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Determination of Rare-Earth, Yttrium, and Scandium Abundances in Rocks and Minerals by an Ion Exchange-X-Ray Fluorescence Procedure

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The method involves the dissolution of a geologic sample in an appropriate acid medium, separation of the rare earths, yttrium, scandium, and barium by a strong acid cation exchange procedure, removal of the barium as a barium sulfate precipitate, and collection of the remaining ions on ion exchange paper. The concentrations of the individual elements are determined by X-ray fluorescence. Single element standards are used to establish corrections for the various interferences in the complex rare-earth X-ray spectrum. The method yields a precision of ± 10 to $\pm 20\%$ for all elements down to concentrations of 1 to 2 $\mu\text{g}/\text{gram}$. Detection limits normally range from 0.5 to several $\mu\text{g}/\text{gram}$. Comparison with literature values for the U.S.G.S. standard rocks indicates relatively good agreement (10–30%) at the ppm level.

DURING THE PAST ten to fifteen years, trace elements have come to play an important role in the delineation of geologic processes. These elements, which are present in very small amounts (usually 0.1 to several hundred parts per million), are considered to be more responsive to changes in the geologic environment than are the major elements which compose the bulk of the rock system. Among the most useful, and the most popular, of these trace elements are the rare earths, yttrium, and scandium.

The widespread use of trace element data has been occasioned mainly by the development of precise and extremely sensitive methods of analysis. Rare-earth abundances, in geologic materials, are usually obtained by neutron activation (1–3) or isotope dilution (4, 5) procedures. Spark source mass spectrography (6, 7) is also currently used. Few X-ray fluorescence procedures have been developed for the deter-

mination of trace amounts of the rare-earth elements in geologic materials. Rose and Cuttitta (8) have described a method for the determination of semimicrogram concentrations of the rare-earth elements but the technique has not been extended to the microgram level. Russian investigators have long used X-ray fluorescence procedures but descriptions of their methods (9) are few and the procedures apparently require a significant amount of preconcentration.

Although neutron activation and isotope dilution procedures yield excellent precision and high sensitivity, they are both tedious and time consuming, and the general applicability of the methods is somewhat limited by the availability of equipment. The procedure described below permits the determination, with sufficient precision, of rare-earth, yttrium, and scandium abundances in most rocks and minerals. The method is roughly five times as fast as neutron activation or isotope dilution procedures and does not require any special equipment beyond a good X-ray fluorescence spectrometer.

EXPERIMENTAL

Apparatus. The X-ray fluorescence spectrometer used in this study was a General Electric XRD-6VS. The operating conditions are listed in Table I. A vacuum path was used for all determinations. A Baird Atomic beta counter was used to determine the activity of the ^{154}Eu tracer. Both Vycor and Pyrex ion exchange columns were used. The inside diameter of these columns was 2.1 cm and they were filled with resin to a height of 15 cm. Vycor glassware, platinum dishes, and Polypropylene and Teflon beakers were used throughout the procedure.

Reagents and Standards. Vapor distilled hydrochloric, sulfuric, and nitric acids were used throughout the chemical procedure. The hydrofluoric acid was commercial ACS reagent grade.

Dowex 50W-X8, 200–400 mesh cation exchange resin was used in the ion exchange portion of the method. Reeve Angel SA-2 ion exchange paper was used as the ion collector and support for the X-ray portion of the procedure. The ion exchange resin used in this paper is Amberlite IR-120.

