

MAJOR AND TRACE ELEMENT ABUNDANCES IN STANDARD ROCK

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Nondestructive photon activation analysis with high-resolution gamma-spectrometry has been used to determine 7 major and 10 minor elements in Japanese standard rock, JB-1 basalt. The rock sample and the multielement standards were irradiated simultaneously with 30 MeV bremsstrahlung and the (γ , n) and (γ , p) reaction products were measured by the Ge(Li) detector. Elements found to be suited to determination by this method include barium, calcium, cerium, chromium, cobalt, iron, magnesium, manganese, nickel, niobium, potassium, rubidium, sodium, strontium, titanium, yttrium and zirconium. The abundance values obtained are in good agreement with published data.

Introduction

The determination of a number of constituents in standard rocks has been performed by various analytical methods, and, as a result, a considerable amount of the data has been accumulated until recently. The availability of high-resolution solid-state detectors, referring exclusively to lithium-drifted germanium, and of the computerized gamma-spectrometer system for processing complex spectral data acquired by pulse-height analyzer has greatly increased the applicability of nondestructive analysis and a considerable amount of work has been reported on its application to geological (Cobb, 1967; Gordon et al., 1968; Dale et al., 1970; Kuncir et al., 1970; Filby et al., 1970; Hertogen et al., 1971; Randa et al., 1972), biological (Nadkarni et al., 1969; 1970; 1971; Sato, 1975) and environmental materials (Zoller et al., 1970; Dams et al., 1970). In thermal neutron activation analysis, however, the number of the elements determinable by nondestructive technique is limited because of high swamping activities either from the abundant elements or trace elements with high thermal neutron capture cross sections such as manganese, sodium, scandium and cobalt. This approach could only be achieved when a strictly instrumental technique was introduced in sequential activation procedures (Schmitt et al., 1970) or when chemical group separations were combined with high-resolution gamma-spectrometry (Morrison, 1969; 1972).

High-energy photon activation shares the advantages of homogeneous activation as well as thermal neutron activation, but produces an entirely different range of nuclides. Alternate products induced by (γ , n) or (γ , p) reactions have, in some cases, more convenient half-lives or gamma-ray energies than those produced by (n, γ) reactions.

Schmitt et al. (1970) introduced bremsstrahlung activation technique in their sequential activation procedures based on an instrumental method and determined the abundances magnesium, calcium, titanium and nickel in rock materials.

Hislop and Williams (1971) have also applied this technique to the intact analysis of several standard rocks and the Apollo 12 returned lunar materials for 6 elements.

A considerable volume of work has been devoted in the past to the collection of the specific activity data for photonuclear reactions of various types induced by bremsstrahlung with various maximum energies by using our linear electron accelerator of the Tohoku University (Kato, 1972). Utilizing the experience gained in these work, we are developing the nondestructive method of analysis of multielement materials by bremsstrahlung activation, and, in a previous paper (Sato et al., 1972: 1975), the elemental abundances of several standard rocks have been reported. In the present work, this technique was further applied to the nondestructive determination of a number of the elements in the standard silicate rock issued by the Geological Survey of Japan, JB-1 basalt.

The versatility and applicability of the method have been demonstrated by presenting the abundance data on 7 major and 10 minor elements in this rock.

Experimental

The standard rock examined in this experiment was provided in a finely powdered form. Rock samples were individually placed in small pieces of aluminum foil and made into discs 9 mm in diameter with a thickness of about 4 mm. An amount of the rock loaded was 350–400 mg. The two kinds of comparative standards used in this work were the synthetic multielement standards. One of them has a similar elemental composition to the rock materials to be analysed and the other contains four compounds mixture. The former standards were prepared in such manner that an aliquot of a mixed solution of the minor or trace elements was added to a known amount of a solid mixture of the major constituents. In preparing them, the reagents with chemical purity of 99.99% or better were used. This solid standard was a mixture composed of SiO_2 (66.51%), MgO (5.92%), TiO_2 (1.06%), Fe_2O_3 (5.29%), Na_2CO_3 (11.91%) and CaCO_3 (9.31%). To ensure homogeneity, the compounds were mixed in a "V-form" mixing tube by rotating it for a period of 2 days. Three multielement standard solutions were prepared, the first containing Co (9.95), Mn (89.5), and Rb (116) and the second Ba (419), Sr (118), Y (8.50) and Ni (6.42) and the third Zr (74.1) and Nb(6.91), where values in brackets show the amount of each element (μg) in a 0.1 ml aliquot of each solution. Besides, a standard solution of cerium was prepared by dissolving $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ in water ($102\mu\text{g}$ Ce/0.1 ml). Onto a 150 mg amount of the solid standard placed in a small aluminum container made from thin foil, 0.1 ml each of the standard solutions were pipetted. The latter standard was a mixture composed of SiO_2 (85.05%), K_2CO_3 (13.74%), BaCO_3 (0.54%), Cr_2O_3 (0.36%) and NiO (0.29%). They were dried at 110°C and then made into a disc with a diameter of 9 mm and 4 mm high.

