

LIQUID SCINTILLATION COUNTING
RECENT APPLICATIONS AND DEVELOPMENT
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DETERMINATION OF TOTAL ACTIVITY BY LIQUID
SCINTILLATION COUNTING AND ITS APPLICATION
TO AQUEOUS EFFLUENT SAMPLES

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An analytical method for determining total activity in water samples is described. The method depends on the direct relationship between the average energy deposited in a liquid scintillator solution and the channels ratio recorded for two different portions of the total energy spectrum. Calibration curves are constructed using single energy beta emitters. Samples are first counted at low gain for medium to high energy activity, followed by a second count at high gain to record total activity. Results obtained by this method for both synthetic and reactor effluent samples were quantitative (3-7%) compared with results obtained by low-background beta counting (42-100%).

I. INTRODUCTION

Conventional methods used to measure total activity in liquid samples are seldom adequate for any useful purpose and the data obtained are usually impossible to interpret. Evaporation of the sample in preparation for counting can result in losses of volatile nuclides such as ^3H , ^{14}C , ^{106}Ru , and ^{131}I . Large uncertainties are usually introduced due to absorption and scattering of the beta particles in the deposited salts on the planchet. Low energy radiation, emitted by such common nuclides as ^{14}C , ^{55}Fe , ^{45}Ca , ^{147}Pm , ^{241}Pu , ^{63}Ni and ^{51}Cr , is not normally detected by these methods.

The most reproducible and accurate results for total activity measurements can be obtained with a detector that is

relatively energy-independent. Liquid scintillation systems offer essentially 4π counting and should provide substantial improvement for gross activity determinations. This technique has been applied to rapid measurements of environmental samples (Prochazka and Jilek, 1971) and for total beta and alpha assay (Bogen and Welford, 1971). Samples containing mixtures of ^3H , ^{14}C , and ^{32}P have been analyzed by beta spectrum analysis (Oller and Plato, 1972) utilizing a liquid scintillation spectrometer coupled to a multichannel analyzer. The usefulness of these procedures for the determination of total activity in samples containing both beta and gamma activity has not been determined.

The calibration of any counter for measuring total activity of mixed fission and activation products is a difficult problem primarily due to the potentially wide energy range involved. The usual practice is to use a ^{40}K or ^{90}Sr - ^{90}Y standard with the assumption that the average energy of that standard is the best approximation of the average energy for mixed fission and activation products. The purpose of this paper is to: (1) demonstrate that serious errors occur when a single efficiency is adopted for gross activity counting and (2) present an improved liquid scintillation method which will provide more reliable and accurate estimates of gross activity in reactor effluent and aqueous environmental samples.

II. EXPERIMENTAL

A. *Equipment*

The commercial liquid scintillation analyzer (LSA) used was a Packard Model 3385. The LSA has three independent single-channel analyzers that permit a certain amount of energy discrimination as well as the auto background subtract and channels ratios features. A Beckman wide-beta counter was used to compare evaporated standards and samples with results from the LSA.

B. *Radioisotope Standards*

All radioactive standard solutions were obtained from Amersham-Searle.

C. *Reagents*

All reagents used were A.C.S. reagent-grade materials.

III. DESCRIPTION AND DISCUSSION OF PROCEDURES

The determination of total activity in effluent water samples is made difficult by the emission of both weak and energetic beta, positron or alpha particles from unidentified nuclides present in unknown proportions. Whatever type of detector is used, there is a "threshold" energy below which no particle can be detected and above which most of the particles entering the sensitive volume will be counted. Charged particles, whatever their energy, are detected with better efficiency by a liquid scintillation counter than by a thin-window Geiger-Muller tube due to the absence of absorption and to the 4π geometry of the phosphor in which the activity is dissolved. The threshold of the liquid phosphor cannot be reduced enough to enable all nuclides to be detected with the same efficiency. Therefore no one particular efficiency should be adopted to calculate the total activity in a sample containing an unknown mixture of nuclides. Any method claimed to measure "total beta activity" or "gross activity" is the result of a compromise. Some nuclides are overestimated and the remainder are underestimated. The underestimated nuclides could easily contribute a major proportion of the total activity. Many samples received by this laboratory contain large percentages of such low energy nuclides as ^{51}Cr , ^{58}Co , ^{54}Mn , and ^{55}Fe . An accurate assessment of the total activity in these samples is impossible if the counting efficiency is based exclusively on one nuclide such as ^{40}K or ^{90}Sr . The following procedure incorporates a calibration technique utilizing several standard beta emitters with average energies ranging from 6 KeV (^3H) to 583 KeV (^{89}Sr). Counting efficiencies are subsequently compared with the pertinent channels ratios to produce calibration curves. These calibration curves are then used to predict total activity in samples containing mixtures of unknown nuclides in various proportions.

