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An Internal-Reference Method for the Determination of Rubidium by Photon-Activation Analysis with Strontium Used as the Reference Element*[1]

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We have studied a method for the determination of rubidium by activation analysis with bremsstrahlung photons, with strontium used as the internal-reference element. This method is based on the γ-ray spectrometric measurement of the ^{84}Rb activities produced by the ^{85}Rb(γ,n) reaction and on the comparisons of those activities with that of ^{83}Rb arising from strontium as a result of the (γ,p) reaction. The yields of various photonuclear reactions in rubidium and in strontium have also been examined as a function of bremsstrahlung maximum energies up to 60 MeV, and the best conditions for the determination of rubidium are proposed. When the maximum energy was set at 18 to 20 MeV, no interfering reactions occurred; a rubidium content down to about 2 μg can be determined accurately. A comparison of solid-state and scintillation γ-ray spectrometry in this method has also been included with respect to the sensitivity and the selectivity.

A minute amount of rubidium can be determined by a thermal neutron activation method by inducing ^{86}Rb activity in an irradiated sample; this technique has been applied to the determination of rubidium in a number of materials of geochemical interest[1-3] The contents of rubidium and strontium in terms of the rubidium-to-strontium ratios have been utilized for the age-determination of these materials.[4] An accurate and precise analytical method was required in this work.

The work described here was undertaken for the purpose of establishing an accurate method for the determination of rubidium by photon-activation analysis, using strontium as the internal-reference element. In order to determine the best conditions for the determination of rubidium by this method, 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 18 to 20 MeV, no interfering reactions occurred, and traces of rubidium down to about 2 μg could be determined accurately. A comparison of the solid-state detection by means of the scintillation-detection method is also included with respect to the sensitivity and the selectivity.

Experimental

Materials and Irradiation. The rubidium chloride was a guaranteed reagent grade. Strontium carbonate of a guaranteed reagent grade was further purified by repeated reprecipitations. Synthetic mixtures of these two compounds, with known weight ratios of rubidium to strontium ranging from 1.3×10^{-1} to 5.4×10^{-3}, were prepared in order to examine the sensitivity and the accuracy of the method. Each sample (weight, about 100 mg) was placed in a quartz tube with an internal diameter of 4 mm for bremsstrah-

*1 Study of the Activation Analysis using the Internal-Reference Method. XIV., A part of this work was presented at the 17th Annual Meeting of the Analytical Chemistry Society of Japan, Hiroshima, October, 1968. Part XIII: H-T. Tsai, T. Kato and Y. Oka, This Bulletin, **43**, 2482 (1970).

1) M. J. Cabell and A. A. Smales, *Analyst*, **82**, 390 (1957).

2) A. A. Smales, T. C. Hughes, D. Mapper, C. A. J. McInnes and R. K. Webster, *Geochim. Cosmochim. Acta*, **28**, 209 (1964).

3) K. Tomura, H. Higuchi, H. Takahashi, N. Onuma and H. Hamaguchi, *Anal. Chim. Acta*, **43**, 523 (1968).

4) E. Anders, *Rev. Mod. Phys.*, **34**, 287 (1962).

lung irradiation. All the irradiations were terminated in 1 hr. The linear electron accelerators of Tohoku University and of the Japan Atomic Energy Research Institute were used as the bremsstrahlung sources. 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 paper.[5]

Separation Procedure. The irradiated sample was dissolved in a small amount of 0.1 N hydrochloric acid, along with 20 mg of a rubidium carrier. The solution was evaporated to dryness, and the residue was dissolved with dilute aqueous ammonia (pH 8) and then subjected to cation-exchange separation. The resin used was Dowex 50W×8, 100 to 200 mesh size. This was fed into a column 25 cm long and with an internal diameter of 8 mm. The rubidium was eluted with a 0.5 M ammonium acetate solution and was precipitated by the addition of 0.1 N perchloric acid with ice-cooling. The rubidium perchlorate was filtered and dried in a vacuum.

