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Determination of Niobium by Photon-Activation Analysis Based on Internal-Reference Method*1

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The internal-reference method proposed previously has been applied to the photon-activation analysis of niobium using molybdenum as the reference element. For the determination of niobium, ^{92m}Nb produced by the (γ,n) reaction was utilized and ^{95m}Nb or ^{96}Nb activities coming from molybdenum by the (γ,p) processes were used as reference. A series of molybdenum and niobium mixtures with known compositions were irradiated by bremsstrahlung photons with a maximum energy of 17 MeV for an hour. After niobium activities were separated chemically, their γ-ray spectra were measured with a lithium-drifted germanium detector. A good proportionality was obtained between the activity ratio, R_{A_0}, and the weight ratio, R_W. Niobium down to 50 μg can be determined with a relative error within $\pm 3\%$ under the present experimental conditions.

Thermal neutron activation analysis for niobium has been studied by several workers.[1-3] Kim and

*1 Study on the Activation Analysis using Internal-Reference Method. XII., Part XI: Y. Oka, T. Kato and Y. Konami, *Bunseki Kagaku*, **18**, 971 (1969).

1) C. K. Kim, "Production and Use of Short-lived Radioisotopes from Reactors," I.A.E.A., 1963, Vol. II, 73.

Meinke,[2] and Verbeek[3] measured the 16.6 KeV X-ray of 6.3 min-^{94m}Nb produced by (n,γ) reaction. Rapid separation is necessary in their methods, and low energy of the X-ray makes the measurement difficult. Athavale *et al.*[4] have taken advantage of the reaction ^{93}Nb(n,α)^{90}Y induced by fast neutrons in a pile. Tomita and Saisho[5] used the ^{93}Nb(p,n)^{93m}Mo reaction for the same purpose.

In the present paper we describe a method of photon-activation analysis using molybdenum as the internal-reference element.

Experimental

Materials and Irradiation. Niobium, in the form of metallic powder of analytical-reagent grade was supplied from Johnson Mathey Co. Molybdenum was metallic powder of 99.9% purity from Wako Pure Chemical Industries, Ltd.

A linear electron accelerator of the Tohoku University and that of the Japan Atomic Energy Research Institute were the bremsstrahlung sources.

0.1—1.5 g of each element or mixtures of known compositions were sealed either in small quartz or pyrex tubes with an internal diameter of 6 mm. They were placed in a target holder immediately behind the converter*[2] and irradiated. Typical irradiation was performed for an hour.

Measurement of Radioactivity. For measurements of γ-ray spectra a lithium-drifted germanium detector with a sensitive volume of 36 cm^3 coupled to a TMC 1024-channel pulse-height analyzer was used. Nuclide identification was made by energies and decay curve analysis of the specified γ-ray photopeaks.[6]

Separation of Niobium. Niobium activities were separated from irradiated samples with anion exchange

TABLE 1. NUCLEAR REACTION AND MASS THRESHOLD

Target nuclide (abundance)	Reaction type	Product nuclide	Threshold energy (MeV)	Coulomb barrier (MeV)	Half-life	γ-Ray energy (MeV)		
^{93}Nb(100%)	(γ, n)	^{92m}Nb	8.95[7]		10.16d	0.90	0.934	1.83
	(γ, 2n)	^{91m}Nb	17.18[7]		62d	1.21		
	(γ, 3n)	^{90}Nb	28.78		14.6 hr	0.142	0.511	1.14
						1.30	2.18	2.32
^{92}Mo(15.16%)	(γ, p)	^{91m}Nb	7.45[7]	6.72	62d	1.21		
	(γ, pn)	^{90}Nb	19.65	6.73	14.6 hr	0.142	0.511	1.14
						1.30	2.18	2.32
	(γ, d)	^{90}Nb	17.28[7]	6.71	14.6 hr	0.142	0.511	1.14
						1.30	2.18	2.32
^{94}Mo(9.12%)	(γ, pn)	^{92m}Nb	17.45	6.70	10.16d	0.90	0.934	1.83
	(γ, d)	^{92m}Nb	15.09[7]	6.66	10.16d	0.90	0.934	1.83
^{96}Mo(16.50%)	(γ, p)	^{95m}Nb	9.53[7]	6.64	90 hr	0.235		
	(γ, p)	^{95}Nb	9.30[7]	6.64	35d	0.765		
^{97}Mo(9.45%)	(γ, p)	^{96}Nb	9.18[7]	6.62	23.35 hr	0.459	0.569	0.778
						0.811	0.851	1.092
						1.200	1.499	
	(γ, pn)	^{95m}Nb	16.44	6.64	90 hr	0.235		
	(γ, d)	^{95m}Nb	14.13	6.61	90 hr	0.235		
	(γ, pn)	^{95}Nb	16.20	6.64	35d	0.765		
	(γ, d)	^{85}Nb	13.89[7]	6.61	35d	0.765		
^{98}Mo(23.75%)	(γ, p)	^{97}Nb	9.79[7]	6.59	72 min	0.655		
	(γ, pn)	^{96}Nb	17.60	6.62	23.35 hr	0.459	0.569	0.778
						0.811	0.851	1.092
						1.200	1.499	
	(γ, d)	^{96}Nb	15.60[7]	6.59	23.35 hr	0.459	0.569	0.778
						0.811	0.851	1.092
						1.200	1.499	
^{100}Mo(9.62%)	(γ, pn)	^{98}Nb	17.97	6.58	51 min	0.720	0.787	1.16
						1.44	1.52	1.68
						1.88	1.93	
	(γ, d)	^{98}Nb	15.81[7]	6.55	51 min	0.720	0.787	1.16
						1.44	1.52	1.68
						1.88	1.93	

