Photon-Activation Analysis for Zirconium with Molybdenum Used as the Internal-Reference Element[1)]

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A method for the determination of zirconium has been studied by activation analysis with bremsstrahlung photons, with molybdenum used as the internal-reference element. This method is based on the γ-ray spectrometric measurement of the ^{89}Zr activity produced by the ^{90}Zr(γ,n) reaction and on the comparison of this activity with the ^{88}Zr activity formed by the (γ,α) reaction on molybdenum. The reaction products and their rates of production in zirconium and in molybdenum have also been examined as functions of bremsstrahlung maximum energies up to 60 MeV, and the best conditions for the determination of zirconium are proposed. When the maximum energy was set at 20 MeV, no interfering reactions occurred; under the present experimental conditions, a zirconium content down to about 18 μg can be determined accurately. The reliability and the versatility of this method are demonstrated.

A minute amount of zirconium can be determined by photon-activation analysis using ^{89}Zr activity induced in an irradiated sample. This technique has been applied to the determination of zirconium in hafnium samples, using the non-destructive internal-reference method.[2,3)]

In a previous report,[4)] a method for the determination of niobium by photon-activation analysis has been proposed, with molybdenum used as the internal-reference element. The activity of the ^{92m}Nb produced by the (γ,n) reaction was utilized for the determination, while ^{95m}Nb or ^{96}Nb activities coming from molybdenum by the (γ,p) processes were used as references. On the basis of similar principles, methods for the determination of arsenic,[5)] rubidium,[6)] and cesium[7)] have also been established. Besides the (γ,n) and the (γ,p) reactions, the (γ,α) reactions can be induced by activation with photons in the giant resonance-energy region; the yields of (γ,α) reactions in several medium-weight nuclei for 20 MeV bremsstrahlung were given previously.[8)]

Thus, an element can be determined by comparing the activity of its (γ,n) reaction product with the activity induced by the (γ,α) reaction on the reference element having an atomic number higher by two.

The present work concerns a method for the determination of zirconium using molybdenum as the internal-reference element. In order to determine the best conditions for this purpose, some work has also been carried out on the yields of photonuclear reactions over the energy range of bremsstrahlung photons up to 60 MeV. When a maximum energy was set at 20 MeV, no interfering reactions occurred, and traces of zirconium down to about 18 μg could be determined accurately.

Experimental

Materials and Irradiation. The zirconium oxide was of an analytical-reagent grade and was from the Johnson Mathey Corp. The molybdenum was a metallic powder of 99.9% purity, from Wako Pure Chemical Industries, Ltd. Synthetic mixtures of these two samples, with known zirconium-to-molybdenum weight ratios ranging from 2.46×10^{-3} to 2.49×10^{-5}, were prepared in order to examine the sensitivity and the accuracy of the method. Each sample, weighing from 0.1 to 2 g, was placed either in a silica or Pyrex tube with an internal diameter of 8 mm. The tube was then placed in a water-cooled target holder immediately behind the bremsstrahlung generator, a 3-mm-thick platinum plate, and was irradiated. The irradiation periods varied between 1 and 3 hr.

Two kinds of linear-electron accelerators of Tohoku University were the bremsstrahlung sources. One of them provided a 20 MeV-electron beam. The other machine, which was capable of accelerating electrons with much higher energies, was used as the 30-to-60 MeV bremsstrahlung source. The experimental method, involving bremsstrahlung-flux monitoring, and the details of the irradiation were essentially the same as have been described in detail in a previous report.[9)]

Separation of Zirconium. The separation of zirconium activities from an irradiated sample was performed, after the addition of a zirconium carrier (10 mg), by means of the anion-exchange method, with a mixture of hydrofluoric and hydrochloric acid as the eluent.

The method was essentially the same as has been described in a previous report.[4)] The zirconium activities were eluted from a Dowex 1×8 column[10)] with 80 m*l* of a 0.01 N hydrofluoric acid - 9 N hydrochloric acid mixture. To this fraction, 5 m*l* of a saturated aqueous solution of boric acid were added. The zirconium hydroxide was precipitated from this solution by the addition of aqueous ammonia, filtered, washed, and then ignited to give zirconium oxide. This was wrapped with a thin sheet of aluminum for γ-ray counting. The chemical yield was determined, if needed.