After the elution of the rubidium, the strontium was eluted from the column with 1 N nitric acid and precipitated as strontium carbonate by means of an aqueous ammonium carbonate solution. The precipitate was filtered and dried at 500°C. Either rubidium perchlorate or strontium carbonate was wrapped with a thin sheet of aluminum in order to determine the chemical yield, if needed, and for γ-counting.

Counting Equipment. A lithium-drifted germanium detector with an active volume of 36 cm^3, ORTEC 8101-30P, was 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 counting efficiency of this detector has been determined as a function of the source distance and the γ-ray energy by counting a series of calibrated sources of known activities. A sample was measured at a fixed position, 9 mm from the active 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. For the determination of the photonuclear yields where a much greater resolving power was required, the Ge(Li) detector was used exclusively; for analytical purposes, both counting systems were employed.

Yield Determination. A yield was defined as the production rate of nuclide due to a certain photonuclear reaction in dps at the end of the irradiation of one mole of a parent nucleous when a standard amount of bremsstrahlung radiation with a given maximum energy has passed through the target during the irradiation period. The initial decay rates of the various activities produced were determined from a decay-curve analysis of the counting rate of the relevant photopeak area. The corresponding saturation rates were computed and normalized for the bremsstrahlung intensity, which was measured by means of the amount of of ^{196}Au activity produced by the $^{197}Au(\gamma,n)^{196}Au$ reaction in a gold foil irradiated together with the sample. After correcting for chemical yields, counting efficiencies, branching ratios,[6] and the internal conversion electrons,[7] the yields were expressed relative to that of the $^{87}Rb(\gamma,n)^{86}Rb$ process or of the $^{84}Sr(\gamma,n)^{83}Sr$ process.

Results and Discussion

Photonuclear Reaction. Rubidium has two naturally-occurring isotopes, ^{85}Rb(72.15%) and ^{87}Rb(27.85%), while strontium has four isotopes, ^{84}Sr(0.56%), ^{86}Sr(9.86%), ^{87}Sr(7.02%), and ^{88}Sr-(82.56%). The experimental results showed that the rubidium nuclides formed in the irradiations of the two elements by bremsstrahlung with maximum energies up to 60 MeV were ^{82m}Rb ($T_{1/2}$= 6.3 hr), ^{83}Rb ($T_{1/2}$=83d), ^{84}Rb ($T_{1/2}$=33.0 d), ^{84m}Rb ($T_{1/2}$=20 min), and ^{86}Rb ($T_{1/2}$=18.66 d). In addition, the production of ^{81}Rb($T_{1/2}$=4.7 hr) was also observed in an irradiated strontium sample. In this experiment, γ-rays from ^{81m}Rb could not be measured because of its lower energies (0.085 MeV with IT) and its relatively short half-life (31 min). The ^{84m}Rb activity could not be detected from strontium since it has decayed away during the separation processes.

From the threshold-energy considerations, the main reactions which can occur in both elements with bremsstrahlung and with maximum energies below 20 MeV are the (γ,n) and (γ,p) reactions. Thus, when irradiated with 17.6 MeV bremsstrahlung, ^{84}Rb, ^{84m}Rb, and ^{86}Rb, the (γ,n) reaction products, were measured. No nuclides other than the above were produced at 20 MeV. Since the ^{84}Rb activity was used in the determination of rubidium, the irradiation conditions leading to the production of ^{84}Rb from strontium had to be avoided. The only possible reaction producing ^{84}Rb in the irradiation with bremsstrahlung below 20 MeV is the $^{86}Sr(\gamma,d)^{84}Rb$ reaction ($-Q$=17.84 MeV). The experimental results showed that the production of ^{84}Rb from strontium with 20 MeV bremsstrahlung could not be observed in any appreciable amount.

