

Standardization of a ^{32}P solution containing pure-beta impurities using the TDCR method in liquid scintillation counting

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Abstract

The liquid scintillation counting standardization of pure-beta solutions containing pure-beta emitter impurities is a difficult task because, unlike that which can be achieved by using gamma-ray spectrometry, the continuous characteristics of beta spectra and the poor intrinsic resolution of LSC spectrometers do not allow an easy identification and precise determination of the activity concentration of these impurities. This problem was recently encountered in the standardization of a ^{32}P solution in the framework of an international comparison, where the activity contribution of the impurities was over 10% of the main nuclide activity at the reference date. This paper describes the method used to identify the impurities in this ^{32}P solution and the calculation of the detection efficiencies using the triple to double coincidence ratio model. Details on the calculation of the uncertainties of each activity and the covariances between these activities are given.

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1. Introduction

Liquid scintillation counting (LSC) is a widely used method for the standardization of pure-beta nuclides. Detection efficiency can be calculated, under some assumptions, using the triple to double coincidence ratio method (TDCR) or the CIEMAT/NIST method (Broda et al., 1988, Grau Malonda et al., 1988). Both methods are based on the same physical assumptions and models, and the detection efficiency is a function of the average energy spectrum absorbed by the liquid scintillator. For the standardization of pure-beta emitters, as the range of electrons in the scintillator is small versus the dimensions of the vial, this energy spectrum can be calculated directly from the theoretical beta spectrum of the nuclide. Even for high-energy beta

nuclides, where a significant number of electrons interact with the glass envelope of the vial, the influence of this “wall effect” is negligible if the quenching of the source is not extreme (Cassette, 2002).

Of course, the implicit assumption behind these models for calculating detection efficiency is that the nuclide to be measured is the expected one. If the radioactive solution contains a non-negligible amount of impurities, the calculated spectrum must be modified accordingly. This means that, if the impurity of radioactive concentration is not negligible versus the expected uncertainty of the measurement, a qualitative and quantitative impurity evaluation is necessary.

The routine procedure in our laboratory is to measure the gamma-ray emission of the radioactive solution. However, this procedure can only reveal gamma-emitting impurities but not pure-beta impurities, even at a high concentration level. The LSC standardization of pure-beta solutions containing pure-beta emitters impurities is thus a difficult task because, unlike that which can be achieved using gamma-ray spectrometry,

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the continuous characteristics of beta spectra and the poor intrinsic resolution of LSC spectrometers do not allow an easy identification and precise determination of the activity concentration of these impurities.

This situation is illustrated in an example recently encountered during an international activity comparison of a ^{32}P solution, where the solution disseminated to the participants contained a notable amount of radioactive impurities. The analysis procedure used in our laboratory is detailed hereafter.

2. Identification of the nature of the possible impurities in the ^{32}P solution

A preliminary impurity assessment was made using a commercial liquid scintillation spectrometer (Guardian[®], Perkin Elmer[®]). The spectrum clearly revealed a peak in the low-energy range (Fig. 1). The reference spectrum for a pure ^{32}P solution in the same counting conditions is shown in Fig. 2. This indicates that, at the reference date, there was a significant amount of beta impurities in the solution. From the spectrum, the relative impurity concentration was estimated to be about 10% of the total activity concentration of the solution.

The presence of impurity in this case is obvious, even with a low-resolution LS-spectrometer, because the overlap of the main radionuclide and the impurity spectra is small and the impurity concentration is high. It must be pointed out that a similar case but with a larger degree of overlap between the spectra would be

much more difficult to solve. For example, the presence of ^3H in a ^{14}C solution, even at a high level, is difficult to detect using LSC spectrometry.

From the supposed production mode of this nuclide ((n,p) reaction on ^{32}S), the possible pure-beta impurities could be ^{33}P and ^{35}S . The reference spectrum for a pure ^{35}S solution in the same counting condition (Fig. 3) cannot be exactly adjusted on the lower energy part of the spectrum of the ^{32}P solution. Nevertheless, the resolution of LSC spectra is not sufficient to get an unambiguous characterization of the nuclides present.

