Comparison of C-14 liquid scintillation counting at NIST and NRC Canada

Denis E. Bergeron,^{1,*} Raphael Galea,² Lizbeth Laureano-Pérez,¹ and Brian E. Zimmerman¹

¹*Radiation Physics Division, National Institute of Standards and Technology, Gaithersburg, MD, USA*

²*National Research Council of Canada, Ottawa, ON, Canada*

denis.bergeron@nist.gov

+1(301)975-2282

Abstract

An informal bilateral comparison of ^{14}C liquid scintillation (LS) counting at the National Research Council of Canada (NRC) and the National Institute of Standards and Technology (NIST) has been completed. Two solutions, one containing ^{14}C -labeled sodium benzoate and one containing ^{14}C -labeled n-hexadecane, were measured at both laboratories. Despite observed LS cocktail instabilities, the two laboratories achieved accord in their standardizations of both solutions. At the conclusion of the comparison, the beta spectrum used for efficiency calculations was identified as inadequate and the data were reanalyzed with different inputs, improving accord.

Keywords: efficiency tracing; CNET; triple-to-double coincidence ratio; TDCR; ^{14}C ; bilateral comparison; benzoate; hexadecane; cocktail instability; beta spectrum shape; shape factor

1. Introduction

One of the first β -particle-emitting radionuclides standardized using a liquid scintillation (LS)-based efficiency tracing method was ^{14}C (Grau Malonda and Garcia-Toraño, 1982; Coursey et al., 1986). Its commercial and technical importance, simple decay scheme, and relatively high LS counting efficiency ($\approx 94\%$) made it an attractive target for the development and demonstration of the CIEMAT/NIST efficiency tracing (CNET) method of LS counting. Similarly, ^{14}C has often been featured in the demonstration of new instruments or methods for LS counting via the triple-to-double coincidence ratio (TDCR) method (for example, Broda and Pochwalski, 1992; Wanke et al., 2012).

Recently, the National Institute of Standards and Technology (NIST) and the National Research Council of Canada (NRC) undertook an informal bilateral comparison of LS counting capabilities. A solution of ^{14}C -benzoate was standardized at NRC and sent to NIST. In the past, researchers have found that adsorption of organic salts to the walls of LS vials can lead to measurement bias as a result of counting losses (Wigfield, 1974; 1975). In the early stages of our bilateral comparison, we found that some LS cocktail formulations suffered counting losses of several percent. This prompted us to add a second phase to the comparison, centered on a ^{14}C -hexadecane solution. Since hexadecane dissolves directly in the organic phase of a scintillant, it is expected to form more stable cocktails than aqueous samples accommodated in organic scintillants via micellization.

Herein, we describe the methods used for sample preparation, LS counting, and data analysis at NRC and NIST. The ^{14}C activities determined by the laboratories were in accord for both the benzoate and hexadecane solutions.

2. Experiment

2.1. Comparison solutions

2.1.1. Benzoate

A solution of ^{14}C -sodium benzoate in $0.1 \text{ mol}\cdot\text{L}^{-1}$ sodium hydroxide was standardized at NRC-Canada and designated as Certified Reference Material 2013-C14-A13203 (Galea, 2013). An ampoule of the solution containing nominally 500 kBq of ^{14}C was shipped to NIST for measurement in November of 2013. To preserve the blind comparison, only a nominal “shipping” activity was provided to NIST.

2.1.2. Hexadecane

Two ampoules of a ^{14}C -n-hexadecane solution, NIST Standard Reference Material (SRM) 4222C (Calhoun and Coursey, 1991), were acquired for the comparison. One ampoule was shipped to NRC and one was kept at NIST. Since the certified activity for this SRM was available, this phase of the comparison cannot be considered truly “blind”. The participants responsible for analyzing the data did not look at the standard activity before completing their analyses, but the comparison can be guaranteed as “blind” only by invoking an “honor system”.

2.2. Source preparation

2.2.1. NIST

For all counting samples, radioactive materials were added gravimetrically and non-radioactive materials were added volumetrically via dispensette or micropipette. All samples contained 10 mL of scintillant in 20 mL glass scintillation vials. Unquenched sources were prepared for TDCR counting (efficiency variation was achieved with gray filters). For CNET counting, a series of five nitromethane-quenched sources were prepared with each scintillant. The chemical compositions of the ^3H tracer and ^{14}C sources were precisely matched via addition of nitromethane (approximately 1:5 or 1:10 by volume in ethyl alcohol), NaOH carrier solution (containing no benzoate), water, and/or hexadecane. Similarly, blanks were matched to have the same composition as the ^3H and ^{14}C samples.