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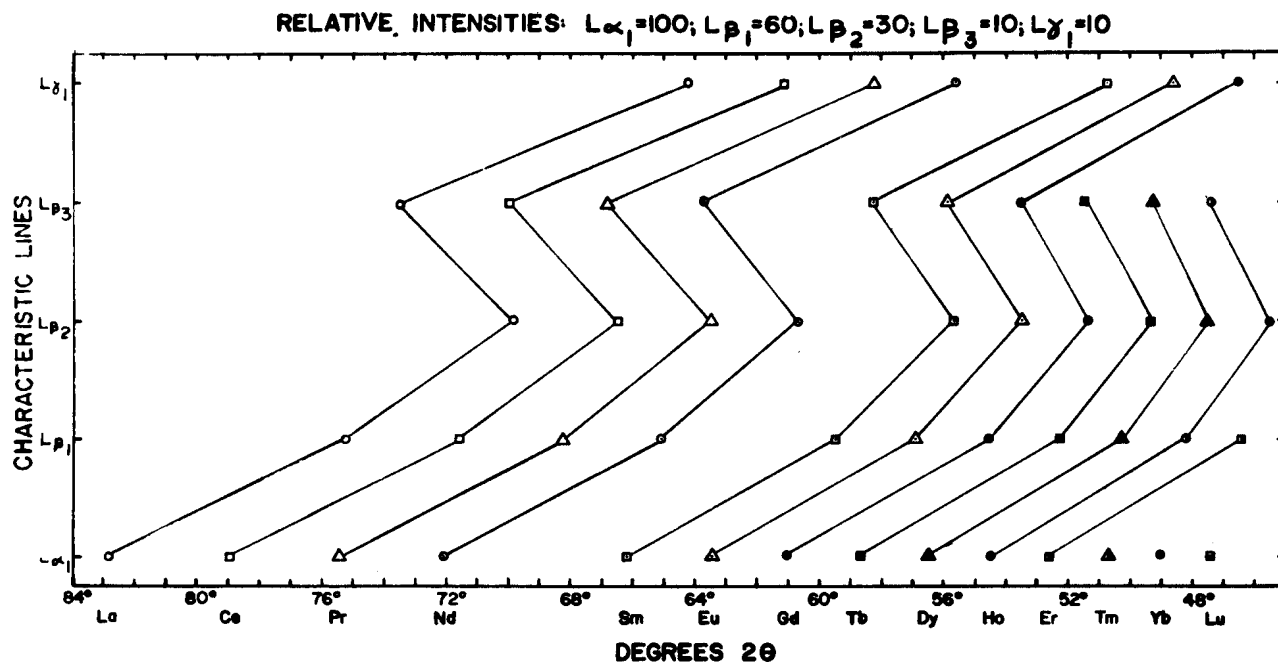


Figure 1. L series emission line interferences for the rare-earth group. Dispersing crystal is LiF (200)

Table I. X-Ray Spectrographic Conditions

	Rare earths (La-Lu)	Scandium	Yttrium
Target	W	Cr	W
Voltage	60 KV	50 KV	60 KV
Current	60 mA	60 mA	60 mA
Crystal	LiF (200)	PET	LiF (200)
Detector	Flow proportional counter, P10 gas		Scintillation counter
Pulse height analyzer			
Base level	2.0 V	2.0 V	2.0 V
Window	14.0 V	14.0 V	14.0 V

The standards were prepared from high purity (>99.9%) oxides of the rare earths, yttrium, and scandium which were obtained from Research Chemicals, Phoenix, Ariz. The desired amount of rare-earth, yttrium, or scandium oxide was weighed to four places and transferred to a Teflon beaker. The oxide was dissolved in 1:1 HNO₃ and the solution was evaporated almost to dryness. The solution was then diluted to 250 ml with distilled water. These stock solutions were standardized by EDTA titration against a Cu standard solution, PAN being used as the indicator.

The stock solutions were diluted so that standards were prepared with the following concentrations: 1, 10, 50, 125, and 250 μg. The desired amount of diluted stock solution was pipetted into a 20-ml beaker and evaporated to dryness. The residue was taken up in 15 ml of 0.01N HCl and an ion exchange paper (2.5 × 1.9 cm, converted to the H⁺ form) was added to the solution. The beaker was then covered and placed on a gently vibrating sieve table for three days (sufficient time for essentially 100% recovery of the ions from solution). At the end of this time period, the paper was removed from the solution, rinsed with distilled water, gently dried under a heat lamp, and then pressed flat between filter papers. Intensities for the analytical lines and interferences were subsequently determined from these standards.

¹⁵⁴Eu, in the form of a 0.5M HCl solution, was purchased from New England Nuclear, Boston, Mass., and was used to determine the chemical yield. The original solution was di-

luted to yield an Eu standard solution which had an activity of approximately 0.5 μCi per ml. One ml of the Eu standard solution contained 0.04 μg of europium, a value which is well below the detection limit of the analytical method.

A yield standard was prepared by equilibrating an ion exchange paper with 1 ml of Eu standard solution which had been diluted to 15 ml with distilled water. The ion exchange paper was placed in the solution, on the vibrating table, for three days. At the end of this time, no residual activity was noted in the solution, all of the ¹⁵⁴Eu having been adsorbed by the paper. This paper now served as a standard which represented 100% recovery.