2) C. K. Kim and W. W. Meinke, *Anal. Chem.*, **35**, 2135 (1963).

3) A. A. Verbeek, *Anal. Chim. Acta*, **33**, 131 (1965).

4) V. T. Athavale, H. B. Desai, S. Gangadharan, M. S. Pendharkar and M. Sankardas, *Analyst*, **91**, 638 (1966).

5) I. Tomita and H. Saisho, *Nature*, **195**, 1189 (1962).

*2 3 mm thick platinum plate (Tohoku University linac) or 2 mm thick platinum plate (JAERI linac).

6) "Table of Isotopes" was used for specification: C. M. Lederer, J. M. Hollander and I. Perlman, "Table of Isotopes," 6th Ed., John Wiley & Sons, Inc., New York (1967).

7) C. Maples, G. W. Goth and J. Cerny, 'Nuclear Reaction *Q*-Values,' "Nuclear Data," K. Way Ed., Sec. A, Vol. 2, Academic Press, Inc., New York (1966), p. 429.

resin using hydrofluoric acid-hydrochloric acid mixture as the eluting agent.[8] The irradiated sample was dissolved in 3 m*l* of 40 (w/v) % hydrofluoric acid containing a few drops of nitric acid in a teflon beaker, and the content was evaporated to dryness under an infrared lamp. After dissolving the residue with 5 m*l* of 1N hydrofluoric acid, 9.711 mg of niobium in 1N hydrofluoric acid solution was added as carrier. The resulting solution was poured into a Dowex 1×8 column.*3 Yttrium activities were eluted with 1N hydrofluoric acid, and zirconium activities were eluted with 80 m*l* of 0.01N hydrofluoric acid-9N hydrochloric acid mixture. Niobium was then eluted with 80 m*l* of 0.2N hydrofluoric acid-9N hydrochloric acid mixture. To this niobium fraction, 5 m*l* of saturated boric acid solution was added. The solution was heated nearly to boiling for about 1 min and niobium was precipitated by the addition of aqueous ammonium hydroxide solution. The precipitate was filtered and washed with dilute ammonium hydroxide solution and then ignited to obtain niobium oxide. The chemical yield of niobium was 90—95%.

Results and Discussion

Photonuclear Reaction. The photonuclear reactions on niobium and molybdenum were studied with Bremsstrahlung of several different maximum energies. The nuclear characteristics of radionuclides of present importance, mass threshold energies of possible reactions and the Coulomb barrier heights are summarized in Table 1.

When niobium samples were irradiated with Bremsstrahlung, with maximum energies 17, 30, 45 and 60 MeV, the γ-ray spectra of the resultant activities were obtained as shown in Fig. 1. As shown in spectrum I in Fig. 1, an intense photopeak at 0.934 MeV was observed. Minor peaks at 0.90 and 1.83 MeV were also measured. From the γ-ray energies and decay curve analysis, the production of ^{92m}Nb could be confirmed. This might be acceptable from the threshold consideration listed in Table 1. With 30 MeV bremsstrahlung, the production of ^{91m}Nb by (γ,2n) reaction could also be expected. However, as seen in spectrum II in Fig. 1, the activity strength of the 1.21 MeV γ-ray photopeak was very weak. This would be due to the fact that the irradiation period was too short to produce enough 62 d-^{91m}Nb activity and that the branching decay ratio of the 1.21 MeV γ-ray is only 3%. From mass threshold energy, the ^{93}Nb (γ,3n) ^{90}Nb reaction may not be expected at 30 MeV, but it was apparent with 45 and 60 MeV bremsstrahlung.