NIST performed two experiments with the benzoate solution. In the first, two scintillants, Hi Safe 3 (HS3) and Hionic Fluor (HiF) were used (all scintillants are from PerkinElmer, Waltham, MA, USA)¹. Count rates were observed to decrease with time (see section 3.1), especially for the HiF cocktails, and so in the second experiment, HS3 and Ultima Gold (UG) were used. The total aqueous fractions ($f = \frac{v_{\text{aq}}}{v_{\text{tot}}}$, where v_{aq} and v_{tot} are the aqueous and total volumes, respectively) in the first experiment were 0.09 and 0.05 for the HiF and HS3 cocktails, respectively. In the second experiment, lower values for f were adopted: ≈ 0.025 and ≈ 0.01 for HS3 and UG, respectively. It was expected that lower f would help to minimize cocktail instabilities.

¹ Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

NIST also performed two experiments with the hexadecane material. In the first, HiF and UG were used. The CNET ^{14}C sources and blanks each had $f \approx 0.005$ (in the typical 10 mL of scintillants used in NIST cocktails) to match the ^3H tracing samples; the tracing samples and blanks each contained nominally 0.015 g of hexadecane (natural isotopes) to match the ^{14}C sources. The TDCR sources and blanks contained no added water. In the second experiment, HiF and Ultima Gold AB (UGAB) were used for CNET, while HiF and Ultima Gold F (UGF) were used for TDCR. The CNET samples were matched as before, but the UGAB sources were prepared with $f \approx 0.1$ in order to assure micellization and avoid the complications that can arise in UGAB samples with lower f (Zimmerman and Collé, 1997; Bergeron, 2012; 2014).

2.2.2. NRC

All additions were made volumetrically with gravimetric confirmation to monitor any loss due to evaporation. Dilution factors and massic activities were calculated with the mass data. All samples contained 20 mL of scintillant in 20 mL glass vials. Samples were initially prepared with scintillants and radioisotope and counted before quenching with nitromethane (undiluted). The ^3H tracer and ^{14}C sources were precisely matched via addition of nitromethane, water, and/or NaOH carrier (containing no benzoate). No non-radioactive (natural isotopes) hexadecane was added to ^3H tracer sources. Blanks were similarly matched.

The benzoate solution was standardized via CNET. Initial measurements used UG as the scintillant, with no added water ($f < 0.01$). In addition to the UG cocktails, subsequent experiments added HiF and OptiFluor (OF), again with no added water. Count rates were found to be very unstable for the OF cocktails.

The hexadecane solution was standardized via CNET and TDCR. The scintillants were UG, HiF, and OF with no other components added ($f \approx 0$). Matching sets of ^3H tracer sources were prepared for CNET counting. Quenching was achieved with nitromethane addition, and the same ^{14}C sources were used for CNET and TDCR counting.

2.3. Counting

2.3.1. NIST

CNET measurements were performed with a Wallac 1414 WinSpectral and a Beckman-Coulter LS7800. A detailed description of these counters is given elsewhere (Laureano-Pérez et al., 2007). All samples were run for 5 cycles on each counter on two or more occasions, for measurement sets spanning > 80 d. Tritium counting efficiencies ($\epsilon_{\text{H-3}}$) ranged from approximately 0.12 to 0.46.

TDCR measurements were performed on the NIST TDCR counter, which has been described previously (Zimmerman et al., 2004). Data were acquired simultaneously with a system utilizing the MAC3 (Bouchard and Cassette, 2000) unit to process coincidence pulses and with a home-built FPGA-based system. Efficiency variation was achieved with gray filters, with typical TDCR values (K) of 0.80 to 0.92 in the benzoate studies and 0.80 to 0.95 in the hexadecane studies.

2.3.2. NRC

CNET measurements were performed with a Wallac 1410 LSC counter. Each source was measured at least three times and $\epsilon_{\text{H-3}}$ ranged from approximately 0.10 to 0.37.

