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Further investigations of a simple counting technique for measuring mixtures of two pure β-emitting radionuclides

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Abstract

A simple liquid scintillation counting technique to measure the activity composition of a mixture containing two known pure β-emitting radionuclides was recently developed at the NMISA. The method has been applied to various two-component mixtures of ^{32}P, ^{33}P and ^{35}S, primarily to gauge the effect of spectral energy differences on the method's ability to extract the individual activities. Excellent results were obtained for mixtures of ^{33}P and ^{35}S, radionuclides with similar, low β energies. Mixtures containing the high-energy β-emitter ^{32}P were more difficult to resolve, although quenching of the counting sources with CHCl$_3$ improved mixture resolution.
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Keywords: Pure β-emitting radionuclides; Mixtures; TDCR efficiency calculation; CIEMAT/NIST; Liquid scintillation counting; Phosphorus-32; Phosphorus-33; Sulphur-35

1. Introduction

A simple counting technique to measure the activity composition of a mixture containing two known pure β-emitting radionuclides was recently devised at the National Metrology Institute of South Africa (NMISA) and the feasibility of the method demonstrated in practice with a variety of mixture combinations of ^{14}C and ^{63}Ni (Van Wyngaardt and Simpson, 2006). For this paper, the effect of spectral energy differences on the method's ability to extract the individual activities was investigated. For small energy differences, various mixtures of the low-energy β-emitters ^{33}P ($E_{max} = 248.50$ keV) and ^{35}S ($E_{max} = 167.14$ keV) (Bé et al., 2004) were measured. The applicability of the method for radionuclide pairs with large energy differences was investigated by measuring mixtures of ^{32}P ($E_{max} = 1\,710.66$ keV) (Bé et al., 2004) with both ^{33}P and ^{35}S. The experiments were facilitated by the ready availability of stock solutions of these radionuclides in chemically compatible form.

2. The basic method

2.1. Overview

The method is based on elements of two liquid scintillation techniques that are widely used to measure single-radionuclide solutions, namely the triple-to-double coincidence ratio (TDCR) technique (Simpson and Meyer, 1992, 1994) and the CIEMAT/NIST efficiency tracing method (Grau Malonda and Garcia-Toraño, 1982; Coursey et al., 1985). The radionuclide activity composition of a mixture source is determined from the double- and triple-coincidence count rates, N_d and N_t, combined with the double- and triple-coincidence detection efficiencies of the component radionuclides, ε_d, ε_t, ε'_d and ε'_t. Thus,

$$N_d = N_0\varepsilon_d + N'_0\varepsilon'_d, \tag{1}$$

and

$$N_t = N_0\varepsilon_t + N'_0\varepsilon'_t, \tag{2}$$

where N_0 and N'_0 are the activities of the component radionuclides. The efficiencies are calculated from theoretical expressions that are functions of the figure-of-merit (Simpson and Meyer, 1994). The figure-of-merit, P, is

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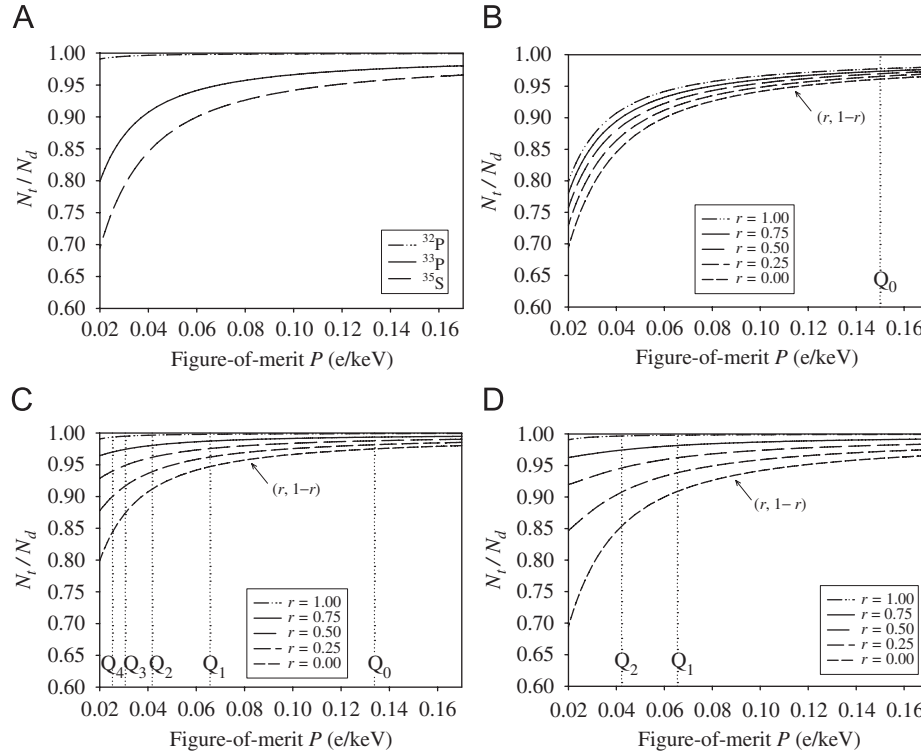E-mail address: FvWyngaardt@nmisa.org (W.M. van Wyngaardt).

