≪Original≫ # Reactor Neutron Activation Analysis
by a Single Comparator Method

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Abstract

A method of activation analysis, based on the irradiation and counting of an iron wire which contains manganese impurity as the single comparator. has been elaborated by critical evaluation of nuclear data involved in activation and activity measurement. The variation of effective cross section is investigated as a function of the spectral index and other parameters such as a measure of the proportion of epithermal neutrons in the reactor spectrum. The errors induced by shifts in the neutron spectrum in the irradiation positions are discussed. The known amount of each element is irradiated simultaneously together with the single comparator, and the obtained values are compared with the known amount of each element. The results show that in general the random errors are not greater than those obtained by using the conventional relative method, but the systematic errors were up to about 20%.

This method is applied to the determinations of fourteen rare earth elements in monazite as well as other seven elements in the standard kale powder. The satisfactory reproducibility of the present method makes possible the determination of the elements with an accuracy attainable with the conventional relative method.

요   약

중성자 방사화 및 방사능 계측에 관계하는 핵데타를 세밀히 연구검토하여 망간을 불순물로 함유하고 있는 철선을 단일비교체로 한 중성자 방사화분석법을 발전시켰다. 유효반응 단면적의 변화를 원자로 내부 스펙트럼의 열외 중성자의 비율과 같은 스펙트럼 지표및 그외 다른 변수의 함수로 검토하였으며 조사위치에서 중성자 스펙트럼의 변위로 생기는 오차를 토의 하였다. 각원소의 이미 아는양을 취하여 단일비교체와 함께 조사한 다음 본법에 의해서 그 함량을 산출하여서 원래 취한 양과 비교하였다. 그 결과 우연오차는 일반적인 비교법으로 얻은 오차보다 크지 않았으나 계통적 오차는 대략 20%이내였다. 본법을 모나자이트 중에 함유된 14개 희토류 원소의 정량과 표준배추시료 중에 있는 다른 7개의 원소정량에 적용하였다. 그결과 분석치는 만족할만한 재현성을 나타내었으며 종래의 비교법으로 얻을 수 있는 정도의 정확성으로 이들 원소를 분석할 수 있었다.

1. Introduction

In the neutron activation analysis the relative method is generally used. In this method the treatments of the standard for each element to be determined, *i.e.*, prepara-

tion, dissolution, counting, etc., are very cumbersome and time consuming, especially when determining a great number of elements in one sample. Moreover, when the irradiation of a sample takes place with many standards, the voluminous target will cause inhomogeneous irradiation, giving rise to different reaction rates in the sample and standards.

For these reasons the single comparator method was first used by Girardi *et at.*[1] who evaluated socalled K values, *i.e.*, the ratios of the specific photopeak activities of the isotopes investigated to the specific photopeak activity of the comparator. Recently Kim *et al.*[2,3] determined spectral indices in the irradiation positions instead of determining the K values, applying the Westcott convention[4] for the evaluation of the effective activation cross section. In their works the cobalt wire (1% Co, 9% Mg and 90% Al) and gold wire (0.12% Au and 99.88% Al) were used as the comparator. Cobalt wires were to be lefe for about one day for the activity due to the reaction $^{27}Al(n, \alpha)^{24}Na$ to decay. The gold has also the disadvantage that it is much sensitive on the flux fluctuation because of the large resonance integral of this element.

In our laboratory the iron wire was used as the comparator, which homogeneously contains sufficient manganese to produce a suitable ^{56}Mn activity as described in the previous report[5]. Using this comparator fourteen rare earth elements in the monazite were recently determined.[6]

In this paper, the method has been further elaborated for the broad application of the manganese as the comparator, with emphasis on the evaluation of effective activation cross section using a gamma-ray spectrometry with NaI (Tl) detector. The errors induced by shifts in the neutron spectrum in the irradia-

tion positions were discussed. The present method was applied to analyse the rare earths in a monazite sample as well as mercury and the other elements in the standard kale powder.

The most recent values published in the literatures for various nuclear constants have been used for the evaluation of the experimental data obtained in this study. The satisfactory reproducibility of the present method makes possible the determination of the elements with an accuracy attainable with the conventional relative method.

2. Principle and Methodology

When a sample is irradiated in the reactor the induced counting rate of a certain nuclide can be expressed by the well known relation:

$$A = \Phi \cdot \hat{\sigma} \cdot W \cdot N \cdot f \ (1/M) \ \varepsilon \cdot b \cdot S_t \cdot D, \qquad (1)$$

where Φ = neutron flux

$\hat{\sigma}$ = effective activation cross section

W = weight of element

N = Avogadro's number

f = fractional isotopic abundance of target nuclide

M = atomic weight of element

ε = efficiency of the detector for a particular gamma-ray measured

b = gamma-ray abundance in decay scheme

S_t = saturation factor; $1 - e^{-\lambda_1 t_1}$ (λ_1 = decay constant, t_1 = irradiation time)

D = decay factor; $e^{-\lambda_1 t_2}$ (t_2 = decay time).