In the determination of magnesium through the use of the $^{25}\text{Mg}(\gamma, p)^{24}\text{Na}$ reaction, the $^{27}\text{Al}(n, \alpha)^{24}\text{Na}$ reaction causes interferences, and, hence, an aluminum container is a source of interference. The magnesium determination was, there-

fore, carried out independently of the other elements by irradiating a rock sample and magnesium oxide standards. These standards were discs of about 100 mg each wrapped in a small piece of aluminum foil and made into a disc with a thickness of 9 mm. The rock sample and the multielement or magnesium oxide standards were encapsulated into a silica tube so that the standards were placed on the front and back of the sample (face to face) for simultaneous irradiation. An aluminum disc weighing 100 mg was also contained and irradiated together with the sample for an interference study. The tube was placed in a water-cooled sample holder for bremsstrahlung irradiation by the linear electron accelerator of the Tohoku University and was aligned along the beam axis with the front face of the tube immediately behind the photon-producing converter.

From a knowledge of the basic study regarding the sensitivity and interferences in photon activation analysis, (Kato, 1972), an electron energy of 30 MeV was selected in the present work. The energy region of 30 MeV bremsstrahlung covers a substantial part of the excitation functions of the (γ, n) and (γ, p) reactions for most of nuclei, whereas suppresses the production of the (γ, pn) , (γ, α) and $(\gamma, 2n)$ reactions which would cause interferences. The electron beam, the peak current being 90 mA, produced bremsstrahlung in a platinum converter with a thickness of 3 mm located 3 cm from the beam exit window. The average beam current in a typical operating condition was 70 μ A at the position of the converter measured by using a current monitor. The bremsstrahlung intensities were measured by activating copper discs attached to each sample, and the production rate of the ^{64}Cu by the $^{65}\text{Cu}(\gamma, n)^{64}\text{Cu}$ reaction was measured by the area under the 1340 keV gamma-ray photopeak. In a typical irradiation, a dose rate was determined as 4.41×10^6 R/min at the sample position by using the yield value of 4.82×10^6 ^{64}Cu atoms per one mole of ^{65}Cu per roentgen as reported earlier (Kato & Oka, 1972). The full-width at half-maximum of the bremsstrahlung intensity at 30 MeV was about 12 mm at 10 mm downstream from the converter. The experimental result showed that the vertical spread of flux did not have a pronounced effect on the result, if the samples were limited to dimensions of the above size, and that a flux gradient along the length of the sample was 10% or less. Irradiations were terminated in 4–4.7 hours.

Gamma-counting was made with lithium-drifted germanium detector with sensitive volume of 70 cm³ and 24 cm³, Ortec model, and its associated electronics coupled to a Toshiba 4098-channel pulse-height analyzer. System resolution was 2 and 4 keV for the 1334 keV gamma-line of ^{60}Co . After irradiation, the rock sample or the standard was mounted on the detector at a fixed position, and counting was made consecutively for increasing intervals over a period of one month or longer. In the case of magnesium determination, both the rock sample and the magnesium oxide standards were separately transferred into fresh aluminum containers for the gamma-counting. A Lucite plate with an appropriate thickness (10 or 2 mm) was placed between the sample and the detector surface to absorb positions from a number of positron emitting nuclides.

Nuclides were identified from a knowledge of the gamma-ray energies, decay

data, the gamma-spectra obtained by irradiating pertinent pure elements, and nuclear data listed in the Table of Isotopes (Lederer et al., 1967). In obtaining full-energy peak areas, total peak counts were computed and background contributions were subtracted, assuming linear variation of background over the peak of interest. Interferences from overlapping peak were corrected by decay curve analysis. The decay-corrected peak areas were then used to determine elemental abundances in the standard rocks as compared to the multielement standards. A mean specific activity for any specified gamma-ray from standards on both sides was used for calculation.

