

A Single Comparator Method Using Reactor Neutron and Its Errors

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원자로 중성자를 이용한 단일 비교체법과 오차

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Abstract

A single comparator method with its accuracy has been studied for determining multielement by reactor neutron activation analysis. Spectral index at the irradiation position of each sample was determined using two flux monitors of Au and Co, one of which was used as a single comparator. The uncertainties of nuclear data related to the method were investigated for 18 elements and the error of the analytical result due to the uncertainties of nuclear data related is found to be less than 6%. The analytical results of 4 USGS reference samples agree well within 15% deviation with the results evaluated by USGS.

초 록

원자로 중성자 방사화 분석법으로 다중 원소들을 분석하기 위한 단일 비교체법을 그에 따른 오차와 함께 조사하였다. 각 시료의 조사 위치에서 스펙트럴 지수는 Au와 Co 두개의 모니터를 이용하여 결정하였으며 이중 한개는 단일 비교체로 사용하였다. 18개 원소에 대하여 이 방법에 사용된 핵 자료의 불확실도를 조사하였으며, 이 값들에 의한 분석 결과의 오차는 6% 이하 이었다. 4개의 USGS 표준시료의 분석 결과는 USGS에서 평가한 분석결과와 15%의 편차 이내에서 잘 일치하였다.

1. Introduction

Neutron activation analysis is suitable for the multielement determination. The relative method

is convenient for the determination of one or two elements. But applying this method to the determination of multielement is cumbersome and time-consuming. Different approaches have been suggested to solve the problem; the use of

synthetic multielement standard, standard reference material[1] or single comparator method [2-13]. In the first approach, the preparation of multielement in one solution involves the problems of stability of individual ions during storage and adsorption of elements on container wall. [14-16] Although the use of standard reference method is convenient to simulate conditions of irradiation, cooling and counting of samples, it is not easy to have proper reference materials and the benefit is impaired by uncertainties in the analytical data of those.

Single comparator method is based on Westcott's effective activation cross section[17,18] and needs only one standard element as a single comparator instead of many individual standards. The method is, therefore, suitable for the determination of multielement in large series of samples and particularly for the case in which relative variation of trace concentrations are of primary analytical interest. Several methods have been suggested to determine the effective activation cross section such as cadmium ratio method [2,3,7,8] or two monitors method[4-6, 9-13]. In the cadmium ratio method, the cadmium ratios of individual elements have to be determined prior to the analysis of samples. This is not to be a simple task and implies large systematic error stemmed from the neutron flux dip near the cadmium cover. In the two monitors method, the effective activation cross sections of individual elements are calculated from the activity ratio of two monitors which are irradiated with sample, either one of which can be used as a single comparator. So the error involved in determining each element comes mainly from the uncertainties in the related nuclear data. Efforts to determine nuclear data have resulted in a large number of data accurate enough to be applied to the single comparator method without serious error.

This paper presents a single comparator method

using two monitors of gold and cobalt, together with uncertainties in the related nuclear data and the experimental data. The accuracy of the method is also discussed by analyzing the well known standard materials.

2. Single Comparator Method

When a sample is irradiated with a known amount of the single comparator (w^*), the photopeak counting rate ratio, Ap_i/Ap^* , of a nuclide in the sample to a single comparator nuclide leads to the evaluation of the weight of the element of concern (w_i).

$$w_i = w^* \frac{Ap_i}{Ap^*} \cdot \frac{R}{C_1 \cdot C_2 \cdot C_3 \cdot C_4},$$

$$\text{where } C_1 = \frac{f_i \cdot M^*}{f^* \cdot M_i}, \quad C_2 = \frac{b_i}{b^*}, \quad C_3 = \frac{\epsilon_i}{\epsilon^*},$$

$$C_4 = \frac{\hat{\sigma}_i}{\hat{\sigma}^*}, \quad R = \frac{(1 - e^{-\lambda^* t_1}) e^{-\lambda^* t_2}}{(1 - e^{-\lambda_i t_1}) e^{-\lambda_i t_2}}$$

$\hat{\sigma}$: effective activation cross section(barn),

ϵ : detection efficiency of a detector for a given gamma-ray energy,

b : gamma-intensity of a given gamma-ray,

f : fractional isotopic abundance of a target nuclide,

M : atomic weight of an element(g),

λ : decay constant (sec^{-1}),

t_1 : irradiation time (sec),

t_2 : cooling time (sec).