It should be noted that knowledge of a mass threshold energy of a given photonuclear reaction gives only the possibility of its production: The relative probability of forming each product by

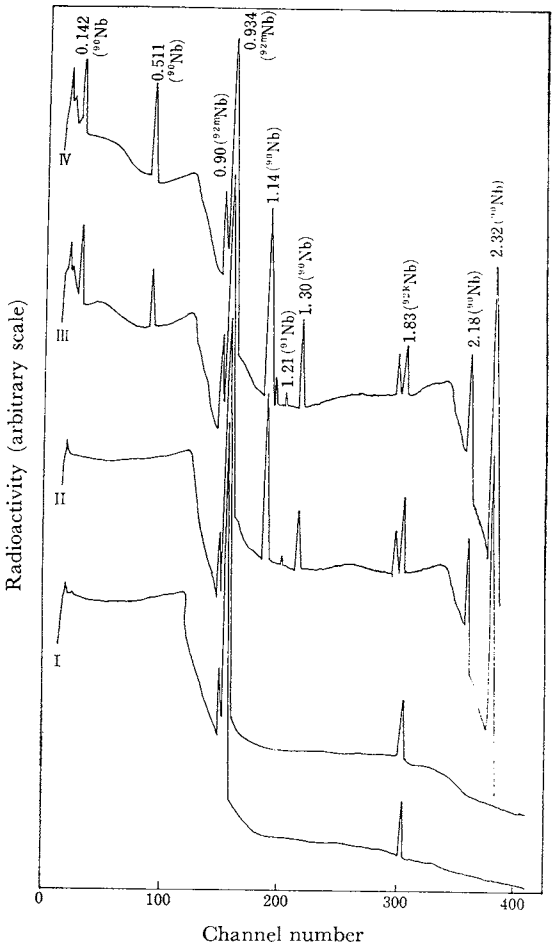

Fig. 1. γ-Ray spectra of niobium targets irradiated by Bremsstrahlung with various maximum energies.
I: 17 MeV bremsstrahlung for 60 min, 10.4 d after irradiation
II: 30 MeV bremsstrahlung for 100 min, 2.0 hr after irradiation
III: 45 MeV bremsstrahlung for 60 min, 1.8 d after irradiation
IV: 60 MeV bremsstrahlung for 105 min, 1.9 d after irradiation

the (γ,x n) reactions depends on the shape of the excitation functions which determines the yield value over the energy range of given Bremsstrahlung.

Studies have been done on the niobium activities produced by the (γ,pxn) reactions in molybdenum samples irradiated with bremsstrahlung of maximum energies varying from 17 MeV to 65 MeV. Their γ-ray spectra are given in Fig. 2. In spectrum I in Fig. 2, the productions of ^{95m}Nb and ^{96}Nb can be seen. The former can be formed by the ^{96}Mo (γ,p), ^{97}Mo (γ,pn) or ^{97}Mo (γ,d) reactions, and the latter by the ^{97}Mo (γ,p), ^{98}Mo (γ,pn) or ^{98}Mo (γ,d) reactions. From mass threshold and Coulomb barrier consideration as given in Table 1,

8) E. J. Dixon and J. B. Headridge, *Analyst*, **89**, 185 (1964).

*3 1 cmϕ×40 cm, 100—200 mesh.