Duplicate analyses were made for each element, and the result was the average with the range from this value. In cases where more than one gamma-ray peak were measured (Ca and Ti), the average values were obtained for each of the peaks, and these values were further averaged to obtain the final result with the range from this value.

Table 1. The nuclear data for determination

Element	Process	Activation product	Half-life of product	Gamma-ray used (KeV)	Peak intensity (cpm/mg) ¹⁾
K	(γ , n)	³⁸ K	7.71 m	2170	1.94×10^4 ²⁾
Fe	(γ , p)	⁵⁶ Mn	2.576 h	{ 847 1811 2100	{ 4.21×10^3 4.29×10^2 1.98×10^2
Sr	(γ , n)	^{87m} Sr	2.83 h	388	2.61×10^6
Mg	(γ , p)	²⁴ Na	15.0 h	1369	4.75×10^3
Ca	(γ , p)	⁴³ K	22.4 h	{ 374 617	{ 1.77×10^3 7.40×10^2
Ba	(γ , n) + (γ , γ')	^{135m} Ba	28.7 h	268	4.47×10^3
Ni	(γ , n)	⁵⁷ Ni	36.0 h	{ 1378 1890	{ 4.50×10^4 4.69×10^4
Ti	(γ , p)	⁴⁸ Sc	1.83 d	{ 983 1040 1314	{ 4.95×10^2 4.67×10^2 3.52×10^2
Zr	(γ , n)	⁸⁹ Zr	3.27 d	913	3.22×10^4
Ti	(γ , p)	⁴⁷ Sc	3.43 d	160	5.63×10^4
Ca	(γ , n)	⁴⁷ Ca	4.53 d	1298	4.05×10^1
Nb	(γ , n)	^{92m} Nb	10.16 d	934	1.03×10^4
Cr	(γ , n)	⁵¹ Cr	27.8 d	319	1.85×10^3
Rb	(γ , n)	⁸⁴ Rb	33.0 d	880	5.08×10^3
Co	(γ , n)	⁵⁸ Co	71.3 d	811	1.46×10^3
Ti	(γ , p)	⁴⁶ Sc	89.3 d	1211	3.38×10^1
Y	(γ , n)	⁸⁸ Y	108 d	1836	8.92×10^2
Ce	(γ , n)	¹³⁹ Ce	140 d	166	1.57×10^4
Mn	(γ , n)	⁵⁴ Mn	303 d	835	6.45×10^2
Na	(γ , n)	²² Na	2.6 y	1275	2.80×10^1

1) At the end of 4h-irradiation with 30 MeV bremsstrahlung with a dose-rate of 4.41×10^6 R/min: 24 cm³ Ge(Li), source-to-detector distance 12 mm.

2) Peak intensity of ³⁸K was measured by 70 cm³ Ge(Li).

Result and Discussion

The elements except potassium determined here were those which gave intermediate or long-lived radioactive products in photon activation analysis. The particulars of the nuclear characteristics of the nuclides of the present importance are listed in Table 1. The peak intensities due to those gamma-rays are also included which were obtained by irradiating each pure element under the identical experimental conditions. Figure 1 and 2 show the typical gamma-spectra of an irradiated JB-1 rock measured 17 min, 5.68 h, 5.96 d and 51.6 d after irradiation. The shapes and the decay properties of the spectra of this sample were quite resemble to those of the former multielement standards measured at comparable decay times.

At shorter decay times after irradiation, the gamma-spectra of both the rock samples and the multielement standards were so strongly dominated by 511-keV annihilation radiations from the positron emitters that no gamma-rays below that energy were observable. The main products observed at this time were those with higher energy gamma-rays, e.g. ^{38}K and ^{24}Na . In the spectra taken at decay

