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Comparison of the French and U.S. National ³H (tritiated H₂O) Standards by $4\pi\beta$ Liquid Scintillation Spectrometry*

B. E. ZIMMERMAN and R. COLLÉ

Physics Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, U.S.A

Radioactivity standards of tritiated water (^3H_2O)—disseminated by the Laboratoire Primaire des Rayonnements Ionisants (LPRI) and the National Institute of Standards and Technology (NIST), the national radionuclidic metrology and standardization laboratories of France and U.S.A., respectively—have been intercompared by liquid scintillation (LS) spectrometry. The ratio of the certified massic activities for the two standards was compared to that obtained from direct measurements on matched sets of LS cocktails prepared from the standards. Seven experimental trials (involving a total of 21 counting sources for each standard) were performed for the comparison. The trials were performed under a wide range of experimental conditions, including use of two different LS spectrometers and three series of LS cocktail compositions (with systematically varied ³H detection efficiencies). The results exhibited an apparent mean disagreement between standards of < 0.4% on a relative basis. For contrast, the relative combined standard uncertainty on the massic activity ratio for the two standards, as obtained from their respective certified uncertainty assessments, is about 0.7%. © 1997 Published by Elsevier Science Ltd

An international measurement intercomparison of ^{63}Ni and ^{55}Fe was recently conducted (Cassette, 1995, 1996). The intercomparison exercise was sponsored by EUROMET, a European collaboration for metrological standardizations, and was organized by the Laboratoire Primaire des Rayonnements Ionisants (LPRI), the national radionuclidic standardization laboratory of France. The primary intent of the exercise was to evaluate the adequacy of liquid scintillation (LS) spectrometry techniques for the assay of nuclides that decay by pure, low-energy β emission (e.g. ^{63}Ni) and pure, low-Z (atomic number) electron capture (e.g. ^{55}Fe). The National Institute of Standards and Technology (NIST), although not a member of EUROMET, participated in the intercomparison at the invitation and concurrence of the member states. For this intercomparison, NIST assayed the EUROMET ^{63}Ni solution by concurrently tracing the ^{63}Ni detection efficiency against both a LPRI ³H standard and a NIST ³H standard using the well-known CIEMAT/NIST protocol

(Grau Malonda and Garcia-Torano, 1982; Coursey *et al.*, 1986), and thus had occasion to directly intercompare the extant ³H (tritiated H_2O) standards disseminated by these two laboratories (Table 1). This note summarizes the results of our comparative measurements on the two standards. The findings given herein may serve to be of value to other researchers who employ such ³H standards.

As noted, the current work is an adjunct to our participation in the EUROMET intercomparison, but is also related to recent ^{63}Ni standardization activities and extensive evaluations of LS cocktail stability, cocktail composition, and cocktail mismatching effects for low-energy β-emitting nuclides (Collé and Zimmerman, 1996a, b; Zimmerman and Collé, 1996, 1997a, b; and Collé, 1997a, b). These references describe in greater detail many of the experimental aspects of the present ³H standard comparisons.

The comparative ³H measurements were based on $4\pi\beta$ LS spectrometry of gravimetrically-determined aliquants of the two standards. The routine gravimetric procedures used in our laboratory as they apply to the preparation of LS counting sources, as well as estimations of their associated uncertainties, have been treated at length previously (Collé, 1993, 1997a; Collé and Thomas, 1993; Collé *et al.*, 1995).

Table 1. Summary of the LPRI and NIST ^{3}H standards

	LPRI standard	NIST standard
Identification	94/R-007E*	SRM 4927E†
Composition	^{3}H$_2$O/H$_2$O	^{3}H$_2$O/H$_2$O
^{3}H/^{1}H mol fraction	1.1 (10^{-14})	3.6 (10^{-15})
Massic activity	209.8 kBq g^{-1}	69.23 kBq g^{-1}
Relative standard uncertainty	0.52%	0.50%
Reference time	1200 UT 27 January 1994	1700 UT 15 August 1995

*See LPRI, 1994.