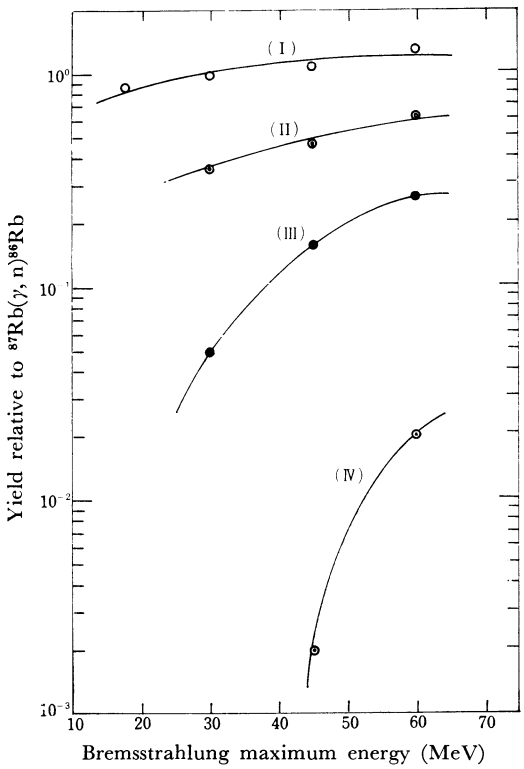
The yields of various reactions are given as a function of the bremsstrahlung maximum energy in Figs. 1 and 2. Since an excitation energy beyond 30 MeV covers the giant resonance region well for most nuclei, and since the main nuclear event in this energy region is the emission of one neutron,[8] the yield value of the (γ,n) reaction remains almost unchanged throughout this energy region. The yield of the reaction with the emission of more than one nucleon appeared to be strongly

5) Y. Oka, T. Kato and N. Sato, This Bulletin, **42**, 387 (1969).

6) The decay schemes used were those listed in G. M. Lederer, J. M. Hollander and I. Perlman, "Table of Isotopes," Sixth Ed., John Wiley & Sons, New York (1967).

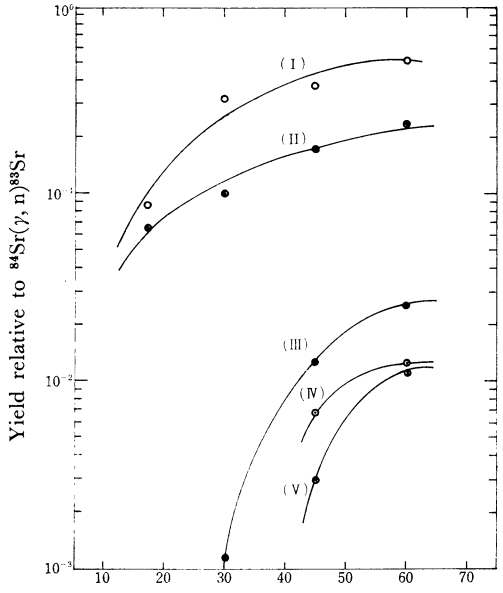
7) The tables in M. E. Rose, "Internal Conversion Coefficients," North-Holland Publ. Co., Amsterdam (1958), were used.

8) R. Montalbetti, L. Katz and J. Goldenberg, *Phys. Rev.*, **91**, 659 (1953).



(I): $^{85}Rb(\gamma,n)^{84}Rb$. (III): $^{85}Rb(\gamma,2n)^{83}Rb$.
(II): $^{85}Rb(\gamma,n)^{84m}Rb$. (IV): $^{85}Rb(\gamma,3n)^{82m}Rb$.

Fig. 1. The yield of rubidium nuclides produced from rubidium as a function of bremsstrahlung maximum energy.



(I): $^{84}Sr(\gamma,p)^{83}Rb$. (IV): $^{84}Sr(\gamma,pn)^{82m}Rb$.
(II): $^{87}Sr(\gamma,p)^{86}Rb$. (V): $^{84}Sr(\gamma,p2n)^{81}Rb$.
(III): $^{86}Sr(\gamma,pn)^{84}Rb$.

