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Half-Life and Beta Spectrum of Rb^{87}†

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Liquid-scintillation counting techniques have been applied to the measurement of the specific activity and the beta spectrum of the natural radioactivity of rubidium. The measured Rb^{87} half-life is $(47.0\pm1.0)\times10^9$ yr, and the observed maximum beta energy is 272±3 kev.

INTRODUCTION

An accurate value for the decay constant of Rb^{87} is of considerable interest in the measurement of the ages of geologic specimens. From the ratio of radiogenic Sr^{87} to Rb^{87} in the specimen and the half-life of Rb^{87} the age can be determined directly, and it is believed that this method applied to mica provides the most reliable ages for common rocks.[1] Unfortunately, the half-life of Rb^{87} is uncertain, and values by specific-activity measurements ranging from 43×10^9 to 64×10^9 years have been reported in the literature. A summary of these measurements has been given by Aldrich *et al.*[1,2] who correlated the ages of minerals from single-mineral assemblages as determined by the decay of U^{238}, U^{235}, Th^{232}, Rb^{87}, and K^{40}. They measured the ratios Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Sr^{87}/Rb^{87} in each of six samples ranging in age from 375 to 2700 million years. A half-life of $(50\pm2)\times10^9$ years for Rb^{87} was found to be consistent with the Pb^{206}/U^{238} and the Pb^{207}/U^{235} ages. Recent work by Libby[3] using solid-sample beta-counting techniques with corrections for self-absorption and scattering gave a value of $(49\pm2)\times10^9$ years.

In the work described below we have employed the liquid scintillation spectrometer to determine the absolute specific activity of rubidium and to obtain the end point of the Rb^{87} beta rays. The half-life of Rb^{87} is calculated from the specific activity using the relationship $T_{\frac{1}{2}}=0.693N/A$, where N is the number of atoms of Rb^{87} and A is the disintegration rate.

The liquid scintillation counter is particularly useful in determining the disintegration rate of low-energy, low-specific-activity beta emitters since the radioactive substance is dissolved directly in the scintillator. This technique eliminates the uncertainty of self-absorption and scattering corrections which must be made when thick sample counting methods are used. Steyn[4] has shown that absolute disintegration rates determined by liquid scintillation counting agree with those obtained by conventional 4π beta counting of weightless samples for the nuclides Co^{60} (0.3 Mev), I^{131} (0.6 Mev), and P^{32} (1.7 Mev). Results of similar experiments in our laboratory confirm the work of Steyn and indicate a high degree of reliability for this method of absolute-beta counting.

APPARATUS

Two liquid scintillation apparatuses are used in this work. The first consists of a five-inch Du Mont 6364 multiplier phototube mounted vertically, an amplifier, a single-channel pulse-height analyzer, and a scaler. The phototube is enclosed in a light-tight aluminum can and covered with a hemispherical reflector [Fig. 1(a)]. The sample cell containing the scintillator is placed directly on top of the phototube using a few drops of mineral oil to achieve optical coupling. The sides of the sample cell are painted with a highly reflecting

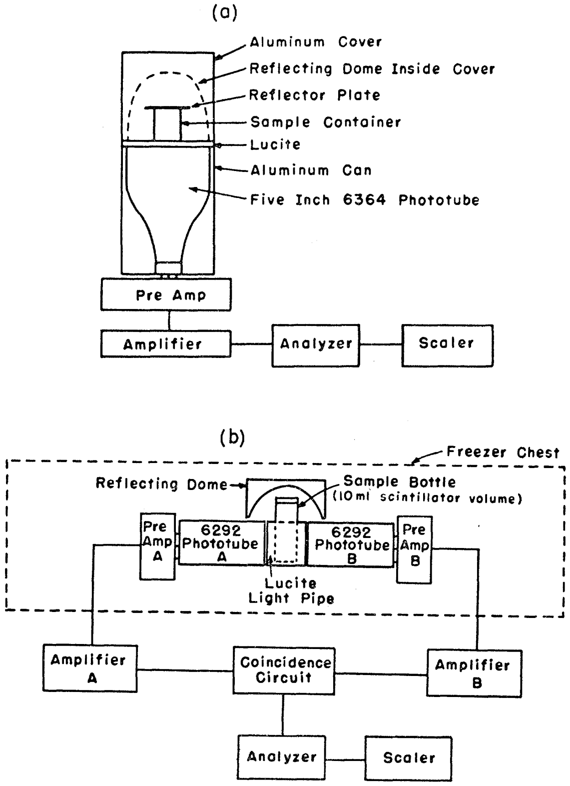

FIG. 1. Diagrams of liquid scintillation spectrometers.