†Based on a gravimetric dilution of SRM 4927E [NIST, 1991], and decay over 16.95 a using a ^{3}H half-life of $T = 12.33$ a ± 0.06 a. The relative standard uncertainty in the ^{3}H primary calibration (in 1978 by internal gas-proportional counting) was 0.18%, which was propagated with relative standard uncertainties of 0.05% for the gravimetric dilution and 0.46% for the ^{3}H decay correction (to the cited reference time) to obtain a relative combined standard uncertainty in the massic activity of 0.50% (Collé and Zimmerman, 1996b).

Two different LS spectrometers (designated 'B' and 'P') were employed. Their principal operating characteristics are outlined in Table 2. Descriptions of these operating characteristics, their respective performance, and use within this laboratory for various radionuclidic calibrations are available (Collé, 1993, 1996a; Collé and Thomas, 1993; Collé et al., 1995). Specific aspects of the LS procedures as they apply to this work have been given by Zimmerman and Collé (1996, 1997b), and Collé and Zimmerman (1996a, b). The LS counting sources (i.e. cocktails) contained aliquants of the two ^{3}H standard solutions, ranging from about 30 to 60 mg, in approx. 10 g of a commercially-prepared scintillation fluid (Ultima Gold), a DIPN (di-isopropyl-napthalene)-emulsifier-based scintillant that utilizes PPO (2,5-diphenyloxazole) and bis-MSB [p-bis(o-methylstyryl)benzene] fluors (Packard Instrument Co., 1994). The cocktails were contained in glass, nominal 20 mL LS vials having cork-backed, aluminum-foil liners on plastic screw caps. Three series of cocktails with differing composition were prepared. Each series contained $n_s = 7$ matched sources of each standard. The specific cocktail compositions are tabulated by Zimmerman and Collé (1997b). They included compositions with both low H$_2$O mass fractions (0.003 $< f_w <$ 0.008), and larger fractions (0.05 $< f_w <$ 0.08) which were obtained by the addition of blank water. All cocktails also contained trace quantities of HCl and Ni^{2+} carrier

cations (for matching with the ^{63}Ni cocktails). Additionally, one of the three series contained about 0.009 mol of an EDTA^{-2} (ethylenediaminetetraacetate) chelating agent in each cocktail. To vary the efficiencies within a series, variable quantities (0–200 mg) of a 10% solution of CH$_3$NO$_2$ in ethanol, as an imposed chemical quenching agent, were added to the cocktails. The additions within a series of $n_s = 7$ cocktails had nominal 10–15 mg increments in added CH$_3$NO$_2$ solution mass. Blank cocktails of comparable composition and volume were also prepared for each of the cocktail series, and were used for background subtractions. The three cocktail series are designated: 'A' for high f_w with the chelate; 'B' for high f_w; and 'C' for low f_w.

Each cocktail within a given series was replicately measured initially on either one or the other spectrometer (and ultimately on both spectrometers) from $n_m = 4$ to $n_m = 10$ times (over typically 2–4 days). Counting time intervals ranged from 15 to 40 min per cocktail. The counting sources (with blanks interspersed) were sequentially measured in pairs (e.g. LPRI ^{3}H sample 1, NIST ^{3}H sample 1, followed by LPRI ^{3}H sample 2, NIST ^{3}H sample 2, followed by LPRI ^{3}H sample 3, etc.) such that adjacent samples were paired to those of comparable quenching. Hence, each cocktail in any given sequence was measured once before initiation of its next replication. The replication measurements of any one cocktail were separated by time intervals of

Table 2. Characteristics of the NIST LS spectrometers employed for the ^{3}H standard comparisons

