MASTER

INVESTIGATION OF CERENKOV COUNTING
OF ENVIRONMENTAL STRONTIUM-90

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The usefulness of Cerenkov counting for measurement of energetic beta radiation has been recognized for some time. However, little has been reported on detection of low levels of $^{90}\text{Sr-Y}$, of importance in environmental monitoring. Consequently, a typical liquid scintillation counter was evaluated for this purpose. A "blank" of about 5 cpm and ^{90}Y efficiency of 42% were obtained for 20-ml samples. The corresponding minimum detectable concentration for a 100-minute count is 0.03 pCi/ml, so that measurement of water samples can readily be made at the maximum permissible concentration for ^{90}Sr , 0.3 pCi/ml. The efficiency for ^{90}Sr is less than 0.4%, 1.4% for ^{137}Cs , and less than 0.04% for gamma-emitting ^{85}Sr , a useful tracer. Some data for ^{90}Y efficiencies and blanks are given for other liquid scintillation counters.

Chemical treatments are necessary in some cases to concentrate $^{90}\text{Sr-Y}$, to remove colored substances which cause quenching, or to eliminate interfering radionuclides. However, the manipulations need not be as elaborate as in conventional radiochemical analysis methods for ^{90}Sr . Ferric ion (yellow) quenches at the 5 ppm level, but the interference can be eliminated by adding a reducing agent. The Rn daughter ^{214}Bi , an interfering radionuclide, disappears by decay in 2-3 hours after removal of Rn by sweeping with air or gas. Concentration-separation methods studied have included precipitation and ion exchange.

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I. INTRODUCTION

Strontium-90 is one of the most toxic radionuclides associated with nuclear energy because of its retention by the body, its half-life of about 29 years, and the 2.28-MeV beta radiation of its 64-hour daughter, ^{90}Y . Determination of the latter by Cerenkov counting is attractive, as was recognized by Yamada (1962), who obtained a detection limit of about 0.2 dpm/ml using 8-litre water samples. Ross and Rasmussen (1974) reported 36-50% efficiency for ^{90}Y , and Carmon (1979) described the measurement of both ^{89}Sr and ^{90}Sr , but little attention has been given to low levels of ^{90}Sr .

It was decided to investigate the utility of a typical liquid scintillation spectrometer for the Cerenkov determination of simulated natural environment water samples containing ^{90}Sr . Short-lived nuclides such as ^{89}Sr were negligible. The counter employed was a 3000 series Packard Instrument Co. liquid scintillation spectrometer with EMI 6255B photomultiplier tubes operated in the coincidence mode. Voltage, gain, and discriminator settings were optimized with respect to efficiency and background at 1600, 70%, and 100-1000, respectively, somewhat as described by Haberer (1966). The refrigerator temperature was 0°C. Radionuclides were prepared by diluting reference materials from the National Bureau of Standards (NBS) or were measured using equipment calibrated with NBS materials.

II. BACKGROUNDS AND EFFICIENCIES FOR YTTRIUM-90

Backgrounds and ^{90}Y efficiencies were measured using four types of vials: (1) Wheaton polyethylene, (2) Fisher linear polyethylene, (3) Wheaton low-potassium glass, and (4) locally fabricated quartz. Capacities of vials varied from about 15 to 23 ml; aqueous volumes were limited to 20 ml. The count rate with the chamber empty was typically 7.3 cpm. Count rates with empty vials and with vials almost filled with 0.1 N HCl are given in Table I, which also includes ^{90}Y efficiencies. From these data, the minimum detectable activity, MDA (defined as $2.8 \sigma_b$), for a 100-minute count is 1.5 dpm, or 0.68 pCi. The corresponding concentration in a 20-ml sample is 0.034 pCi/ml, well below the maximum permissible concentration (MPC) for ^{90}Sr , 0.3 pCi/ml.