If the sample is irradiated together with the manganese comparator the activity ratio of a nuclide of interest in the sample to that of the manganese nuclide is given by

$$\frac{A}{A'} = \frac{\hat{\sigma} \cdot W \cdot f \cdot M' \cdot \varepsilon \cdot b \cdot S_t \cdot D}{\hat{\sigma}' \cdot W' \cdot f' \cdot M \cdot \varepsilon' \cdot b' \cdot S_t' \cdot D'}, \qquad (2)$$

where the indication(') refers to manganese comparator. If the constants are separated,

equation(2) may be written as

$$W = W' \cdot \frac{A \cdot S_t' \cdot D'}{A' \cdot S_t \cdot D} \cdot K_1 \cdot (C_2 \cdot C_3)^{-1}, \quad (3)$$

where

$$K_1 = \frac{f' \cdot M \cdot b'}{f \cdot M' \cdot b}, \quad C_2 = \frac{\varepsilon}{\varepsilon'}, \quad C_3 = \frac{\hat{\sigma}}{\sigma'}.$$

K_1 is the absolute constant and can be found from the literature, whereas C_2 varies with the detector and the counting geometry used. C_3 varies with the spectral index at the irradiation site, namely, the ratio of epithermal to thermal flux.

(1) The C_3 Value and the Effective Activation Cross Section.

The effective activation cross section $\hat{\sigma}$ is given by Westcott convention[4] as follows,

$$\hat{\sigma} = \sigma_o (g + r \sqrt{T/T_o} \cdot S_o) \quad (T_o = 293.6°K), \quad (4)$$

where σ_o is the thermal cross section at neutron velocity of 2200 m/sec and $r\sqrt{T/T_o}$ spectral index which shows the relative strength of the epithermal component of the mixed neutron spectrum at temperature T. g and S_o are the factors depending on the departure of the cross-section law from the $1/v$ form. For a cross section following the $1/v$ law in the thermal region g is one and S_o is zero. For a reactor neutron spectrum S_o is defined[4] by

$$S_o = \frac{2}{\sqrt{\pi} \cdot \sigma_o} \int_{\mu kT}^{\infty} (\sigma(E) - g\sigma_o \sqrt{E_o/E}) \frac{dE}{E}$$

$$\equiv \frac{2 \cdot I_o'}{\sqrt{\pi} \cdot \sigma_o}, \quad (5)$$

where $\sigma(E)$ is the cross section as a function of neutron energy. The integral I_o' in equation (5) is the resonance integral of the usual type with an effective lower energy limit of μkT, where k is Boltzman constant, and with a $1/v$-term subtracted. For a well-moderated reactor the constant μ is given as 5.[7]

(2) Spectral Index

As is seen from Eq. (4) the spectral index $r\sqrt{T/T_o}$ must be determined in order to evaluate the effective cross section. For an irradiation position in a reactor of steady operation the index remains constant. The spectral index can be determined with the knowledge of Cd-ratios(CR) and S_o values of a standard nuclide by the following relation

$$r\sqrt{T/T_o} = \frac{g}{(CR-1)S_o + CR \cdot 1/K} \quad (6)$$

where the constant K is 2.073 for the 0.020 inch thickness of cadmium[7]. For the calculation of the spectral indices the data used are shown in Table 1. With these data and cadium ratios determined for the standards, the spectral indices were calculated as shown in Table 1.

Table 1. Spectral index in the pneumatic tube

Nuclides produced from standards	Half life	σ_o	S_o	I (barn)	K[1]	Cd ratio	$r\sqrt{T/T_o}$
[198]Au	2.70 d	98.8	17.01[17]	15.35[17]	2.073	1.99±0.02	0.0560±0.001
[56]Mn	2.58 h	13.3	0.778	15[13]	//	14.5±0.06	0.0572±0.0003

Table 2. Spectral index of the pneumatic tube, measured during a long period of time

Position in rabbit	$r\sqrt{T/T_o}$ measured in				mean
	Feb. '72	March '72	June '72	Sep. '72	
upper part (A)	0.0549	0.0571	0.0567	0.0561	0.0562±0.0008
lower part (B)	0.0597	0.0591	0.0585	0.0579	0.0588±0.0007

The spectral indices determined by different standards agree well each other as shown in Table 1. Therefore manganese can be used as a standard similar to gold for the determination of the spectral indices. The spectral indices for the pneumatic tube of the TRIGA MARK II reactor, determined for four months, are summarized in Table 2.

As shown in this Table the reactor is operated steadily and the spectral index remains constant on irradiation positions A and B of the rabbit. The distance between the upper and lower parts is ca. 6 cm. The contribution of the discrepancy in the indices between A and B to the effective activation cross section of gold results in an error of about 4% in the cross section. If manganese is used as the standard, however, the same contribution to the effective activation cross section of manganese results in an error of about 0.4%.