Twelve spectra were then recorded at different dates (six are shown in Fig. 1). The decay curve of the counting rate of these spectra in a low-energy window (channels 1–300) was recorded versus time. In this spectral region, as the spectrometer has a logarithmic energy axis, the contribution of the ^{32}P spectrum is negligible and the counting rate evolution is mostly dominated by the impurities. This decay curve was fitted using the 3 following functions:

- One exponential with the half-life of ^{33}P .
- One exponential with the half-life of ^{35}S .
- A linear combination of these two exponentials.

The fitting procedure is a χ^2 minimization (Press et al., 1992). The experimental decay curve could not be fitted with a single exponential but could be fitted with a good χ^2 value when using the linear combination of the two exponentials. This confirms the presence of both ^{33}P and ^{35}S in the solution.

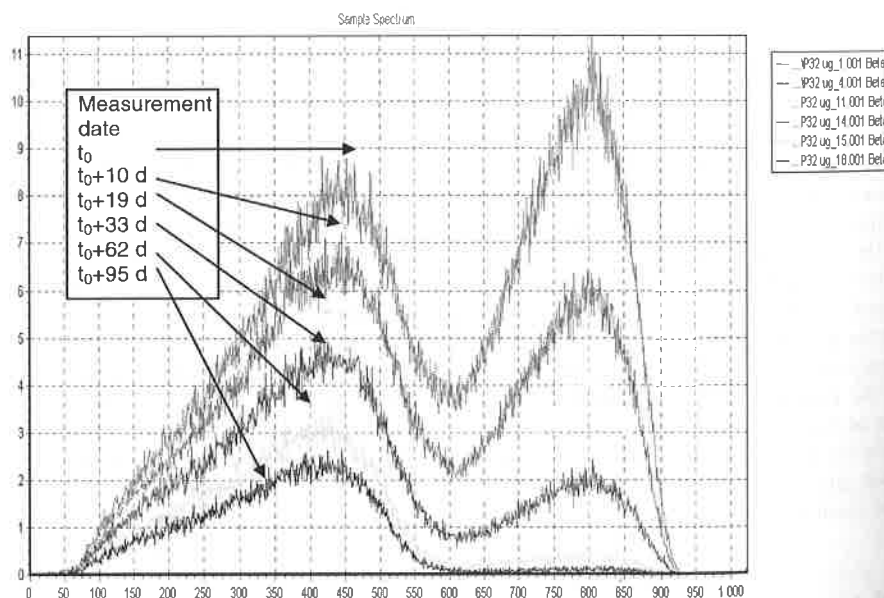


Fig. 1. Examples of LSC spectra of the ^{32}P solution with impurities at various measurement dates: x-axis, channel number; y-axis, number of pulses recorded in the channel.

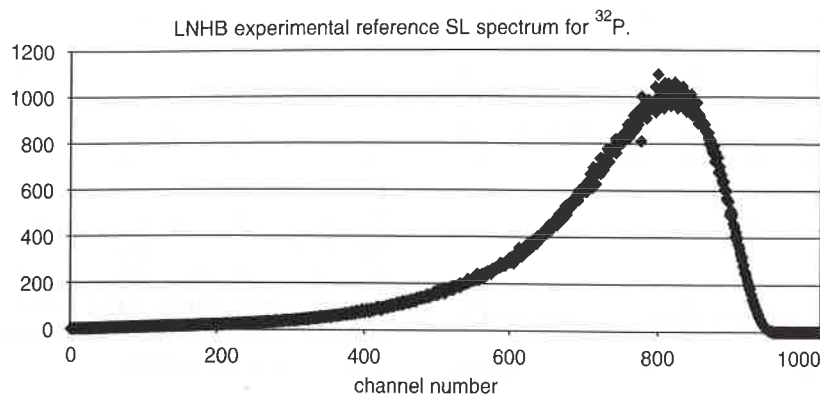


Fig. 2. ^{32}P LSC reference spectrum: x-axis, channel number; y-axis, number of pulses recorded in the channel.

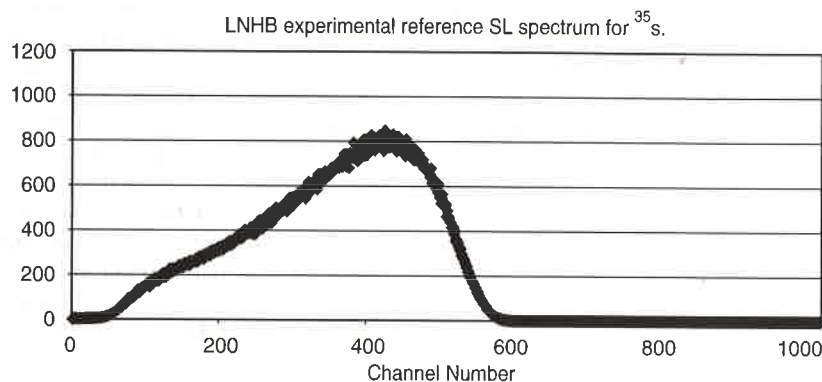


Fig. 3. ^{35}S LSC reference spectrum: x-axis, channel number; y-axis, number of pulses recorded in the channel.