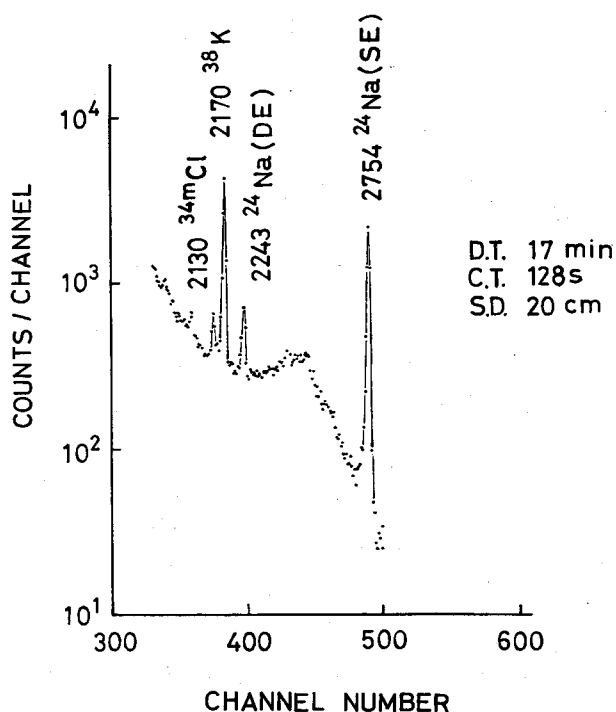


Fig. 1 Gamma-ray spectra of standard rock, JB-1 (I). D. T., C.T. and S. D. indicate time interval between irradiation and counting, counting period, and source-to-detector distance, respectively. SE and DE designate single and double annihilation-photon escape peaks, respectively. Bg indicates peaks occurring in background. Values on each peak are energies in keV.

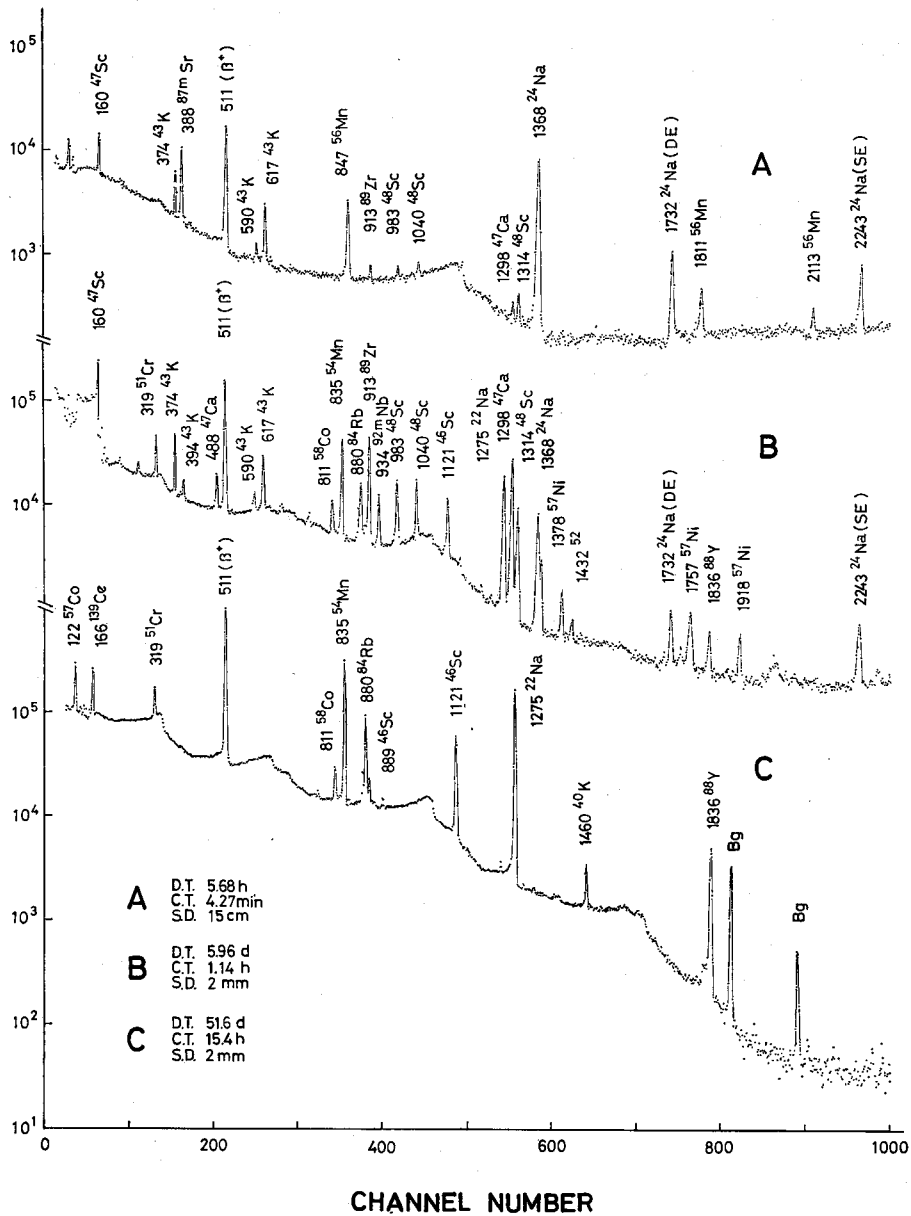


Fig. 2 Gamma-ray spectra of standard rock, JB-1 (II).
 D.T., C.T. and S.D. indicate time interval between irradiation and counting, counting period, and source-to-detector distance, respectively. SE and DE designate single and double annihilation-photon escape peaks, respectively. Bg indicates peaks occurring in background. Values on each peak are energies in keV.