(3) The S_o Value

The resonance integral excluding the $1/v$ tail, i.e., I_o' in Eq. (5), is related with the thermal cross section by the following relation

$$I_o' = I_o - 0.45\sigma_o, \qquad (7)$$

where I_o is the resonance integral including $1/v$ component and $0.45\sigma_o$ is the $1/v$ component of the resonance integral[8]. If I_o is known I_o' is easily calculated by Eq. (7). Once I_o' is known S_o is simply calculated by Eq. (5). The thermal cross sections for many nuclides are rather well known whereas the reported values for the resonance integrals are not only scanty but also largely different each other. When S_o is not well known or inaccurately known for a given nuclide this may also be determined with the knowledge of the cadmium ratio and spectral index by the following relation

$$S_o = \frac{1}{(CR-1)}\left(\frac{g}{r\sqrt{T/T_o}} - CR\cdot\frac{1}{K}\right), \qquad (8)$$

which is obtained by rearrangement of Eq. (6).

Provided that no resonance peak appears near Cd-cut-off energy and the resonance self-shielding which occurs in the target is negligible, Eq. (8) usually fits well for the determination of S_o-value of a nuclide. In the present study the determinations of S_o-values

Table 3. The S_o values determined and taken from literature and the contribution of its error to the effective activation cross section.

Reaction	S_o This work	S_o Other work	$\sigma_o^{(20)}$ (barn)	$\dfrac{\Delta\hat{\sigma}}{\hat{\sigma}}\times 100$ (%)
²³Na(n,r)²⁴Na	0.348±0.002	0.158[13]	0.534±5	1.2
³⁷Cl(n,r)³⁸Cl	0.144±0.050	—	0.430±0.1	
⁴¹K(n,r)⁴²K	0.67±0.02	—	1.2	
⁵⁵Mn(n,r)⁵⁶Mn	0.780±0.024	0.778[13]	13.3±0.1	0.2
⁵⁹Co(n,r)⁶⁰Co	1.94±0.003	1.78[13]	37.2±0.6	0.97
⁶³Cu(n,r)⁶⁴Cu	0.741±0.035	1.00[13]	4.51	1.3
⁷⁵As(n,r)⁷⁶As	12.3±0.4	9.55[13]	4.5	8.7
⁸¹Br(n,r)⁸²Br	15.8±0.8	—	3.1±0.4	
¹⁹⁶Hg(n,r)¹⁹⁷Hg	0	0[19]	3092±211	0
¹⁹⁷Au(n,r)¹⁹⁸Au	16.9±0.8	17.3[13]	98.8	1.6
¹³⁹La(n,r)¹⁴⁰La	1.04±0.22	1.06[13]	8.2±0.8	0
¹⁴²Ce(n,r)¹⁴³Ce	0.85±0.02	0.85[18]	0.95±0.05	
¹⁴¹Pr(n,r)¹⁴²Pr	1.270±0.004	1.04[13]	10.9±1.1	1.7
¹⁴⁸Nd(n,r)¹⁴⁹Nd	14.1±0.9	15.4[13]	2.9±0.5	4.0
¹⁵²Sm(n,r)¹⁵³Sm	14.0±0.4	16.51[13]	210±10	7.0
¹⁵¹Eu(n,r)¹⁵²Eu	0.38±0.04	0.39[17]	2951±85	0
¹⁵⁸Gd(n,r)¹⁵⁹Gd	10.8±0.3	—	3.5±1.0	
¹⁵⁸Tb(n,r)¹⁵⁹Gd	26±2	24.6[18]	22±2	3.0
¹⁶⁴Dy(n,r)¹⁶⁵Dy	0	—	2700±200	
¹⁶⁵Ho(n,r)¹⁶⁶Ho	10.0±1.6	—	64±6	
¹⁷⁰Er(n,r)¹⁷¹Er	3.71±0.135	—	9±2	
¹⁶⁹Tm(n,r)¹⁷⁰Tm	6.09±0.02	—	125	
¹⁷⁴Yb(n,r)¹⁷⁵Yb	0.406±0.003	—	55	
¹⁷⁶Lu(n,r)¹⁷⁷Lu	0	—	2100±150	

for some nuclides have been made and the results are compared with the reported values in Table 3. The effective activation cross sections, which are calculated using both of S_o values, are different each other as shown in the last column in this Table.

(4) The C_3 Value

The effective activation cross section $\hat{\sigma}$ was calculated by Eq. (4). The C_3 values as a function of the spectral indices are then calculated and illustrated in Fig. 1.
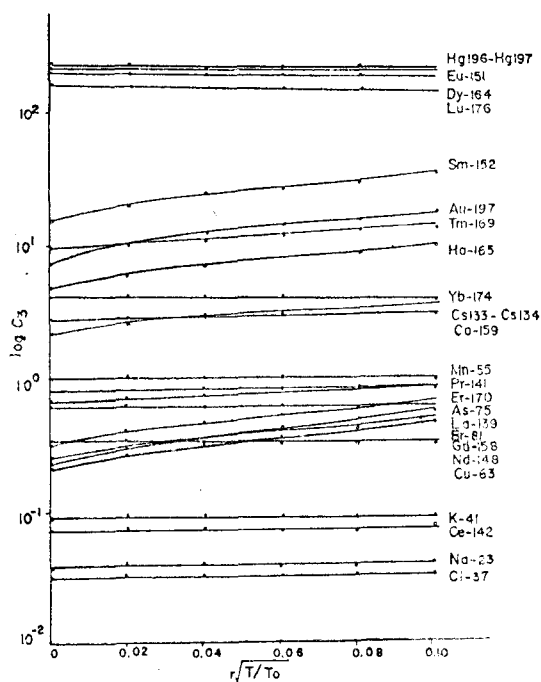

Fig. 1. Ratios of the effective cross sections relative to manganese *vs.* the neutron spectral index.