Procedure. A 0.1- to 1-gram sample, depending upon the expected concentration of the rare earths, yttrium, and scandium, is weighed into a platinum dish and 1 ml of ¹⁵⁴Eu standard solution is added by pipet. Silicate samples are dissolved in 10 to 20 ml of HF by digestion on a steam bath. Calcite samples are dissolved in 15 ml of cold 5% acetic acid and subsequently filtered to remove any insoluble material. After dissolution, the solution is evaporated to dryness and 50 ml of 2N HCl is added. This solution is evaporated to dryness and 30 ml of 2N HCl is added. When the solution has evaporated to approximately 5 ml, it is removed from the steam bath and diluted to 20 ml with distilled water.

The ion exchange columns are cleaned with 350 ml of 6.6N HCl and re-equilibrated with 250 ml of 2N HCl. The sample is loaded, by pipet, directly onto the resin bed. The sample is washed through the column with 450 ml of 2N HCl and the rare earths, yttrium, scandium, and barium are removed with 280 ml of 6.6N HCl. The eluent is evaporated almost to dryness and then diluted to 60 ml with distilled water. Two drops of H₂SO₄ are added and the solution is heated for several hours on a steam bath. The resulting BaSO₄ precipitate is removed by filtering the solution through a MF-Millipore HA filter. The filtrate is evaporated almost to dryness and then diluted to 15 ml with distilled water. An ion exchange paper is placed in the solution and the beaker is then covered and placed on a gently vibrating sieve table for three days. At the end of this time period, the paper is removed from the solution, gently dried under a heat lamp, and then pressed flat between filter papers.

The chemical yield is determined by comparing the radioactive intensity of the sample to that of a yield standard which

represents 100% recovery of the amount of ^{154}Eu initially added. The absolute concentration of the rare earths, yttrium, and scandium is determined by X-ray fluorescence. Three samples and a blank ion exchange paper are placed on the X-ray spectrometer. The intensity of the radiation at the various analytical wavelengths is determined, in consecutive order, starting with La. After the intensities have been determined for all of the elements, the papers are turned over and the intensities are determined for the reverse sides. The values obtained for both sides of the papers are averaged to give an intensity in counts per second. The intensities observed for the blank paper are used as the background intensities. Both 100 sec/side and 40 sec/side counting intervals are used. The raw data are reduced using a computer program written in Fortran IV and run on an IBM 360/50 computer. The program determines the total background correction (background value determined on the blank plus corrections due to interferences) and then the concentration in ppm, by correcting the observed intensities for background, calculating the concentration in $\mu\text{g/g}$, and then converting these values to ppm by considering the chemical yield and the original weight of the samples.

RESULTS AND DISCUSSION

Ion Exchange Procedure. The separation procedure used in this study has been outlined by Schnetzler *et al.* (4). Strelow (10) and Strelow *et al.* (11) have reported distribution coefficients for many cations between hydrochloric acid solutions, of varying normality, and strong acid cation exchange resins. According to these data, elution with 2N HCl, through strontium, will remove all of the cations except the rare-earth elements, yttrium, barium, scandium, thorium, and zirconium. The rare-earth elements, yttrium, barium, and scandium are readily removed with 6.6N HCl. Scandium is the first element to come off the column followed by yttrium, barium, and the rare earths (starting with lutetium and ending with lanthanum). Thorium and zirconium are more strongly adsorbed and will remain on the column.

The columns were initially calibrated by preparing a mixture of scandium, yttrium, europium, and lanthanum to which was added 1 ml of Eu standard solution and several ml of a ^{84}Sr tracer solution. A beta counter was used to monitor the appearance of ^{84}Sr in the eluent and elution with 2N HCl was stopped after the appearance of ^{84}Sr . The columns were then eluted with 6.6N HCl until all of the elements of interest were recovered. Lanthanum exhibited a tail so that excessive amounts of 6.6N HCl were used to ensure the total recovery of lanthanum.

Determination of Chemical Yield. Several different approaches were utilized to check the validity of using ^{154}Eu as a recovery monitor for Sc, Y, and the rare earths. During the initial calibration of the columns, ^{154}Eu was used to monitor the recovery of a mixture of Sc, Y, Eu, and La. The initial concentrations of this mixture and those determined after eluting the column agreed to within $\pm 5\%$. Barium (0.01 gram) was added to this same mixture and, following precipitation of the barium as a sulfate, the concentrations of the initial and final mixtures agreed to within $\pm 5\%$. There is no reason to expect any of the other elements to behave differently from these four elements so that ^{154}Eu is considered to be a reliable tracer. In addition, the reproducibility of the results for the U.S.G.S. standard rocks, and the agreement of

these results with published values, is taken as further support for the reliability of ^{154}Eu as a recovery monitor.