interval of 2-5 h, the products of interest were ^{87m}Sr , ^{56}Mn , ^{43}K , ^{24}Na and ^{47}Sc . At longer decay times, photopeaks due to the (γ, n) reaction products of a number of elements could be observed. Below is a discussion of special problems associated with determinations of the abundances of the respective elements.

Sodium can be determined by the $^{23}\text{Na}(\gamma, n)^{22}\text{Na}$ reaction. The 1275 keV peak of ^{22}Na was measured precisely at longer decay times. The photopeak of potassium coming from the reaction $^{39}\text{K}(\gamma, n)^{38}\text{K}$ was observed at earlier decay time. The 1369 keV peak of ^{24}Na was used for magnesium determination. High energy photoneutrons generated in the vicinity of the converter can produce the $^{27}\text{Al}(n, \alpha)^{24}\text{Na}$ which would cause interferences in the magnesium determination. This interference is particularly serious for the sample with a high Al/Mg ratio. A separate irradiation of each definite amount of magnesium and aluminum under identical conditions produced a ratio of ^{24}Na specific activities of 206:1. The $^{27}\text{Al}(n, \alpha)^{24}\text{Na}$ contribution to the total ^{24}Na activity could be estimated to be 0.8% for this rock. The results may be accurate without correction for aluminum contributions for JB-1 with an ratio Al/Mg less than 2.0. The $^{23}\text{Na}(n, \gamma)^{24}\text{Na}$ contribution to the total ^{24}Na activity was found to be negligible by irradiating a definite amount of sodium carbonate together with the sample. Calcium was determined either by the $^{44}\text{Ca}(\gamma, p)^{43}\text{K}$ or by the $^{48}\text{Ca}(\gamma, n)^{47}\text{Ca}$ reaction. Of the peaks of ^{43}K and ^{47}Ca , the 374 and 617 keV peaks of ^{43}K and the 1298 keV peak of ^{47}Ca were found to produce precise values of calcium concentration. Table 2 shows the results using these three different peaks. For titanium, three different scandium isotopes, ^{46}Sc , ^{47}Sc and ^{48}Sc , produced by (γ, p) reactions could be used for quantifications. A ratio of the relative yields for (γ, p) reactions on ^{47}Ti , ^{48}Ti and ^{49}Ti expressed as those per mole has been determined as 0.54:0.20:0.12 (Oka et al., 1969). The 160 keV gamma-ray of ^{47}Sc , however, gives the highest full energy peak. In the titanium determination using ^{47}Sc , the $^{51}\text{V}(\gamma, \alpha)^{47}\text{Sc}$ reaction is the possible source of interferences. A separate irradiation of vanadium and titanium showed that the production rate (cpm/mg) of ^{47}Sc by the $^{51}\text{V}(\gamma, \alpha)^{47}\text{Sc}$ turned out to be only 4% of that by the $^{48}\text{Ti}(\gamma, p)^{47}\text{Sc}$. Correction required for this rock with V/Ti ratio was 0.14%. Although ^{47}Sc can also be produced by the process $^{48}\text{Ca}(\gamma, n)^{47}\text{Ca} \xrightarrow{\beta^-} ^{47}\text{Sc}$, interferences from its decay were not significant at earlier decay times. At longer decay times, the 1121 keV peak of ^{46}Sc can also be used (Table 2). Manganese can be determined by the $^{55}\text{Mn}(\gamma, n)^{54}\text{Mn}$ reaction. The major source of interference in the use of ^{54}Mn is from iron by the $^{56}\text{Fe}(\gamma, pn)^{54}\text{Mn}$ reaction. When an amount of pure iron was irradiated with

Table 2. Calcium and titanium concentrations determined by using different gamma-ray photopeaks

