

# The standardization of $^{33}\text{P}$ by the TDCR efficiency calculation technique

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## Abstract

The activity of the pure beta-emitter phosphorus-33 ( $^{33}\text{P}$ ) has been directly determined by the triple-to-double coincidence ratio (TDCR) efficiency calculation technique, thus extending the number of radionuclides that have been standardized by this simple, non-extrapolation liquid scintillation (LS) method. The major advantage of inherently accounting for chemical quenching without the need for additional external measurements is demonstrated.

The  $^{33}\text{P}$  solution activity concentration was verified by tracing with cobalt-60, utilizing  $4\pi(\text{LS})\beta\text{-}\gamma$  coincidence counting. Agreement to within 1.2% confirmed the reliability of the TDCR measurements.

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*Keywords:* Phosphorus-33; Activity measurement; Liquid scintillation coincidence counting; TDCR technique

## 1. Introduction

Phosphorus-33 ( $^{33}\text{P}$ ) is a useful radionuclide for radiolabeling and medical treatment. Being a pure beta-emitter, specialized techniques are required to accurately determine the disintegration rate. The triple-to-double coincidence ratio (TDCR) efficiency calculation technique (Simpson and Meyer, 1994; L'Annunziata and Kessler, 1998) was selected for this purpose, thereby extending the number of radionuclides that have been standardized by this simple, non-extrapolation liquid scintillation (LS) method. With this method, the measured double- and triple-coincidence count rates provide sufficient data to allow the extraction of the source activity irrespective of the quenched state. This major advantage of inherently accounting for the chemical quenching without the need for additional external measurements, was verified for  $^{33}\text{P}$  by heavily quenching sources with different amounts of chloroform.

Since this was the first time that  $^{33}\text{P}$  had been measured with the TDCR efficiency calculation technique, the solution activity concentration was also

determined by efficiency tracing utilizing the  $4\pi(\text{LS})\beta\text{-}\gamma$  coincidence counting method. Cobalt-60 ( $^{60}\text{Co}$ ) was selected as the tracer because of the comparable beta spectrum energies and shapes (both allowed).

## 2. Review of the TDCR efficiency calculation technique

A LS source is viewed by a three-phototube detection system and the double-tube coincidence counting rate  $N_d$  and the triple-tube rate  $N_t$  are recorded simultaneously. If  $N_0$  is the  $^{33}\text{P}$  disintegration rate, then

$$N_d = N_0 \varepsilon_d \quad (1)$$

and

$$N_t = N_0 \varepsilon_t, \quad (2)$$

where  $\varepsilon_d$  and  $\varepsilon_t$  are the double- and triple-tube detection efficiencies, respectively. The efficiencies can be determined without recourse to prior calibration nor the use of a reference standard. Instead this is achieved in an absolute way by combining the experimental measurement with theory. Although the efficiencies are initially unknown, their ratio  $R$  is given by the measured

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counting rates. Thus

$$\frac{\varepsilon_t}{\varepsilon_d} = \frac{N_t}{N_d} = R. \quad (3)$$

In a LS counting system the efficiencies can be expressed theoretically as a function of a single floating parameter  $P$ , the so-called figure-of-merit, that in effect is an indicator of the light output/electron emission process. Therefore, Eq. (3) can be rewritten as

$$\frac{\varepsilon_t(P)}{\varepsilon_d(P)} = R \quad (4)$$

and  $P$  is found by solving the equation to the desired accuracy by the method of iteration. Having obtained  $P$  for the specific value of  $R$  determined by measurement, the corresponding efficiencies follow directly and the source activity is given by

$$N_0 = \frac{N_d}{\varepsilon_d(P)} = \frac{N_t}{\varepsilon_t(P)}. \quad (5)$$

### 3. Activity measurements

A high-purity  $^{33}\text{P}$  solution in the form of  $\text{H}_3\text{PO}_4$  in 0.01 M HCl was obtained from the Nuclear Energy Corporation of South Africa (NECSA). All counting sources were prepared by dissolving accurately weighed aliquots of the  $^{33}\text{P}$  solution in 12 ml of liquid scintillator (Quicksafe A from Zinsser Analytic) to which 3 ml/l of 3 M HCl had been added to minimize adsorption to the glass counting vials.