3. Modeling the radioactive decay data

As the composition of the radioactive source was assumed to be a mixture of ^{32}P , ^{33}P and ^{35}S , the global activity decay model can be described by the following function:

$$N(t) = A_{32\text{P}}\epsilon_{32\text{P}} \exp\left(-\frac{t}{\tau_{32\text{P}}}\right) + A_{33\text{P}}\epsilon_{33\text{P}} \exp\left(-\frac{t}{\tau_{33\text{P}}}\right) + A_{35\text{S}}\epsilon_{35\text{S}} \exp\left(-\frac{t}{\tau_{35\text{S}}}\right),$$

× with $\tau_i = T_{1/2}/\ln(2)$, (1)

where $N(t)$ is the global count rate of the source, A_{xx} is the activity of the radionuclide xx at $t = 0$, ϵ_{xx} is the detection efficiency of the radionuclide xx and τ_{xx} the half-life of the radionuclide xx .

It was assumed that the detection efficiency of each radionuclide remains constant versus time and thus that the products $A_{xx}\epsilon_{xx}$ are a single variable, N_{xx} , meaning the count rate produced by the nuclide xx at $t = 0$. This assumption is reasonable if the sources are stable. This

stability was a posteriori checked by the consistency of the decay-curve analysis of each nuclide. It was also observed that, for a given measurement date, the relative standard deviation of the counting rate of five sources was not exceeding 0.2%, which is, from our experience, a good indicator of the stability of the sources.

Eq. (1) can thus be rewritten as

$$N(t) = N_{32\text{P}} \exp\left(-\frac{t}{\tau_{32\text{P}}}\right) + N_{33\text{P}} \exp\left(-\frac{t}{\tau_{33\text{P}}}\right) + N_{35\text{S}} \exp\left(-\frac{t}{\tau_{35\text{S}}}\right). \quad (2)$$

A χ^2 fitting of the experimental decay data of Eq. (2), gives the right values for the half-lives of the considered nuclides would be a good proof of the consistency of the assumptions made. Nevertheless, this kind of fit is known to be an ill-defined problem if all parameters are allowed to vary freely (Enderlein and Erdmann, 1997). A resolution using a nonlinear Levenberg–Marquardt method (Press et al., 2001) confirms this fact: in this

case, many combinations of the unknowns give good χ^2 fitting values.

The only way to solve the degeneracy of the parameters in Eq. (2) is to impose the values of the half-lives of the three nuclides. This supposes the stability of the source, but this hypothesis is already implicit in Eq. (2), and also the correct identification of the impurities present in the source.

4. Calculation of the detection efficiency of each nuclide

This curve fitting gives the count rate for each nuclide versus time. This count rate is the ratio of the activity of each nuclide to the detection efficiency of each nuclide. Using the TDCR method (Cassette et al., 2003), the coincidence detection efficiencies for a known radionuclide can be calculated, if the figure of merit of the counter (i.e. the average number of photoelectrons emitted at the photocathodes of the PMTs per unit of energy absorbed in the scintillator) is known. In double (logical sum) coincidences, assuming a perfect symmetry of the three photomultiplier tubes, the detection efficiency formula is

$$\varepsilon_D = \int_{\text{spectrum}} S(E) ((3(1 - e^{-\eta})^2 - 2(1 - e^{-\eta})^3)) dE \quad (3)$$

$$\text{with } \eta = \frac{v}{3} \int_0^E \frac{A dE}{1 + kB \frac{dE}{dx}} \quad (4)$$

where $S(E)$ is the energy spectrum absorbed by the scintillator and kB the ionization quenching parameter.

The free parameter is, in this formulation, vA , the product of the average quantum efficiency (v) of the photocathodes of the PMTs by the average number (A) of photons produced after the absorption of 1 keV in the scintillator.