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10) 1 cm $\phi\times40$ cm, 100—200 mesh.

TABLE 1. NUCLEAR DATA FOR ZIRCONIUM NUCLIDES

Target nuclide (abundance, %)	Reaction type	Product nuclide	Mass threshold ($-Q$, MeV)	Coulomb barrier (MeV)	Half-life of product	Decay mode	Principal γ-rays
^{90}Zr (5.46)	(γ, n)	^{89}Zr	12.00	—	78.4 hr	EC, β^+	0.910, 1.710
	(γ, 2n)	^{88}Zr	21.14	—	85 d	EC	0.394
	(γ, 3n)	^{87}Zr	33.81	—	1.6 hr	EC, β^+	1.220
	(γ, pn)	^{88}Y	20.20	6.44	108.1 d	EC, β^+	0.898, 1.836
	(γ, d)	^{88}Y	17.63	6.15	108.1 d	EC, β^+	0.898, 1.836
	(γ, αn)	^{85}Sr	18.22	11.43	64.0 d	EC	0.514
^{91}Zr (11.23)	(γ, 2n)	^{89}Zr	19.19	—	78.4 hr	EC, β^+	0.910, 1.710
	(γ, 3n)	^{88}Zr	30.18	—	85 d	EC	0.394
	(γ, p)	^{90m}Y	6.86	6.40	3.1 hr	IT, β^-	0.202, 0.482
^{92}Zr (17.11)	(γ, p)	^{91m}Y	9.40	6.38	50 min	IT	0.551
	(γ, pn)	^{90m}Y	17.33	6.40	3.1 hr	IT, β^-	0.202, 0.482
	(γ, d)	^{90m}Y	15.10	6.11	3.1 hr	IT, β^-	0.202, 0.482
^{94}Zr (17.40)	(γ, p)	^{93}Y	10.33	6.35	10.3 hr	β^-	0.267, 0.940
^{96}Zr (2.80)	(γ, n)	^{95}Zr	7.84	—	65.5 d	β^-	0.724, 0.756
^{92}Mo (15.86)	(γ, α)	^{88}Zr	5.46	13.65	85 d	EC	0.394
	(γ, αn)	^{87}Zr	17.65	13.69	1.6 hr	EC, β^+	1.220
^{94}Mo (9.12)	(γ, αn)	^{89}Zr	14.06	13.62	78.4 hr	EC, β^+	0.910, 1.710
^{100}Mo (9.62)	(γ, αn)	^{95}Zr	11.02	13.40	65.5 d	β^-	0·724, 0.756

Measurement of Radioactivity. The γ-ray measurements were made with a Ge(Li) detector, with a sensitive volume of 36 cm^3, coupled to a TMC 1024-channel pulse-height analyzer. The counting system had a resolution of 4 keV for the 661.6 keV γ-line of ^{137}Cs. The sample was measured at a fixed position, 1 cm from the sensitive surface of the detector.

A 3″ dia.×3″ NaI(Tl) crystal was also used as the detector. This was coupled to an 800-channel pulse-height analyzer made by the Tokyo Shibaura Electric Co., Ltd. The sample was located at a distance of 1 cm from the crystal surface.

For the study of various photonuclear reaction products, in which a much greater resolving power was required, the Ge(Li) detector was used exclusively. For analytical purposes, the NaI(Tl) detector was used.

Results and Discussion

Photonuclear Reaction. The nuclear data of present importance are given in Table 1. For a zirconium sample irradiated with 20 MeV bremsstrahlung, ^{89}Zr and ^{95}Zr produced by the (γ,n) reactions and ^{91m}Y produced by the (γ,p) reaction were measured at a cooling time of 45 min. At 30 MeV, ^{88}Zr was produced by the (γ,2n) reaction and ^{90m}Y and ^{93}Y were produced by the (γ,p) reactions, beside the above products. With this energy, ^{88}Y formed by the (γ,pn) and (γ,d) reactions on ^{90}Zr was also recognized after the relatively short-lived products had decayed away. In addition, the ^{90}Zr(γ, 3n)^{87}Zr reaction occurred for an energy beyond 45 MeV. These zirconium and yttrium activities are summarized in terms of their γ-ray photopeak intensities, and are plotted against bremsstrahlung maximum energy, in Fig. 1. All the activity data are expressed in counts per minute per milligram of zirconium at the end of an 1-hr irradiation by bremsstrahlung with the given maximum energies, after being normalized to a standard dose rate required to produce 1.0 μCi ^{196}Au by the 1-hr irradiation of 1 mg of gold. It is clear that the