Fig. 2. The yield of rubidium nuclides produced from strontium as a function of bremsstrahlung maximum energy.

energy-dependent. In the energy region higher than 45 MeV, the $^{85}Rb(\gamma,3n)^{82m}Rb$ and $^{85}Rb(\gamma,4n)^{81m,81}Rb$ reactions occurred; the ^{81}Rb and ^{82m}Rb activities were also measured from an irradiated strontium sample. An increase in the yields of the (γ,pn) reactions can be seen beyond 45 MeV. The $^{84}Sr(\gamma,pn)^{81}Rb$ reaction contributes mainly to the production of ^{81}Rb from strontium. At 60 MeV, however, the additional contribution to the total production rate comes from the $^{86}Sr(\gamma,p4n)^{81}Rb$ reaction. The main reaction leading to the production of ^{82m}Rb in this energy region is the $^{84}Sr(\gamma,pn)$ reaction.

For analytical purposes, the ^{84}Rb activity as a result of the (γ,n) reaction can be used effectively with respect to the sensitivity at a given maximum energy investigated here. Table 1 shows the photopeak activities of ^{84}Rb, together with those of ^{83}Rb from strontium, as a function of the bremsstrahlung maximum energy. In the determination of rubidium by the use of strontium as a reference, however, it is necessary to avoid interferences due to the production of ^{84}Rb from strontium through the (γ,d) and (γ,pn) reactions. As has been stated earlier, the irradiation by bremsstrahlung with maximum energies below 20 MeV gives no such trouble.

Determination of Rubidium. The 0.880 MeV γ-ray photopeak of ^{84}Rb can be utilized for the determination of rubidium, while the ^{83}Rb activity arising from strontium can be used as a reference. A comparison of the scintillation detection by the solid-state detection method can be discussed in terms of the sensitivity and the selectivity by processing the synthetic mixtures.

When a 3″ dia.×3″ NaI(Tl) detector was used, we obtained the typical γ-ray spectrum shown in Fig. 3. The sample was irradiated with 20 MeV bremsstrahlung in this case. It can be seen that the photopeak appearing at 0.525 MeV is the compound peak of the 0.511 MeV γ-ray from ^{84}Rb and the 0.521, 0.530, and 0.553 MeV γ-rays of ^{83}Rb. The area under the latter three different γ-rays of ^{83}Rb were determined from these spectra by the following sequences:

1) from the spectrum in Fig. 3, the background activity due to the 1.078 MeV γ-ray of ^{86}Rb was subtracted by the graphical subtraction method;[9]

2) the area under the 0.880 MeV photopeak, A_{detn}(cpm), was obtained;

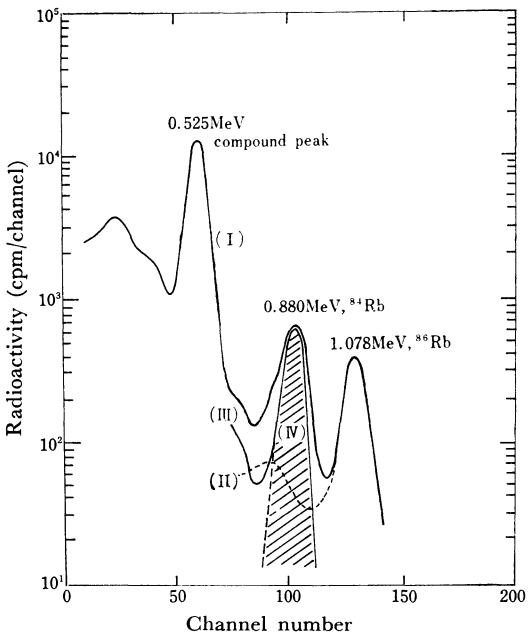
3) the 0.511 MeV photopeak area due to ^{84}Rb,

9) "Guide to Activation Analysis," ed. by W. S. Lyon, Jr., D. Van Nostrand Co., Princeton, N. J. (1964), p. 104.