Several yield standards were prepared. Each standard was counted for a total of 120 seconds (60 seconds per side) and these results agreed to within $\pm 1\%$. The samples were counted for an equal length of time and reproducibility of these results, over a span of several months, was $\pm 1\%$. The background intensity was negligible relative to the count rate of the samples and was neglected when making the calculations. A direct determination of the chemical yield was made by comparing the count rates of the samples to those of the yield standard. The average chemical yield was 90% and ranged from a low of 78% (barium rich sample) to a high of 99%.

Equilibration of Ion Exchange Paper. The ion exchange papers were initially equilibrated by filtration. This procedure, however, was somewhat unsatisfactory since the ions were not equally distributed on both sides of the paper. The result was a marked difference in X-ray intensity for the two sides of the ion exchange paper. This problem was eliminated by gently shaking the papers in a solution containing the rare earths, yttrium, and scandium ions. Using the activity of ^{154}Eu as a monitor, it was found that after 1 day 95 to 97% of the ions were adsorbed on the paper, after 2 days 99%, and after three days no residual activity was found in the solution.

Complex Rare-Earth Spectrum. One of the major problems in determining, by X-ray fluorescence, the concentration of the individual elements in a rare-earth element mixture is the interference of the various emission lines of the L spectral series. Figure 1 is a plot of the various L series emission lines vs. 2θ degrees. It is evident from this plot that some of the $L\beta$ and $L\gamma$ lines of the lighter rare-earth elements have 2θ values close to those of the $L\alpha$ lines of the heavier rare-earth elements. In general, if these lines are within 1.5 degrees 2θ of one of the $L\alpha$ lines, they can contribute to the intensity of the $L\alpha$ emission line and therefore produce a spuriously high intensity. Rose and Cuttitta (8) have developed a method for the determination of the concentration of the individual rare-earth elements in which they correct for these inter-element interferences, assuming that matrix effects are negligible.

Campbell *et al.* (12, 13) have thoroughly investigated the use of ion exchange papers as both ion collectors and supports for the X-ray emission determination of the concentrations of various elements. The use of these papers can greatly increase the sensitivity of a particular determination and reduce the matrix effects (in particular, absorption).

Construction of Working Curves and Correction for Inter-Element Interferences. The ion exchange papers are not sufficiently thick for 100% absorption of the primary radiation to occur. For this reason, it was necessary to place a beam stop behind the sample. The beam stop was of simple design consisting of a $1\frac{1}{4}$ inch deep Plexiglas box whose inside dimensions were somewhat greater than the opening in the aluminum mask of the sample holder. This box was lined with lead foil and placed beneath the aluminum mask of the sample holder. Scans over a wide 2θ range, with and without the beam stop in position, indicated that it was responsible for a substantial reduction in background intensity.

Sample holders were constructed from $\frac{1}{4}$ -inch Plexiglas strips. These holders were cut to fit between the beam stop and the aluminum mask of the sample holder. A rectangular opening, slightly larger than the opening in the aluminum

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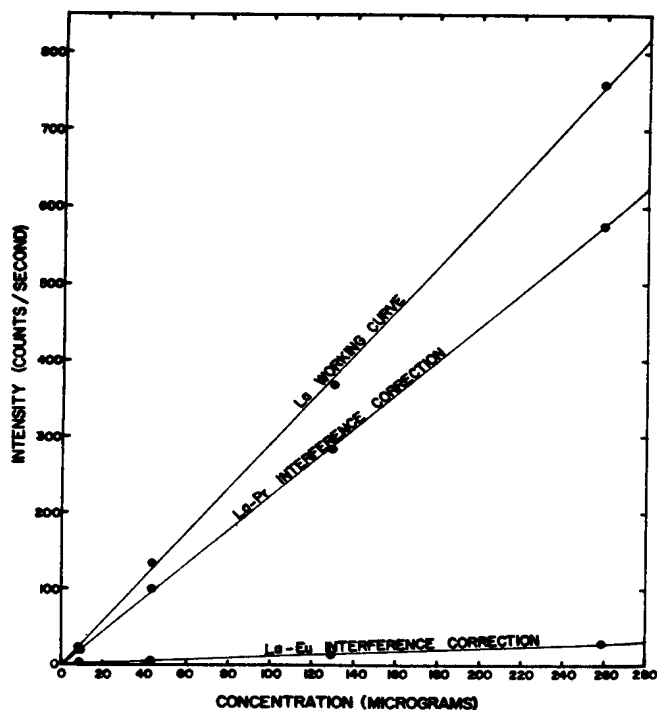