As the global spectrum of the mixture of radionuclides is not known a priori, an iterative two-step process is used to determine it. This process is described hereafter and summarized in Fig. 4.

Step 1: The global spectrum is calculated as a sum of the theoretical spectra of ^{32}P , ^{33}P and ^{35}S weighted by their respective relative count rates. This procedure supposes that, at a first approximation, the detection efficiency of each nuclide is unity.

The value of the free parameter is obtained by solving the general TDCR equation in which, the experimental ratio of observed count rates in TDCR is equal to the calculated ratio of triple and double detection probabilities:

$$\text{TDCR} = \frac{\int_{\text{spectrum}} S(E)(1 - e^{-\eta})^3 dE}{\int_{\text{spectrum}} S(E)((3(1 - e^{-\eta})^2 - 2(1 - e^{-\eta})^3)) dE} \times \text{with } \eta \text{ defined in Eq. (4).} \quad (5)$$

Step 2: The free parameter vA is then injected in Eq. (3) using the spectrum of ^{32}P , in order to calculate the detection efficiency of ^{32}P and the same procedure is used to calculate detection efficiency of ^{33}P and ^{35}S .

This gives a first estimate for the activity of the three radionuclides by using the respective detection efficiencies of each nuclide in Eq. (1). Steps 1 and 2 are then iterated but in Step 1 the new global spectrum is calculated as a sum of the theoretical spectra of ^{32}P , ^{33}P and ^{35}S weighted by their respective relative estimated activity concentrations. The process converges toward a stable solution after two iterations and gives the activity of the three radionuclides.

5. Experimental results

Two sets of five liquid scintillation sources were prepared using Ultima Gold[®] and Hionic Fluor[®] cocktails from Perkin Elmer[®]. The decay was followed over a period of 94 days.

The detection efficiencies obtained following the previously described procedure for Ultima Gold[®] LS-cocktail are (0.9985 ± 0.0001) for ^{32}P , (0.9512 ± 0.0032) for ^{33}P and (0.9166 ± 0.0053) for ^{35}S ($k = 1$). The uncertainty on each value is the experimental standard deviation observed from the analysis of the 15 measurements. The activity of each radionuclide versus time was then calculated taking into account the calculated values of detection efficiencies.

An exponential decay curve fitting was made on these results in order to check the consistency of the analysis procedure. A χ^2 minimization procedure was undertaken with the half-life, τ , as a free parameter.

$$Y = a \exp\left(\frac{-\ln(2) \cdot t}{\tau}\right).$$

The results obtained are listed in Table 1, in comparison with the published evaluated half-life values (Bé et al., 1998). The relative difference between the experimental and the evaluated half-life values are lower than 10^{-4} for ^{32}P , about 0.6% for ^{33}P and 2.8% for ^{35}S .

The relative activity concentration of ^{32}P , ^{33}P and ^{35}S at the reference date are respectively, 90.6%, 6.9% and 2.5% of the total activity of the solution.

6. Evaluation of uncertainties

The uncertainty budget of this measurement is detailed in Table 2. The contribution of the ionization-quenching factor, kB , was deduced by considering a uniform distribution of this parameter on the 0.007 to 0.015 cm MeV⁻¹ range. This contribution is, as expected, negligible for ^{32}P but reaches 1% for ^{35}S . It must be observed that this evaluation is fast but very