Fig. 1. The curves demonstrating the relationship between N_t/N_d and P for ^{32}P, ^{33}P, ^{35}S 1(A) and various two-component mixtures of these radionuclides (1B ^{33}P:^{35}S, 1C ^{32}P:^{33}P, 1D ^{32}P:^{35}S) were generated as described by Van Wyngaardt and Simpson (2006). The concept of the method can be visualised as measuring N_t/N_d for a mixture source and determining P from a tracer; the curve where the two values intersect then indicates the fractional composition, $r = A_0/(A_0 + A'_0)$ and $(1-r) = A'_0/(A_0 + A'_0)$, of the mixture. Once r is known, A_0 and A'_0 can be calculated (Van Wyngaardt and Simpson, 2006). The figures-of-merit where measurements were undertaken are indicated on each plot.

determined experimentally from a pure β-emitting tracer standard of similar quench to the prepared source, along the lines of the CIEMAT/NIST method. The activity concentrations of the component radionuclides, A_0 and A'_0, are calculated from

$$A_0 = cN_0 = c\left(\frac{N_t\varepsilon'_d - N_d\varepsilon'_t}{\varepsilon_t\varepsilon'_d - \varepsilon_d\varepsilon'_t}\right), \tag{3}$$

and

$$A'_0 = c'N'_0 = c'\left(\frac{N_d\varepsilon_t - N_t\varepsilon_d}{\varepsilon_t\varepsilon'_d - \varepsilon_d\varepsilon'_t}\right), \tag{4}$$

where N_0 and N'_0 are given by equations derived in Van Wyngaardt and Simpson (2006) and c and c' are factors transforming the activities to activity concentrations on a specific reference date. This facilitates the comparison of results from sources prepared from the same solution but measured at different times.

2.2. TDCR parameter computation

It is a simple matter to show from Eqs. (1) and (2) that for a binary mixture the TDCR parameter N_t/N_d is given by (Van Wyngaardt and Simpson, 2006)

$$\frac{N_t}{N_d} = \frac{r\varepsilon_t + (1-r)\varepsilon'_t}{r\varepsilon_d + (1-r)\varepsilon'_d}, \tag{5}$$

where $r = A_0/(A_0 + A'_0)$ is the activity fraction of one component of the mixture and $(1-r) = A'_0/(A_0 + A'_0)$ is the remainder. Using Eq. (5), plots of N_t/N_d vs. P were generated for the three pure components ^{32}P, ^{33}P and ^{35}S (Fig. 1A, where $r = 1$) as well as for various mixtures of the three radionuclide pairs (Fig. 1B–D). It can be seen from Fig. 1A that the line for the high-energy β-emitter ^{32}P is almost straight and horizontal, curving slightly downwards at a very low figure-of-merit. The ratio N_t/N_d reaches a minimum of 0.99 at $P = 0.02$ e/keV. As the β energy of the radionuclide decreases, the slope of the line at high P and the downward curvature at lower P increases so that $N_t/N_d = 0.80$ for ^{33}P and $N_t/N_d = 0.70$ for ^{35}S at 0.02 e/keV. For plots 1B–D continua of lines are in fact possible as the fractional compositions change from $r = 0$ to 1, i.e. incrementally from one pure component to the other.

3. Experimental approach

The approach followed in the experiment is summarised in Fig. 2. Stock solutions of ^{32}P, ^{33}P and ^{35}S were purchased from AEC-Amersham and diluted in two steps to give solutions, which were suitable for further work. For each pair of radionuclides the dilutions were mixed in various ratios to give three series of mixed radionuclide solutions. The activity concentration of each dilution was measured by conventional means. The mixed radionuclide
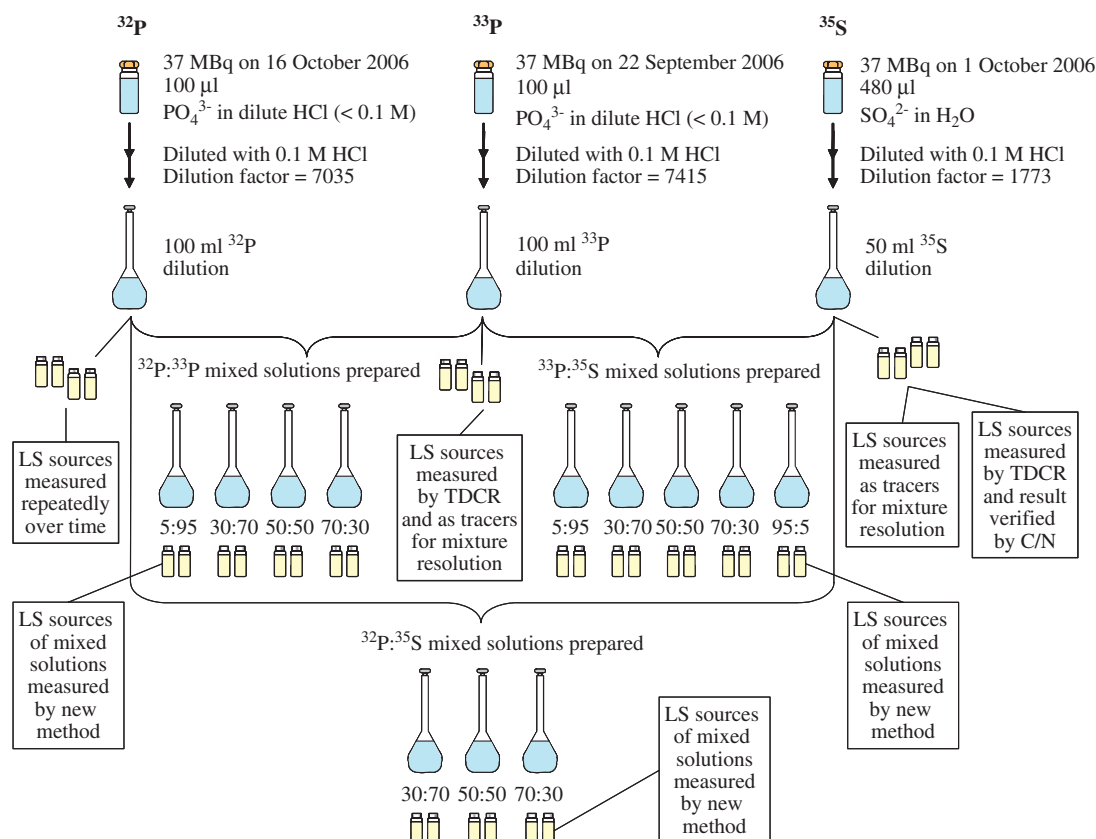
Fig. 2. Summary of the experimental procedure followed. The numbers given with the mixture solutions indicate the approximate activity compositions at the measurement reference date.