TDCR measurements were performed with a Hidex 300 LS-METRO, the use of which for metrology has recently been demonstrated at other national metrology institutes (Wanke et al., 2012; Kossert et al., 2014). Each source ($n = 15$) was measured ten times. For the benzoate samples (stability tests only), K ranged from 0.75 to 0.93. For the hexadecane samples, K ranged from 0.73 to 0.93.

2.4. Efficiency models

Both NRC and NIST used the MICELLE2 code (Kossert and Grau Carles, 2008; 2010) to calculate CNET and TDCR efficiencies. The SCINTL.DAT input file was edited for each scintillant with elemental composition data from the manufacturer (PerkinElmer, 2007). The value of the Birks parameter, kB , was selected to give the least variance in recovered activity across the experimental efficiencies (realized by chemical quenching or gray filters). The typical value used at NRC and NIST in these studies was $kB = 0.0075 \text{ cm} \cdot \text{MeV}^{-1}$, which is consistent with findings reported by Kossert and Grau Carles (2010). All of the efficiency models used the Birk's formula for the quenching function. In the initial comparison, an "allowed" beta spectrum shape (i.e., the shape factor, $C(W_e) = 1$) was used; the data were later reevaluated (see Section 3.2) with different shape factors input into MICELLE2. For each MICELLE2 calculation, $5 \cdot 10^4$ events were simulated.

In addition, NIST used the CN2003 code (Günther, personal communication) for CNET efficiencies. The CN2003 calculations, with a value of $kB = 0.0075 \text{ cm} \cdot \text{MeV}^{-1}$, were used in the final CNET analysis and the beta spectrum was calculated with an allowed shape. The CN2003

efficiencies were in agreement with MICELLE2 efficiencies over the range of experimental efficiencies, returning final activities that agreed to 0.30 %.

NIST also used a Mathematica-based code developed in-house (Zimmerman, 2008) for the calculation of TDCR efficiencies. The Mathematica program calculates the doubles and triples counting efficiencies at each efficiency point using the average counting rates for coincidences between each of the three detector pairs, as well as the logical sum of double coincidences and triple coincidences. The methodology applied in the program allows for corrections for phototube detection asymmetry to be made. The input beta spectrum was calculated using the SPEBETA program (Cassette, 1992) using the evaluated endpoint energy (Bé et al., 2013) and (in the initial comparison) assuming an allowed shape with screening corrections. As with the MICELLE2 calculations, kB was selected to give the minimum variance in recovered activity across the efficiency series (i.e., across different gray filters) and was equal to $0.0075 \text{ cm} \cdot \text{MeV}^{-1}$. The stopping power equations, dE/dx , for electrons in the LS cocktails were calculated by fitting functions of the form

$$dE/dx = (a + cE^{0.5} + eE + gE^{1.5} + iE^2 + kE^{2.5}) / (1 + bE^{0.5} + dE + fE^{1.5} + hE^2 + jE^{2.5}), \quad (1)$$

where E is the value of the midpoint energy for each bin of the calculated beta spectrum (with a low-energy cut off of 100 eV), to data from the NIST ESTAR database (NIST, 2015) again using composition data from the manufacturer (PerkinElmer, 2007). The Mathematica-calculated efficiencies were used in the final TDCR analysis and were in agreement with MICELLE2 efficiencies over the range of experimental efficiency points to the extent that the final recovered activities from the two codes agreed to 0.43 % for ^{14}C -benzoate and to 0.05 % for ^{14}C -

hexadecane; the small differences arise partially from PMT asymmetries which are treated in the Mathematica-based program, but not in MICELLE2.

3. Results

All uncertainties are calculated by adding the individual components in quadrature and are reported as expanded uncertainties with $k = 2$.

3.1. Benzoate

From CNET, NRC determined a final massic activity, C_A , of $105(2) \text{ kBq}\cdot\text{g}^{-1}$ for the benzoate solution at the comparison reference time, 13 September 2013 13:00:00 EST. A summary uncertainty budget is presented in Table 1 with a detailed version available in the online supplemental material (Table S1). The activity was based on measurements with UG.

From TDCR, NIST determined $C_A = 106(1) \text{ kBq}\cdot\text{g}^{-1}$ for the benzoate solution. A summary uncertainty budget is presented in Table 2 with a detailed version available online (Table S2).

The activity was based only on measurements with HS3. HiF sources were found to exhibit signs of short-term instability. Samples were agitated before each measurement cycle. The average difference between the activities recovered from the first and third of three sequential 720 s measurements on HiF samples was 0.96 %; for HS3 samples it was 0.30 %. The average difference between the activities recovered from the second and third measurements was 0.29 % for HiF samples and 0.01 % for HS3 samples.