| Characteristic	System B	System P
LS spectrometer model	Beckman LS7800	Packard Tri-carb A2500TR
Operating mode	Sum-coincidence	Sum-coincidence
Photomultiplier tubes	Hamamatsu R331-05	Hamamatsu R331-08
Operating temperature	Ambient	Ambient
Coincidence resolving time	22 ns	18 ns
Sum-coincident pulse amplification	Logarithmic	Linear
Pulse resolving time	5–33 μs (Variable with pulse height)	12 μs (Fixed)
Spectral analog-to-digital converter (ADC) capacity	1000 Channels	2048 Channels
Nominal conversion gain (energy per channel)	Variable (with logarithmic energy)	1 keV
Detection threshold (nominal)	≤ 1 keV	≤ 1 keV
Live-time determination method (and uncertainty)	Gated oscillator (scaled) (± 0.1%)	Gated oscillator (scaled) (± 0.1%)
Quench indicating parameter (QIP)	Horrocks number (H)	Transformed Spectral Index of the External Standard (tSIE) (proprietary)
External γ-ray source for QIP determination (and location)	^{137}Cs (side)	^{133}Ba (bottom)
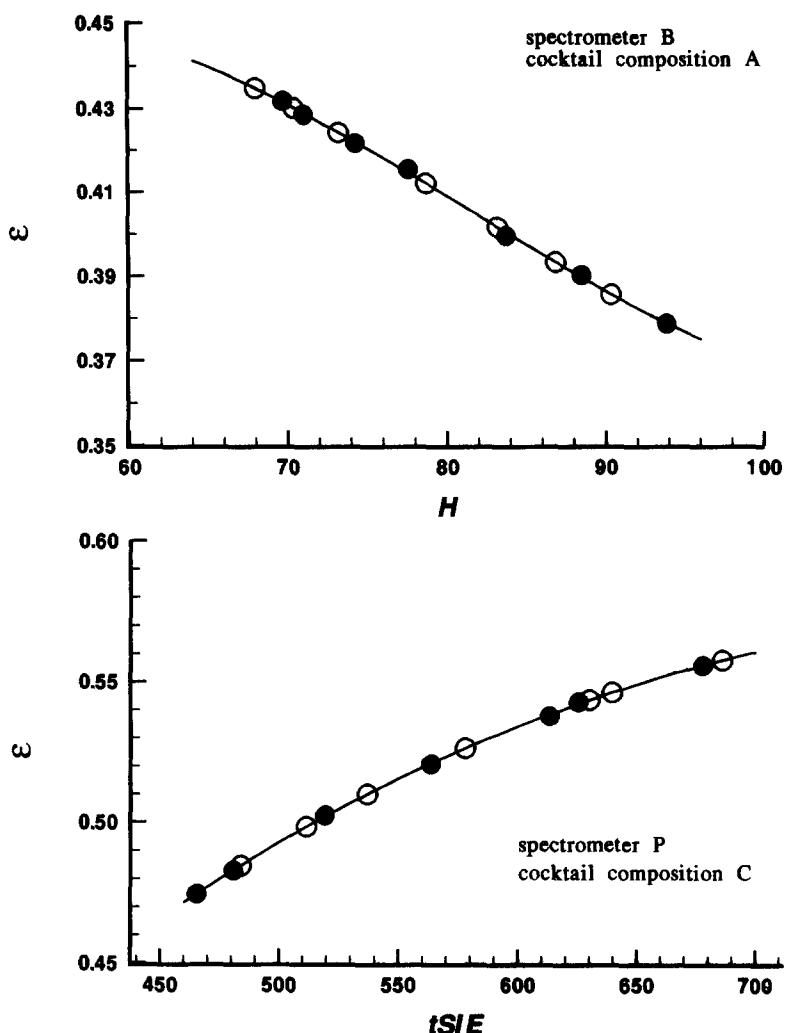
Fig. 1. Representative quench curves [ε vs either H for spectrometer B (upper) or $tSIE$ for spectrometer P (lower)] as obtained for two of the seven trials (with cocktail compositions A and C). The solid circles represent data used to develop the F_q function from the NIST ³H-standard cocktails. The open circles represent interpolated points on the curves for the matched LPRI ³H-standard cocktails.

typically 4 or more hours. Typical relative standard deviations of the mean for five replicate measurements (after appropriate background and decay corrections) on any one cocktail were generally < 0.1%. The cocktails were counted at varying 'ages' t_{age} (i.e. the interval between the preparation time and counting time): 1 day > t_{age} < 4 days; 3 days < t_{age} < 7 days; and 15 days < t_{age} < 18 days. Variations in ³H detection efficiency ε and corresponding quench indicating parameters (QIP) amongst the cocktails covered a range: 0.38 < ε < 0.56 with QIPs of 63 < H < 94 for spectrometer B and 673 > $tSIE$ > 420 spectrometer P. In all, the comparison results were based on seven sets of experimental trials, i.e. measurements of each of the three cocktail series A, B, and C on both the B and P spectrometers plus the re-measurement of series B with spectrometer B after t_{age} > 15 days.