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† Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] L. T. Aldrich and G. W. Wetherhill, *Annual Review of Nuclear Science* (Annual Reviews, Inc., Palo Alto, 1958), Vol. 8, p. 257.

[2] Aldrich, Wetherhill, Tilton, and Davis, Phys. Rev. **103**, 1045 (1956).

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TABLE I. Standardization of the liquid scintillation counters against a 4π β proportional counter.

Isotope	4π β proportional counter (counts/min)	Liquid scintillation counters 5-inch (counts/min)	Tri-Carb (counts/min)
P^{32} (1.7 Mev)	47 400	46 800	47 200
Cs^{137} (0.5 Mev)	40 500	39 400	41 200
Pm^{147} (0.22 Mev)	125 500	126 000	126 000
S^{35} (0.167 Mev)	64 880	64 500	65 000

titanium dioxide paint,[5] and the cell is covered with a reflecting plate. This apparatus is operated at room temperature.

The second apparatus consists of a Tri-Carb Liquid Scintillation Spectrometer, model 314.[6] This instrument uses two 2-inch Du Mont 6292 multiplier phototubes mounted horizontally inside a refrigerated chest set to operate at 0°C. The cell containing the sample is placed between the phototubes in a Lucite light pipe to obtain good optical coupling [Fig. 1(b)]. The pulses from the phototubes are then fed into an amplifier, a coincidence circuit, pulse-height analyzer, and a scaler. Both the low temperature and the coincidence circuit act to reduce the phototube noise background of the instrument.

In both cases the scintillator used is a toluene solution containing 4 grams of terphenyl and 0.1 gram of 1,4-di-[2-(5-phenyloxazoyl)]-benzene (POPOP) per liter. The latter material is used to shift the wavelength of the emitted light into the region of maximum response for the photomultipliers.[7,8]

EXPERIMENTAL

Absolute Beta Counting

Experiments to determine the reliability of the liquid-scintillation counter as an absolute beta counter were undertaken. Samples of P^{32}, Cs^{137}, Pm^{147}, and S^{35} were counted in both liquid scintillation counters (Fig. 1) under conditions similar to those used for the Rb^{87} counting and in a 4π beta proportional counter. The samples in the liquid scintillation counters were counted at several pulse-height discriminator settings and after subtracting off background plots were made of counting rate *versus* pulse height. These curves were then extrapolated to zero pulse height to obtain the true-disintegration rates of the samples. Typical curves for S^{35} are given in Fig. 2. The results of these experiments (Table I) indicate that the liquid scintillation counter behaves as an absolute beta counter at least down to a maximum-beta energy of 0.167 Mev. Further work to establish the counting efficiency in the lower energy region is in progress. In order to minimize errors, 50-microliter samples were taken for each of the above measurements and each sample was counted to 0.2% counting statistics. The largest error involved was in the extrapolation of the integral counting curve. A conservative estimate of the over-all reliability of absolute beta counting by the liquid scintillation method would be of the order of 2%.

Rb^{87} Half-Life Determination

In order to obtain a uniform distribution throughout the scintillating solution it is necessary to convert the material to be counted into a form which is soluble in the liquid scintillator. Ronzio, Cowan, and Reines[9] found that the 2-ethylhexanoic acid (octoic acid) salts of metal ions are soluble in scintillator solutions and do not cause appreciable quenching. The rubidium salt of octoic acid was made by the following technique. A slight excess of barium hydroxide was slowly added to a hot rubidium sulfate solution which was then centrifuged to remove the barium sulfate. The excess barium was precipitated as the carbonate by carbon dioxide gas and removed by filtration. The filtrate containing the rubidium hydroxide was evaporated under vacuum to a small volume and contacted with a 10% excess of octoic acid. The rubidium octoate solution was evaporated under vacuum several times with absolute ethanol to remove water. The final salt re-