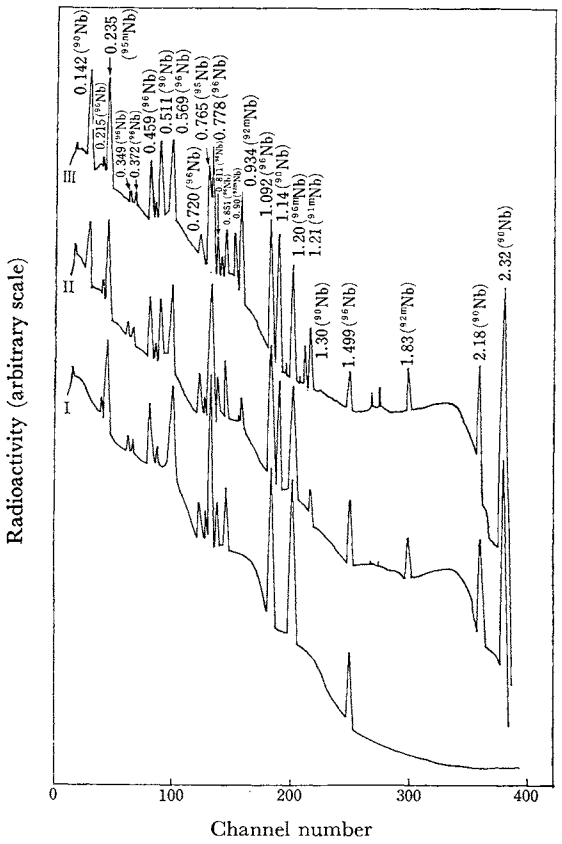

Fig. 2. γ-Ray spectra of niobium fractions separated from irradiated molybdenum targets.
I: Irradiated with 17 MeV bremsstrahlung for 60 min, spectrum obtained 1.33 d after irradiation
II: Irradiation with 30 MeV bremsstrahlung for 30 min, spectrum obtained 3.03 d after irradiation
III: Irradiated with 65 MeV bremsstrahlung for 25 min, spectrum obtained 3.96 d after irradiation

the possible reactions to produce ^{95m}Nb and ^{96}Nb can be concluded to be (γ,p) reactions on ^{96}Mo and ^{97}Mo respectively at 17 MeV. From a similar consideration, ^{95}Nb may be formed only by the (γ,p) reaction on ^{96}Mo at 17 MeV. Its production rate would not be appreciable in a short irradiation period. With bremsstrahlung maximum energies above 30 MeV, the formation of ^{90}Nb, ^{92m}Nb and small amount of ^{95}Nb can be found as shown in Fig. 2.

As has been stated on the yields of the (γ,n), (γ,p), (γ,2n), (γ,pn) and (γ,α) reactions with 20 MeV Bremsstrahlung, the (γ,n) reaction gives the highest yield for most of nuclei in the medium-to-heavy mass region.[9-11] Accordingly, ^{92m}Nb, the (γ,n) reaction product, should be preferably used for the determination of niobium with respect to sensitivity. The formation of ^{92m}Nb, therefore, should be necessarily avoided in an irradiated molybdenum sample. As seen in Table 1, the possible reactions leading to the production of ^{92m}Nb from molybdenum are the (γ,pn) or the (γ,d) reaction on ^{94}Mo. The sum of their mass threshold energies and Coulomb barrier heights are 24.15 and 21.75 MeV, respectively, which are both well beyond an excitation energy of 20 MeV. Hence interference of this sort could be avoided in the irradiation with 20 MeV bremsstrahlung, provided that the tunnel effect was not taken into account. Figure 3 shows the experimental results.

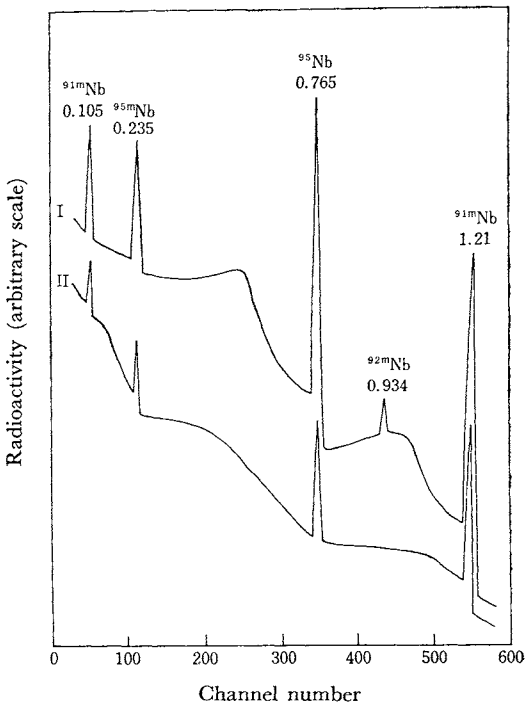

Fig. 3. γ-Ray spectra of niobium fractions separated from irradiated molybdenum targets.
I: Irradiated with 20 MeV bremsstrahlung for 1 hr, spectrum obtained 1.83 d after irradiation
II: Irradiated with 17 MeV bremsstrahlung for 1 hr, spectrum obtained 10.4 d after irradiation

The 0.934 MeV γ-ray of ^{92m}Nb can still be found as shown in spectrum I but its formation was completely suppressed at 17 MeV. Consequently, the irradiation was performed by 17 MeV bremsstrahlung in the determination of niobium using

9) Y. Oka, T. Kato, K. Nomura and T. Saito, This Bulletin, **40**, 575 (1967).

10) Y. Oka, T. Kato, K. Nomura, T. Saito and H.-T. Tsai, *ibid.*, **41**, 380 (1968).