Figure 2. Lanthanum working curves

mask, was cut out of the middle of the Plexiglas holder. Two pieces of 0.00015-inch Spectro-film were stretched across the holder and secured with Scotch tape. The upper layer could be removed so that an ion exchange paper could be sandwiched between the two sheets of Spectro-film. This arrangement proved to be quite successful and kept extraneous absorption and scattering effects to a minimum.

The $L\alpha_1$ lines were used as the analytical lines for the determination of rare-earth element concentrations. Three standards and a blank could be loaded on the X-ray spectrometer at one time. Each standard, and the blank, was counted for 100 seconds. The papers were turned over and the reverse sides were counted for 100 seconds. The total counts obtained on both sides were added, and then divided by the total counting time, to give an average value in counts per second. The count rate obtained on the blank at each 2θ position was used as the background value.

Corrections were established for the inter-element interferences following the procedure outlined by Rose and Cuttitta (8). As an illustrative example, the preparation of the lanthanum working curves will be considered (see Figure 2). The goniometer was set at 82.88 degrees (2θ value for lanthanum $L\alpha_1$) and the standards and the blank were each counted for 200 seconds (100 seconds per side). The average count rate for the blank was considered to be equivalent to the background value and was subtracted from the average count rate for each of the standards. The resulting working curve plots counts per second above background *vs.* concentration. As can be seen from Figure 1, the $L\beta_1$ line of lanthanum will interfere with the $L\alpha_1$ line of praseodymium and the $L\gamma_1$ line of lanthanum will interfere with the $L\alpha_1$ line of europium. The contribution of these lanthanum lines to the intensities of the praseodymium $L\alpha_1$ and europium $L\alpha_1$ lines is found by setting the goniometer at the 2θ values corresponding to these $L\alpha$ lines and then determining the intensity of the $L\beta_1$ and $L\gamma_1$ lines, respectively, at these positions. This results in the construction of the lanthanum-

Table II. Intensities and Backgrounds Determined for the Various Analytical Lines

Element	Analytical line	$2\theta^a$ (degrees)	Average background (c/s)	Line intensity above background (c/s/ μ g)
La	$L\alpha_1$	82.88	8.14	2.91
Ce	$L\alpha_1$	79.00	16.59	3.91
Pr	$L\alpha_1$	75.41	11.55	4.70
Nd	$L\alpha_1$	72.11	27.30	5.40
Sm	$L\alpha_1$	66.22	25.46	7.90
Eu	$L\alpha_1$	63.56	40.64	7.50
Gd	$L\alpha_1$	61.08	35.06	8.51
Tb	$L\alpha_1$	58.76	50.74	10.38
Dy	$L\alpha_1$	56.59	51.75	10.38
Ho	$L\alpha_1$	54.53	56.82	10.67
Er	$L\alpha_1$	52.61	65.77	10.70
Tm	$L\alpha_1$	50.77	86.50	6.95
Yb	$L\alpha_1$	49.06	125.64	6.66
Lu	$L\alpha_1$	47.43	138.15	7.00
Y	$K\alpha$	23.80	505.17	10.16
Sc	$K\alpha$	40.55	45.84	11.56

^a LiF (200) dispersing crystal for all elements except Sc (PET).

praseodymium and lanthanum-europium interference curves. For any given concentration of lanthanum, the intensity of the interference (in counts per second) can be obtained from the working curves. This value is then subtracted from the intensity of the analytical line in question, resulting in a total intensity which has been corrected for the lanthanum contribution.

All inter-element interferences were determined in the same manner and a series of working curves were constructed to correct for these interferences. There are no interference effects in the case of the yttrium and scandium $K\alpha$ lines. The working curves were constructed by finding the linear regression equation for each set of data points. The slope of the resulting line was used in the computer program. Table II lists the intensity and average background for the analytical line of each element.

All of the 250- μ g standards were checked for inter-element interferences. Only the $L\beta$ and $L\gamma$ lines contributed measurable intensities to the analytical lines of any of the other rare-earth elements. Since this value represents the maximum concentration that should be encountered for any single element, the contributions of the weaker X-ray lines to the measured intensities were not significant.