solutions were measured with the new method, mainly using appropriate sources of ^{33}P and ^{35}S as tracers.

The liquid scintillation cocktail to be used in the entire experiment was made up in a single batch to minimise differences in quenching due to variation in the cocktail composition. The cocktail consisted of 3 ml of 3 M HCl, which was added to 1 l of Quicksafe A from Zinsser Analytic to reduce possible adsorption effects. Counting sources were prepared by adding accurately weighed aliquots of the dilutions or mixtures to 12 ml liquid scintillation cocktail in Wheaton glass scintillation vials and mixed thoroughly. Sources were stored in the dark, at least over night, before measurement. CHCl$_3$ was added as a quenching agent to some of the sources to reduce afterpulsing and to study the effect of the reduction of the counting efficiency on mixture resolution.

All sources were measured in the NMISA three-phototube detection system described by Meyer and Simpson (1990), with the RCA 8850 phototube 3 replaced by a new BURLE 8850 high-gain phototube. Outputs from the phototubes, after being fed through the usual pre-amplifiers, amplifiers and timing single-channel analyzers, were mixed in a locally designed and built two- and three-fold coincidence unit (Simpson and Morris, 2004). After-pulsing was measured (Simpson, 2002) simultaneously with counting for each double-coincidence channel in turn. Before each series of measurements the detection system

was reproducibly set up in terms of phototube efficiency matching using a source of the low-energy β-emitter ^{63}Ni. This entailed setting the counting thresholds just below the single-electron peak and adjusting the positions of the sources relative to the phototubes so as to match the double-coincidence count rates to within 0.5% after correcting for the background and afterpulses when present. All changing of sources was done in the dark, illumination provided only by red light, to prevent the phototubes and sources from being exposed to white light.

4. Measurement of the individual radionuclide solutions

The ^{33}P and ^{35}S solutions were expected to be free of impurities and the solutions were measured by the TDCR efficiency calculation technique to establish the activities. This method had been previously used and verified for ^{33}P (Simpson and Morris, 2004) and gave the activity concentrations of the present solutions as $A(^{33}P) = 46.67 \pm 0.23$ kBq/g and $A(^{35}S) = 43.23 \pm 0.22$ kBq/g at 12h00 SAST on 29 September 2006. The uncertainties specified are the standard combined uncertainties. The result obtained for ^{35}S was validated by also analysing the counting data using a variation of the CIEMAT/NIST method. Sources of ^{63}Ni and ^{33}P with quench states similar to that of the ^{35}S sources of interest were measured as tracer standards to determine the figure-of-merit and thus the ^{35}S detection efficiency.

Dividing the measured ^{35}S count rate concentrations by the calculated efficiencies produced activity concentrations of 43.03 kBq/g (from ^{63}Ni) and 43.47 kBq/g (from ^{33}P). These activity concentrations agree with the TDCR result to within the stated experimental uncertainty.

To determine possible impurities of ^{33}P and ^{35}S, the decay of the ^{32}P solution was followed over a 46-day period, using the method described in Simpson and Van Wyngaardt (2006a). Analysis of 108 individual measurements gave the composition of the solution as $A(^{32}\text{P}) = 42.74 \pm 0.30$ kBq/g and $A'(^{33}\text{P}) = 0.70 \pm 0.23$ kBq/g at 12h00 SAST on 23 October 2006, with the ^{35}S component being essentially zero. The uncertainties specified are the standard combined uncertainties.

5. The measurement of mixtures

The activity concentrations of the mixtures were calculated algebraically from those determined for the original dilutions by taking into account the mass portions weighed out, as detailed further. For each mixture solution a mass m_1 of the higher-energy emitter was mixed with a mass m_2 of the lower-energy emitter to prepare a mass m_{total} of the mixture. For the ^{33}P:^{35}S mixtures, the gravimetric activity concentrations, $A_G(^{33}\text{P})$ and $A_G(^{35}\text{S})$, were calculated from

$$A_G(^{33}\text{P}) = A(^{33}\text{P})m_1/m_{total} \quad \text{and}$$
$$A_G(^{35}\text{S}) = A(^{35}\text{S})m_2/m_{total}. \tag{6}$$

For the ^{32}P:^{33}P mixtures, the gravimetric activity concentrations, $A_G(^{32}\text{P})$ and $A_G(^{33}\text{P})$, were calculated from

$$A_G(^{32}\text{P}) = A(^{32}\text{P})m_1/m_{total} \quad \text{and}$$
$$A_G(^{33}\text{P}) = [A(^{33}\text{P})m_2 + A'(^{33}\text{P})m_1]/m_{total}, \tag{7}$$

where the ^{33}P impurity from the ^{32}P solution was simply added to the ^{33}P component. For the ^{32}P:^{35}S mixtures, the gravimetric activity concentrations were calculated from

$$A_G(^{32}\text{P}) = A(^{32}\text{P})m_1/m_{total} \quad \text{and}$$
$$A_G(^{35}\text{S}) = A(^{35}\text{S})m_2/m_{total}, \tag{8}$$

with the ^{33}P impurity being given by

$$A_G(^{33}\text{P}) = A'(^{33}\text{P})m_1/m_{total}. \tag{9}$$

The latter activity concentration was used to correct the acquired count rates for the contribution of the impurity so that a two-component mixture could be assumed. The results obtained from the measurement of the mixed solutions were subsequently compared against these gravimetrically determined activity compositions (i.e. gravimetric compositions).