Long-term instabilities were also observed in the NIST samples, undermining confidence in the NIST CNET results. The NIST CNET measurements were taken over a period of three weeks, and during that time the observed count rates and recovered activities decreased by approximately 3 %.

Follow-up TDCR measurements on HS3 sources also found a drop of approximately 3 % in the recovered activity after approximately four months. NRC observed a drop of comparable magnitude in UG samples after approximately five months; agitation of this source increased the measured count rate by only 0.3 %, leaving the recovered activity ≈ 3 % lower than the value determined five months previously. To further investigate cocktail instability effects, NIST prepared and studied two UG and two HS3 sources and measured them on the LS7800 for more than two weeks. The count rates for all four sources dropped precipitously with time.

NRC also investigated cocktail instability effects, preparing three HiF and three OF sources. Over a period of three days, the average count rates for the HiF sources were stable to < 0.1 %, while the count rates for the OF sources dropped by up to 50 %. Agitation of the OF sources increased the count rates to within 10 % of their original values.

The combined observations indicate effects from reversible and irreversible mechanisms of instability. Something like a settling or phase separation process might account for the short-term (reversible) instabilities seen at NIST and NRC. A longer-term process like adsorption to the vial walls might explain the longer-term (irreversible) instabilities.

It is difficult to make a correction for or assign an uncertainty to the effects of cocktail instability since it is unknown what shape any extrapolation to a reference time should take. If the drop in count rate is due to adsorption (where the rate equation would take the form of an exponential), then any correction would have to be based on a detailed knowledge of the effect of the geometry change (including wall effects) on the counting efficiency. So, the NRC and NIST activities for the benzoate solution do not include any corrections or estimated uncertainties for cocktail instability effects. Over the timescale of the experiments, it can be assumed that any unseen variability due to cocktail instability (which, to emphasize, is not evident in the data used to calculate C_A) is embodied in the statistical uncertainty components (i.e., measurement repeatability and reproducibility).

It is our opinion that if a correction appears to be required for cocktail instability or if such instability appears to be a dominant source of uncertainty, the data should be treated as suspect. We do not think a correction for cocktail instability effects is ever appropriate.

Despite concerns over LS cocktail instability with the ^{14}C benzoate solution, the standard massic activities recovered from measurements on the most stable cocktails at the two laboratories (TDCR-based for NIST and CNET-based for NRC) differ by $(1.1 \pm 1.9) \%$.

3.2. Hexadecane

From CNET, NRC determined a final C_A of $53.1(8) \text{ kBq}\cdot\text{g}^{-1}$ for the ^{14}C hexadecane material at the comparison reference time, 10 September 2014 12:00:00 EST. From TDCR, NRC determined $C_A = (53.5 \pm 1.1) \text{ kBq}\cdot\text{g}^{-1}$. The uncertainty budgets are presented in Tables 1 and S1.

The activities were based on measurements with UG, HiF, and OF. Over a period of 5 months, no systematic losses in the count rates were observed; for most samples, the count rates varied by $< 0.2 \%$, and for no sample was a variation of more than 1% observed.

From CNET, NIST determined $C_A = 53.4(6) \text{ kBq}\cdot\text{g}^{-1}$ for the ^{14}C hexadecane material. From TDCR, NIST determined $C_A = 53.9(3) \text{ kBq}\cdot\text{g}^{-1}$. The uncertainty budgets are presented in Tables 2 and S2. The CNET activities were based on measurements with HiF and UGAB. The TDCR activities were based on measurements with HiF and UGF.

The NIST TDCR samples were monitored for instabilities on two timescales. To look for short-term instabilities, 50 successive 900 s TDCR acquisitions were taken overnight at NIST for one UG source and one HiF source. The HiF source appeared to be stable in terms of the recovered C_A , but a possible decrease in the measured TDCR value (K) was seen; the MICELLE2 model recovers the correct activity, appropriately handling the decrease in counting efficiency indicated by the decreasing K . The UG source showed a slight decrease in the recovered C_A and in the measured K ; in this case, the MICELLE2 model does not account for the efficiency change indicated by the data.