#### 3.1. TDCR technique

Three counting sources were prepared in commercial glass vials. The sources were counted with a detection system comprising three RCA 8850 high-gain phototubes that were connected in coincidence through a locally designed and built electronic module providing a triple- and three double-coincidence signal outputs. The thresholds for all three phototube channels were set to just below the single electron peak so that the conditions for the efficiency calculation were fulfilled. To satisfy the criterion that each phototube should have the same

figure-of-merit, the efficiencies were matched by ensuring that the three double-coincidence counting rates were as similar as possible after accounting for the background rates. This was achieved by the proper placement of the counting vial relative to the phototubes.

Data analysis was accomplished with a locally modified version of the computer programme EFFY 2 (García-Toraño and Grau Malonda, 1985). Information is given in Table 1 concerning that portion of the computation related to deriving the  $^{33}\text{P}$  beta-particle spectrum. The ensuing efficiency curves determined by the programme are shown in Fig. 1, where the relationship between the measured TDCR value and the efficiencies becomes evident. The recorded data were analyzed by first correcting for background, deadtime (1.0  $\mu\text{s}$ ) and coincidence resolving time (0.47  $\mu\text{s}$ ). After-pulsing was found to be negligible. The average of the three corrected double-coincidence rates was utilized in the subsequent analysis procedure described in the previous section. The results of the activity measurements are given in Table 2. The total uncertainty ( $1\sigma$ )

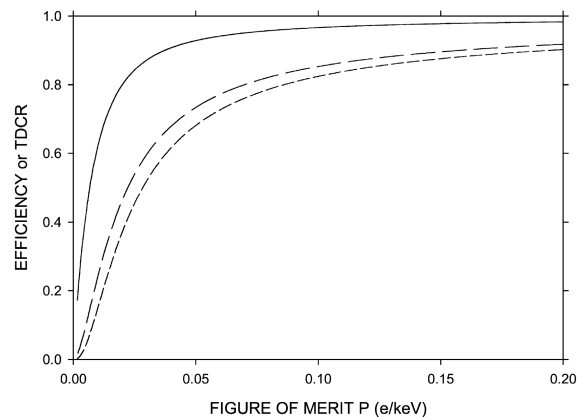


Fig. 1. Calculations for  $^{33}\text{P}$  of the two-phototube efficiency  $\varepsilon_d$  (long dashes), three-phototube efficiency  $\varepsilon_t$  (short dashes) and the TDCR  $\varepsilon_t/\varepsilon_d$  (solid curve), expressed as a function of the figure-of-merit. The ionization quenching function (Gibson and Gale, 1968) required for these calculations was based on a value for the Birks constant of  $k_B = 0.0100 \text{ g}/(\text{cm}^2 \text{ MeV})$ .

Table 1  
Parameters relating to the calculation of the  $^{33}\text{P}$  beta-particle spectrum

Prohibition parameter	Maximum energy (keV)		Number of energy steps	Average energy (keV)		
	NCRP (1985)	Audi and Wapstra (1993)		Computed	NCRP (1985)	ENSDF <sup>a</sup>
0	249.0 ± 2.0	248.5 ± 1.1	923	76.51	76.6 ± 0.7	76.4 ± 0.5

The beta-decay energy used in the computation was 249.0 keV.

<sup>a</sup>Evaluated Nuclear Structure Data File (ENSDF) from the National Nuclear Data Center, Brookhaven National Laboratory, Upton, NY, USA.