5.1. The measurement of mixtures of ^{33}P and ^{35}S

Two sources were prepared from each of the five ^{33}P:^{35}S mixture solutions. The sources prepared from the ^{33}P:^{35}S (70:30) mixture were selected for a preliminary, detailed investigation and were measured together with pure sources of ^{63}Ni, ^{35}S and ^{33}P as tracers to estimate the figure-of-merit of the mixed sources. The sources were measured on two separate days and for each day the figure-of-merit was determined from each of the three tracers by TDCR analysis of the individual radionuclide counting data using a locally modified version (Simpson and Meyer, 1994) of the programme EFFY 2 (García-Toraño and Grau Malonda, 1985). For all measurements the afterpulse correction was consistent with zero. The data collected for the mixed radionuclide sources were corrected for background, deadtime ($\tau_D = 1.0$ μs) and coincidence resolving time ($\tau_R = 0.47$ μs) to obtain the double- and triple-coincidence count rates, N_d and N_t, required for further analysis. The double- and triple-coincidence detection efficiencies for ^{33}P and ^{35}S were calculated for each value of P extracted from the tracer measurements using the same efficiency calculation routines used for TDCR data analysis. The activity concentrations on the reference date, A_0 and A'_0, were calculated from Eqs. (3) and (4).

The results obtained are summarised in Table 1. The various tracers gave results that varied from one another, particularly those from ^{63}Ni, with those from ^{35}S giving excellent agreement between the gravimetric source composition and the activity concentrations extracted by the method. The variation obtained with the different tracers indicates a possible imperfection in the model used to calculate the efficiencies, although small differences in chemical quenching between the various sources could also have contributed to the variation. The effect of these

Table 1
Activity concentrations extracted for the mixture solution ^{33}P:^{35}S (70:30) are compared for different tracer standards used

Tracer	Measurement date					
	29 September 2006			6 October 2006		
	P (e/keV)	$A_0(^{33}\text{P})$ (kBq/g)	$A'_0(^{35}\text{S})$ (kBq/g)	P (e/keV)	$A_0(^{33}\text{P})$ (kBq/g)	$A'_0(^{35}\text{S})$ (kBq/g)
^{63}Ni	0.162	26.7	18.9	0.162	28.2	16.8
^{35}S	0.151	32.1	13.5	0.154	32.4	13.1
^{33}P	0.147	34.0	11.6	0.151	33.6	12.1

The gravimetrically determined composition of the solution was $A_G(^{33}\text{P}) = 32.2$ kBq/g and $A_G(^{35}\text{S}) = 13.4$ kBq/g. All concentrations are given on the reference date of 29 September 2006, 12h00 SAST.
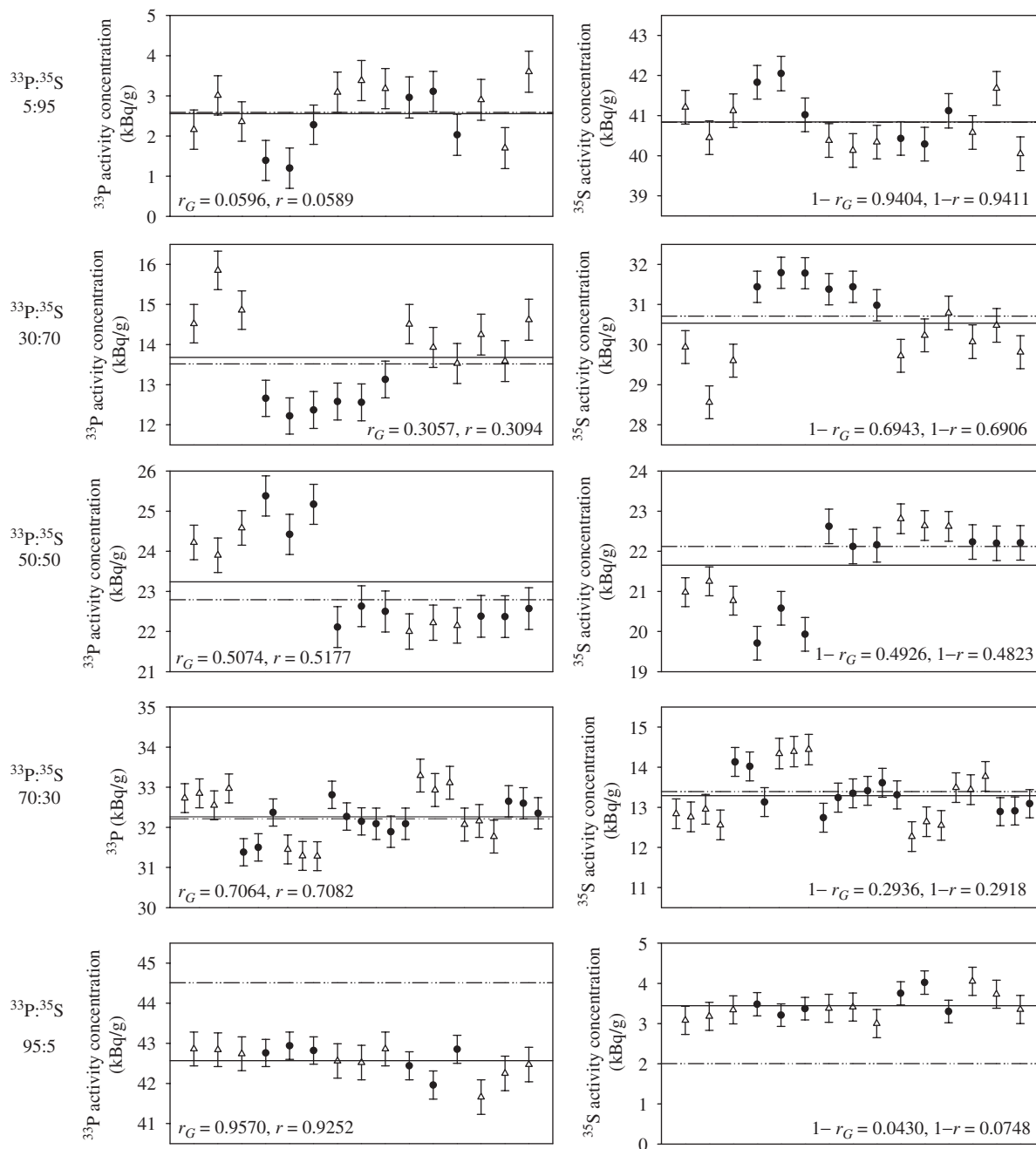
Fig. 3. The plots show the activity concentration and statistical uncertainty obtained from each individual measurement of the $^{33}P{:}^{35}S$ mixture solutions using ^{35}S as the tracer. Results from two different sources in each case are indicated by unfilled triangles and filled circles, respectively. The ^{33}P components are given on the left and the ^{35}S components on the right-hand side. The dash-dot-dotted lines give the gravimetric concentrations and the solid lines the average value of all measurements of the same solution. The ratios, r_G and r, given on each ^{33}P plot and the ratios, $(1-r_G)$ and $(1-r)$, given on each ^{35}S plot indicate the gravimetric and measured activity fractions determined for each solution.