To look for longer-term instabilities, the time-dependence of the measurements over the 5 d duration of the NIST TDCR experiment were studied. One HiF source showed a discrete change in K over time from day 1 to day 5, which seems to track with a real change in the double efficiency, since the recovered C_A is constant; i.e., the MICELLE2 model seems to appropriately describe the efficiency change. An UG source showed no change in K but a definite change of

0.74(2) % in the recovered C_A . For reference, C_A for the HiF source changed by 0.02(29) % over the same period. It appears that the change in efficiency in the UG source is not accompanied by the K change that would be expected from the MICELLE2 model. In the second NIST TDCR experiment, no short- or long-term instabilities were observed for the UGF sources.

In the second NIST CNET experiment, count rate losses were observed for both UGAB and HiF. Three measurements were taken over a period of 20 d, showing a decrease in the measured count rates of 0.6 % for UGAB and 0.4 % for HiF. To check for longer-term instabilities, an additional measurement was performed approximately 64 d later, showing a decrease of ≤ 0.1 % for both UGAB and HiF.

It is not clear why NIST observed long-term instabilities in UG cocktails while NRC did not, but the standard massic activities reported by the two laboratories are in accord to within the stated uncertainties, as seen in Figure 1. Figure 1 also shows the certified activity for SRM 4222C, decay corrected to the comparison reference time, $53.9(4) \text{ kBq}\cdot\text{g}^{-1}$.

SRM 4222C (Calhoun and Coursey, 1991) was standardized at NIST between 1990 and 1991, with additional experiments performed in 1992. The standardization was a relatively early application of the CNET method, following the procedures outlined in the 1986 standardization of a ^{14}C -tartaric acid solution (Coursey et al., 1986). The main scintillant used was UG (though the commercial formulation may have been different from what is used today), with efficiency variation achieved by chemical quenching with chloroform. The EFFY code (Garcia-Toraño et al., 1985) was used for efficiency calculations. In the early 1990s, precise cocktail matching was

not common practice at NIST or anywhere else. The series of quenched ^{14}C -hexadecane samples did not include additional water for matching with the tritiated water tracer samples. However, water was added to one sample of the series as an additional quencher, and notes indicate that this addition had an effect on cocktail stability. Contemporaneous measurements on a ^3H -n-hexadecane solution indicate a loss in counting efficiency with time. Losses in counting efficiency for hexadecane-based samples were generally less than for tritiated water samples in the same scintillants (Calhoun et al., 1992). Figure 1 illustrates the accord between current NRC and NIST determinations and the certified activity for SRM 4222C.

Finally, Figure 1 also shows that at both laboratories, TDCR returns a higher activity than CNET. For the ^{14}C -benzoate solution, the TDCR-based activity (from NIST) was again higher than the CNET-based activity (from NRC). It is possible that this systematic difference between the techniques indicates a problem with the beta spectrum used in the efficiency calculations. Kossert and Mougeot recently showed that the inclusion of atomic screening and exchange effects in the beta spectrum calculations brought TDCR and CNET measurements on ^{63}Ni into accord, revealing a general overestimate of the counting efficiencies (resulting in an underestimate of the activities) resulting from the use of the uncorrected beta spectrum (Kossert and Mougeot, 2015).

As we discovered, the ^{14}C beta spectrum is known to deviate from a purely allowed shape, with several discrepant shape factors reported in the literature based on experiment and calculation (Sonntag et al., 1970; Genz et al., 1991; García and Brown, 1995; Alimonti et al., 1998; Kuzminov and Osetrova, 2000). We reanalyzed our data with six different sets of shape factor

coefficients (including allowed) from the literature, input into MICELLE2 for efficiency calculations. We found that the ratio of the values for C_A recovered by the two techniques, $A_{\text{CNET}}/A_{\text{TDCR}}$, varied from 0.988 with the allowed shape to 1.016 with the Sonntag (1970) shape ($C(W_e) = 1 - 4.67*W_e + 3/W_e + 2*W_e^2$). In the CNET data, the variability due to efficiency variation (i.e., source-to-source variability across the chemically quenched series) reached a clear minimum (0.160 %) with the shape factor limit reported by the Borexino collaboration (Alimonti et al., 1998)

$$C(W_e) = 1 + aW_e \quad (2)$$

where W_e is the total energy of the emitted β -particle in natural units (i.e., electron rest mass, m_e) and $a = -0.37$ (alternatively expressed as -0.72 MeV^{-1}). In other words, the experimental efficiency curve is best modeled by MICELLE2 when the Borexino limit is used for the ^{14}C beta spectrum shape factor.