Table I. Backgrounds and Efficiencies with Various Vials

Vial type	Background, cpm		Yttrium-90 Efficiency, %
	Empty	Filled	
1	5.7	5.2	42
2	4.6	4.3	42
3	8.9	8.5	37
4	7.3	7.1	27

A "blank" vial (type 1) was prepared with the quenching agent Fe^{3+} (Section IV) at 0.25 mg/ml. Background dropped to 4.1 cpm. Even more pronounced effects were seen with glass and quartz vials. An opaque solution-suspension of ink in a type 1 vial showed a background of 1.2 cpm. It was concluded that electronic noise is minor, but that Cerenkov light is produced in system components and glass and quartz vials by external gamma and cosmic radiation (and by beta in glass).

Pulse height spectra of Cerenkov pulses were taken by means of a Nuclear Data 6603 analyzer. Data for ^{90}Y and a type 1 blank are shown in Figure 1 with an unquenched liquid-scintillation spectrum of ^3H for comparison. It is apparent that the pulse height distribution of the ^{90}Y sample is similar to that of the ^3H , and that pulses from the blank cover a wide range of amplitudes, with a secondary maximum at a location equivalent to about 1.7 MeV. These observations are similar to those reported by Francois (1972). It is clear from these data that changing voltage and gain have little effect on figure of merit for ^{90}Y , but discriminator levels are important. The spectral data support empirical observations during optimization.

Measurements were made on the same counter (A) at room temperature, and backgrounds were substantially higher, as shown in Table II, which also contains data for other instruments. Noise seems to increase with temperature. Low blanks might have been achieved by optimization, which was not feasible for these systems because they were in use for other work.

Table II. Backgrounds and Efficiencies of Several Counters

System	Refrig.	Background, cpm		Efficiency, %
		Blank	Ink	
A	No	26	19	--
B	No	17	9	75 ^a
C	Yes	12	1.5	75 ^a
D	No	10	5	44
E	Yes	17	2.4	43
F	Yes	8	--	56

^a7ml, others 20

FIGURE 1. Spectra of ³H (LSC) and Cerenkov counts for ⁹⁰Y and blank.

Table III. Efficiencies for Various Nuclides

Nuclide	Efficiency, %
^{85}Sr	<0.04
^{90}Sr	<0.4
^{137}Cs	1.4
^{60}Co	3.3
^{89}Sr	15
$^{222}\text{Rn}^a$	22
$^{106}\text{Ru-Rh}$	49

^a Beta-gamma daughters

III. EFFICIENCIES FOR OTHER RADIONUCLIDES

Efficiencies are given in Table III for several nuclides sometimes of significance in analysis of environmental samples. The low efficiency of ^{85}Sr , consistent with that reported by Carmon (1979), makes possible the use of ^{85}Sr as tracer to measure recoveries in complicated separation procedures. Determination of the efficiency of ^{90}Sr required the separation of the ^{90}Y daughter and correction for regrowth before and during counting. Separations may not have been complete, hence an upper-limit value is presented in the table. ^{226}Ra solution was used in the estimation of the efficiency for ^{222}Rn daughters, principally ^{214}Bi . Since Rn was not in equilibrium with Ra in the solution, it was necessary to place aliquots in vials and wait for ingrowth of Rn and daughters. It was found that Rn penetrated the plastic vial walls, markedly in type 1, and less in type 2; it did not penetrate glass. This phenomenon is shown in Figure 2 (type 2 vial) in which Rn and daughters contained in the walls of the empty vial disappear more rapidly than expected (Rn half-life: 3.8 days).

Interference from Rn daughters can be minimized by removal of Rn by bubbling air through a water sample, then waiting two to three hours for the Rn daughters to decay. If the activities of other radionuclides are known, corrections can be estimated. Separations can also be used (see Section VI). If ^{89}Sr is present, ^{90}Sr may be determined by complete separation of Sr, and initial count for ^{89}Sr , then counting of ^{90}Y after ingrowth (Carmon, 1979).

FIGURE 2. Radon daughter growth in solution and decay after emptying vial.

