—
Ba	61ppm±21	32ppm±18	—

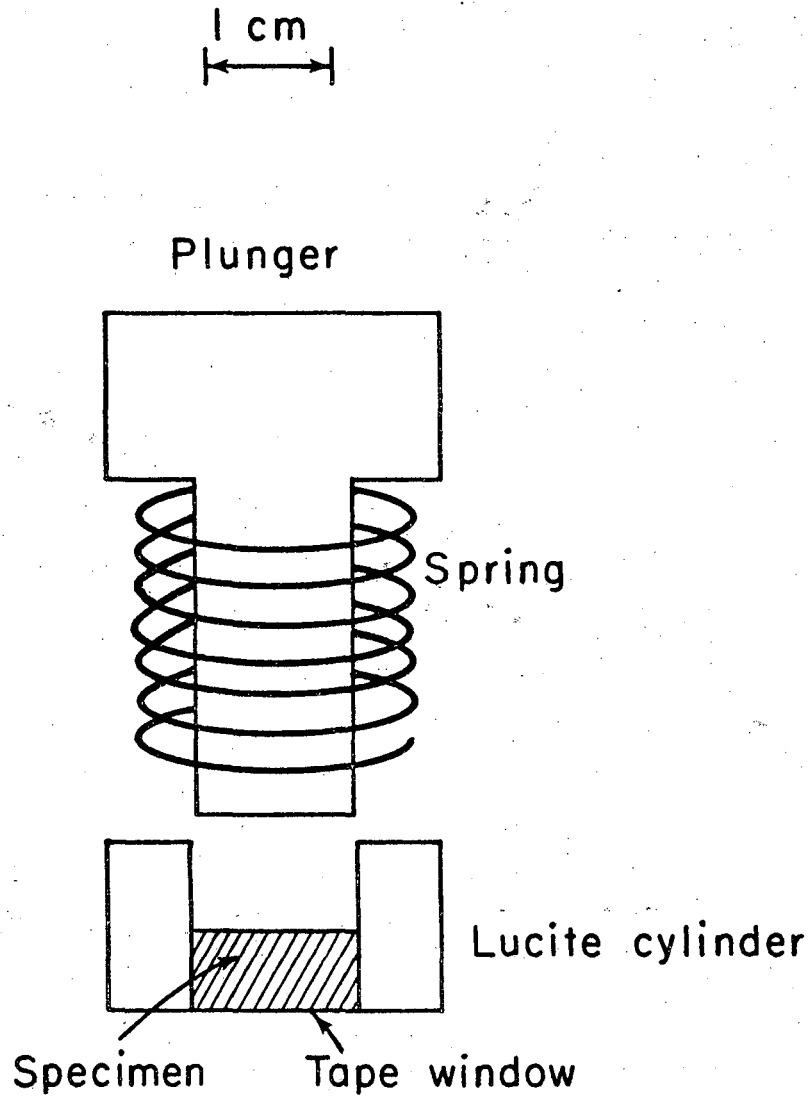
FIGURE CAPTIONS

- Fig. 1. Schematic of x-ray fluorescence analysis system.
- Fig. 2. Apparatus employed to prepare geochemical specimens.
- Fig. 3. Spectral background curve established for nickel using five powdered materials. All background counts are normalized to 1000 sec count periods and an x-ray tube current of 100 μ amps.
- Fig. 4. Total mass absorption coefficient curves for reference standards BCR-1, AGV-1, and Standard Pottery.
- Fig. 5. Standard curves which illustrate the relationship between concentration and the ratio of spectral line counts to true background.
- Fig. 6. Apparent mass absorption coefficient curve established for Fe $K\alpha$ x-rays using experimental spectrum/true background ratios and calculated apparent total mass absorption coefficients.
- Fig. 7. X-ray spectrum obtained on Granite GA for the determination of the elements Ti-Zr.
- Fig. 8. X-ray spectrum obtained on Granite GA for the determination of the elements Pd-Ba.