Table 2  
Results of activity measurements on <sup>33</sup>P samples as given by the TDCR technique

Source	Solution mass (mg)	CHCl <sub>3</sub> (ml)	Measured rates (cps)		TDCR	Extracted from data analysis				
			Double	Triple		Figure-of-merit <i>P</i> (e/keV)	Two-tube efficiency $\epsilon_d$	Three-tube efficiency $\epsilon_t$	Source activity $N_0$ (Bq)	Solution activity (kBq/g)
1	57.831	—	1106.2	1077.8	0.9743	0.1302	0.8823	0.8597	1254	21.68
1	57.831	—	1107.4	1079.9	0.9752	0.1349	0.8858	0.8639	1250	21.62
2	101.039	—	1929.4	1880.7	0.9748	0.1324	0.8840	0.8617	2183	21.60
2	101.039	—	1928.6	1880.7	0.9752	0.1346	0.8856	0.8636	2178	21.55
3	167.242	—	3179.9	3092.4	0.9725	0.1216	0.8753	0.8512	3633	21.72
3	167.242	—	3184.7	3098.2	0.9728	0.1231	0.8766	0.8528	3633	21.72
1	57.831	1.0	963.0	907.4	0.9422	0.0606	0.7737	0.7290	1245	21.52
1	57.831	1.0	966.8	910.7	0.9420	0.0603	0.7729	0.7281	1251	21.63
1	57.831	1.5	899.2	831.4	0.9246	0.0478	0.7232	0.6687	1243	21.50
1	57.831	1.5	898.9	830.6	0.9241	0.0475	0.7219	0.6671	1245	21.53
1	57.831	2.0	829.8	749.4	0.9031	0.0384	0.6681	0.6033	1242	21.48
1	57.831	2.0	832.6	751.8	0.9029	0.0383	0.6676	0.6028	1247	21.56

The samples were first measured in the unquenched state before being quenched with chloroform. The measured rates have been decay corrected to the reference date, 3 July 2002.

was 0.39% comprising mainly the components due to counting statistics (0.06%), background (0.10%), photo-tube mismatch (0.25%) and the efficiency calculation (0.25%).

When sources are chemically quenched, the scintillation output is inhibited resulting in lowered detection efficiency. Experimentally, this manifests in a reduction in the measured count rates and is accounted for in the theoretical determination of the counting efficiency through the figure-of-merit *P* modified by an energy-independent relative quenching factor (Gibson, 1976; Simpson and Meyer, 1992). It is clear that as a result of this, the TDCR efficiency calculation technique extracts the source activity directly irrespective of the quench state. Although demonstrated previously for other radionuclides, this has now been verified for <sup>33</sup>P by using chloroform as the quenching agent (see Table 2).

### 3.2. Tracer measurements

The <sup>33</sup>P solution activity concentration as given by the TDCR technique was verified by tracing with <sup>60</sup>Co, utilizing the 4π(LS)β-γ coincidence extrapolation method. Counting sources were prepared in custom-made flat-faced cylindrical counting vials, each being viewed in turn by two RCA 8850 phototubes coupled in coincidence. The 4π count rate of the mixed source is given by

$$B = N_1 \epsilon_1 + N_1(1 - \epsilon_1)P_\gamma + N_2 \epsilon_2, \tag{6}$$

where  $N_1$  and  $N_2$  are the source activities of the tracer and <sup>33</sup>P, respectively,  $\epsilon_1$  and  $\epsilon_2$  are the corresponding detection efficiencies and  $P_\gamma$  is the gamma-ray interaction probability. The <sup>60</sup>Co activity was obtained by first