Absorption Effects. In order for the method outlined above to be successfully used, absorption effects must be kept at a minimum. Since the maximum acceptable analytical error is 10%, the magnitude of the absorption effects, for any mixture of elements, should be kept at a value of less than 10%. It is possible to calculate the magnitude of the absorption effects for various elemental mixtures.

For ion exchange resin-loaded papers, the intensity per microgram of collected element is a function of the X-ray transmission characteristics of the paper for the primary and secondary X-rays of interest. For a constant incident radiation:

$$I = \frac{K \left(1 - e - \left[\left(\frac{\mu}{\rho} \right)_1 \csc \theta_1 + \left(\frac{\mu}{\rho} \right)_2 \csc \theta_2 \right] \rho t \right)}{\rho \left[\left(\frac{\mu}{\rho} \right)_1 \csc \theta_1 + \left(\frac{\mu}{\rho} \right)_2 \csc \theta_2 \right]} \quad (1)$$

Table III. Absorption Effects for Various Rare-Earth, Yttrium, and Scandium Mixtures

Element	Concn, μg	Trans. %	Concn, μg	Trans. %	Concn, μg	Trans. %	Concn, μg	Trans. %	Concn, μg	Trans. %	Concn, μg	Trans. %
La	82	97	69	97	168	95	119	95	177	94	30	91
Ce	165	97	162	96	298	94	311	94	396	92	137	91
Pr	19	96	21	96	32	94	33	93	50	91	33	90
Nd	66	96	83	96	106	94	122	93	214	91	229	90
Sm	10	97	14	97	14	95	20	94	31	92	84	91
Eu	2	95	8	95	3	91	6	91	3	88	34	90
Gd	6	94	10	94	7	90	11	90	15	86	94	88
Tb	1	95	2	94	1	90	2	90	2	87	10	88
Dy	3	95	5	94	2	91	5	91	5	87	69	89
Ho	1	95	1	94	1	91	1	91	1	88	12	89
Er	2	95	3	95	1	91	2	91	3	88	35	89
Tm	1	95	1	95	1	92	1	91	1	89	7	89
Yb	1	95	1	95	1	92	1	92	1	89	32	89
Lu	1	96	1	95	1	93	1	92	1	90	5	89
Y	14	99	31	99	9	98	26	98	26	98	410	97
Sc	4	97	11	97	2	96	40	95	6	94	3	90
Total concn	378		423		647		701		932		1224	

where

I = counts per second per microgram

K = a constant consisting of a measure of the absorption and conversion of incident to characteristic radiation and the intensity of the incident radiation

$\left(\frac{\mu}{\rho}\right)_1$ = mass absorption coefficient for the incident radiation

$\left(\frac{\mu}{\rho}\right)_2$ = mass absorption coefficient for the fluorescent radiation

θ_1 = angle of incident radiation

θ_2 = angle of fluorescent radiation

t = thickness of the paper

ρ = density of the paper

For any particular wavelength:

$$\left(\frac{\mu}{\rho}\right)_j = \sum_i \left(\frac{\mu}{\rho}\right)_i W_i \quad (2)$$

where

$\left(\frac{\mu}{\rho}\right)_j$ = incident radiation ($j = 1$) or fluorescent radiation ($j = 2$)

$\left(\frac{\mu}{\rho}\right)_i$ = mass absorption coefficient of element i for the wavelength of interest

W_i = weight fraction of element i

Additionally

(ρt) = weight of one square centimeter of paper plus weight per centimeter squared of additional elements

$$\rho = (\rho t)/t \quad (3)$$

A value for K is not required since it is the ratios between intensities which will be calculated.

A computer program was written in Fortran IV, and run on an IBM 360/50 computer, which solved the above equations for various mixtures of rare-earth elements, yttrium, and scandium. The concentrations were selected to be representative of abundances which might be found in geologic materials. For the General Electric XRD-6VS