The Borexino limit also gave $A_{\text{CNET}}/A_{\text{TDCR}} = 0.994$, resulting from an increase of approximately 0.4 % in the C_A recovered from the CNET data and 0.2 % in the C_A recovered from the TDCR data (these values are based on the NIST data; the impact of varying the shape factor increases at lower efficiencies, so that the NRC data show increases of approximately 0.7 % and 0.2 % for the CNET- and TDCR-recovered C_A s, respectively). A slightly lower (larger in absolute magnitude) coefficient gives slightly better agreement between the techniques, but with greater variability due to efficiency variation in the CNET data. In general, the TDCR data were not as sensitive to changes in the shape factor coefficient, with less change in C_A and variability due to efficiency variation (i.e., gray filter dependence).

A complete reanalysis of the comparison data with $a = -0.37$ gave better accord between TDCR and CNET, as shown in the red triangles in Figure 1. Our data are more consistent with the Borexino beta spectrum shape factor limit (Alimonti et al., 1998) than with the allowed or Sonntag (1970) shape factors, but our results should not be interpreted as a true shape factor determination.

4. Conclusions

With the ^{14}C -benzoate samples, some LS cocktail formulations were more stable than others. Instabilities were observed over different timescales for all cocktail formulations, but it is unclear what form any extrapolation of count rate losses should take. In this study, we have relied on data collected with the most stable cocktails and assumed that the uncertainty due to small instabilities (which we do not see in the data used to calculate C_A) should be encompassed in the other statistical components of uncertainty (repeatability and reproducibility). Without any corrections or added uncertainty for cocktail instabilities, activities determined by NRC using CNET and by NIST using TDCR differed by $(1.1 \pm 1.9) \%$, indicating accord.

Even with the ^{14}C -hexadecane samples, some cocktail formulations, particularly those containing added water for matching with CNET ^3H tracer sources, exhibit long-term instability. Without any corrections or added uncertainty for cocktail instabilities, activities determined by NRC and NIST using CNET and TDCR were in accord. NRC recovered activities $(-1.4 \pm 1.6) \%$ (CNET) and $(-0.7 \pm 2.2) \%$ (TDCR) different from the certified activity for SRM 4222C. NIST recovered activities $(-0.9 \pm 1.3) \%$ (CNET) and $(0.1 \pm 1.0) \%$ (TDCR) different from the certified activity.

The observation that TDCR-derived activities were consistently higher than CNET-derived activities prompted a reevaluation of the data using the beta spectrum shape factor limit reported by Alimonti et al. (1998) in the efficiency calculations. With the revised efficiencies, NRC recovered activities $(-0.7 \pm 1.6) \%$ (CNET) and $(-0.5 \pm 1.5) \%$ (TDCR) different from the certified activity and NIST recovered activities $(-0.5 \pm 1.2) \%$ (CNET) and $(0.3 \pm 1.2) \%$ (TDCR) different from the certified activity.

This informal bilateral comparison has demonstrated equivalence in LS counting of ^{14}C samples at NRC and NIST.

Acknowledgements

The laboratory notebooks of B.M. Coursey, J.T. Cessna, and J.M. Calhoun (NIST) were consulted for the description of the 1990 to 1992 experiments. We are grateful to the participants in the Liquid Scintillation Working Group of the International Conference on Radionuclide Metrology and its Applications (ICRM) for discussions on the topic of ^{14}C liquid scintillation counting. We thank R.P. Fitzgerald (NIST) for a critical reading of the manuscript.

References

- Alimonti, G., Angloher, G., Arpesella, C., et al., 1998. Measurement of the ^{14}C abundance in a low-background liquid scintillator. *Phys. Lett. B* 422, 349-358.
- Bé, M.-M., Chisté, V., Dulieu, C., Mougeot, X., Chechev, V.P., Kondev, F.G., Nichols, A.L., Huang, X., Wang, B., 2013. Monographie BIPM-5: Table of Radionuclides (Vol. 7 - A = 14 to 245).