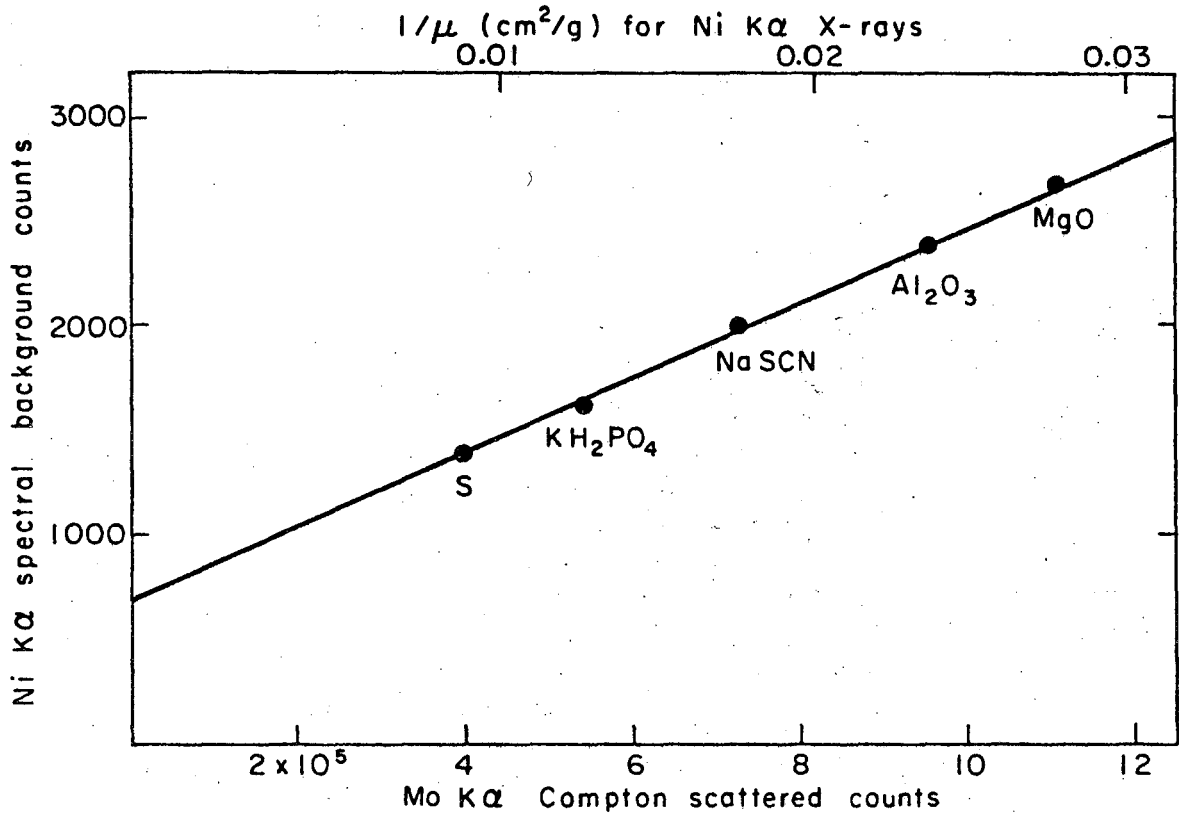
XBL 768-2928

Fig. 1



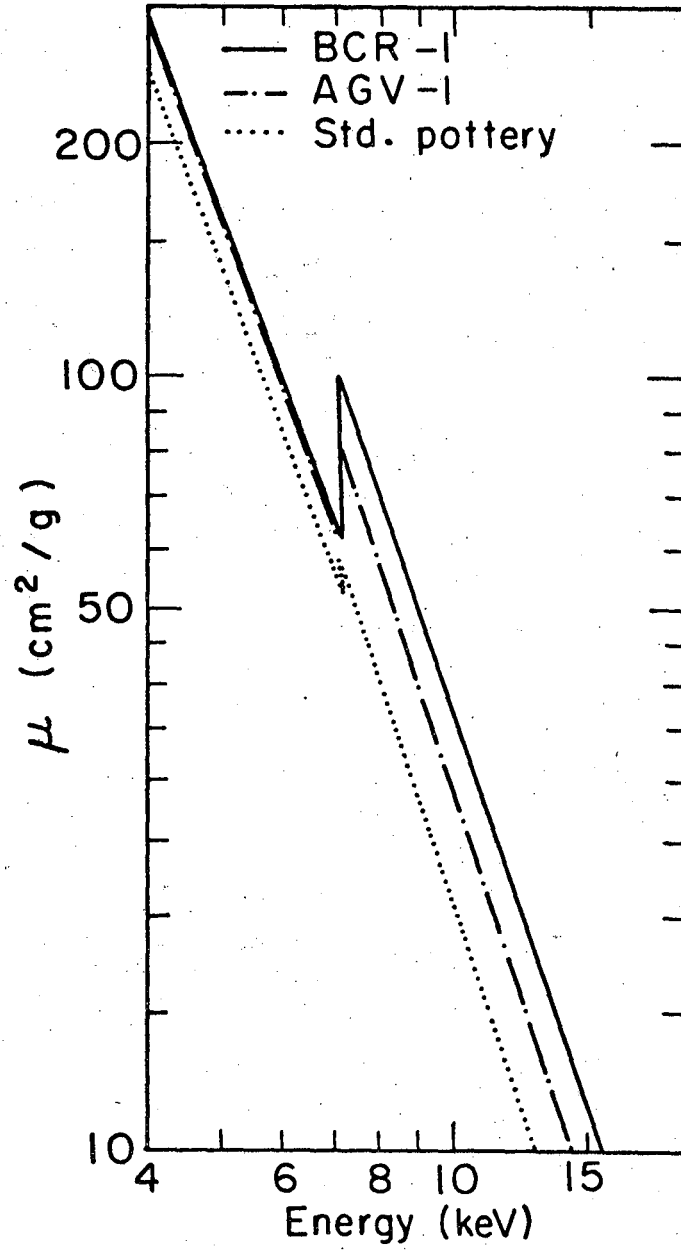
XBL 766-2927