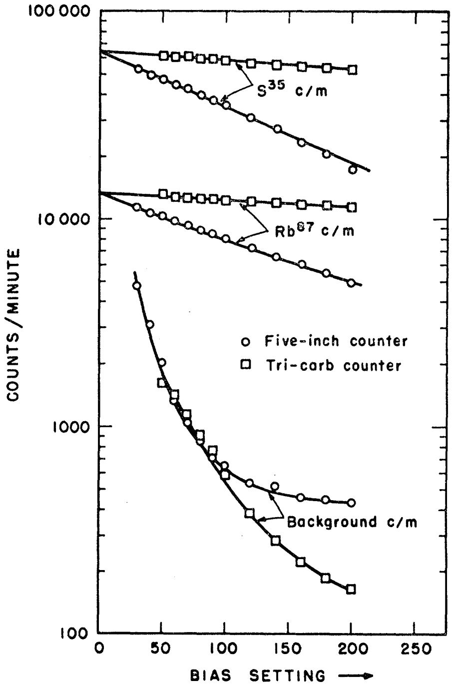

FIG. 2. Integral counting rate curves.

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[5] D. L. Horrocks and M. H. Studier, Anal. Chem. **30**, 1747 (1958).

[6] Packard Instrument Company, P. O. Box 428, La Grange, Illinois.

[7] Hayes, Ott, Kerr, and Rogers, Nucleonics **13**, No. 12, 38 (1955).

[8] Hayes, Ott, and Kerr, Nucleonics **14**, No. 1, 42 (1956).

[9] A. R. Ronzio, Intern. J. Appl. Radiation and Isotopes **4**, 196 (1959).

mained as a viscous syrup which was mixed with an equal volume of ethanol to convert it to a free-flowing liquid. Aliquots of this solution were then added to the scintillator solution and counted. Other aliquots were gravimetrically analyzed for rubidium content.

Four sources of rubidium were used for half-life determinations. The first was a sample of DeRewal International Rare Metals Company rubidium chloride which was shown by optical spectrochemical analysis to be 98.5% pure. The remaining 1.5% was made up of potassium and cesium for which a correction was made in the final gravimetric analysis. Since the specific activity of K^{40} in natural potassium is only 1.94 d/m/mg the correction to the counting rate of the sample due to the presence of natural potassium was neglected. The other three samples were Fairmount Chemical Company rubidium chloride, A. D. Mackay Company rubidium nitrate, and DeRewal Company rubidium chloride, each of which was further purified by ion-exchange separation.[10] Dowex-50 cation columns were used with 0.5*N* HCl as the eluting agent. The rubidium chloride eluate was metathesized to the sulfate by evaporation to dryness with sulfuric acid and converted to the octoate as described above.

Aliquots of the rubidium octoate solutions containing approximately 230 mg Rb^+ were added to 10 ml of liquid scintillator in the counting cell and allowed to cool in the dark for about twenty minutes. This quantity of rubidium gave about 12 000 counts/min and quenched the pulse-height output of the scintillator by 25%. These samples were then counted integrally at several pulse-height-discriminator settings down to the region of phototube noise. Background counts were taken under identical conditions and subtracted from the gross counting rate to obtain the net counting rate of the Rb^{87}. The background cell was filled with scintillator, and a solution of ethanol and octoic acid was added until the pulse-height output as measured by the Ba^{137m} electron line was the same for the background cell as for the sample cell, i.e., until the amount of quenching in the two solutions was identical. The observed net counting rates were plotted against pulse height and extrapolated through the region of phototube noise to zero pulse height to obtain the true disintegration rate of the sample. The extrapolation amounted to a correction of about 12% in the case of the five-inch counter and about 5% in the case of the Tri-Carb counter. A typical curve for each counter is given in Fig. 2.