(5) The C_2 Value and the Counting Efficiency

The detector is a $3'' \times 3''$ Na I (Tl) crystal coupled to Dumont 6363 photomultiplier. It is placed in the center of a lead shield of $60 \times 60 \times 60$ cm³ internal dimensions and thick-

ness of 6 cm.

The disintegration rate of radioisotope formed during irradiation can be deduced from the experimental measurement of the photopeak counting rate. The absolute emission rate of a gamma-ray A_o is related to its photopeak counting rate A_p through the relationship

$$A_o = A_p/\varepsilon, \qquad (9)$$

where ε is the efficiency of the detector for that particular gamma-ray energy. From A_o the disintegration rate A is then calculated by the following relation

$$A = A_o/b, \qquad (10)$$

using the literature data on gamma-ray abundances b.

The photopeak counting rates of the calibrated standard sources are measured under a well defined geometrical condition. The efficiency ε is then determined by means of Eq. (9). This method requires the availability of standardized sources. The detector efficiency *vs.* gamma-ray energy was first plotted as shown on the curve 1 in Fig. 2
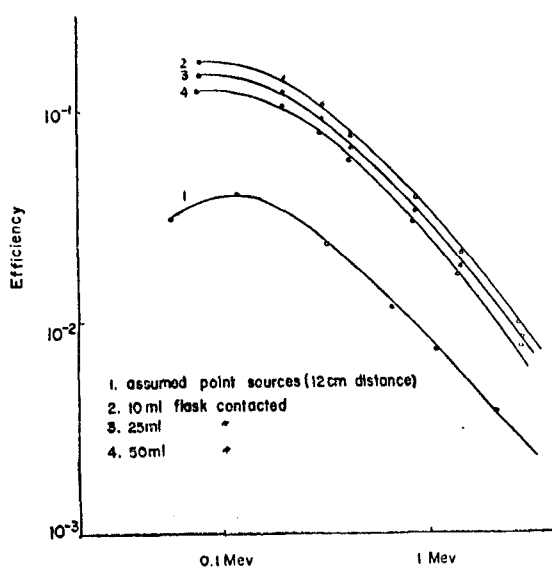

Fig. 2. Efficiencies in various geometries using $3'' \times 3''$ NaI(Tl)

using the calibrated standard sources of ^{241}Am, ^{57}Co, ^{203}Hg, ^{22}Na, ^{137}Cs, ^{54}Mn, ^{60}Co and ^{88}Y, which were supplied from the IAEA laboratory.

The distance between the sources and the detector was 12.0 cm. Each solution of ^{197}Hg, ^{51}Cr, ^{198}Au, ^{56}Mn, ^{24}Na, ^{60}Co and ^{65}Zn was prepared by irradiating the appropriate solutions of these elements. 100λ of each solution were pipetted on a polyethylene sheet and dried under an infra-red lamp. The sheet was folded to fit the counting condition of the IAEA standard sources as mentioned above. The absolute disintegration rates of the prepared samples were determined using the efficency curve 1 of Fig. 2.

The counting efficiencies at different geometries were determined as follows. 100λ aliquots of each irradiated soltion were pipetted to 10ml, 25ml and 50ml volumetric flasks and diluted to the volumes. The flasks were measured for the gamma-ray activities. Then the efficiencies at these geometries were determined using the absolute disintegration rate obtained as described above. The efficiencies were plotted *vs.* gamma-ray-energies as shown on the curve of 2,3 and 4 in Fig. 2. The relative counting efficiencies, *i.e.*, $C_2=\varepsilon/\varepsilon'$, are then easily calculated from these curves.

(6) Evaluation of the Photopeak Areas

When the peak was sufficiently well-defined, the method shown in Fig. 3 was used to inscribe the gamma peak in a triangle. The error of the triangle was found to be negligible. When peaks were overlapped a subtraction procedure[9] was adopted. It consists of determining the shape of the spectrum of a single gamma-ray at any given energy by interpolation between different spectra, obtained experimentally from isotopes emitting a single gamma-ray. This procedure
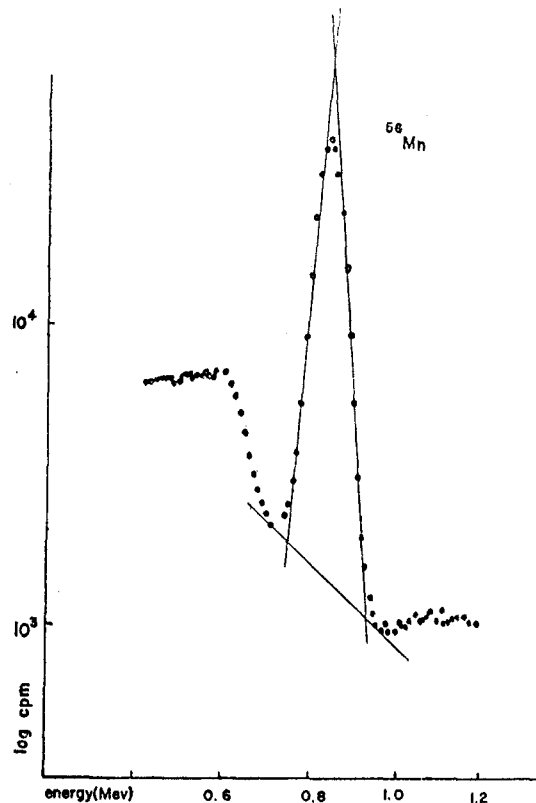