Fig. 2



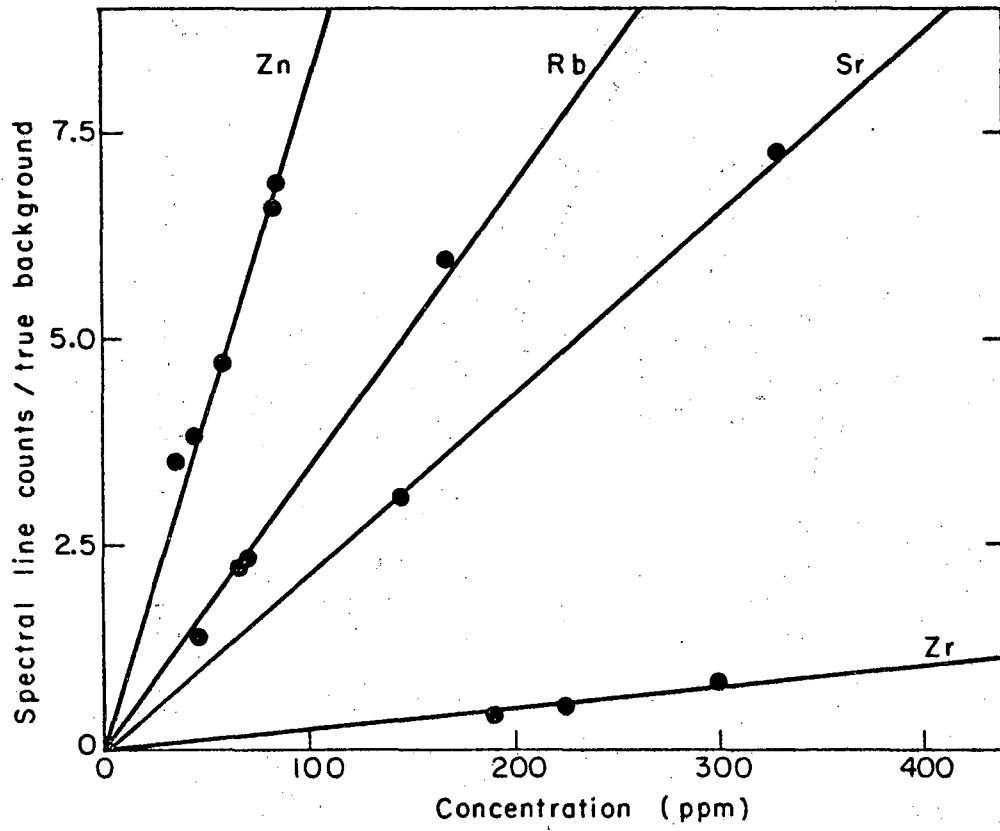
XBL 766-2932

Fig. 3



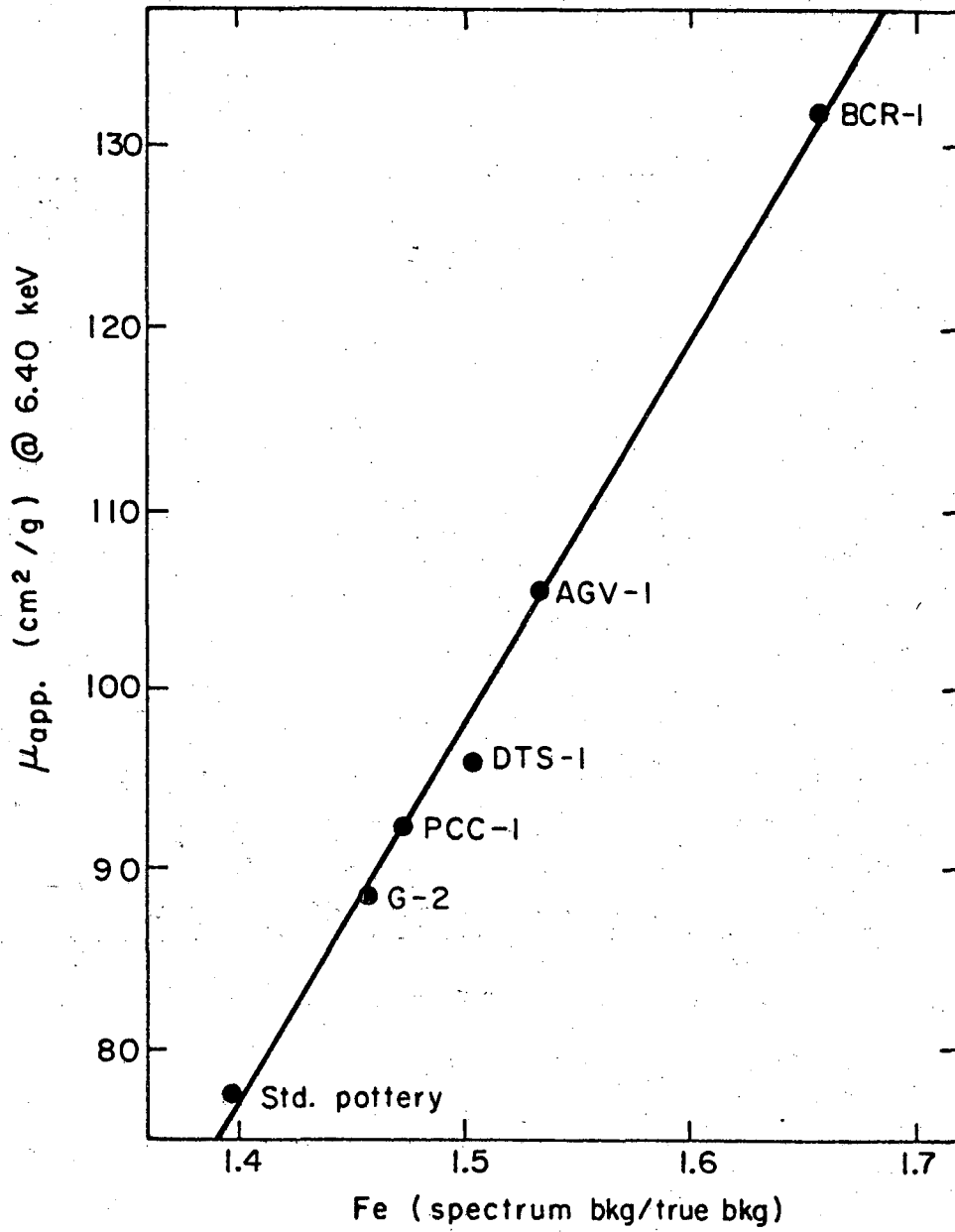
XBL 766-2930