A. Sample Preparation

The matrix for liquid scintillation counting of standards and samples consisted of 10 mL of 0.3 M HCl mixed thoroughly with 10 mL of Insta-gel¹ in 22-mL low-potassium-glass vials. The samples were placed in the counter's holding chamber for one hour for dark adaptation and temperature equilibration before counting. All counting was done at 10°C. Color and

¹Packard Instrument Company.

chemical quenching should be avoided because of possible spectrum shifting and subsequent changes in channels ratios. New calibration curves are required for any significant change in acid concentration.

B. Instrument Settings

The LSA used in this work was a three-channel instrument which allowed for a sufficient degree of energy discrimination. The first channel (A) was used to count all activity from very low energy ^3H through the highest energy beta emitters. Channel A records true "gross" or "total" activity because it includes those counts associated with compton and auger electrons as well as alpha and beta activity.

A second channel (B) was optimized to measure total activity but with the exclusion of low energy ($E_{\text{ave}} < 10 \text{ KeV}$) emitters. In many samples 95% or more of the total activity is tritium. Channel B thus eliminates a potentially large interference in the accurate measurement of higher energy activity.

The third channel (C) was used in conjunction with channels A and B. The window chosen for channel C was meant to cover a large portion of the medium and high energy region while excluding all low energy activity. Maximum sensitivity is thus assured for changes in average beta energy from sample to sample as monitored by the channels ratios A/C and C/B. The following discriminator settings were used for this work:

Channel A	5 - infinity
Channel B	120 - infinity
Channel C	100 - 800

C. Calibration Procedures

Seven nuclides (^3H , ^{63}Ni , ^{129}I , ^{147}Pm , ^{90}Sr , ^{36}Cl , and ^{89}Sr) with single beta transitions ranging in average energy from 6 KeV to 583 KeV were chosen for calibration of channels A and B. Counting efficiencies for channel A were plotted against the corresponding channels ratio of A/C with a gain of 100% found to be optimum. In a similar manner the counting efficiencies in channel B for the standard beta emitters were related to the channels ratio C/B with an optimum gain of 10%.

Figures 1 and 2 illustrate the relationship between counting efficiencies of the beta standards and the channels ratios for channels A and B respectively. Background should be subtracted from each channel before computation of channels ratios for increased accuracy. In computing channels ratios for low activity samples, it is very important to use net rather than gross counts.