11) Y. Oka, T. Kato, K. Nomura, T. Saito and H.-T. Tsai, *ibid.*, **41**, 2660 (1968).

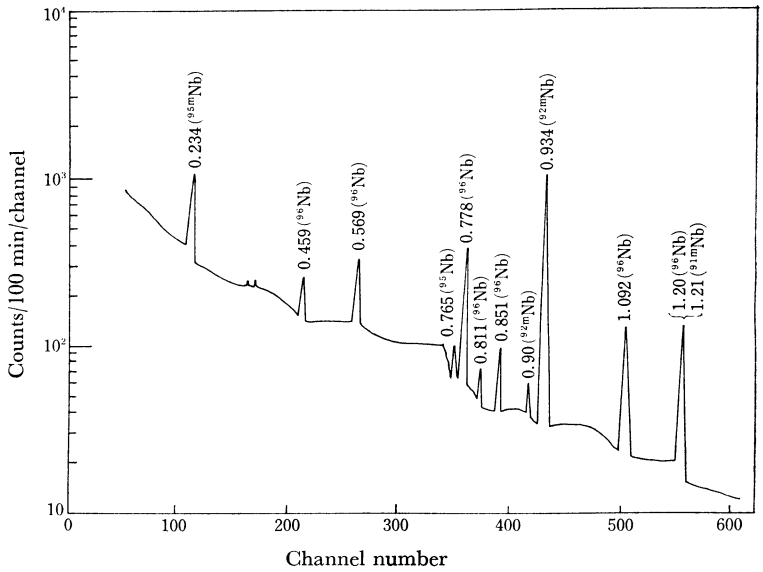

Fig. 4. γ-Ray spectrum of niobium fraction separated from irradiated niobium-molybdenum mixture (Nb/Mo=2.36×10^{-3}). Spectrum obtained
2.1 d after irradiation.

TABLE 2. R_W *vs.* R_{A_0} FOR NIOBIUM-MOLYBDENUM MIXTURES

R_W (Nb/Mo)	R_{A_0}		R_W/R_{A_0}	
	$\frac{^{92m}\text{Nb (0.932 MeV)}}{^{95m}\text{Nb (0.235 MeV)}}$	$\frac{^{92m}\text{Nb (0.934 MeV)}}{^{96}\text{Nb (1.092 MeV)}}$	$\frac{^{92m}\text{Nb}}{^{95m}\text{Nb}}$	$\frac{^{92m}\text{Nb}}{^{96}\text{Nb}}$
4.356×10^{-3}	9.74×10^{-1}	2.55	4.47×10^{-3}	1.71×10^{-3}
3.190×10^{-3}	6.78×10^{-1}	1.99	4.71×10^{-3}	1.60×10^{-3}
1.117×10^{-3}	2.41×10^{-1}	6.63×10^{-1}	4.63×10^{-3}	1.68×10^{-3}
5.694×10^{-4}	1.21×10^{-1}	3.51×10^{-1}	4.71×10^{-3}	1.62×10^{-3}
1.470×10^{-4}	3.33×10^{-2}	8.78×10^{-2}	4.41×10^{-3}	1.67×10^{-3}
		Mean:	4.59×10^{-3}	1.66×10^{-3}
		Std. dev.:	$\pm0.12\times10^{-3}$	$\pm0.04\times10^{-3}$

molybdenum as the internal-reference element.

The Determination of Niobium. The synthetic niobium-molybdenum mixtures were irradiated with 17 MeV Bremsstrahlung for an hour at a photon flux of 4.3×10^5 roentgens/min. After irradiation, niobium activities were separated chemically as described above. In Fig. 4, a typical γ-ray spectrum of niobium fraction is shown. Photopeak area under the 0.934 MeV photopeak of ^{92m}Nb was measured against that of either the 0.235 MeV photopeak area from ^{95}Nb or the 1.092 MeV photopeak area from ^{96}Nb.

The results are shown in Table 2. In each case, a good proportionality was obtained between R_W and R_{A_0}, where R_W is the weight ratio of niobium to molybdenum and R_{A_0} is the ratio of photopeak activities corrected at the end of one hour irradiation. The determination of niobium content in a sample can be achieved by using this relationship.

When a 10 cpm of photopeak activity is selected as the limit of determination, niobium content down to about 50 μg in a 1.5 g sample of molybdenum will be determined with a relative error within $\pm3\%$. Further applicability of this method will be found in the determination of niobium content in various samples by adding a proper amount of molybdenum as internal-reference element. An increase in sensitivity would be expected by using the higher bremsstrahlung dose and with a longer period of irradiation.