The rubidium octoate solutions were analyzed gravimetrically for total rubidium content by fuming with sulfuric-perchloric acid to destroy the organic material, taking to dryness in a platinum dish, and weighing the rubidium as the sulfate. The number of atoms of Rb^{87} present was calculated from the known isotopic abundance of 27.85%.[11]

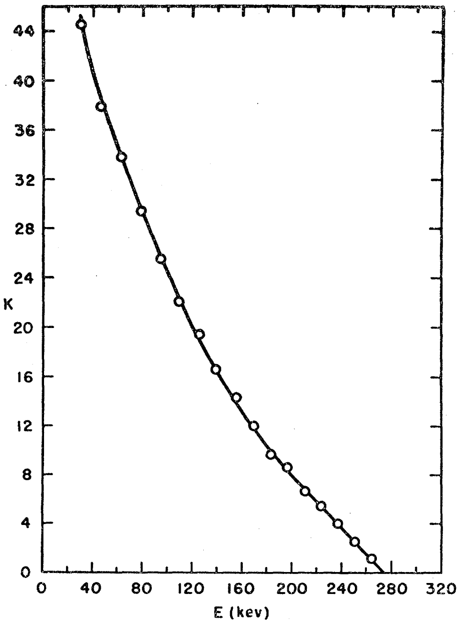

FIG. 3. Kurie plot for Rb^{87}.

Analysis of the Beta Spectrum

The differential analysis of the Rb^{87} beta spectrum was done using the five-inch liquid scintillation spectrometer [Fig. 1(a)]. The high-voltage and amplifier gain were adjusted so that the total spectrum was spread over about half of the full discriminator range. Differential counts were taken at intervals of 2% of the range using a 2% window width from zero up to the maximum energy of the β rays. The linearity of the window width with discriminator setting was checked by feeding the pulses from a precision pulse generator into the pre-amplifier. Background counts were taken under identical conditions using a scintillator solution containing octoic acid and ethanol to simulate the sample. The position of the Ba^{137m} electron line was used to ensure that the quenching in the background cell was the same as in the sample cell and to calibrate the pulse-height scale. The discriminator settings were converted to energy values using a pulse height *vs* energy calibration curve established with the aid of monoenergetic sources.[12] The data were corrected for resolution using a second-derivative correction formula[13] which has been shown to be applicable to liquid scintillation spectrometry.[12] A Kurie plot[14] was made of

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[10] W. A. Brooksbank and G. W. Leddicote, J. Phys. Chem. **57**, 819 (1953).

[11] A. O. Nier, Phys. Rev. **79**, 450 (1950).

[12] E. P. Steinberg and L. E. Glendenin, Argonne National Laboratory (to be published).

[13] G. E. Owen and H. Primakoff, Phys. Rev. **74**, 1406 (1948).

[14] Tables for the Analysis of β Spectra, National Bureau of Standards Applied Mathematics Series Report No. 13 (U. S. Government Printing Office, Washington, D. C., 1952).

TABLE II. Data for determination of half-life of Rb^{87}.

Rubidium source	Counter	Activity [(dis/min)/ml]	Weight of Rb ($mgRb_2SO_4$/ml)	Specific activity of Rb [(dis/min)/mg]	Half-life (10^9yr)
DeRewal RbCl (98.5% purity)	5-inch	12 400	365.2×0.985=359.7	54.13	47.75
	Tri-Carb	12 500			
	5-inch	12 500			
		Av 12 470±43			
DeRewal RbCl (Purified by ion exchange)	5-inch	11 800	342.5	54.97	47.03
	5-inch	12 000	341.9		
	5-inch	12 200	343.6		
	5-inch	12 000			
	Tri-Carb	12 300	Av 342.7±0.6		
		Av 12 060±152			
Mackay $RbNO_3$ (Purified by ion exchange)	5-inch	12 300±100	348.6	55.28	46.77
			345.5		
			348.8		
			Av 347.6±1.4		
Fairmount RbCl (a) (Purified by ion exchange)	5-inch	13 600	378.0	56.14	46.04
	Tri-Carb	13 650	377.5		
	5-inch	13 500			
			Av 377.8±0.25		
		Av 13 580±57			
Fairmount RbCl (b) (Purified by ion exchange)	5-inch	12 450	361.7	54.36	47.56
	5-inch	12 700	361.3		
		Av 12 580±125	Av 361.5±0.2		
				Av 55.0±0.6	Av 47.0±0.5

the final data and extrapolated to obtain the maximum beta energy. The Rb^{87} Kurie plot is shown in Fig. 3.