Fig. 3. Evaluation of the photopeak area

was used for example in the case of ^{60}Co where peaks at 1.17 and 1.33 Mev were overlapped.

(7) Effect of Coincidences Between Different Gamma-rays

A certain number of the isotopes studied emit two gamma-ray quanta in cascade. These gamma-rays can penetrate simultaneously into the detector and produce a coincidence peak. Therefore some loss will occur on the photopeak areas of the measured main peaks. A correction for this loss has been made by the method described by Heath[10] and Crouthamel[11] by the following equation

$$A_1\cdot\text{corr.} = A_1+A_s/P_2, \qquad (11)$$

where A_1.corr. is the corrected value of the photopeak area, A_1 peak area under one of the main peaks, A_s the area under the

Table 4. The K_1 values and the gamma-ray energies used for spectrometric determination

| Nuclide	γ-ray energy (Mev)	Half life	f	b	K_1
^{24}Na	1.37	15 h	1.00	1.00	0.414
^{38}Cl	2.16	38 m	0.245	0.47	5.55
^{42}K	1.52	12.4 h	0.0677	0.018	57.8
^{56}Mn	0.845	2.58 h	0.99	1.00	1.00
^{60}Co	1.33	5.27 y	1.00	1.00	1.06
^{64}Cu	0.511	12.8 h	0.691	0.38	4.36
^{76}As	0.559	26.4 d	1.00	0.43	3.14
^{82}Br	0.777+0.807	35.3 h	0.495	1.08	2.69
^{197}Hg	0.077+0.066	65 h	0.146×10^{-2}	0.999	2.50×10^3
^{198}Au	0.412	64.8 h	1.00	0.95	3.74
^{140}La	1.597	40.2 h	0.999	0.6	4.18
^{143}Ce	0.294	33 h	0.111	0.46	49.6
^{142}Pr	0.158	19.2 h	1.00	0.037	68.6
^{149}Nd	0.27(0.24+ 0.266+0.22)	1.9 h	0.0572	0.26	175
^{153}Sm	0.103+0.07	46.8 h	0.266	0.334	30.5
^{152}Eu	0.963	9.3 h	0.478	0.15	3.82
^{169}Gd	0.364	18 h	0.249	0.09	126
^{160}Tb	0.88+0.97	72 d	1.00	0.62	4.62
^{165}Dy	0.361	139.2 m	0.282	0.011	945
^{166}Ho	1.37	27.3 h	1.00	0.009	330
^{171}Er	0.308+0.294	7.52 h	0.148	0.91	22.2
^{170}Tm	0.084	127 d	1.00	0.033	92.3
^{175}Yb	0.396	4.2 d	0.318	0.06	163
^{177}Lu	0.208	6.8 d	0.026	0.061	1990
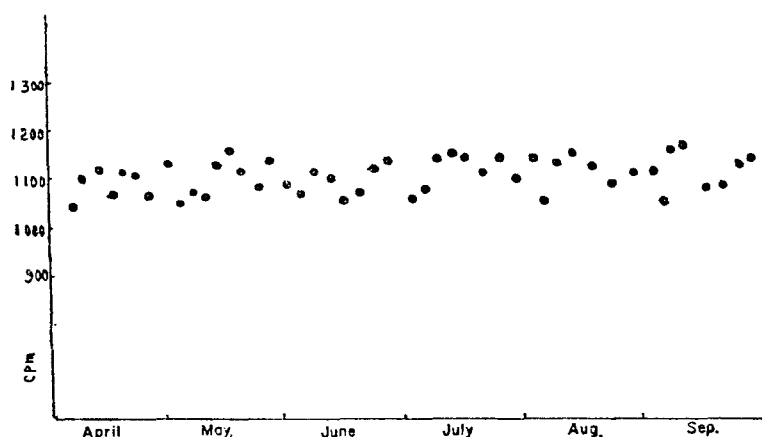
Fig. 4. Counting rates obtained from ^{56}Mn in iron wire under 0.84Mev. photopeak during 6 months of 1972

sumpeak due to the coincidence effect and P_2 the peak-to-total ratio of the another peak. The correction has been applied for some isotopes, *i.e.*, ^{60}Co, ^{38}Cl and ^{24}Na.