inconsistencies is minimised when the tracer standard used is the same as the low–energy component of the mixture. The results extracted from the individual (70:30) source measurements, using ^{35}S as a tracer, are plotted together with the predicted statistical uncertainties in the fourth row of plots in Fig. 3. These uncertainties, $\sigma(A_0)$ and $\sigma(A'_0)$, were calculated from equations given by Van Wyngaardt and Simpson (2006), modified similarly to Eqs. (3) and (4)

from activities to activity concentrations on a specific reference date.

The remaining $^{33}P{:}^{35}S$ mixed sources were measured over 3 days using only ^{35}S sources as tracers. The result obtained for each individual measurement is displayed in Fig. 3. For each solution the *average* measured values can be compared with the prepared gravimetric activity concentrations in Fig. 3 and in Table 2. The table also gives

Table 2
The averaged results of measurements of the ^{33}P:^{35}S mixtures are given, with A_G the gravimetrically determined activity concentrations and A_0 and A'_0 the values extracted from measurement using ^{35}S as the tracer

Mixture	$A_G(^{33}$P$)$ (kBq/g)	$A_0(^{33}$P$)$ (kBq/g)	$\Delta(^{33}$P$)$ (%)	Dev(^{33}P) (%)	$A_G(^{35}$S$)$ (kBq/g)	$A'_0(^{35}$S$)$ (kBq/g)	$\Delta(^{35}$S$)$ (%)	Dev(^{35}S) (%)
5:95	2.6	2.6	11	−1.2	40.8	40.8	0.52	0.0
30:70	13.5	13.7	1.6	1.2	30.7	30.5	0.62	−0.6
50:50	22.8	23.2	0.91	2.0	22.1	21.7	0.81	−2.1
70:30	32.2	32.3	0.55	0.1	13.4	13.3	1.4	−0.8
95:5	44.5	42.6	0.37	−4.4	2.0	3.4	5.4	72

The figures-of-merit extracted were 0.1477 and 0.1487 e/keV on the different measurement days. Uncertainty estimates for the extracted activities are indicated by $\Delta(^{33}$P$)$ and $\Delta(^{35}$S$)$. The relative deviations were calculated from Dev = $[(A_0 - A_G)/A_G] \times 100$.
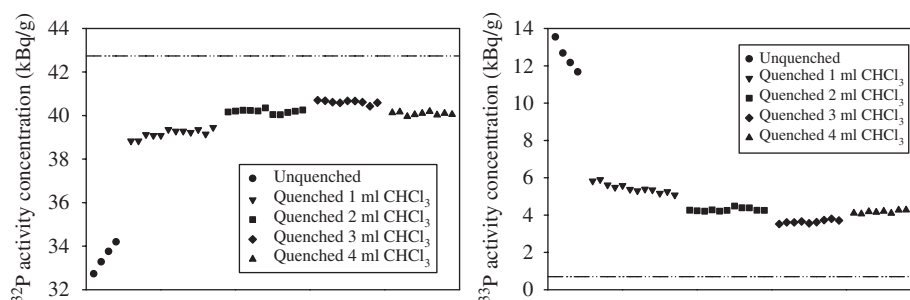

Fig. 4. The plots show the activity concentration obtained from each individual measurement of sources prepared from the original ^{32}P dilution in various quench states. The dash-dot-dotted lines show the gravimetric activity concentrations, $A_G(^{32}$P$) = 42.74$ kBq/g and $A_G(^{33}$P$) = 0.70$ kBq/g.

uncertainty estimates that are primarily due to counting statistics (shown in Fig. 3) and possible differences in quenching between the mixture and tracer sources leading to variation in the actual figure-of-merit used. For this mixture combination, the deviations from the prepared activities were not significantly different from that expected based on the uncertainties. The results show excellent agreement between the prepared and extracted activity concentrations for all mixtures except for the mixture containing only 5% ^{35}S, where the deviations are nevertheless smaller than 2 kBq/g.