To perform these comparisons, the decay-corrected net counting rate concentration for any ³H sample j

(with j = 1,2,3...n_s) during measurement cycle i (with i = 1,2,3...n_m) was obtained from $R_{j,i} = [C_{j,i} - C_{B(j)}]/$ [exp($- \lambda T_i$)$t_i m_j$] where $C_{j,i}$ is the gross integral counts in the full-energy LS spectrum for the jth cocktail at measurement time T_i; $C_{B(j)}$ is the corresponding gross integral counts (averaged over all n_m counting cycles) for background obtained from spectra of a matched blank LS cocktail; λ is the ³H decay constant which was assumed to be λ = ln(2)/(12.34 a ± 0.02 a); T_i is the decay time interval from the midpoint of the measurement time interval to a common reference time (taken to be 1200 UT 1 January 1996); t_i is the counting (live) time interval for measurement of both the jth cocktail and matched blank; and m_j is the mass of the ³H standard aliquant used in the jth cocktail. Averaging over all n_m measurement cycles results in mean R_j values for each jth cocktail (within an experimental trial). Given the certified values (Table 1) of the massic activities for the LPRI and NIST ³H standards with appropriate decay correc-

tions to the 1200 UT 1 January 1996 reference time ($A°_{LPRI}$ and $A°_{NIST}$, respectively), one can obtain the obvious relations $\varepsilon_{j(LPRI)} = R_{j(LPRI)}/A°_{LPRI}$ and $\varepsilon_{j(NIST)} = R_{j(NIST)}/A°_{NIST}$. Either set of measured efficiencies ε_j may be combined with their respective experimentally-determined QIP values, such as H, to establish a 'quench curve' having a fitted functional form $\varepsilon_j = F_q(H_j)$. The F_q quench-curve function obtained from cocktails of one standard may then be applied to perform small QIP-adjusted quench corrections to assay the massic activity of the other standard's cocktails. Arbitrarily, we selected the NIST ^{3}H standard to obtain $R_{j(NIST)}/A°_{NIST}$ $= \varepsilon_{j(NIST)} = F_q(H_{j(NIST)})$, which was then applied to derive an apparent massic activity of the LPRI standard: $A_{LPRI} = R_{j(LPRI)}/F_q(H_{j(LPRI)})$. The agreement between the two ^{3}H standards can then be expressed by a comparison ratio $K = A_{LPRI}/A°_{LPRI}$, which is equivalent to the ratio of the apparent (measured) massic activities A_{LPRI}/A_{NIST} to the decay-corrected certified massic activities $A°_{LPRI}/A°_{NIST}$: $K = (A_{LPRI}/A_{NIST})/(A°_{LPRI}/A°_{NIST})$. Evaluations of the $\varepsilon_{j(NIST)}/\varepsilon_{j(LPRI)}$ ratios directly for the comparison of the two standards is not as valid as the K used here because of slight composition (and quenching) differences between the LPRI and NIST ^{3}H cocktails. Alternative selection of the LPRI ^{3}H standard (to establish $\varepsilon_{j(LPRI)} = F_q(H_{j(LPRI)})$, and thereby to derive $A_{NIST} = R_{j(NIST)}/F_q(H_{j(NIST)})$ and $K = A°_{NIST}/A_{NIST}$) yields results that are equivalent and redundant. The agreement between the two ^{3}H standards could also be inferred from the results of efficiency tracing the EUROMET ^{63}Ni against the LPRI ^{3}H standard compared to those obtained from tracing against the NIST ^{3}H standard (see below).

Figure 1 gives two representative quench curves (of the seven trials) obtained from use of the NIST ^{3}H standard cocktails to derive the F_q function by fitting the data to 3rd order polynomials. The figure also exhibits the interpolated efficiencies $\varepsilon_{j(LPRI)}$ used to obtain $A_{j(LPRI)}$ and K_j for each cocktail.