(8) Other Constants

Additional constants to be introduced for the single comparator method are K, S and

Table 5. Accuracy of the present method

Element	Amount added $\mu g (W_i)$	Isotope	W_d/W_i*	std. dev., %	Number of determination
Na	10.2	²⁴Na	1.09	1.52	3
Cl	10.5	³⁸Cl	1.10	2.3	4
K	20.3	⁴²K	1.40	4.5	5
Mn	10.3	⁵⁶Mn	0.982	1.2	5
Co	20.6	⁶⁰Co	1.02	2.5	3
Cu	25.6	⁶⁴Cu	0.851	3.7	3
As	17.3	⁷⁶As	1.05	5.0	4
Br	16.2	⁸²Br	0.931	2.3	3
Hg	10.1	¹⁹⁷Hg	0.862	1.6	5
Au	3.2	¹⁹⁸Au	1.03	1.4	3
La	8.23	¹⁴⁰La	0.875	1.2	3
Ce	8.56	¹⁴³Ce	1.01	1.0	3
Pr	8.23	¹⁴²Pr	1.10	2.5	3
Nd	8.95	¹⁴⁹Nd	0.89	5.0	4
Sm	1.02	¹⁵³Sm	1.19	4.2	3
Eu	1.09	¹⁵²ᵐEu	0.86	3.3	3
Gd	10.2	¹⁵⁹Gd	0.89	7.6	4
Tb	15.3	¹⁶⁰Tb	0.95	2.3	3
Dy	1.05	¹⁶⁵Dy	0.842	3.5	3
Ho	10.2	¹⁶⁶Ho	1.10	4.5	4
Er	10.3	¹⁷¹Er	1.20	3.2	4
Tm	12.5	¹⁷⁰Tm	0.81	4.5	5
Yb	13.5	¹⁷⁵Yb	1.46	3.2	5
Lu	14.5	¹⁷⁷Lu	1.25	4.5	5

*W_d Amount μg determined by the present method

D. K_1 remains constant and can be calculated from the data of literatures[12]. The calculated K_1 is given in Table 4. S_t and D depend on irradiation and decay times and are easily determined with a good accuracy.

3. Experiment

(1) Pneumatic Tube

The pneumatic tube which transfers a polyethylene rabbit to the core of the TRIGA MARK II reactor has a thermal flux of about 3.0×10^{12} n·cm⁻²·sec⁻¹ with a spectral index of 0.0565. As shown in Fig. 4 the variation in thermal flux shows little fluctuation during a period of several months.

(2) Procedure for the Determination of Each Element

The solution containing the known amount of the element was sealed in polyethylene vials. An accurately weighed iron wire was attached with Scotch tape on the outside wall of the each vial. The irradiations were performed in the pneumatic tube of TRIGA MARK II reactor. The irradiation time was varied from a few minutes to 1 hour. The photopeak counting rates of iron wire and the radioisotopes formed were measured after diluting the samples to the specified conditions.

The weights of the elements were calculated from the activities of iron wire and samples by Eq. (3) using the values of K_1, C_2, C_3, S_t and D. The calculated results were compared with the added amounts of the element as shown in Table 5.

(3) Determination of Rare Earths in Monazite

A 0.1-gr weight of the finely ground monazite(dried at 110°C) was accurately weighed into a platinum crucible fitted with a cover. The content was digested with 1 ml of concentrated sulfuric acid for 3 hours on a hot plate at ca. 250°C. When cool, the digested mass was quantitatively transferred with a jet of water into a 150 ml beaker containing ca. 60 ml of water. The solution was filtered into a 100 ml volumetric flask through a hardened filter (Whatman No, 542) using gentle suction. The clear filtrate was diluted to 100ml with water. 50 ml of the solution were loaded on a cation exchange resin column, Dowex, 50W ×8, 200-400 mesh, 6 cm long by 5 mm diameter, for the group separation of rare earths. The whole elements, except rare earths and thorium, were eluted out by eluting the column with 150ml of 1 N hydrochloric acid. The rare earths were then eluted with 60 ml of 3 N hydrochloric acid and the eluate was collected into a 100ml beaker. The solution was evaporated to near dryness under an infra-red lamp. The residue was digested with 1ml of concentrated nitric acid and the digested solution was evaporated to near dryness. The digestion and evaporation were repeated once more. Finally the residue was dissolved with distilled water. The solution was transferred quantitatively into a 10 ml volumetric flask and diluted to the volume. A 0.5-ml volume of the above sample solution was taken into a ca. 1 ml polyethylene vial. A weighed iron wire was attached on the outside wall of the vial. The vial was irradiated for 1 hour. The exact amount 250λ of the irradiated rare earth sample solution were loaded on the resin calumn for the individual separation of rare earths. The column was then eluted as

Table 6. The contents of the rare earths in Koksung monazite(%)

Element	Results of this work	Previous results[6]
La	12 (±4.5%)	10.0
Ce	25 (±1.0%)	28
Pr	2.3 (±1.5%)	2.3
Nd	10.2 (±5.2%)	9.9
Sm	1.6 (±7.5%)	1.6
Eu	0.082(±3.2%)	0.074
Gd	1.2 (±4.2%)	1.4
Tb	0.10 (±3.5%)	0.12
Dy	0.52 (±3.2%)	0.44
Ho	0.087(±3.7%)	0.084
Er	0.15 (±2.5%)	0.12
Yb	0.085(±3.5%)	0.083
Lu	0.0097(±4.2%)	0.0099

described under "Standardization of Rare Earths" in the previous report[6]. Each test tube was counted for 30 sec and an elution curve was obtained by plotting the activity of each test tube number. The eluted portions of each rare earth were collected into a 25 ml volumetric flask and the activity was counted with 400 channel analyzer at the respective gamma-ray-energies as described in Table 4. The content of each rare earth in monazite sample was calculated as described above under the section of "(2) Procedure". The results were compared with previous results in Table 6.