5.2. The measurement of mixtures of ^{32}P and ^{33}P

Because it was known from following the decay that the ^{32}P solution contained about 1.6% of ^{33}P as an impurity, the new method was applied to this *mixture* solution to assess its usefulness under these particularly stringent conditions. Previously, measurements of the high-energy β-emitters ^{89}Sr and ^{90}Y (Simpson and Van Wyngaardt, 2006b) had shown that the TDCR method was particularly sensitive to inexact corrections in the flat region of N_t/N_d vs. P curves. This sensitivity was expected to be even more so for mixtures. Since the curve for ^{32}P ($r = 1$ in Fig. 1C) is quite flat, the strategy applied was to quench sources, particularly if afterpulse emission was high, to undertake measurements in a more favourable efficiency region.

Three sources were prepared from the ^{32}P dilution. Source 1 was measured without quenching and gave an afterpulse correction for channel 1 that was high (1.71%). CHCl$_3$ was then added to all three sources as a chemical

quenching agent in increments of 1 ml from 1 to 4 ml to reduce the detection efficiency and so also afterpulsing. The ^{32}P sources, with ^{33}P sources as tracers, were measured in each of the different quench states. In all cases the tracer standards were filled with CHCl$_3$ to the same volume as the mixture sources.

The data analysis was performed as for the ^{33}P:^{35}S mixtures. The result of each individual measurement is given in Fig. 4. The results obtained from the unquenched source were particularly poor and showed significant variation between the repeat measurements. An insufficiently accurate afterpulse correction in this flat region (quench Q_0 in Fig. 1C) certainly contributed to the large deviations observed. The best results were obtained from the sources quenched with 3 ml of CHCl$_3$, where the ^{32}P activity concentration was under-estimated by 2.5 kBq/g and the ^{33}P activity concentration over-estimated by 3.1 kBq/g. These results are quite reasonable if it is considered that measurements were completed in just a few days, compared to the 46 days required to determine the solution composition by following the decay.

For the measurement of the ^{32}P:^{33}P mixture solutions, two sources were prepared from each of the four mixtures. Since the previous measurements had confirmed the expectation that better mixture resolution would be obtained by quenching, the sources from the 5:95 mixtures were measured with 3 and 4 ml of CHCl$_3$ added and the sources with the more equal mixture fractions each with 2 and 3 ml of CHCl$_3$. Each source was counted in both quench states. A significant afterpulse contribution was measured for channel 1, with larger corrections generally required for mixtures
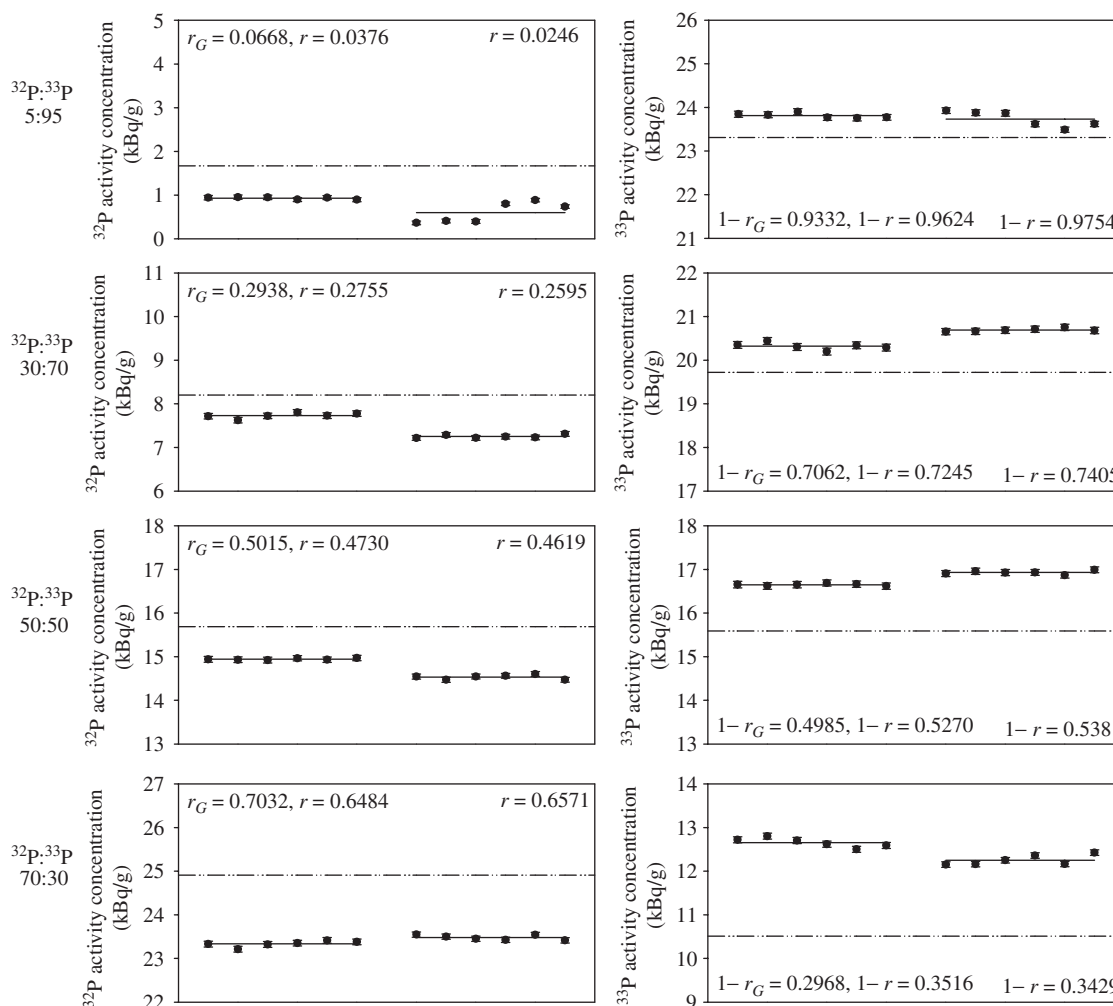
Fig. 5. The plots show the activity concentration obtained from each individual measurement of the ^{32}P:^{33}P mixture solutions with the ^{32}P components given on the left and the ^{33}P components on the right-hand side. The statistical uncertainties are given and are of the same size as the markers. In each plot, two sets of measurements are given, with the measurements from the less quenched source on the left and the more highly quenched source on the right. The dash-dot-dotted lines give the gravimetric concentrations and the solid lines the average value of each set of measurements of the same solution. The ratios, r_G and r, given on each ^{32}P plot and the ratios, $(1-r_G)$ and $(1-r)$, given on each ^{33}P plot indicate the gravimetric and measured activity fractions determined for each solution.