- Bergeron, D.E., 2012. Determination of micelle size in some commercial liquid scintillation cocktails, *Appl. Radiat. Isotop.* 70, 2164-2169.
- Bergeron, D.E., 2014. Identification of phase boundaries in surfactant solutions via Compton spectrum quenching. *J. Phys. Chem. A* 118, 8563-8571.
- Bouchard, J., Cassette, P., 2000. MAC3: an electronic module for the processing of pulses delivered by a three photomultiplier liquid scintillation counting system. *Appl. Radiat. Isotop.* 52, 669-672.
- Broda, R., Pochwalski, K., 1992. The enhanced triple to double coincidence ratio (ETDCR) method for standardization of radionuclides by liquid scintillation-counting. *Nucl. Inst. Meth. A* 312, 85-89.
- Calhoun, J.M., Coursey, B.M., 1991. Standard Reference Material 4222C Radioactivity Standard for Liquid Scintillation Counting.
- Calhoun, J.M., Cessna, J.T., Coursey, B.M., 1992. A system for intercomparing standard solutions of beta-particle emitting radionuclides. *Nucl. Instrum. Meth. A* 312, 114-120.
- Cassette, P., 1992. SPEBETA program, personal communication.
- Coursey, B.M., Mann, W.B., Grau Malonda, A., Garcia-Toraño, E., Los Arcos, J.M., Gibson, J.A.B., Reher, D., 1986. Standardization of Carbon-14 by $4\pi\beta$ liquid scintillation efficiency tracing with Hydrogen-3. *Appl. Radiat. Isotop.* 37, 403-408.
- Galea, R., 2013. Certified Reference Material 2013-C14-A13203. NRC Report Number: PIRS-2013-1817.
- Garcia, A., Brown, B.A., 1995. Shape of the β spectra in the $A = 14$ system. *Phys. Rev. C* 52, 3416-3427.

- Garcia-Toraño, E., Grau Malonda, A., 1985. EFFY- a new program to compute the counting efficiency of beta-particles in liquid scintillators. *Comp. Phys. Comm.* 36, 307-312.
- Genz, H., Kühner, G., Richter, A., Behrens, H., 1991. Phenomenological wave functions for the $A = 14$ system and a consistent description of beta decay observables. *Z. Phys. A* 341, 9-24.
- Grau Malonda, A., Garcia-Toraño, E., 1982. Evaluation of counting efficiency in liquid scintillation counting of pure β -ray emitters. *Int. J. Appl. Radiat. Isotop.* 33, 249-253.
- Kossert, K., Grau Carles, A., 2008. Study of a Monte Carlo rearrangement model for the activity determination of electron-capture nuclides by means of liquid scintillation counting, *Appl. Radiat. Isotop.* 66, 998-1005.
- Kossert, K., Grau Carles, A., 2010. Improved method for the calculation of the counting efficiency of electron-capture nuclides in liquid scintillation samples. *Appl. Radiat. Isotop.* 68, 1482-1488.
- Kossert, K., Capogni, M., Nähle, O.J., 2014. Bilateral comparison between PTB and ENEA to check the performance of a commercial TDCR system for activity measurements. *Appl. Radiat. Isotop.* 93, 38-44.
- Kossert, K., Mougeot, X., 2015. The importance of the beta spectrum calculation for accurate activity determination of ^{63}Ni by means of liquid scintillation counting, *Appl. Radiat. Isotop.* 101, 40-43.
- Kuzminov, V.V., Osetrova, N.Ja., 2000. Precise Measurement of ^{14}C beta spectrum by using a wall-less proportional counter. *Phys. Atom. Nucl.* 63, 1292-1296.
- Laureano-Pérez, L., Collé, R., Fitzgerald, R., Outola, I., Pibida, L., 2007. A liquid-scintillation-based primary standardization of ^{210}Pb . *Appl. Radiat. Isotop.* 65, 1368-1380.