(4) Determination of the Mercury and Other Elements in a Standard Kale Powder

One gr of the standard powder was irradiated along with the iron wire for one hour. The irradiated powder was digested by adopting a modified Smith's method[14] as follows.

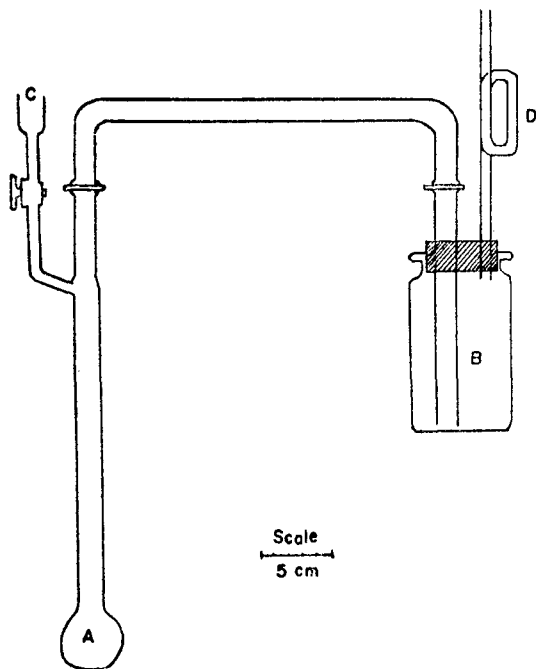The sample with 0.7 ml of the concentrated

Fig. 5. Apparatus for the destruction of biological samples.

sulfuric acid and 3 ml of concentrated nitric acid was heated in the flask A in Fig. 5. During heating more nitric acid was added. The total nitric acid added was 7 ml. The time needed for the digestion was 55-60 min. During the digestion mercury and bromine were distilled and gathered into a bottle which contained 30 ml of 10 N NaOH solutton. Recoveries of both elements were determined by the tracer work, *i.e.*, by following these procedures with the the radioactive tracers of mercury and bromine.

It was also found by the similar tracer method that the arsenic was quantitatively remained in the reaction flask[14]. Recovery of bromine was 100% and that of mercury was more than 95%.

10 N NaOH solution containing mercury and bromine was transferred into 50 ml volumetric flask and diluted with the distilled water to the volume. The gamma-ray spectrometry was performed for the activity

of bromine using a 400 channel analyzer which was connected to $3''\times3''$ Na I (Tl) crystal. After counting bromine the distilled solution in the flask was quantitatively transferred to a 500 ml beaker, 20 mg of mercury carrier were added and adjusted to pH 8-9 with 6N hydrochloric acid solution. The precipitation of Hg was then carried out with the thioacetamide from hot solution[15]. The precipitation was allowed to settle for at least 2 hours and centrifuged. The precipitate was dissolved in a saturated Na_2S solution, transferred into 50 ml volumetric flask and finally counted with the analyzer.

The digested sample solution in a round bottomed flask was transferred into a 50 ml volumetric flask and diluted to the volume with distilled water. 25 ml of the solution were loaded on a cation exchange resin column (Dowex 50 ×8, 50-100 mesh, 15 cm×6 mm) and eluted with 10 ml of water and with 25 ml of 0.1 N HCl for the quantitative separation of arsenic. The flow rate was 1 ml/min. The eluate in the fraction of 60 drops was taken into a test tube by means of a fraction collector. The activity of each tube was measured for 1 min with a well type scintillation counter and was plotted against the number of the test tube.

The column was eluted with 200 ml of 0.45 N HCl for the quantitative separation of Na and K. The alkaline earth portion was then separated into a group by eluting the column with 100 ml of 1 N HCl. Each portion was collected into 50 ml volumetric flask after reducing the volume by heating if necessary.