Averaging across all n_s cocktails (within a trial) results in a mean K for the trial as given in Fig. 2. The grand mean across all seven trials, as shown in Fig. 2, is $K = 0.9963$ with a relative standard deviation of 0.36%. Given that the propagated relative standard uncertainty on the ratio $A°_{LPRI}/A°_{NIST}$ is of the order $\sqrt{2}(0.5\%) \gtrsim 0.7\%$ (see Table 1), one may conclude that the two ^{3}H standards, based on these comparative LS measurements, are in 'perfect' agreement within their certified uncertainties. Nevertheless, across all seven trials, the assayed massic activity of the LPRI ^{3}H standard with respect to the NIST ^{3}H standard is low compared to the LPRI certified value. The magnitude of this systematic difference can be generalized as being a few tenths of one percent, and is well within the bounds of the certified standard uncertainty on either standard (LPRI, 1994; NIST, 1991).

For completeness, the cumulative probability distribution of Fig. 3 gives the experimental results of all 49 individual K determinations (for the 7 cocktail × 7 trial matrix). The variance is $s_K^2 = 2.2(10^{-5})$ for the mean $K = 0.9963$ which corresponds to a relative standard deviation of 0.47%. Close examination of Fig. 3 clearly demonstrates the systematic, but slight offset between the two standards.

The above comparative measurement findings on the two ^{3}H standards comport excellently with that previously reported by Zimmerman and Collé (1997b) for the efficiency tracing of the EUROMET ^{63}Ni solution. Over the same seven experimental trials, they found that the assayed massic activity of the EUROMET ^{63}Ni solution traced against the LPRI ^{3}H standard $A_{63/LPRI}$ compared to that obtained
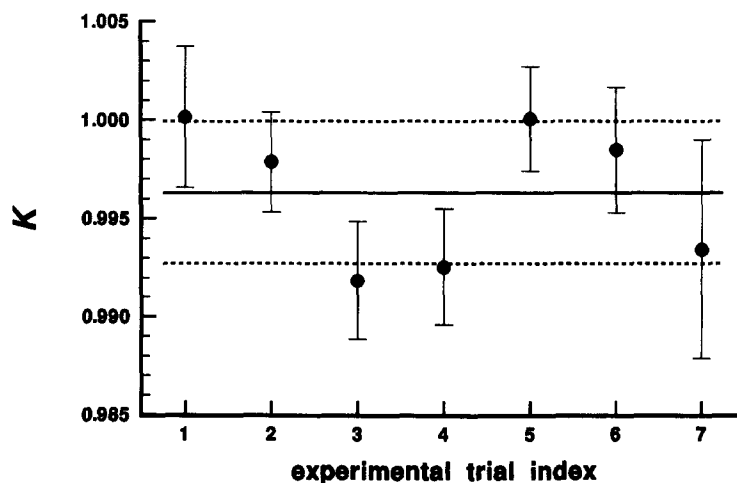

Fig. 2. Mean values of the ^{3}H standard comparison ratio $K = (A_{LPRI}/A_{NIST})/(A°_{LPRI}/A°_{NIST})$ as obtained from the seven experimental trials. The uncertainty bars on each data correspond to the standard deviation interval on each mean K as calculated for the $n_s = 7$ cocktails in each trial. The horizontal solid and broken lines correspond to the grand mean and its standard deviation interval, respectively.
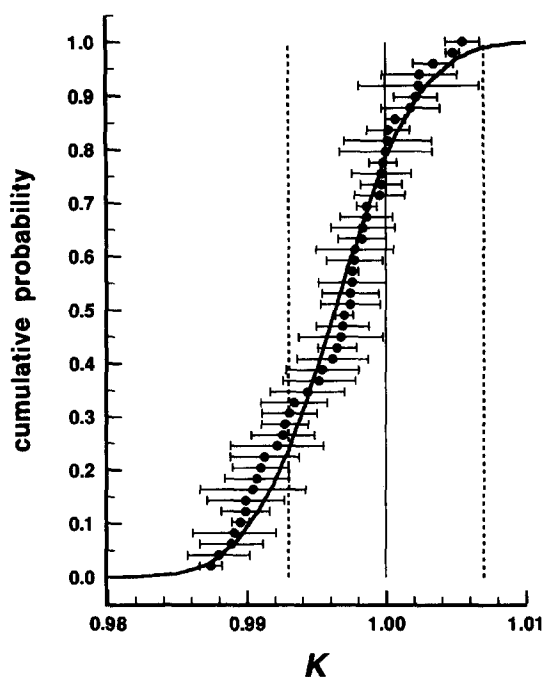
Fig. 3. Ogive of 49 determinations of $K = (A_{\mathrm{LPRI}}/A_{\mathrm{NIST}})/(A'_{\mathrm{LPRI}}/A'_{\mathrm{NIST}})$ for the comparison of the LPRI and NIST ^{3}H standards. The uncertainty bars on each datum correspond to the standard deviation on each K as calculated for the n_m measurements on each determination. The solid curve corresponds to a calculated normal distribution having a mean $\mu_K = 0.9963$ and variance of $\sigma_K^2 = 2.2(10^{-5})$. The vertical line at $K = 1$ corresponds to 'perfect' agreement between the certified values of the massic activity of the standards, while the broken vertical lines represent the uncertainty bounds for the propagated standard uncertainty on K as obtained from the certified uncertainty in each standard.