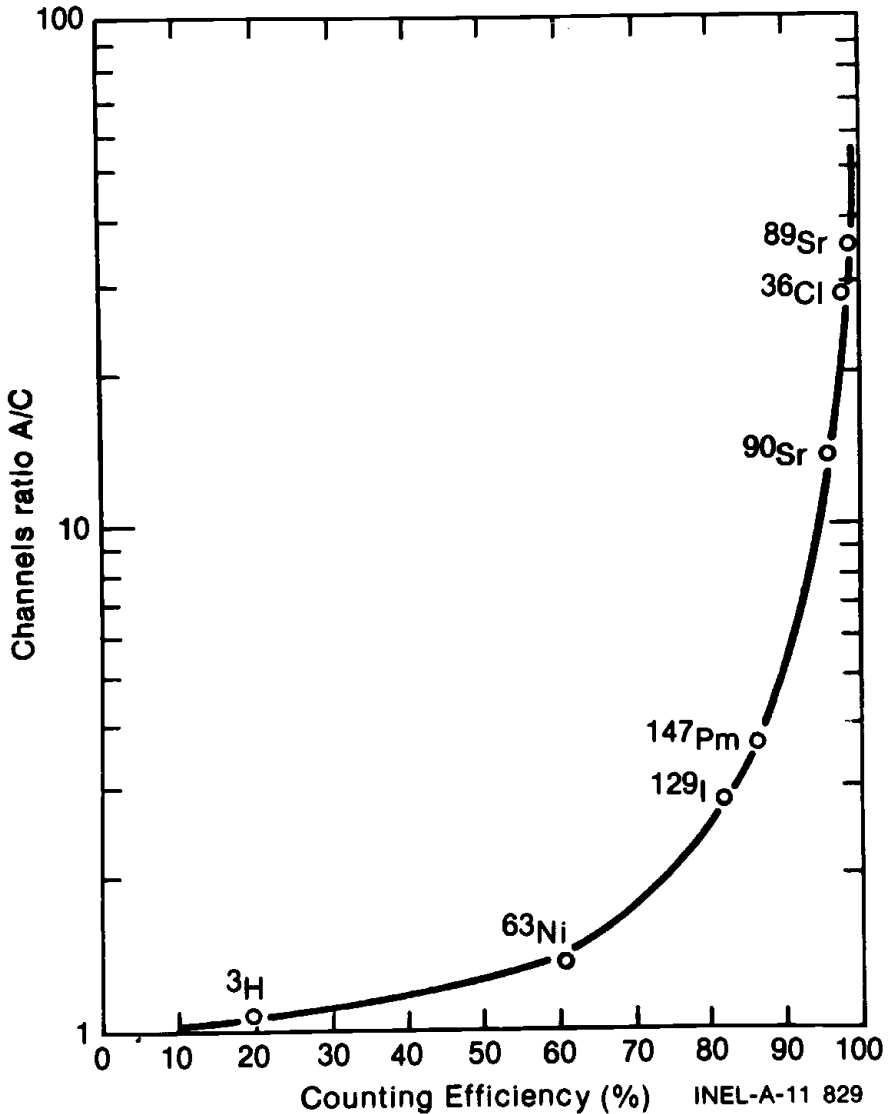


FIGURE 1. Channel A counting efficiencies for standard beta emitters.