- NIST, 2015. Electron stopping power and range tables, available online at <http://physics.nist.gov/PhysRefData/Star/Text/ESTAR.html>.
- PerkinElmer, 2007. Application Note: LSC Cocktails—Elemental Composition.
- Sonntag, C., Rebel, H., Ribbat, B., et al., 1970. Experimental evidence for nonstatistical shape of beta spectrum of ^{14}C . Lett. Nuovo Cimento 4, 717.
- Wanke, C., Kossert, K., Nähle, O.J., 2012. Investigations on TDCR measurements with the HIDEX 300 SL using a free parameter model. Appl. Radiat. Isotop. 70, 2176-2183.
- Wigfield, D.C., 1974. The determination of the radioactivity of ^{14}C samples adsorbed on glass vials by direct liquid scintillation counting. Anal. Biochem. 59, 11-15.
- Wigfield, D.C., 1975. On the myth that benzoic acid is adsorbed on the walls of liquid scintillation counting vials. Anal. Biochem. 63, 286-289.
- Zimmerman, B.E., Collé, R., 1997. Standardization of ^{63}Ni by $4\pi\beta$ liquid scintillation spectrometry with ^3H -standard efficiency tracing. J. Res. Natl. Inst. Stand. Technol. 102, 455-477.
- Zimmerman, B.E., Collé, R., Cessna, J.T., 2004. Construction and implementation of the NIST triple-to-double coincidence ratio (TDCR) spectrometer, Appl. Radiat. Isotop. 60, 433-438.
- Zimmerman, B.E., 2008. The use of *Mathematica* in analyzing data from the triple-to-double coincidence ratio method (TDCR) for the standardization of radionuclides, LSC 2008, Advances in Liquid Scintillation Spectrometry. Davos, Switzerland.

Table 1 Uncertainty budget for the NRC LS-based standardizations of a ^{14}C -benzoate solution and a ^{14}C -hexadecane solution. See Table S1 for detailed descriptions of the uncertainty components. Note that these are the uncertainties for the comparison values, which were determined before any beta spectrum shape factor studies were carried out. Thus, no uncertainty due to the shape factor is included.

Uncertainty Component	Type	%		
		benzoate	hexadecane	
		CNET	CNET	TDCR
Repeatability	A	0.1	0.1	0.1
Background	A	0.02	0.02	0.02
Weighing; dilution	B	< 0.002	< 0.002	< 0.002
Weighing; calibration of balance	B	0.03	0.03	0.03
Efficiency tracer ^3H activity	B	0.1	0.1	-
Quenching model	B	0.7	0.7	1.0
^{14}C half-life	B	< 0.0002	< 0.0002	< 0.0002
Live time	B	< 0.05	< 0.01	< 0.03
Combined standard uncertainty; $u_c = (\sum u_i^2)^{1/2}$		0.7	0.7	1.0
Expanded uncertainty; $U = k \cdot u_c$; $k = 2$		1.4	1.4	2.0

Table 2 Uncertainty budget for the NIST LS-based standardizations of a ^{14}C -benzoate solution and a ^{14}C -hexadecane solution. See Table S2 for detailed descriptions of the uncertainty components. Note that these are the uncertainties for the comparison values, which were determined before any beta spectrum shape factor studies were carried out. Thus, no uncertainty due to the shape factor is included.

Uncertainty Component	Type	%		
		benzoate	hexadecane	
		TDCR	CNET	TDCR
LS measurement precision	A	-	0.29	-
Repeatability	A	0.19	-	0.09
Reproducibility	A	0.05	-	0.09
Background	B	$2.6 \cdot 10^{-3}$	-	$2.6 \cdot 10^{-3}$
Weighing	B	0.05	0.05	0.05
Live time	B	-	0.08	-
Efficiency tracer ^3H activity	B	-	0.03	-
Quenching model / kB	B	0.42	0.30	0.11
Data collection system	B	0.11	-	0.18
Data analysis code	B	0.43	0.30	0.05
^{14}C half-life	B	$1.4 \cdot 10^{-6}$	$1.4 \cdot 10^{-5}$	$1.2 \cdot 10^{-6}$
^3H half-life	B	-	$2.6 \cdot 10^{-3}$	-
$E_{\beta\text{max}}$	B	$3.3 \cdot 10^{-4}$	< 0.0001	$1.4 \cdot 10^{-4}$
Combined standard uncertainty; $u_c = (\sum u_i^2)^{1/2}$		0.64	0.52	0.26
Expanded uncertainty; $U = k \cdot u_c$; $k = 2$		1.29	1.05	0.51

Figure 1 NRC and NIST results from LS-based standardizations of a ^{14}C -hexadecane solution, SRM 4222C. The certificate activity is shown as a solid line, with its expanded ($k = 2$) uncertainty shown as dotted lines. The open diamonds represent the (original) activities calculated with an allowed shape for the ^{14}C beta spectrum. The open triangles result from the reanalysis of the data with the beta spectrum shape factor limit from the Borexino collaboration report (Alimonti et al., 1998). Uncertainty bars express expanded ($k = 2$) uncertainties.