with higher ^{32}P content and lower quench states. Two ^{33}P sources were prepared and measured in the same quench states as the mixed sources to serve as tracers to estimate the figure-of-merit of the system.

All data analysis was performed as described previously. The result of each individual measurement is displayed in Fig. 5. For each solution the *average* measured values can be compared with the gravimetric activity concentrations, calculated from Eq. (7), in Fig. 5 and in Table 3. The results show reasonable agreement between the prepared and measured activity concentrations, although not as good as that obtained for the ^{33}P:^{35}S mixtures. The estimated uncertainties are also given in Table 3 and are smaller than those obtained for the ^{33}P:^{35}S mixtures, as expected from the higher detection efficiencies and the larger differences between the energies of the component radionuclides. However, the relative deviations are generally significantly larger than the uncertainties, indicating a possible inconsistency in the model

used for the efficiency calculation. The absolute deviations are below 2 kBq/g for all of the results but one.

5.3. The measurement of mixtures of ^{32}P and ^{35}S

Two sources were prepared for each of the three ^{32}P:^{35}S mixture solutions and counted in two different quench states, with 1 and 2 ml of CHCl$_3$ added. Afterpulses showed the same trends observed for the other ^{32}P-containing mixtures. One ^{33}P and one ^{35}S source were prepared and measured in the same quench state as the mixed sources as tracers to estimate the figure-of-merit of the system.

Before determining the mixture activity concentrations, A_0 and A'_0, from Eqs. (3) and (4), the contributions from the ^{33}P impurity to the measured count rates as given by

$$N_d(^{33}\text{P}) = \left[A_G(^{33}\text{P})\varepsilon_d(^{33}\text{P}) \right] \frac{m}{\mathrm{e}^{-\lambda'' t}} \qquad (10)$$

Table 3
The averaged results of measurements of the ^{32}P:^{33}P mixtures are given, with A_G the gravimetric activity concentrations and A_0 and A'_0 the measured values

Mixture and quench state	P (e/keV)	$A_G(^{32}P)$ (kBq/g)	$A_0(^{32}P)$ (kBq/g)	$\Delta(^{32}P)$ (%)	Dev(^{32}P) (%)	$A_G(^{33}P)$ (kBq/g)	$A'_0(^{33}P)$ (kBq/g)	$\Delta(^{33}P)$ (%)	Dev(^{33}P) (%)
5:95 Q$_3$	0.0311	1.7	0.9	11	−44	23.31	23.81	0.39	2.1
5:95 Q$_4$	0.0252	1.7	0.6	53	−64	23.3	23.7	1.4	1.8
30:70 Q$_2$	0.0421	8.20	7.73	0.50	−5.8	19.72	20.32	0.19	3.1
30:70 Q$_3$	0.0311	8.2	7.3	1.3	−12	19.72	20.69	0.37	4.9
50:50 Q$_2$	0.0421	15.69	14.94	0.21	−4.8	15.59	16.65	0.23	6.8
50:50 Q$_3$	0.0311	15.69	14.53	0.50	−7.4	15.59	16.93	0.40	8.6
70:30 Q$_2$	0.0421	24.91	23.33	0.14	−6.3	10.51	12.66	0.32	20
70:30 Q$_3$	0.0311	24.91	23.48	0.27	−5.7	10.51	12.25	0.48	17

The mass of CHCl$_3$ added per source is indicated as the quench state, with Q$_3$ indicating that 3 ml of CHCl$_3$ had been added, etc. Uncertainty estimates for the extracted activities are indicated by $\Delta(^{32}P)$ and $\Delta(^{33}P)$ The deviations were calculated from Dev $= [(A_0−A_G)/A_G] \times 100$.