IV. QUENCHING

Chemical quenching is of no consequence in Cerenkov counting, however color quenching, whether of near-ultraviolet or visible light, can be significant. For example, the effect of ferric ion is shown in Figure 3. This effect was removed by heating with hydroxylamine hydrochloride. Nitrate ion quenches by ultraviolet absorption. With type 1 vials, 0.5 M HNO_3 caused a loss of about 5% in the ^{90}Y count rate, and 1.3 M HNO_3 reduced the count rate by 9%.

FIGURE 3. Quenching by ferric ion.

V. SURVEILLANCE FOR HARD-BETA EMITTERS

Cerenkov counting can be a useful method of surveillance because of its simplicity and its high sensitivity for hard beta radiation and insensitivity to weak beta radiation. Typical water samples from ORNL experimental facilities were measured directly by Cerenkov counting, and radiochemical analyses (Sunderman and Townley, 1960) were performed, with measurements by means of conventional low-background beta counters. Results in Table IV are in good agreement except in two cases, where ^{137}Cs and ^{60}Co were identified, and other nuclides may have been present.

Table IV. ^{90}Sr concentrations by direct Cerenkov and radiochemistry

Sample	Measured activity, dpm/ml ^a	
	Cerenkov	Radiochemical
1	95+5	102+6
2	0.8+0.2	0.80+0.07
3	1.1+0.2	1.0+0.1
4	1.3+0.2	1.2+0.1
5	39+3 34 ^b	30+2
6	2.3+0.4	2.0+0.1
7	192+11	210+12
8	26+2	25+1
9	8.4+0.6 6.8 ^c	3.9+0.2
10	2.0+0.3	1.9+0.1
11	267+14	298+16

^aUncertainties: counting plus 5% intrinsic, 95% C.L.

^bApprox. corrected for ^{137}Cs only.

^cApprox. corrected for ^{60}Co only.

Table V. Comparison between Cerenkov and conventional measurements

Sample	Measured activity, dpm	
	Cerenkov	Conventional
1	2.9+1.5 ^a	3.8+2.6 ^a
2	4.1+1.6	4.1+0.3
3	19+2	21+1
4	62+4	59+4
5	115+4	119+7
6	151+4	161+12

^aCounting errors at 95% C.L.

VI. CHEMICAL CONCENTRATION AND SEPARATION

Chemical treatments are necessary in some cases to concentrate ^{90}Sr -Y from large volumes, to remove quenching substances, or to eliminate interfering radionuclides. A conventional determination (Sunderman and Townley, 1960) involves addition of Sr carrier, precipitation as carbonate followed by nitrate, scavenging by precipitation of $\text{Fe}(\text{OH})_3$ and BaCrO_4 , and final precipitation as oxalate, which is deposited on a small filter disc, dried, weighed, and the activity counted. Such analyses were done on six samples, and, following beta counting, ^{90}Y daughter was allowed to grow in the precipitates, which were subsequently dissolved in HCl and Cerenkov counts were made. Data in Table V show good agreement.

A much simpler scheme is under development involving acidification of a water sample to pH 1 with HNO_3 , and allowing the solution to stand to assure equilibrium between ^{90}Y and ^{90}Sr . Concentration and partial separation are effected by adsorption on a cation resin column. Strontium and Y are then eluted from the column and coprecipitated with calcium oxalate, which is dissolved in HCl for Cerenkov counting. Testing and modification of the scheme are currently in progress.

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REFERENCES

- Carmon, B. (1979). *Int. J. Appl. Rad. Isotopes*, 30, 97.
- Francois, B. (1972). *Int. J. Nucl. Med. Biol.*, 1, 1.
- Haberer, K. (1966). "Measurement of Beta Activities in Aqueous Samples Utilizing Cerenkov Radiation." Packard Instrument Co., Downers Grove, IL.
- Ross, H.H., and Rasmussen, G.T. (1974). In "Liquid Scintillation Counting, Recent Developments," p. 363. Academic Press, New York.
- Sunderman, D.N., and Townley, C.W. (1960). "The Radiochemistry of Barium, Calcium, and Strontium." Report NAS-NS-3010. National Academy of Sciences - National Research Council, Washington, DC.