$$\theta_1 = 60^\circ; \csc \theta_1 = 1.1547$$

$$\theta_2 = 30^\circ; \csc \theta_2 = 2.000$$

For Reeve Angel SA-2 papers in the hydrogen form, the composition (in weight per cent) is as follows: hydrogen, 6.0; carbon, 43.7; oxygen, 44.2; and sulfur, 6.1. The weight of an ion exchange paper, cut to fit the mask in the sample holder, is 0.06207 gram. This represents a surface area of 4.5 cm² so that the weight of an ion exchange paper having a surface area of 1 cm² is 0.01397 gram. The weights of the various elements per cm² of surface area are (in grams): hydrogen, 0.000828; carbon, 0.006028; oxygen, 0.006097; and sulfur, 0.000841. The thickness of the paper is 0.029 cm. The mass absorption coefficients were taken from the tables in Jenkins and DeVries (14). For any particular element, the wavelength of the incident radiation was selected to be just on the short wavelength side of the absorption edge for the characteristic radiation of that element. Initial " I " values were calculated for each of the rare-earth elements, yttrium, and scandium. The tabulated values (Table III) list the per cent intensity of the radiation for the element of interest relative to the intensity which would be expected from an unreacted ion exchange paper.

As can be seen from the calculated intensities in Table III, in all cases where the total concentration is less than 500 μg, the absorption effects do not exceed 10% (greater than 90% transmission). Absorption effects, therefore, may be disregarded as long as the total concentration of the elemental mixture does not exceed 500 μg.

Reagent Blanks. Reagent blanks were occasionally run during the analytical procedure. This involved the dissolution and subsequent chemical treatment of a hypothetical 1-gram sample. In all cases, the concentrations of the rare-earth elements, yttrium, and scandium were below the detection limits of the method.

Analytical Results. The precision of the analytical method was determined by analyzing three of the U.S.G.S. standard rocks; G-2, AGV-1, and BCR-1 in triplicate and by analyzing GSP-1 in duplicate. The average values obtained for these rocks are listed in Table IV along with values determined by other investigators for the same standard rocks. The errors listed are one standard deviation based on the variation from the mean of the replicate analyses.

Relative standard deviation varies from approximately 10% for the more abundant elements to 50% for some of

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Table IV. Comparison of Reported Rare-Earth, Yttrium, and Scandium Abundances in Rock Standards G-2, GSP-1, AGV-1, and BCR-1, in ppm

	This work ^a	Flanagan (15)	Morrison <i>et al.</i> (16)	Higuchi <i>et al.</i> (17)	Gast <i>et al.</i> (5)	Haskin <i>et al.</i> (18)	Philpotts and Schnetzler (19)
G-2							
La	81.5 ± 5.2	82, 81, 84	78	95, 87
Ce	165.0 ± 10.0	144, 167	110	185, 175
Pr	18.7 ± 0.5	20
Nd	65.5 ± 2.8	...	67	42, 51
Sm	10.0 ± 1.1	7.3, 8.7, 9.1	7.0	7.78, 6.73
Eu	2.3 ± 0.9	1.6, 1.37	1.3	1.60, 1.50
Gd	6.0 ± 1.0	...	3	6.22, 6.53
Tb	0.9 ± 0.3	0.52	0.5	0.49, 0.50
Dy	2.6 ± 0.3	2.05	5.2	1.98, 2.11
Ho	<0.3	...	0.7
Er	1.7 ± 0.9
Tm	<0.5	0.4	0.3
Yb	...	0.56	0.9	0.72, 0.65
Lu	<0.5	0.18	0.13	0.131
Y	14.4 ± 1.8	10, 10
Sc	3.4 ± 1.4	3.4, 4.5, 3.31
GSP-1							
La	176.7 ± 18.4	181, 171, 170	...	225, 198
Ce	396.0 ± 40.4	390, 414	...	451, 536
Pr	49.9 ± 4.2	40
Nd	213.9 ± 21.7	178, 169
Sm	31.3 ± 5.0	33, 23.2, 37.6	...	25.0, 31.4
Eu	2.5 ± 0.5	3.5, 2.0	...	2.38, 2.75
Gd	15.0 ± 3.3	15.7, 13.9
Tb	1.5 ± 0.1	1.3	...	1.27, 1.35
Dy	5.0 ± 0.5	5.66	...	5.66, 5.66
Ho	<0.5
Er	3.0 ± 1.8
Tm	<0.9	0.5
Yb	1.54, 1.93
Lu	<0.9	0.17	...	0.22, 0.23
Y	25.5 ± 2.5	35, 20
Sc	6.2 ± 2.4	5.0, 6.0, 6.1
AGV-1							
La	29.9 ± 0.4	33, 33	37	40.7, 46.5
Ce	58.5 ± 3.6	57, 73	58	79.7, 84.6
Pr	7.6 ± 0.4	5
Nd	32.5 ± 1.5	...	49	39, 47
Sm	6.0 ± 0.5	6.6, 5.4, 5.32	6.5	6.45, 6.93
Eu	2.2 ± 0.7	1.7, 1.55	1.6	1.95, 2.00
Gd	5.3 ± 0.3	...	5	5.91, 5.60
Tb	1.2 ± 0.1	0.77	0.8	0.73, 0.71
Dy	3.2 ± 0.6	3.46	4.5	3.28, 3.63
Ho	0.5 ± 0.2	...	0.8
Er	1.2 ± 0.1
Tm	<0.4	0.6	0.4
Yb	1.9	1.76, 1.60
Lu	<0.4	0.37	0.36	0.258, 0.255
Y	17.4 ± 0.3	30, 10
Sc	11.4 ± 2.6	11.4, 11.7, 11.7
BCR-1							
La	25.9 ± 1.3	22, 23, 23.7	23, 23	22.1, 25.1	26.2, 26.0	25.8	...
Ce	51.9 ± 3.4	46, 53	47, 39	62.5, 61.8	54.9, 54.9	54.2	53.9
Pr	7.1 ± 0.9	5
Nd	32.3 ± 3.9	...	27, 36	22, 34.4	28.8, 28.8	30.5	32.1
Sm	7.3 ± 0.3	7.4, 5.9, 5.5	6.6	7.50, 7.11	6.74, 6.74	7.23	7.44
Eu	2.2 ± 0.4	2.3, 1.95	2.1, 1.8	2.35, 2.42	1.98, 1.95	1.97	1.942
Gd	7.8 ± 0.7	...	5, 5	7.30, 6.73	...	8.02	6.47
Tb	0.9 ± 0.2	1.0	1, 1	1.14, 1.20	...	1.15	...
Dy	6.0 ± 0.2	6.25	6	6.25	6.22, 6.18	6.55	6.36
Ho	1.0 ± 0.1	...	1, 1	1.34	...
Er	3.2 ± 0.1	3.69, 3.73	3.51	3.58
Tm	<0.4	0.6	0.6, 0.6	0.6
Yb	2.9 ± 0.6	...	3.2, 3.0	3.66, 3.50	3.74, 3.63	3.48	3.38
Lu	<0.5	0.6	0.62, 0.46	0.560, 0.531	0.634, 0.547	0.526	0.536
Y	32.7 ± 2.9	60, 20
Sc	37.5 ± 11.8	31.0, 32.5, 33.2