Table 1. Photopeak activity of the rubidium nuclides with a Ge(Li) detector

Nuclide	Production reaction	γ-Ray (MeV)	Photopeak activity (cpm/mg)*			
			17.6 MeV	30 MeV	45 MeV	60 MeV
^{84}Rb	^{85}Rb(γ,n)	0.880	5.02×10^{3}	7.71×10^{3}	1.95×10^{4}	1.21×10^{4}
^{83}Rb	^{84}Sr(γ,p)	0.553	5.76×10^{-1}	3.03×10^{0}	4.92×10^{0}	6.02×10^{0}

* cpm at the end of 1 hr-irradiation with a standard dose rate of bremsstrahlung photons with a given maxinum energy incident on 1 mg of the element: With this dose rate, 1.0 μCi ^{196}Au is produced by the (γ,n) process in 1 mg Au.



(I): The original compound spectrum.
(II): Compton back ground due to the 1.078 MeV γ-ray.
(III): Photopeak due to the 0.880 MeV γ-ray of ^{84}Rb.
(IV): The area under the 0.880 MeV photopeak.

Fig. 3. γ-Ray spectra of radiorubidium separated from a mixed sample (Rb 7.21 mg+Sr 55.5 mg), 29 days after irradiation with 20 MeV bremsstrahlung with a NaI(Tl) detector.

A(0.511 MeV), was calculated by:

$$A(0.511\ \mathrm{MeV}) = R\,A_{\mathrm{detn}}$$

where R is the activity ratio, $A_{^{84}\mathrm{Rb}}$(0.511 MeV)/$A_{^{84}\mathrm{Rb}}$(0.880 MeV), which has been determined with the aid of ^{84}Rb, and

4) the area under the composite peak of ^{83}Rb used as reference, A_{ref}, was then calculated by:

$$A_{\mathrm{ref}} = A_{\mathrm{m}} - A(0.511\ \mathrm{MeV}) = A_{\mathrm{m}} - R\,A_{\mathrm{detn}}$$

where A_{m} is the observed area under the compound peak at 0.525 MeV. From the spectra obtained from irradiated mixtures, the A_{detn}'s and the A_{ref}'s were determined, and those activity data were corrected for decay to the end of the irradiation through the use of the half-lives of ^{84}Rb and ^{83}Rb respectively. In the present experiment, all separations were performed 12 days after irradiation; all of the 20 min-^{84m}Rb had decayed away to ^{84}Rb.

Table 2 shows the relation between the photopeak activity ratios, $R_{A_0}=(A_{\mathrm{detn}}/A_{\mathrm{ref}})_{t=0}$, and the ratios of the weights, R_W=Rb/Sr. A good

Table 2. R_W *versus* R_{A_0} for rubidium-strontium mixtures with a NaI(Tl) detector

R_W	R_{A_0}	R_W/R_{A_0}
1.30×10^{-1}	21.6	5.99×10^{-3}
6.23×10^{-2}	10.1	6.16×10^{-3}
1.55×10^{-2}	2.61	5.82×10^{-3}
6.87×10^{-3}	1.14	6.04×10^{-3}
2.40×10^{-4}	3.90×10^{-2}	6.16×10^{-3}