CaO (%)	^{43}K	374 KeV	8.78	9.00
	^{43}K	617 KeV	10.72	9.29
	^{47}Ca	1298 KeV	9.36	8.91
	Average		9.62	9.07
TiO ₂ (%)	^{46}Sc	1121 KeV	1.21	1.21
	^{47}Sc	160 KeV	1.28	1.27
	^{48}Sc	983 KeV	1.21	1.34
	^{48}Sc	1314 KeV	1.15	1.01
	Average		1.21	1.21

30 MeV bremsstrahlung, an activity ratio of 1.03×10^{-3} was obtained as the ratio of the 835 keV full-energy peak of ^{54}Mn to the 847 keV full-energy peak of ^{56}Mn at the end of irradiation. The ^{54}Mn activity due to the $^{55}\text{Mn}(\gamma, n)^{54}\text{Mn}$ reaction for a given rock sample was, therefore, calculated by multiplying the count rate under the 847 keV peak by 1.03×10^{-3} and then by subtracting this value from the count rate under the 835 keV peak corrected for decay to the end of irradiation. Correction of 40% was required for this rock sample with high Fe/Mn ratio. Iron was determined by the $^{57}\text{Fe}(\gamma, p)^{56}\text{Mn}$ reaction. The 847 keV peak of ^{56}Mn was used for quantifications, and the 1811 and 2114 keV peaks were used for confirmation. The results of duplicate analyses for the above 7 elements are given in Table 3 together with the data by Ando (1974) for the JB-1 rocks.

Quantifications for 10 trace elements were made by this method and the results obtained were listed in Table 4. No obvious interfering nuclear reactions have been found for all elements determined here. Strontium is one of the elements conveniently amenable to photon activation analysis by the $^{88}\text{Sr}(\gamma, n)^{87\text{m}}\text{Sr}$ reaction. In measuring the 388 keV full-energy peak, a S/N ratio greater than 2.0 was obtained from spectra taken 4 hours after irradiation. Errors based on the counting statistics associated with strontium abundances of this rock were about 1.0%. The practical sensitivity limit at $\pm 10\%$ relative accuracy

Table 3. Concentration of major constituents (%)

Constituent	This work		Range of literature value ¹⁾
Na ₂ O	2.72	2.73	2.80
K ₂ O	1.40	1.43	1.44
MgO	8.03	7.88	7.74
CaO	9.62	9.07	9.24
TiO ₂	1.21	1.21	1.34
MnO	0.13	0.14	0.15
Fe ₂ O ₃ ²⁾	8.70	8.77	8.96

1) Ando et al., 1974 2) Total Fe as Fe₂O₃

Table 4. Concentration of trace constituents (ppm)

Element	This work		Range of literature value ¹⁾
Ba	484	534	490
Ca	68	72	67.3
Co	41	43	39.1
Cr	414	434	405
Nb	16	14	15-27
Ni	140	118	135
Rb	48	44	41.2
Sr	448	447	435.2
Y	27	26	25.5
Zr	146	141	153

1) Ando et al., 1974

under the present experimental conditions is about 20 ppm Sr. For yttrium, zirconium and niobium, nondestructive method by thermal neutron activation is generally not attainable because these elements are not highly activated or because their (n, γ) reaction products are relatively short-lived or emit no gamma-rays. These elements can, however, be measured nondestructively by photon activation analysis even at ppm levels.

Schmitt et al. (1970) recommended the use of the 1920 keV peak of ^{57}Ni in the determination of nickel in rock materials. In the present work, however, this peak was too weak to measure precisely for any rock samples studied. The use of the 1378 keV peak of ^{57}Ni was satisfactory by means of the utilising the high resolution detector, 70 cc Ge(Li), in spite of the overlapping of this peak and the 1369 keV peak of ^{24}Na . Barium can be determined by measuring the 268 keV peak of $^{135\text{m}}\text{Ba}$. The highest S/N ratio was 0.05 for this rock obtained from spectra two day after irradiation, and an error based on the counting statistics associated with quantification was $\pm 6\%$. The practical sensitivity limit at $\pm 10\%$ relative accuracy under the present experimental conditions can be set at 250 ppm Ba.

For all elements in Table 3 and 4, errors based on the counting statistics were within $\pm 10\%$. The average relative deviation for all the elements determined here based on the duplicate samples was 3%. When the results from the duplicate analyses by this method fall in the main within the range of values presented by other workers (Ando et al., 1974). In conclusion, the elements determined here may be amenable to nondestructive photo nactivation analysis of rock materials of various origins. Further applicability and versatility of the method would lie in the determination of many other elements followed by efficient chemical separation, and these problems will be studied in the near future.

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