by tracing with the NIST ^{3}H standard $A_{63\,\mathrm{NIST}}$ differed (systematically) by comparable ratios of $0.9971 < A_{63\,\mathrm{NIST}}/A_{63\,\mathrm{LPRI}} < 1.0000$ with a mean of 0.9986. A re-assay of a NIST ^{63}Ni standard (NIST, 1995) performed at the same time gave identical results of $0.9971 < A_{63/\mathrm{NIST}}/A_{63/\mathrm{LPRI}} < 1.0002$ (Zimmerman and Collé, 1997b). The slightly smaller values for the ratio $A_{63\,\mathrm{NIST}}/A_{63\,\mathrm{LPRI}}$ compared to those for K is just indicative of the sensitivity of the ^{63}Ni detection efficiency in comparison to the ^{3}H efficiency. In these quench ranges, a 1% change in ^{3}H efficiency corresponds to about a 0.55% change in the ^{63}Ni efficiency.

The good agreement between these two national ^{3}H standards is particularly comforting considering the magnitudes of the invoked ^{3}H decay corrections that were applied. The LPRI standard required a correction for a decay time of nearly 2 a from its certified reference time (with a contributing relative standard uncertainty of about 0.02%); while the NIST standard required a correction for a decay time of just over 17 a from its initial 1978 primary calibration (with a contributing relative standard deviation of about 0.46%) (Collé and Zimmerman,

1996b). One should note that subsequent re-issues of NIST ^{3}H standards since 1978, such as for SRM 4927E (NIST, 1991), were based on the initial 1978 internal-gas-proportional counting primary calibration as well as confirmatory LS measurements.

Very recently, ^{3}H standardization capabilities (by primary methods of internal-gas-proportional counting) of two other national laboratories vis-à-vis that of NIST have been intercompared and reported on (Makepeace et al., 1996). Presumably, such primary measurement capabilities should reflect the reliabilities (and associated uncertainties) of national ^{3}H standards disseminated by these laboratories. These intercomparisons between NIST and the Physikalisch-Technische Bundesanstalt (PTB) of Germany (Braunschweig) and the National Physical Laboratory (NPL) of the U.K. (Teddington) indicated relative differences of about 0.3% between PTB and NIST and about 3% between NPL and either PTB or NIST. The relative standard uncertainties u on these intercomparison measurements by any of the three laboratories were in the range $0.4\% < u < 1\%$. The apparent discordance in ^{3}H measurements between NPL and those of NIST and PTB is undergoing evaluations (Unterweger, 1996).

In summary, one may reasonably conclude that the national ^{3}H standards disseminated by LPRI of France and NIST of the U.S.A. are wholly consistent (within their respective measurement uncertainties of about $\pm 0.5\%$, and even over long ($\gtrsim 20$ a) ^{3}H decay time intervals). By extensions, one may equally conclude that these two national ^{3}H standards are also consistent with ^{3}H standardizations of PTB of Germany (within a relative standard uncertainty of about 0.5%) and with that of NPL of the U.K. (within < 3%).

References

Cassette, P. (1995) Comparison of activity measurement methods in liquid scintillation counting and application to the standardization of ^{63}Ni and ^{55}Fe. Progress report for EUROMET Project 297, Laboratoire Primaire des Rayonnements Ionisants (LPRI), Saclay.