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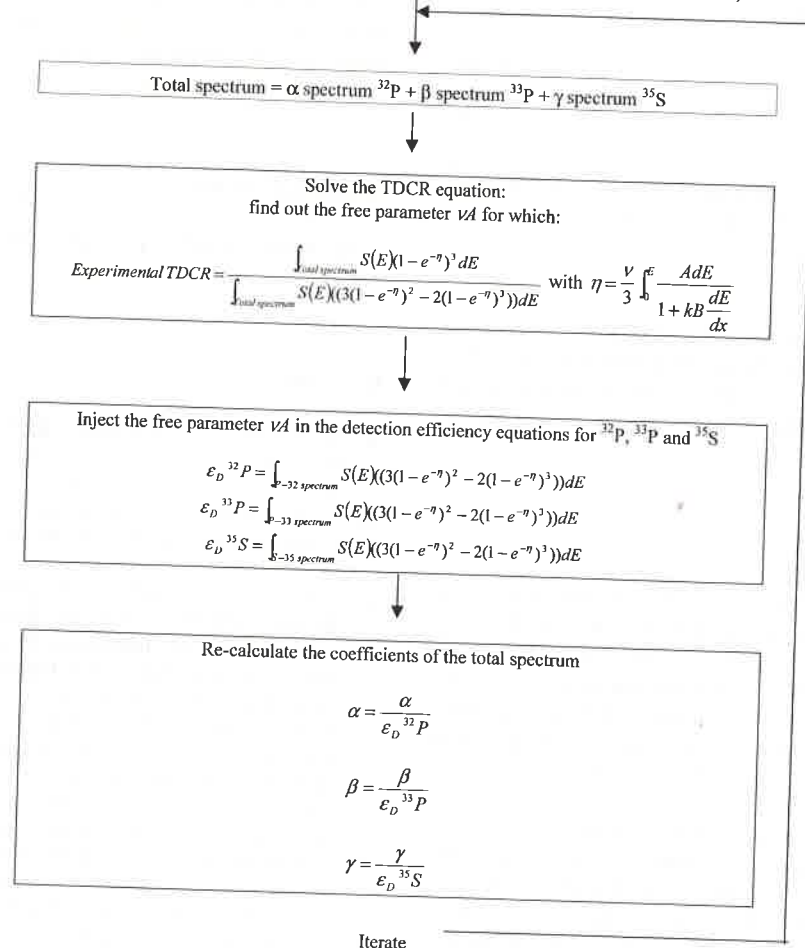


Fig. 4. Method for the calculation of the activities of ^{32}P , ^{33}P and ^{35}S .

Table 1
Experimental and evaluated half-lives of ^{32}P , ^{33}P and ^{35}S (in days) ($k = 1$)

Radionuclide	^{32}P	^{33}P	^{35}S
Experimental half-life	14.261 ± 0.001	25.2 ± 0.1	84.8 ± 1.8
Evaluated half-life	14.262 ± 0.014	25.34 ± 0.12	87.32 ± 0.16

Table 2
Uncertainty budget (in %)

Parameter	^{32}P	^{33}P	^{35}S
Counting statistics	0.2	0.8	1.4
Weighing	0.02	0.02	0.02
Ionisation quenching	0.01	0.6	1.1
Half-life	<10–4	<10–4	<10–4
Curve fitting	0.04	0.6	0.4

conservative. As this only influences the uncertainty of the ^{35}S activity concentration, a more sophisticated evaluation method was considered unnecessary.

The activity concentration values of the three radionuclides are correlated because of the analysis procedure. An underestimation of the activity of one radionuclide must be compensated by an overestimation of another one, for the conservation of the total count rate. The covariance between the three activities was

estimated from the Hessian matrix of the decay-curve fitting analysis. As a first approximation, this covariance was calculated on the count rate of each radionuclide and not on its activity concentration, considering that because of the high detection efficiencies, a more sophisticated procedure was not necessary.

Table 3
Relative uncertainties matrix (in %)

Radionuclide	^{32}P	^{33}P	^{35}S
^{32}P	0.5	$<10^{-3}$ (–)	$<10^{-3}$ (+)
^{33}P		2.5	2.10^{-3} (–)
^{35}S			4

The diagonal terms are relative standard deviations. The non-diagonal terms are the covariances divided by the associated values.

The covariance matrix, expressed for clarity as a relative uncertainty matrix, can be found in Table 3. The diagonal terms are dominant because the non-diagonal terms express only the covariances due to the fitting procedure.

7. Conclusion

The standardization of a ^{32}P solution containing almost 10% of impurities in terms of activity concentration was possible using a decay-curve fitting procedure and an iterative detection efficiency calculation using the TDCR method. The global uncertainty on the main radionuclide is around 0.5%, a value much larger than the one expected for the standardization of a pure solution of ^{32}P .

The method can be extended to other cases. Nevertheless, it must be pointed out that this case is favorable because of the short half-lives of the nuclides, their very different values, their different maximum energy beta spectra and their high counting efficiencies. A similar problem encountered for example with ^3H in a ^{14}C solution would have been much more difficult to solve.

But, in this case, even 10% of ^3H in a ^{14}C solution is hardly detectable using LS spectroscopy, and, as the decay curve analysis requires a long time, the problem would have been probably ignored, resulting in a major error in the ^{14}C activity!

Acknowledgements

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