Manganese and copper can be determined simultaneously in the eluate of 1 N hydrochloric acid solution, without interference from the whole alkaline earths, which are also eluted in this portion. If necessary, rare earths could be eluted with 3 N HCl solu-
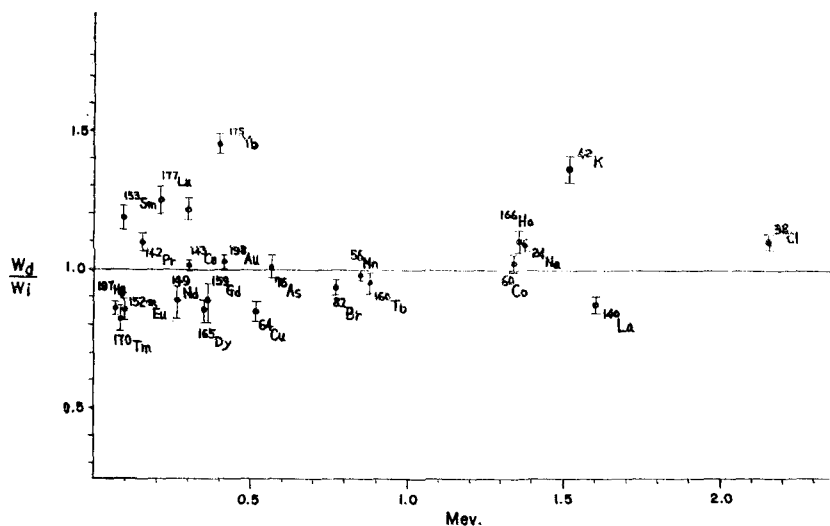
Fig. 6. Accuracy of the present method *vs.* the the gamma ray energy used for the spectrometric determination.

tion[6,16] but omitted in this work.

Radiochemical purities of mercury. bromine, arsenic, copper, manganese, sodium and potassium which are contained in kale sample were confirmed by checking the half lives and gamma-ray energy spectra.

The content of each element in kale powder was calculated as described above under the section of "(2) Procedure". The results are compared with the reported results in Table 7.

4, Results and Discussion

In order to verify the feasibility of the present method, the known amounts of various elements were analyzed. As shown in Table 5, this is indicated in terms of the ratio of W_d to W_i, where W_i is the amount of each element added and W_d is the amount which is determined by the present method. The standard deviations of the measurements for each element W_d are also shown.

Fig. 6 shows the results as a function of the gamma-ray energy of the photopeak measured. This method of presenting the results is particularly useful in visualizing eventual systematic variations arising from errors in

Table 7. Analytical results of of the standard kale powder(p. p. m.)

Element	Results of this work	Previous results[21]
Na	2488 (±4.2%)	2594±617
K	15700(±7.4%)	24630±1,218
Mn	12.0 (±5.0%)	14.9±1.8
Cu	4.81 (±4.3%)	4.81±0.735
As	0.16 (±6.2%)	0.127±0.029
Br	25.2 (±5.5%)	24.3±1.6
Hg	0.131(±11%)	0.150±0.008

the calibration of detector, measurement of effective active activation cross section, etc. The precision in these data obtained by the present method is quite satisfactory, with the exception of potassium and ytterbium. Therefore, within suitable range of concentration, one could hopefully determine simultaneouly as many elements as about twenty with the accuracies in the neighborhood of ±20% for most elements that are analyzed in this work.

On the determination of the ratio of W_d to W_i in the Table 5 the 1/v-law was assumed for absorption cross section of all elements

besides europium and lutetium. The g values used for ^{151}Eu and ^{176}Lu are 0.950 and 2.00 respectively[4]. Because the g value has not been reported for ^{174}Yb, this value was evaluated according to Appendix 1("do it yourself") of AECL-1101[4] using the resonance parameters of BNL-325[20]. According to this calclation the g value of ^{174}Yb was however found to be about 1 which could not explain such a large discrepancy of the ratio of W_d to W_i from unity

If the 1/v-law is assumed for the absorption cross section of lutetium which corresponds to $g=1$, the ratios of W_d to W_i are much deviated from unity by factor of 2.50. Only the data given in AECL-1101 were used for the values of g factors because no other source is available for these data at the present time (C.H. Westcott, private communication). If more recent values are available for g factors, it may be possible that the errors could be further reduced.

The results of rare earth contents in monazite are in good agreement with our recent values[6] obtained by a modified method of Girardi[1]. The analytical results of fourteen rare earth elements in a monazite sample and seven elements in kale powder are given in Table 6 and 7.

The potassium content in kale powder appears lower, by the factor of 1.6, than the reported value[21]. It has been reported by several workers that when potassium is determined by neutron activation analysis, its contents are found to be lower in comparison with the data determined by other method, such as spectrometry or fluorimetry[21]. However, it is rather difficult to assume that an error in the nuclear data associated with ^{42}K nuclide will result in such a large discrepancy in the analytical results for potassium. All other analytical results on the

elements in kale powder are in good agreement with the values determined by other methods.

There are some uncertainties on the S_o values as shown in Table 3. It is, however, found that the difference between the S_o values can not significantly affect the values of the effective activation cross sections with the exception of arsenic and samarium.

As described above under the section of "Spectral index", the advantage of the present method is that the error from the discrepancy in spectral indices can be greatly reduced by the factor of 10 when compared with other method which use gold as a comparator. Simple measurements of Cd ratios of manganese or gold can give the spectral indices $r\sqrt{\dfrac{T}{T_o}}$ in various irradiation sites according to Eq. (6). Using these values the C_3 values, $i.e.$, $\dfrac{\hat{\sigma}}{\sigma'}$ values, can be found in Fig. 1. The weight of element contained can then be simply calculated by Eq. (3) using the C_3 values obtained as well as other values indicated. The present method can thus be used routinely for most elements that are analyzed within accuracies of ±20, which is comparable with the other methods.

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