C_1 and C_2 are absolute constants and can be found in the literature [19]. C_3 and C_4 vary, respectively, with the properties of the detector used as well as the detection geometry and with the energy spectrum of neutron at the irradiation site, but are apparently constant with respect to a definite set of experimental condition. C_3 can be determined for each nuclide for a given experimental condition with a set of well known gamma-ray standard sources. C_4 can be determined from the activity ratio of two monitors irradiated with each sample and the nuclear data related.

With photopeak counting rate ratio of a nuclide in a sample to a single comparator nuclide and the values mentioned above, the right hand side of eq. (1) can be calculated and the concentration in a sample is, therefore, evaluated.

Effective activation cross section

The effective activation cross section, $\hat{\sigma}$, of a nuclide, which is not constant but a function of the neutron energy spectrum, is defined by Westcott [17, 18].

$$\hat{\sigma} = \sigma_0 (g + r \sqrt{T/T_0}) S_0 \quad (2)$$

where σ_0 = activation cross section for 2,200m/sec neutron

$$g = \hat{\sigma}_m / \sigma_0,$$

$$S_0 = (2 / \sqrt{\pi}) \times I_0' / \hat{\sigma},$$

$$\hat{\sigma}_m = \hat{\sigma} \text{ at } r \sqrt{T/T_0} = 0,$$

I_0' = resonance integral with an effective lower energy limit μkT and with a $1/v$ term excluded;

$$r \sqrt{T/T_0} = \text{spectral index.}$$

The effective activation cross section for a given irradiation position of each sample can be calculated when the spectral index is determined. Spectral index for each sample can be determined by irradiating two monitors.

$$r \sqrt{T/T_0} = (g_1 \sigma_{01} - g_2 \sigma_{02} R_{12}) / (S_{02} \sigma_{02} R_{12} - S_{01} \sigma_{01}) \quad (4)$$

where $R_{12} = \hat{\sigma}_1 / \hat{\sigma}_2$, which may be easily determined by the activity ratio of monitors 1 and 2. [13] The related nuclear data of σ_0 , I_0 and g can be found in the literatures [19-23]. C_4 values for all nuclides of interest can be, therefore, calculated for each samples by Eq. (2).

Detection efficiency calibration

The efficiency calibration of a HPGe detector is done by the empirical multi-point method using SPECTRAN-F computer code [24]. The detection efficiency, ϵ , is represented by a simple polynomial function of the form;

$$\log \epsilon = \sum_i b_i (\log E_\gamma)^i \quad (5)$$

Two such equations are used - one for the low

energy efficiency and another for the high energy efficiency - with a single crossover point in common to both. The appropriate value for the crossover energy, E_{cr} , depends on the actual detector. In this work, a Eu-152 source was used for high energy efficiency fitting. For low energy efficiency fitting, three radioactive sources such as Am-241, Ba-133 and Eu-152 were used because there is no single source emitting several low energy gamma-ray of interest. 122 keV of Eu-152 was used as the crossover energy.

Other nuclear data relevant to the method

The absolute gamma intensities of the nuclides used for the evaluation of C_2 values in Eq. (1) are given with uncertainties in the literature [19]. A careful correction for the electron conversion rate is necessary especially for low energy gamma-rays (<200 keV). The conversion rates are also available in the literature.

Other data relevant to the method such as atomic weight (M), fractional isotopic abundance of the nuclide (f), half life ($t_{1/2}$) can be easily found in the same literature.

Monitors

In principle, any element can be used as a monitor (or a single comparator) if the nuclear data of the chosen nuclide is well known. Au and Co are a pair of the most often used monitors. The commercially available alloys of Au-Al and Co-Al are convenient to use for this purpose. In this work, the above two monitors were prepared, respectively, as follows;

An amount of 10-100mg of each metal (Johnson and Matthey, 'spec. pure') was accurately weighed, dissolved in a hot mixture of 2ml nitric acid and 4ml of hydrochloric acid, evaporated nearly to dryness by heating and finally diluted to 50ml in a volumetric flask by distilled water. From this solution, the amount of 100 μ l was pipetted onto polyethylene sheet and dried by an infrared lamp. The polyethylene sheet was wrapped and inserted into a small polyethylene

bag.