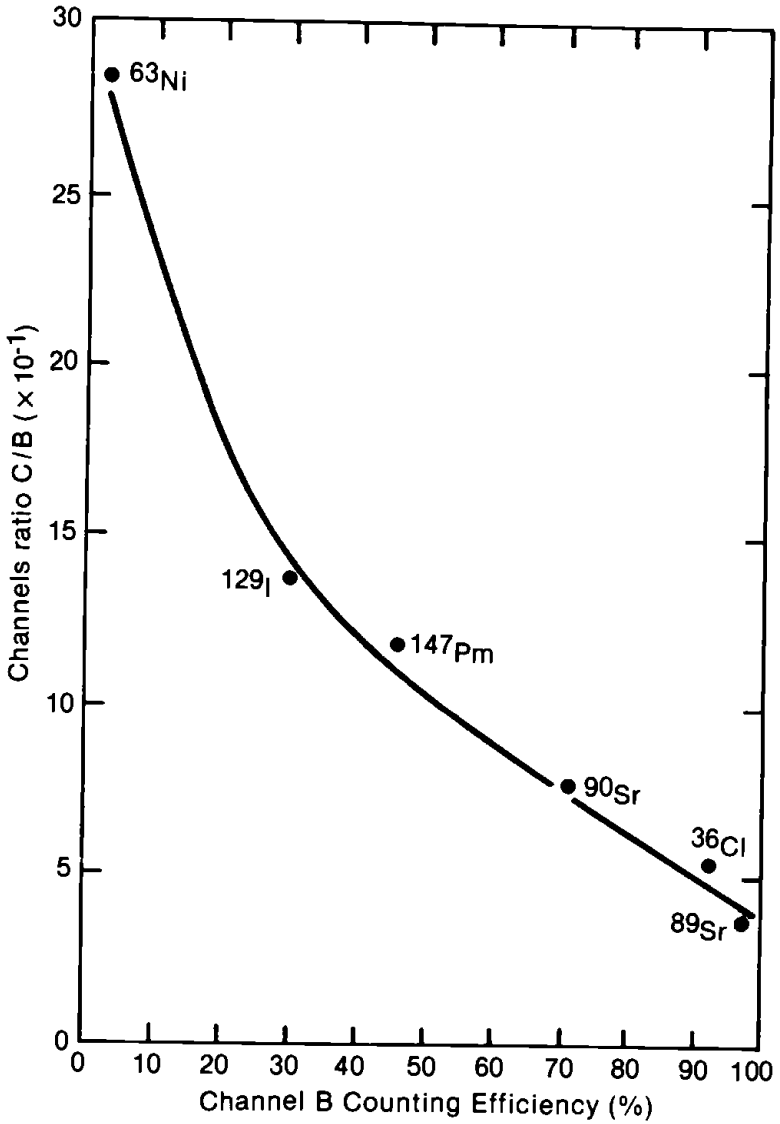


FIGURE 2. Channel B counting efficiencies for standard beta emitters.

D. Activity Determination

The normal procedure for determination of sample activity is as follows:

(1) An initial measurement is made with each channel adjusted to 10% gain. The resultant channels ratio C/B is used to obtain the counting efficiency for channel B from Figure 2.

(2) The sample is then recounted with each channel set for 100% gain. By reference to the channels ratio A/C and Figure 1 the counting efficiency for channel A is obtained.

(3) The medium and high energy activity may be calculated from the expression:

$$A_H, \mu\text{ci/mL} = \frac{b}{e_B \cdot V \cdot 2.2 \times 10^6}$$

where

A_H = medium and high energy activity

b = net cpm, channel B

e_B = channel B counting efficiency (from Figure 2)

V = volume of sample in mL.

(4) The total activity in the sample is expressed as:

$$A_T, \mu\text{ci/mL} = \frac{a}{e_A \cdot V \cdot 2.2 \times 10^6}$$

where

A_T = total activity

a = net cpm, channel A

e_A = channel A counting efficiency (from Figure 1)

V = volume of sample in mL.

E. Detection Limits

Minimum detectable levels of activity (L_D) were calculated at the 95 per cent confidence level for both A_H and A_T using the "working" expression for radioactivity as defined by Currie (Currie, 1968). The detection limit for A_H , for a 10 ml sample counted 100 min with a background of 54 cpm and e_B of 60%, is 1.6×10^{-7} $\mu\text{ci/mL}$. For A_T the L_D is 2.0×10^{-7} $\mu\text{ci/mL}$ with a background of 86 cpm and e_A of 30%.

IV. RESULTS AND DISCUSSION

Calibration curves for this method were constructed by use of single beta transitions only. Further tests of the method were necessary to determine the usefulness of the procedure for measurement of samples that contain radionuclides that emit X-rays, gamma rays, auger and compton electrons, and alpha particles. Table 1 compares those efficiencies predicted from the channels ratio calibration curves with the actual counting efficiencies for several radionuclides which decay by various means. Efficiencies obtained by counting with the wide-beta counter are listed for comparison. The predicted results are in good agreement with the actual efficiencies except in the case of ^{133}Ba and to a lesser extent ^{55}Fe . The discrepancies in these cases may be due to possible differences in energy distribution produced by the electron capture process from that due to normal beta continuum. Wide-beta counter efficiencies are invariably much lower than those obtained by liquid scintillation. Accuracy suffers when wide-beta counting to measure gross activity, especially if ^{90}Sr - ^{90}Y is used as the standard.

Synthetic samples were prepared containing known amounts of beta, beta-gamma, and electron capture activity. The samples were then measured using the channels ratio method and the results are listed in Table 2. These results indicate that various combinations of low, medium, and high energy activity can be estimated within 1-8% by this method.