Mean: $6.0_3\times10^{-3}$
Std. dev.: $\pm0.1_3\times10^{-3}$

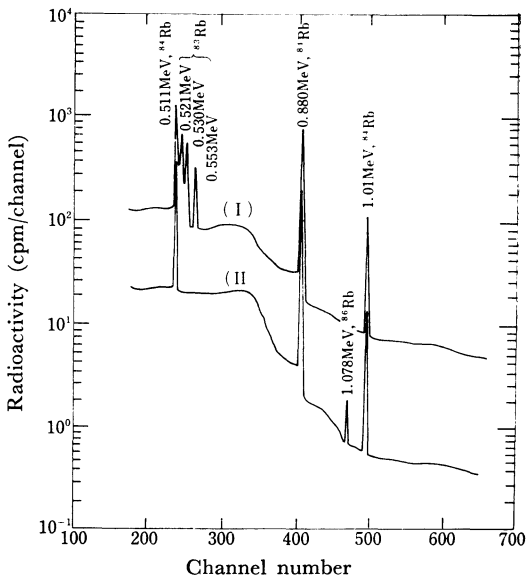


Fig. 4. γ-Ray spectra of radiorubidium with a Ge(Li) detector; (I) separated from a mixed sample (Rb 0.84 mg+Sr 419 mg), 11.9 days after irradiation with 17.6 MeV bremsstrahlung, and (II) of the rubidium sample.

proportionality was held between them, and a relative standard deviation of ±2.1% was obtained under the present experimental conditions:

$$R_W = (6.0_3 \pm 0.1_3) \times 10^{-3} R_{A_0}$$

When the amount of rubidium needed to give a photopeak activity of 10 cpm is selected as the limit of determination, it can be set at 2 μg.

When a 36 cm^3 Ge(Li) detector was used, we obtained the typical γ-ray spectrum shown in Fig. 4, together with that of the rubidium sample. The much greater resolving power of this detector made it feasible to distinguish clearly three different γ-ray photopeaks of ^{83}Rb. The photopeak area under the 0.553 MeV γ-ray was selected as the reference. The ratios of the area under the 0.880 MeV γ-ray to that under the 0.553 MeV γ-ray were computed and corrected for decay to the end of the irradiation. The relation between the R_{A_0}'s and the R_W's was again discussed from these activity data. Table 3 shows the results. The following relationship was obtained:

$$R_W = (1.1_3 \pm 0.0_5) \times 10^{-3} R_{A_0}$$

The relative standard deviation was ±4.8%. A sensitivity of 23 μg for rubidium was obtained in accordance with the definition described earlier.

With a Ge(Li) detector, the method is less sensitive by one order, but the determination of the photopeak areas is quite feasible as compared with scintillation spectrometry. An increase in sensitivity would be expected with a higher bremsstrahlung dose rate and with a longer period of irradiation.

Table 3. R_W *versus* R_{A_0} for rubidium-strontium mixtures with a Ge(Li) detector

R_W	R_{A_0}	R_W/R_{A_0}
5.30×10^{-2}	5.01×10^{1}	1.06×10^{-3}
4.28×10^{-2}	3.86×10^{1}	1.11×10^{-3}
2.95×10^{-2}	2.52×10^{1}	1.17×10^{-3}
1.20×10^{-2}	9.90×10^{0}	1.21×10^{-3}
5.41×10^{-3}	4.90×10^{0}	1.11×10^{-3}

Mean: $1.1_3\times10^{-3}$
Std. dev.: $\pm0.0_5\times10^{-3}$

The general applicability of this method lies in the determination of rubidium in samples of geochemical interest, in biological materials, and in various chemicals. A sample is ready for bremsstrahlung irradiation when it is ground to a powder along with a known amount of strontium carbonate, 100 mg in most cases. Rubidium often accompanies cesium in such samples, and the mutual separation of them can not be performed by the procedure described earlier. Considering the nuclear characteristics of ^{132}Cs ($T_{1/2}$=6.5 d, β^+ 0.6%, γ's), the (γ,n) reaction product, however, does not appear to be a serious source of interference. The γ-ray energies are 0.6678 MeV (96.7%), 0.6303 MeV(0.85%), 0.508 MeV(0.5%), and others (very weak). When a sample contains a large amount of cesium, a lithium-drifted germanium detector may be considered to be superior to a scintillation detector.