In order to check the reliability of the method, the beta spectrum of Ca^{45} was used as a standard. Normal calcium was irradiated with neutrons, purified, and converted to calcium octoate. The calcium octoate was then dissolved in the liquid scintillator and the beta spectrum of Ca^{45} was analyzed under the same conditions used for Rb^{87}.

RESULTS AND DISCUSSION

Half-Life of Rb^{87}

From the number of atoms of Rb^{87} (N) and the absolute disintegration rate of the sample (A) as determined above the decay constant (λ) is obtained from the relationship

$$A=\lambda N.$$

The results of these measurements are given in Table II. The average value for the half-life of Rb^{87} is $(47.0\pm0.5)\times10^9$ yr. The error given is the mean deviation of the five half-life determinations.

Recent work by Kulp[15] in which he incorporates a few additional points with the data of Aldrich *et al.*[2] gives a value for the Rb^{87} half-life of about 48×10^9 yr.

Beta Spectrum of Rb^{87}

From the Rb^{87} Kurie plot (Fig. 3) the maximum beta energy based on two samples is found to be 272±3 kev. A summary of this work compared with the work of other investigators is given in Table III. The shape of the Kurie plot (Fig. 3) is in good agreement with that published by Lewis[16] who used a thalliated rubidium iodide scintillation spectrometer. The agreement on the end-point energy is within the experimental errors of the measurements. The Ca^{45} Kurie plot is shown in Fig. 4. The observed maximum beta energy for Ca^{45} is 253±3 kev. The best literature value is 254±3 kev[17] as determined by β-ray spectrometry.

TABLE III. Values of $E_{\max}$ for Rb^{87} beta spectrum.

$E_{\max}$ (kev)	Method of determination	Reference
272±3	Liquid scintillation spectrometer	This work
275	Thin-lens β spectrometer	a
275	Proportional counter spectrometer	b
275	RbI scintillation spectrometer	c

[a] See reference 20.
[b] See reference 22.
[c] See reference 16.

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[15] J. L. Kulp, Lamont Observatory, Columbia University (private communication).

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[17] Macklin, Feldman, Lidofsky, and Wu, Phys. Rev. **77**, 137 (1950).

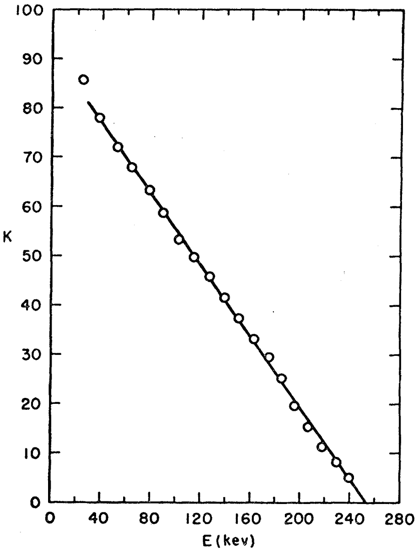

FIG. 4. Kurie plot for Ca^{45}.

A comparison of the Kurie plots for Rb^{87} and Ca^{45} indicates that the Rb^{87} transition is highly forbidden. The Ca^{45} transition is known to be allowed[18] and does in fact give a straight-line Kurie plot. The Rb^{87} Kurie plot has a considerable amount of curvature with an excess of electrons in the low-energy region. The ft value ($\log ft=17.4$ for $E_0=272$ kev and $T_{\frac{1}{2}}=47.0\times10^9$ yr) and the known spin and parity change (3, yes) for this transition indicate a third forbidden transition.[18] Other workers, notably Tomazawa *et al.*[19] and MacGregor and Wiedenbeck,[20] have calculated the third forbidden (tensor only) correction factor from the expressions derived by Greuling.[21] The work of Tomazawa *et al.*[19] was subsequently found to be in error.[20] The factors developed by MacGregor and Weidenbeck were applied to our data without much success. The calculation of the third forbidden correction factor with a V-A mixture involves several adjustable ratios of matrix elements and is exceedingly laborious. This task was not attempted since the significance of the results seemed dubious.

ACKNOWLEDGMENTS

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[22] Curran, Dixon, and Wilson, Phys. Rev. **84**, 151 (1951).