Table 4
The averaged results of measurements of the ^{32}P:^{35}S mixtures are given for ^{35}S as the tracer, with A_G the gravimetric activity concentrations and A_0 and A'_0 the measured values

Mixture and quench state	P (e/keV)	$A_G(^{32}P)$ (kBq/g)	$A_0(^{32}P)$ (kBq/g)	$\Delta(^{32}P)$ (%)	Dev(^{32}P) (%)	$A_G(^{33}P)$ (kBq/g)	$A'_0(^{33}P)$ (kBq/g)	$\Delta(^{33}P)$ (%)	Dev(^{33}P) (%)
30:70 Q$_1$	0.0654	11.82	11.11	0.62	−6.0	25.85	26.59	0.20	2.9
30:70 Q$_2$	0.0422	11.82	11.35	0.51	−4.0	25.85	26.17	0.17	1.2
50:50 Q$_1$	0.0654	19.36	18.43	0.28	−4.8	19.54	20.39	0.22	4.3
50:50 Q$_2$	0.0422	19.36	18.82	0.22	−2.8	19.54	20.05	0.17	2.6
70:30 Q$_1$	0.0654	28.96	27.56	0.16	−4.8	11.52	13.18	0.28	14.4
70:30 Q$_2$	0.0422	28.96	28.00	0.12	−3.3	11.52	12.62	0.21	9.6

The quantity of CHCl$_3$ added per source is indicated as the quench state with Q$_1$ indicating that 1 ml of CHCl$_3$ had been added, etc. Uncertainty estimates for the extracted activities are indicated by $\Delta(^{32}P)$ and $\Delta(^{35}S)$. The deviations were calculated from Dev $= [(A_0−A_G)/A_G] \times 100$.

and

$$N_t(^{33}P) = \left[A_G(^{33}P)\varepsilon_t(^{33}P) \right] \frac{m}{e^{-\lambda'' t}}, \quad (11)$$

were subtracted from the double- and triple-coincidence count rates N_d and N_t. $A_G(^{33}P)$ gives the gravimetrically determined activity concentration of the impurity as calculated from Eq. (9). The efficiencies, $\varepsilon_d(^{33}P)$ and $\varepsilon_t(^{33}P)$, were determined from P as given by the respective tracer standards. The final term converts the count rate concentrations on the reference date to count rates on the later measurement date. The source mass is given by m and λ'' is the decay constant for ^{33}P.

The distribution of the results and the estimated uncertainties were similar to those obtained from the ^{32}P:^{33}P mixtures. In Table 4, the *average* measured values obtained with ^{35}S as tracers for each solution can be compared with the gravimetric activity concentrations calculated from Eq. (8), where a two-component mixture was assumed. The deviations were, on average, 1% smaller when using ^{35}S as the tracer as opposed to ^{33}P and better for the sources quenched with 2 ml of CHCl$_3$ than for those quenched with 1 ml of CHCl$_3$. Again the results showed deviations greater than expected based on the uncertainty estimates, but showed better agreement between the

prepared and measured activity concentrations than was obtained for the corresponding ^{32}P:^{33}P mixtures.

6. Discussion and conclusions

Comparison of results from mixtures with similar fractional compositions showed that the smallest deviations from the gravimetric compositions were obtained for mixtures of the similar, low-energy radionuclides ^{33}P and ^{35}S. For this radionuclide pair, the N_t/N_d vs. P curves (Fig. 1B) are somewhat sloped, even at a high P of 0.148 where measurements were undertaken. These mixtures also gave the largest predicted statistical uncertainties, which can be seen by comparing Figs. 3 and 5 where all plots were drawn so that the Y-axes spanned the same number of activity concentration units. This was due to the energies of the radionuclides being similar and the N_t/N_d vs. P curves therefore close together (Van Wyngaardt, 2007).

The results obtained for the mixtures containing ^{32}P were somewhat worse but improved with increased quenching. Deviations from the gravimetric compositions were larger for mixtures of ^{32}P with ^{33}P (Fig. 1C) than with ^{35}S (Fig. 1D) where the N_t/N_d vs. P curves were further apart and more curved due to the lower β energy of ^{35}S. For higher values of P, the nearly horizontal curve

increases the sensitivity of the method to small inconsistencies between N_t/N_d and P. An extreme case was the measurement of the unquenched ^{32}P source (containing 1.6% ^{33}P), where a small increase in the measured N_t/N_d ratio of 0.0008 (from 0.9930 to 0.9938) between the first and the last measurement translated to an increase in the extracted ^{32}P activity concentration of 1.47 kBq/g and a decrease in the ^{33}P activity concentration of 1.87 kBq/g. By quenching the source with 1 ml of $CHCl_3$, the source was measured at an efficiency where the N_t/N_d vs. P curves are more sloped and curved, reducing the variation between repeat measurements to 0.60 kBq/g for a similar variation in N_t/N_d. However, it is noted that this improvement by quenching must be balanced by the increased uncertainty of the extracted figure-of-merit at lower efficiencies. For example, the uncertainty of P extracted from the tracer increased from about 0.2% to about 0.5% for quenching with up to 3 ml of $CHCl_3$ and increased to 2.5% for sources containing 4 ml of $CHCl_3$.

In conclusion, it was shown that this method is particularly useful for resolving activities of low-energy pure β-emitting mixtures. Such mixtures would be relatively more difficult to measure using methods that rely on some means of spectral de-convolution. For binary mixtures containing a high- and a low-energy β-emitter, more reliable results are obtained at lower detection efficiencies due to the nature of the relationship between the TDCR parameter and the detection system figure-of-merit. Nevertheless, this is still reliant on the figure-of-merit being determined sufficiently accurately.

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