This measurement technique was also tested on liquid samples taken from various power reactor areas. Aliquots were analyzed for individual gamma and beta emitter activity and totalized for comparison with the liquid scintillation and wide-beta methods. The results of these measurements are listed in Table 3. As expected tritium comprises a major share of the total activity in all of the samples. Agreement between the totalized activity and that measured by channel A is very good for all of the samples (3-7%). Measurements made by wide-beta counting are much lower in all cases when compared to the totalized activity values, primarily because the bulk of the activity is tritium and other low energy activity. Little or no agreement is observed between channel B and wide-beta results. This can probably be attributed to losses occurring in the wide-beta sample preparation in addition to errors due to use of a single wide-beta calibration standard.

Standard Nuclide	Average Energy (KeV)	Percent Efficiencies					
		Counting		Liquid Scintillation		Wide Beta	
		Channel A Actual	Channel A Predicted	Channel B Actual	Channel B Predicted	Actual	Predicted
Sr-90	196	96	98	88	92	92	46
Y-90	934						
Co-60	94	95	94	69	61	61	37
Cs-137	195	96	92	64	70	70	25
Ba-137m	IT, CE						
Ru-106	9	92	88	65	72	72	38
Rh-106	1415						
Pb-210	5						
Bi-210	390	87	92	87	91	91	39
Po-210	alpha						
Fe-55	EC	15	20	<0.1	0	0	0
Ba-133	EC	76	89	37	37	37	7
S-35	48	84	84	36	37	37	32
Ce-144	81	96	97	78	88	88	44
Pr-144	1208						
Cs-134	158	94	93	72	77	77	37

TABLE 1. Liquid Scintillation and Wide-Beta Counting Efficiencies.

Sample Description	Activity (dpm)			
	Channel A		Channel B	
	Added	Found	Added	Found
Low energy (^3H and ^{55}Fe)	3.65×10^4	3.69×10^4		
Medium energy (^{147}Pm and ^{60}Co)	9.46×10^3	9.69×10^3	9.46×10^3	9.97×10^3
High energy (^{134}Cs and ^{90}Sr - ^{90}Y)	1.05×10^4	1.06×10^4	1.05×10^4	1.01×10^4
Low-medium	4.59×10^4	4.25×10^4	9.46×10^3	9.74×10^3
Low-high	4.70×10^4	4.55×10^4	1.05×10^4	9.88×10^3
Medium-high	1.99×10^4	2.01×10^4	1.99×10^4	1.94×10^4

TABLE 2. Synthetic Samples.

Sample No.	Type	Principal Isotopes Present	Totalized	Activity $\mu\text{Ci/mL}$		
				Liquid Channel A	Scintillation Channel B	Wide Beta
1.	Chemical Waste	^3H , ^{137}Cs , ^{134}Cs	1.37×10^{-1}	1.42×10^{-1}	7.98×10^{-2}	6.30×10^{-2}
2.	Liquid Waste	^3H , ^{131}I , ^{51}Cr , ^{141}Ce	2.76×10^{-3}	2.65×10^{-3}	2.60×10^{-5}	1.10×10^{-5}
3.	Waste Tank	^3H , ^{60}Co , ^{58}Co , ^{54}Mn	5.41×10^{-2}	5.28×10^{-2}	2.31×10^{-3}	1.47×10^{-3}
4.	Liquid Waste	^{137}Cs , ^{134}Cs , ^{60}Co , ^3H	1.51×10^{-2}	1.61×10^{-2}	1.32×10^{-2}	8.76×10^{-3}
5.	Primary Waste	^3H , ^{131}I , ^{51}Cr , ^{58}Co	8.13×10^{-2}	7.78×10^{-2}	3.24×10^{-2}	4.88×10^{-3}
6.	Waste Pond	^3H , ^{144}Ce , ^{144}Pr , ^{106}Ru , ^{106}Rh , ^{137}Cs	6.25×10^{-2}	6.52×10^{-2}	8.85×10^{-3}	5.44×10^{-3}

TABLE 3. Total Activity in Power Reactor Samples.

V. CONCLUSIONS

An improved method for the determination of total activity by liquid scintillation has been presented. The technique is relatively simple; advantage is taken of the automatic features provided by modern liquid scintillation spectrometers, and the results are considered to be much more accurate than any other gross counting method. Although the detection limit may not be as low as it is for other methods, due to the higher background rates inherent in liquid scintillation counting, the improvement in calibration is considered more advantageous.

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