3. Application of the method

To certify the accuracy of the single comparator method, four USGS reference materials such as SGR-1, SCo-1, SDC-1 and RGM-1 were analyzed as follows;

About 20~50mg of each sample was weighed and sealed in a quartz tube. The samples were irradiated with the two monitors of Au and Co at the Rotary specimen rack of TRIGA Mark III reactor for 9 hours. After irradiation, the samples were transferred into small polyethylene vials and counted by a HPGe detector (CANBERRA, active volume=70cc, FWHM at 1.332MeV of Co-60=1.9keV) connected with a 4096 channel MCA(CANBERRA Model 90). Two gamma-ray spectrums were used in the analysis of each sample; one for medium-lived isotopes (2 days cooling, 1000 sec. counting) and the other for long-lived isotopes (4 weeks cooling, 3000 sec. counting). The photopeak counting rate of each nuclide in the gamma-ray spectrum was calculated with SPECTRAN-F computer code[24]. The content of each element(ppm) in a sample was calculated from the experimental data such as photopeak counting rate, detection efficiency (ϵ), sample weight(w) and times of irradiation (t_1), cooling(t_2) and the nuclear data using the single comparator computer code which was developed for this purpose.

The analytical results are given in Table 1 with the others[25-29]. The present work is represented by "SCM". The values of Katz and Grossmann [25], represented by "RSM", have been obtained by the standard reference method of instrumental neutron activation analysis. Among the values represented by "Others" in Table 1, the values for Fe, Rb, Sc, Zn, As, K, Na and Mn had been obtained by X-ray fluorescence [26], those for Cr and Co by photographed

optical emission spectrometry[27], those for Sb and Hf by instrumental neutron activation analysis[28] and those for U and Th by delayed neutron technique [29]. The values obtained from two kinds of neutron activation analysis, of which one is from the single comparator method and another from standard reference method, agree well within 10% variation except for some elements. The values obtained by other methods have large variations from those obtained by neutron activation analysis. In case of Cs, Cr, Rb and Ta, there are more than 40% variations between the two methods.

4. Discussion

As shown in Table 1, the accuracy of the single comparator method is as good as that of the standard reference method as far as the multielement analysis of large series of samples is concerned. In the standard reference method, only the elements whose contents are accurately known in the standard reference material can be analyzed and thus the accuracy depends mainly on that of the standard reference material used. Whereas, any element in a sample can be determined by the single comparator method if the corresponding photopeak is detected and the related nuclear data are well known. In the related nuclear data the largest uncertainties are frequently found in σ_0 and I_0 , therefore in C_4 . Uncertainties of C_1 and C_3 are less than 0.5% and 2%, respectively, and C_3 can be determined within 1.5% uncertainty for a given set of experimental conditions. In order to illustrate the uncertainties in the related nuclear data in detail, those of σ_0 , I_0 , $t_{1/2}$ and b were investigated for atomic numbers 11-80 and 90,92. Among them, 9 nuclides were excluded because they can hardly be analyzed by this method. The uncertainties in the half lives are less than 0.5 % for most of the nuclides. The uncertainties in

Table 1. The Analytical Results of USGS Standard Materials and The Comparison with Others' (ppm)

Element	SGR-1				SCo-1				SDC-1				STM-1			
	SCM	RSM	Others		SCM	RSM	Others		SCM	RSM	Others		SCM	RSM	Others	
Sb	3.10±0.82	3.05±0.29	3.70±0.31		2.23±0.63	2.40±0.22	2.51±0.13		0.37±0.91	0.36±0.16	0.53±0.01		1.72±0.17	1.88±0.5	1.67±0.06	
Cs	5.08±0.74	4.61±0.36	—		7.16±0.85	6.82±0.68	—		3.90±0.40	3.85±0.24	—		1.60±0.24	1.47±.79	—	
Cr	29.9±5.4	32.5±3.2	20.9±3.2		71.4±5.7	75.3±4.4	59.0±4.5		74.1±5.8	77.4±2.7	67.4±2.9		68.5±3.3	74.1±3.6	2.5±0.33	
Co	10.9±0.6	10.3±0.6	9.96±0.43		10.3±0.79	9.66±0.20	9.30±0.86		14.9±0.7	16.6±0.9	20.3±1.7		0.32±0.09	0.33±0.06	—	
Eu	0.59±0.08	0.52±0.07	—		1.40±0.26	1.24±0.06	—		1.69±0.18	1.86±0.04	—		4.00±0.33	4.03±0.07	—	
Hf	1.46±0.36	1.31±0.26	1.41		4.41±0.62	4.38±0.30	4.73±.17		8.21±0.70	8.14±0.50	8.30±0.04		25.2±1.0	26.4±0.5	28.9±1.6	
Fe (%)	1.69±0.10	1.88±0.09	2.24±0.04		2.81±0.16	3.36±0.11	3.66±0.03		4.87±0.16	4.79±0.13	5.04±0.07		3.56±0.15	3.38±0.73	3.76±.07	
Rb	58.8±20.0	66.5±9.1	92.2±0.9		70.3±19.9	68.9±15.9	122.0±1.0		69.3±22.6	67.9±5.16	129.0±3.5		61.5±24.5	56.0±3.4	113.0±0.7	
Sc	4.41±0.28	4.78±.193	—		10.8±0.7	11.4±0.4	19.3±2.1		14.4±0.6	15.8±0.5	19.0±1.60		0.61±0.05	0.68±0.02	—	
Th	4.42±0.51	4.86±.05	7.66±1.69		9.36±0.71	10.5±0.3	9.52±.95		14.5±1.3	14.2±0.2	11.4±1.1		38.3±1.8	38.8±1.6	26.6±1.1	
Zn	70.4±11.3	—	95.9±9.7		100±16	—	116±2		97.5±9.0	—	105±5		245±19	—	260±8	
U	5.27±1.06	—	5.60±.170		2.85±0.84	3.00±0.70	3.15±0.13		3.00±0.70	—	3.12±0.12		8.41±0.9	—	9.10±0.27	
Sm	2.39±0.17	—	—		4.70±0.27	—	—		6.16±0.36	—	—		10.9±0.7	—	—	
As	73.4±3.5	—	74.5±0.91		9.92±0.91	—	10.8±2.6		18.9±1.0	—	—		21.0±1.4	—	—	
K (%)	1.39±0.50	—	1.42±0.04		2.25±0.29	—	2.21±0.03		2.63±0.36	—	2.72±0.10		3.63±0.76	—	3.55±0.01	
Na(%)	1.88±0.03	—	1.97±0.05		0.57±0.02	—	0.54±0.02		1.41±0.05	—	1.47±0.22		6.20±0.17	—	6.62±0.10	
Mn(%)	0.039±.001	—	0.033±.001		0.040±.001	—	0.047±.001		0.083±.002	—	0.092±.001		0.184±.005	—	0.197±.001	
La	19.9±0.78	—	—		31.8±0.78	—	—		31.8±0.87	—	—		13.4±0.25	—	—	