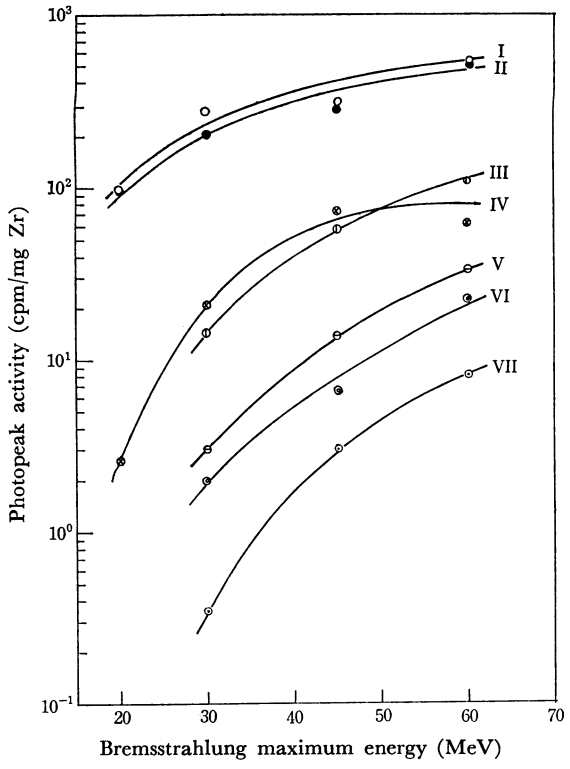

Fig. 1. Photopeak activities of zirconium and yttrium nuclides formed in zirconium as a function of bremsstrahlung maximum energy with a 36 cm^3 Ge(Li) detector.
I: ^{89}Zr 0.910 MeV γ-ray V: ^{90m}Y 0.482 MeV γ-ray
II: ^{89}Zr 0.511 MeV γ-ray VI: ^{93}Y 0.267 MeV γ-ray
III: ^{90m}Y 0.202 MeV γ-ray VII: ^{88}Zr 0.394 MeV γ-ray
IV: ^{91m}Y 0.551 MeV γ-ray

TABLE 2. R_W *versus* R_{A_0} FOR ZIRCONIUM-MOLYBDENUM MIXTURES

R_W (Zr/Mo)	R_{A_0}		R_W/R_{A_0}	
	^{89}Zr(0.511 MeV)	^{89}Zr(0.910 MeV)	^{89}Zr(0.511 MeV)	^{89}Zr(0.910 MeV)
2.460×10^{-3}	9.55×10^{1}	1.33×10^{2}	2.58×10^{-5}	1.85×10^{-5}
2.220×10^{-3}	8.33×10^{1}	1.15×10^{2}	2.64×10^{-5}	1.91×10^{-5}
6.272×10^{-4}	2.27×10^{1}	3.27×10^{1}	2.76×10^{-5}	1.92×10^{-5}
1.902×10^{-4}	7.04×10^{0}	1.02×10^{1}	2.70×10^{-5}	1.86×10^{-5}
1.390×10^{-4}	5.39×10^{0}	6.74×10^{0}	2.58×10^{-5}	2.06×10^{-5}
2.490×10^{-5}	8.99×10^{-1}	1.22×10^{0}	2.77×10^{-5}	2.04×10^{-5}
		Mean :	2.67×10^{-5}	1.94×10^{-5}
		Std. dev. :	$\pm0.08\times10^{-5}$	$\pm0.08\times10^{-5}$

0.910 MeV γ-ray of ^{89}Zr gives the highest photopeak activity for all the bremsstrahlung maximum energies. The annihilation radiation (0.511 MeV) can also be used for the sensitive determination of zirconium.