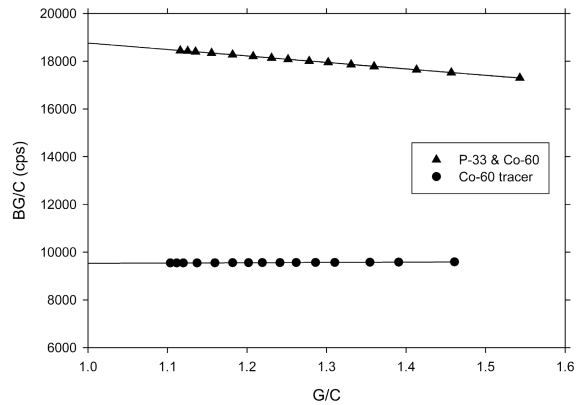


Fig. 2. The 4π count rates, *B*, from the <sup>60</sup>Co liquid scintillation source A before and after the addition of an aliquot of the <sup>33</sup>P solution. The rates are expressed as a function of the inverse of the <sup>60</sup>Co β efficiency, *G/C*, where *G* is the γ-channel rate and *C* the coincidence rate. The error bars are smaller than the symbol size. The analysis indicated that linear fits to the data were appropriate (solid lines).

counting the sample before the addition of <sup>33</sup>P. In this case only the first two terms of Eq. (6) are relevant. The escaping <sup>60</sup>Co gamma-rays were detected with a 75 × 75 mm NaI(Tl) crystal and a window was set to record only the photopeak events, with a net efficiency of  $\epsilon_\gamma$ . Consequently, the gamma rate is  $G = N_1(1 - P_\gamma)\epsilon_\gamma$  and the β-γ coincidence rate is  $C = N_1(1 - P_\gamma)\epsilon_1\epsilon_\gamma$ . Efficiency variation of the 4π events was by threshold discrimination,  $\epsilon_1$  being obtained from *C/G*. Because the counts associated with <sup>33</sup>P are expressed in terms of  $\epsilon_1$ , the efficiency of <sup>33</sup>P is effectively a function of  $\epsilon_1$  and so

Table 3  
The  $^{33}\text{P}$  activity concentration as determined by the liquid scintillation tracer method

Source	$^{33}\text{P}$ solution mass (mg)	Source activity measurements		Extracted $^{33}\text{P}$ activity concentration (kBq/g)
		$N_1$ ( $^{60}\text{Co}$ ) (Bq)	$N_1 + N_2$ ( $^{60}\text{Co}$ and $^{33}\text{P}$ ) (Bq)	
A	431.496	$9531 \pm 9$	$18757 \pm 18$	$21.38 \pm 0.05$
B	205.313	$5705 \pm 7$	$10099 \pm 12$	$21.40 \pm 0.07$

The activity values have been decay corrected to the reference date chosen. The uncertainties shown correspond only to counting statistics.

$\varepsilon_2 = f(C/G)$  such that  $f(C/G) \rightarrow 1$  as  $(C/G) \rightarrow 1$ . Thus extrapolating to  $\varepsilon_1 = 1$  gives the combined activity values and the  $^{33}\text{P}$  activity is found by subtracting the measured  $^{60}\text{Co}$  activity after first being decay corrected to the time of counting the mixed source.

The counting system described in Simpson and Meyer (1988) was used to simultaneously collect 15 data points of varying efficiency for each set. Fig. 2 shows the data collected for a  $^{60}\text{Co}$  source before and after the addition of an accurately weighed aliquot of the  $^{33}\text{P}$  solution. The extracted activity concentration is given in Table 3. The total uncertainty ( $1\sigma$ ) was 0.40% comprising mainly the counting statistics (0.18%) and the data fitting (0.35%). It is evident that the results agree with the TDCR measurements within experimental uncertainty.

#### 4. Conclusions

The activity of  $^{33}\text{P}$  has been measured directly by the TDCR efficiency calculation technique. It was demonstrated that the method extracts accurate results independent of the quenched state of the sources. Chloroform was used as a quenching agent to reduce the double phototube efficiency from 88% to between 67 and 77%. Nevertheless, the activity concentration obtained differed by only 0.5% between the quenched and unquenched counting sources. The activity concentration of the  $^{33}\text{P}$  solution as given by the liquid scintillation tracer method showed agreement to within 1.2%, thus confirming the reliability of the TDCR measurements.

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