*, SCM and RSM represent single comparator method (this experiment) and reference standard method (ref. 25), respectively.

**, The data in the third column of each sample are obtained from ref. 26-29.

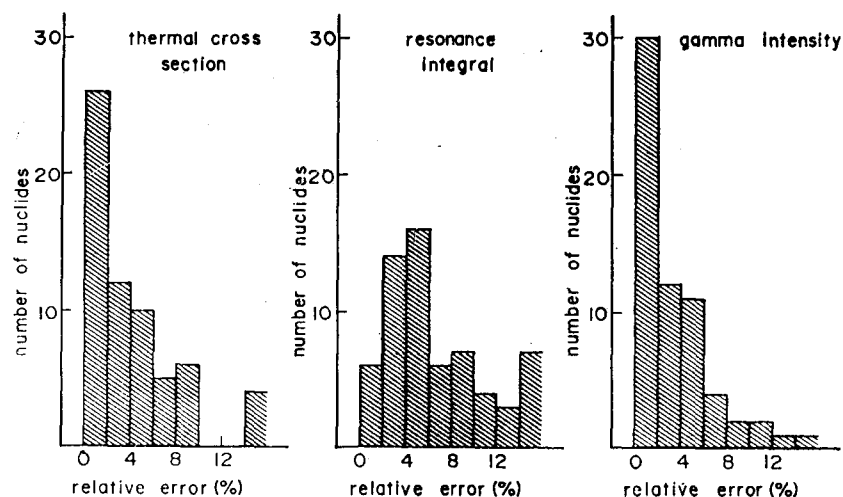


Fig. 1. Relative Errors of Nuclear Data of 63 Nuclides

σ_0 , I_0 and b are shown in Fig. 1. The uncertainties of σ_0 values are within 2% for 40% of the nuclides and within 9% for 94%. Those of b values are within 2% for 47% of the nuclides and within 10% for 94%. As for the resonance integral, the uncertainties are relatively large compared to those in σ_0 and b . About 57% of the nuclides have the uncertainties within 6% and 89% within 14%. These uncertainties contribute to the errors of the effective activation cross sections only by the factor of $1/20 \sim 1/40$ as neutron energy spectrum at the Rotary specimen

rack of TRIGA Mark III reactor is considered.

The errors of the analytical results obtained by the single comparator method are calculated from the uncertainties of the related nuclear data of σ_0 , I_0 , b , f , $t_{1/2}$ and the experimental data of w , ϵ , A_p by the error propagation method. The major sources of the errors in the analytical results are σ_0 , ϵ and A_p . The uncertainties in σ_0 and ϵ are fixed at present. Uncertainty in A_p depends on the matrix effect of sample, time scales of irradiation, cooling, measuring, and the type of detector used. The uncertainties in A_p could, therefore, be reduced less than 1.5% in this experiment. Finally to show the error stemmed only from the uncertainties in the related nuclear data, the errors in the contents of 18 elements in Table 1 are calculated only with the uncertainties in the related nuclear data and are shown in Table 2. They are less than 6% for all the elements. These values are the minimum errors which arise in the single comparator method, and can be reduced further if the more accurate values of nuclear data come.