^a Arithmetic mean of three independent analyses except for GSP-1 which is the arithmetic mean of two independent analyses.

the less abundant elements which were determined near their detection limits. While accuracy can never be absolutely known, abundances determined for the standard rocks using this method exhibit relatively good agreement with abundances obtained by other investigators.

Limitations. The removal of barium as a barium sulfate precipitate is not a completely satisfactory procedure. In particular, if substantial amounts of barium (greater than several per cent) are present in the initial sample, the precipitation of the sulfate results in the coprecipitation of a significant fraction of the total rare-earth elements, yttrium, and scandium. This one step accounts for a large portion of the chemical loss during the analytical procedure. Several other methods were investigated—*i.e.*, the solvent extraction method suggested by Schnetzler *et al.* (4) and an ion exchange procedure using nitric acid as the eluent. These procedures proved to be even less satisfactory than the precipitation of barium as a sulfate. An alternative procedure for the removal of barium would be desirable.

From a consideration of the inter-element interferences, it is evident that more corrections are required for the heavier rare-earth elements. This is of particular importance since most analyses involve mixtures that are enriched in the light rare-earth elements. The greater the amount of light rare-earth enrichment, the larger the correction factors which must be applied to the heavier elements. The result is a

reduction in the precision and accuracy of these determinations.

The method is also somewhat limited by the amount of material which can be collected on the ion exchange paper. This limitation is required in order to keep the absorption effects to a minimum. Under the particular experimental conditions described above, 500 μg was the maximum allowable amount. This amount changes with changes in the total surface area of the ion exchange paper. For mixtures that are significantly enriched in the light or heavy rare-earth elements, the result is a rather high detection limit for some of the less abundant elements. This limitation may be alleviated if the mass absorption coefficients are known with sufficient accuracy to permit the calculation of corrected intensities by iteration procedures.

The ultimate sensitivity of the method will be determined by the statistical capability of distinguishing a weak line from a high background and by the number of corrections which must be applied to any particular analytical line. The latter limitation can be significantly reduced by using an X-ray spectrometer with high resolution capabilities.

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