Cassette, P. (1996) Private communications, and pending final progress report for EUROMET Project 297, to be published, Laboratoire Primaire des Rayonnements Ionisants (LPRI), Saclay.

Collé, R. (1993) Long-term stability of carrier-free polonium solution standards. Radioact. Radiochem. 4(2), 30–40.

Collé, R. (1997a) Systematic effects of total cocktail mass (volume) and H_2O fraction on $4\pi\beta$ liquid scintillation spectrometry of ^{3}H. Appl. Radiat. Isot., in press.

Collé, R. (1997b) Cocktail mismatch effects in $4\pi\beta$ liquid scintillation spectrometry: implications based on the systematics of ^{3}H detection efficiency and quench

indicating parameter variations with total cocktail mass (volume) and H_2O fraction. *Appl. Radiat. Isot.*, in press.

Collé, R. and Thomas, J. W. L. (1993) [36]Cl/Cl accelerator-mass-spectrometry standards: verification of their serial-dilution-solution preparations by radioactivity measurements. *J. Res. Natn. Inst. Stds Technol.* **98**, 653–677.

Collé, R., Lin, Z., Schima, F. J., Hodge, P. A., Thomas, J. W. L., Hutchinson and Coursey, B. M. (1995) Preparation and calibration of carrier-free [209]Po solution standards. *J. Res. Natn. Inst. Stds Tech.* **100**, 1–36.

Collé, R. and Zimmerman, B. E. (1996a) [63]Ni half-life: a new experimental determination and critical review. *Appl. Radiat. Isot.* **47**, 677–691.

Collé, R. and Zimmerman, B. E. (1996b) [63]Ni standardization: 1968–1995. *Radioact. Radiochem.* **7**(2), 12–27.

Coursey, B. M., Mann, W. B., Grau Malonda, A., Garcia-Torano, E., Los Arcos, J. M., Gibson, J. A. B. and Reher, D. (1986) Standardization of carbon-14 by $4\pi\beta$ liquid scintillation efficiency tracing with hydrogen-3. *Appl. Radiat. Isot.* **37**, 403–408.

Grau Malonda, A. and Garcia-Torano, E. (1982) Evaluation of counting efficiency in liquid scintillation counting of pure β-ray emitters. *Int. J. Appl. Radiat. Isot.* **33**, 249–253.

Laboratoire primaire des rayonnements ionisants (LPRI) (1994) Certificate d'étalonnage No. 94/R-007E. LPRI, Gif-Sur-Yvette.

Makepeace, J. L., Day, F. E., Günther, E. and Unterweger, M. P. (1996) Intercomparison of measurement of tritiated water by internal proportional gas counting. *Nucl. Instrum. Meth. Phys. Res.* **A369**, 458–462.

National Institute of Standards and Technology (NIST) (1991) *Certificate, Standard Reference Material 4927E, Hydrogen-3 Radioactivity Standard.* NIST, Gaithersburg, Md.

National Institute of Standards and Technology (NIST) (1995) *Certificate, Standard Reference Material 4226C, Nickel-63 Radioactivity Standard.* NIST, Gaithersburg, Md.

Packard Instrument Co. Inc. (1994) *Material Safety Data Sheet for Ultima Gold AB.* Packard Instrument Co., Downers Grove, Ill.

Unterweger, M. P. (1996) Private communication, National Institute of Standards and Technology, Gaithersburg, Md.

Zimmerman, B. E. and Collé, R. (1996) Standardization of [63]Ni by $4\pi\beta$ liquid scintillation spectrometry with ^{3}H-standard efficiency tracing. *J. Res. Natn. Inst. Stds Technol.* In press.

Zimmerman, B. E. and Collé, R. (1997a) Cocktail volume effects in $4\pi\beta$ liquid scintillation spectrometry with ^{3}H-standard efficiency tracing. *Appl. Radiat. Isot.* **48**, 365–378.

Zimmerman, B. E. and Collé, R. (1997b) A compendium on the NIST radionuclidic assays of the massic activity of [63]Ni and [55]Fe solutions used for an international intercomparison of liquid scintillation spectrometry techniques, to be published.