Table 2. The Minimum Error Occurring in The Elemental Contents Analyzed by The Single Comparator Method (quadratic summation of all uncertainties of the nuclear data used)

Nuclide used	Error(%)	Nuclide used	Error(%)
Sb-124	3.8	Pa-233(Th)	5.7
Cs-134	5.6	Zn-65	2.9
Cr-51	2.0	Np-239(U)	5.1
Co-60	1.2	Sm-153	5.5
Eu-152	4.5	As-76	5.4
Hf-181	2.8	K-42	2.8
Fe-59	4.9	Na-24	3.4
Rb-86	2.9	Mn-56	1.5
Sc-46	6.0	La-140	1.3

References

1. R.A. Nadkiri, G.H. Morrison, J. Radioanal.

- Chem., 43, 347 (1978)
2. J.I. Kim, H.J. Born, J. Radioanal. Chem., 13, 427 (1973)
3. R. Vanderlinden, F. DeCorte, J. Hoste, J. Radioanal. Chem., 20, 729 (1974)
4. F. Girardi, G. Guzzi, J. Pauly, Anal. Chem., 37, 1085 (1965)
5. F. DeCorte, A. Speecke, J. Hoste, J. Radioanal. Chem., 3, 205 (1969)
6. P. Lievens, R. Cornelis, J. Hoste, Anal. Chim. Acta, 80, 97, (1975)
7. N. Yamura, Radiochem. Radioanal. Letters, 18, 135 (1974)
8. F. DeCorte, A. Speecke, J. Hoste, J. Radioanal. Chem., 9, 9 (1971)
9. N.A. Dubinskaya, L.L. Pelekis, J. Radioanal. Chem., 9, 61 (1971)
10. A. Simonits, F. DeCorte, J. Hoste, J. Radioanal. Chem., 24, 31 (1975)
11. D.M. Linekin, J. Appl. Radiation Isotopes, 24, 343 (1973)
12. M. Heutebise, F. Montology, J.A. Libcowitz, Anal. Chem., 45, 47 (1973)
13. J.I. Kim, J. Radioanal. Chem., 63, 121 (1981)
14. A.A. Al-Sibbai, A.G. Fogg, Analyst, 98, 723 (1973)
15. A.W. Struempfer, Anal. Chem., 45, 2251 (1973)
16. A.D. Sherendriker, V. Dharmarajan, H. Walermerrick, P.W. West, Anal. Chim. Acta, 84, 409 (1976)
17. C.H. Westcott, AECL-1106, 1960.
18. C.H. Westcott, W.H. Walker, T.K. Alexander, 2nd Intern. Conf. Peaceful Uses of Atomic Energy, 16, 70, Geneva, 1958.
19. E. Browne, J.M. Dairiki, R.E. Doebler, 'Table of Isotopes', 7th edition, ed. by C.M. Lederer, V.S. Shirley, publ. by John Wiley & Sons, Inc., 1978.
20. E.M. Gryntakis, J.I. Kim, Radiochim. Acta, 22, 128 (1975)
21. J.I. Kim, E.M. Gryntakis, H.J. Born, Radiochim. Acta, 22, 20 (1975)
22. S.F. Mughabghab, M. Divadeenam, N.E. Holden, 'Neutron Cross Section', Vol. 1, Part A, publ. by Academic Press, 1981.
23. S.F. Mughabghab, 'Neutron Cross Section', Vol. 1, Part B, publ. by Academic Press, 1984.
24. Canberra, 'Technical Reference Manual for SPECTRAN-F, Version 2', Canberra Industries Inc., U.S.A., 1981.
25. A. Katz, L. Grossman, 'Description and Analysis of Eight New USGS Rock Standards', compiled and ed. by F.J. Flanagan, pp. 49-57, United States Government Printing Office, 1976.
26. B.P. Fabbi, L.F. Espos, *ibid*, pp. 89-93.
27. F.G. Walthall, A.F. Dorzopf Jr., F.J. Flanagan, *ibid*, pp. 99-115.
28. L.J. Schwarz, J.J. Rowe, *ibid*, pp. 67-70.
29. H.J. Millard Jr., *ibid*, pp. 61-70.