When molybdenum was irradiated with 20 MeV bremsstrahlung and the zirconium activity was separated, only the 0.394 MeV γ-ray was observed; it was attributed to ^{88}Zr produced by the ^{92}Mo(γ,α)^{88}Zr reaction. With 30 MeV bremsstrahlung, γ-rays due to the ^{89}Zr produced by the ^{94}Mo(γ,αn) reaction have also been measured. In addition, ^{87}Zr and ^{95}Zr were produced by the (γ,αn) reactions on molybdenum at energies beyond 45 MeV. Since the ^{89}Zr activity was used in the determination of zirconium, the irradiation conditions leading to the production of ^{89}Zr from molybdenum had to be avoided. Below 20 MeV, only the ^{94}Mo(γ,αn)^{89}Zr reaction ($-Q=14.06$ MeV) can produce ^{89}Zr. The experimental results showed that no appreciable amount of ^{89}Zr was produced from molybdenum with 20 MeV bremsstrahlung.

The Determination of Zirconium. The annihilation radiation or the 0.910 MeV γ-ray photopeak can be utilized for the determination of zirconium, while the ^{88}Zr activity arising from molybdenum can be used as a reference. The accuracy of the method was assessed by processing synthetic zirconium-molybdenum mixtures. They were irradiated with 20 MeV bremsstrahlung for 3 hr at a dose rate of 8×10^{4} R/min.[11] After the irradiation, the zirconium activities were separated chemically as has been described above. Figure 2 shows a typical γ-ray spectrum of the zirconium fraction. The photopeak area of the 0.511 MeV or 0.910 MeV peak of ^{89}Zr was measured and compared with that of the 0.394 MeV peak of ^{88}Zr. The results are given 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 zirconium to molybdenum and where R_{A_0} is the ratio of the photopeak activities corrected at the end of a 3-hr irradiation. The zirconium content can be determined down to 45 μg by this relationship, with a relative error of within 4% under the present experimental conditions.

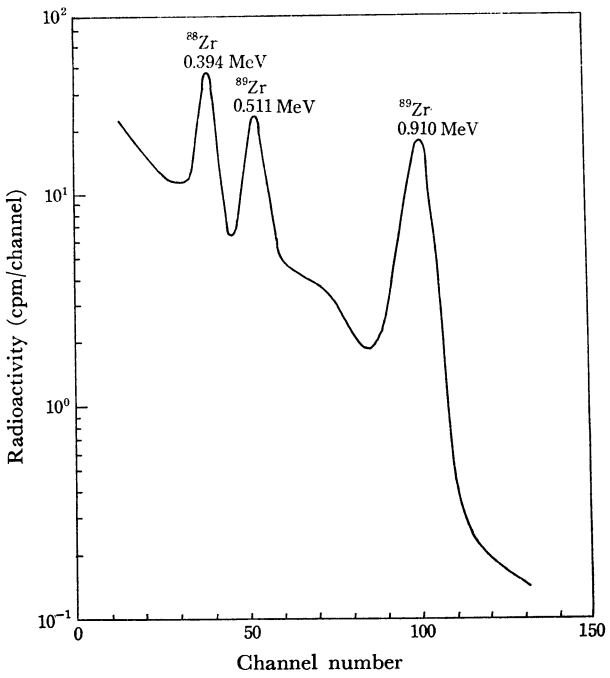

Fig. 2. γ-Ray spectrum of radiozirconium separated from a mixed sample (Zr 45.2 μg + Mo 1.815 g), 23.3 hr after irradiation with 20 MeV bremsstrahlung for 3 hr with a NaI(Tl) detector.

When a photopeak activity of 10 cpm is selected as the limit of determination, about 18 μg of zirconium in 2 g of molybdenum can be determined. With an accelerator giving a higher bremsstrahlung dose rate, the sensitivity is improved. In the energy region of 20 MeV bremsstrahlung, no interfering photonuclear reactions can occur from the coexisting elements. In the present case, the neutron reactions which arise from photoneutrons cause no serious problems.

This method can be used generally for the determination of zirconium when we add a proper amount of molybdenum, 2 g in most cases, to the sample as the reference element. When this method is combined with that reported previously for the determination of niobium,[4] zirconium and niobium may be determined simultaneously with molybdenum used as the reference.

In conclusion, the present authors believe that the method presented here is promising for the accurate

11) The dose-rate determination has been done by means of a method reported earlier.[12]

12) Y. Oka, T. Kato, and I. Nagai, *J. Nucl. Sci. Tech.*, **4**, 300 (1967).

determination of zirconium in samples of various origins, provided that those samples do not contain a large amount of molybdenum.

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