Fig. 4



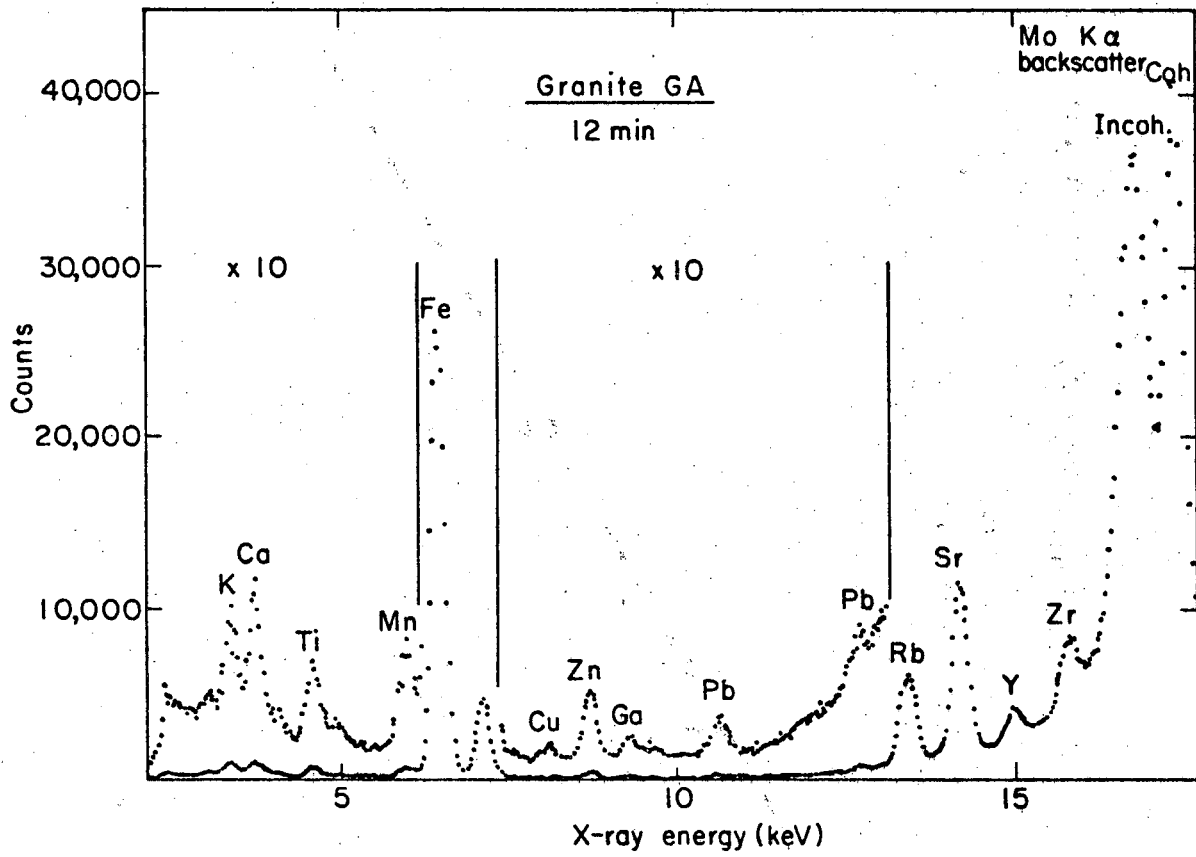
XBL 766-2933

Fig. 5



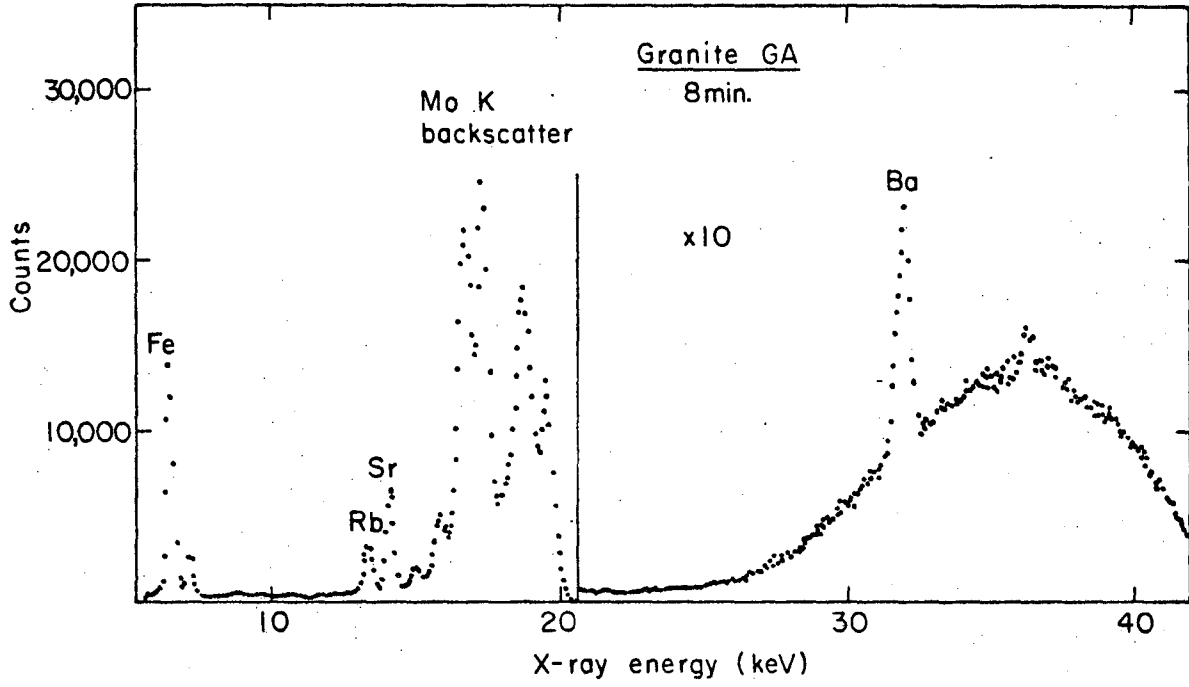
XBL 766-2929

Fig. 6



XBL 766-2931

Fig. 7



XBL 706-2920

Fig. 8

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