

^{63}Ni , its half-life and standardization: Revisited

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Abstract

Recent liquid scintillation (LS) measurements at the National Institute of Standards and Technology (NIST) and at the Laboratoire National Henri Becquerel (LNHB) on a standardized ^{63}Ni solution that has been tracked for nearly 40 years have resulted in several important findings: (i) a ^{63}Ni half-life value of 101.2 ± 1.5 a has been determined with the present decay data. This value is consistent with a previous specific activity determination and with an earlier value from decay measurements; and it appears to be more satisfactory than a recent data evaluator's recommended value of 98.7 a. (ii) All solution standards of ^{63}Ni as disseminated by NIST for the past 38⁺ years are internally consistent with past and recent standardizations. (iii) Primary LS standardizations of ^{63}Ni by the triple-to-double coincidence ratio (TDCR) method and by CIEMAT/NIST ^3H -standard efficiency tracing (CNET) appear to be comparable, although the latter methodology is believed to be inherently inferior. (iv) There is excellent measurement agreement between NIST and LNHB for ^{63}Ni primary standardizations.

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1. Introduction

Primary standardizations of ^{63}Ni have been actively pursued by national radionuclidic metrology laboratories for over 40 years. As a medium-energy² pure-beta emitter, it is often used as a test case for evaluating measurement proficiency in international comparisons. Collé and Zimmerman (1996a) summarized a 27-year history, from 1968 to 1995, of the ^{63}Ni standardization activities at the National Institute of Standards and Technology (NIST). The standardizations over this period involved three series of disseminated solution standards, all of which were gravimetrically related to an identical stock solution. The first NIST standardization was based on microcalorimetry (Barnes

et al., 1971), which was also coupled with mass spectrometry to obtain a precise ^{63}Ni half-life. From measurements obtained in 1968, 1984, and 1995 on the various gravimetrically linked solutions, Collé and Zimmerman (1996b) made the first and only determination of the ^{63}Ni half-life that was based on actually following the radioactive decay of ^{63}Ni . All previously reported determinations were derived from specific activity measurements. The measurements in 1968, 1984, and 1995 also supported the development and dissemination of NIST Standard Reference Materials (SRM) 4226, 4226B, and 4226C (National Institute of Standards and Technology (NIST), 1995). At about the time of the 1995 measurements, an international measurement comparison was conducted under the aegis of EUROMET (Cassette et al., 1998; Collé and Zimmerman, 1997), which indicated good agreement between NIST and the worldwide radionuclidic measurement community.

Fig. 1 shows the origin and devolution of the gravimetrically linked ^{63}Ni solution standards issued by NIST in 1968 (SRM 4226), in 1984 (SRM 4226B), and in 1995 (SRM 4226C), and their relation to the various standardization measurements made over the past 38 years.

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²The endpoint and average energies for the ^{63}Ni beta spectrum are $E_{\beta(\text{max})} = 66.980 \pm 0.015$ keV and $E_{\beta(\text{ave})} = 17.434 \pm 0.004$ keV, respectively (Lee, 2006).

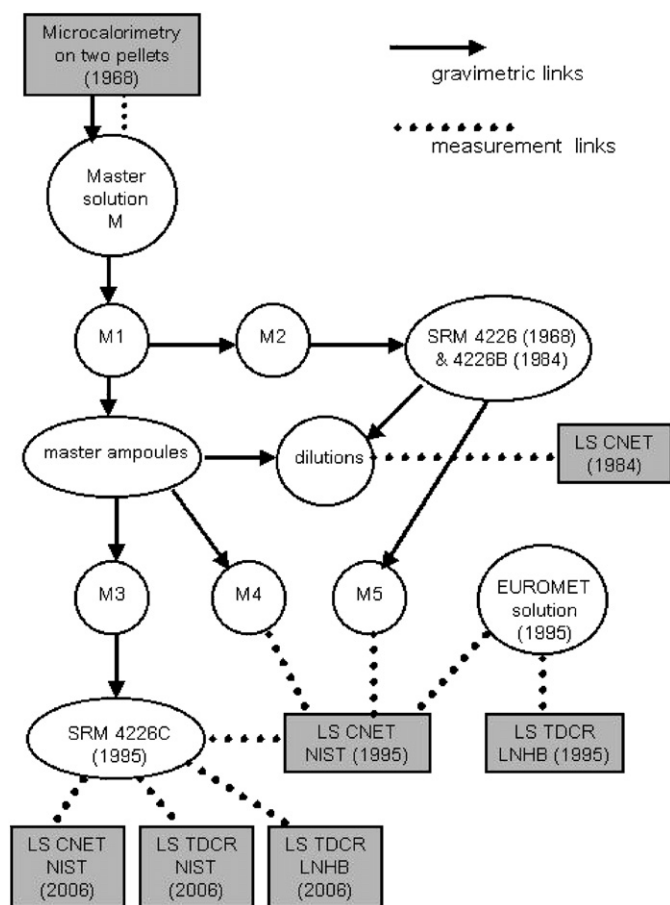


Fig. 1. Schema of the ^{63}Ni gravimetrically linked sources and measurements made by NIST and the LNHB laboratories over the past 38 years. Refer to the text and to Collé and Zimmerman (1996a, b) for details.

The present work (i) constitutes a new re-standardization of these NIST gravimetrically linked ^{63}Ni solutions, (ii) establishes new data points for the ^{63}Ni half-life as determined by decay, (iii) demonstrates reasonably good agreement between the two principal liquid scintillation (LS) primary standardizations methods, and (iv) conveys the results of an informal ^{63}Ni measurement comparison between NIST and the Laboratoire National Henri Becquerel (LNHB) in Saclay.

2. Current experiments and measurement results

Three distinct sets of LS measurements were performed with aliquants of an identical NIST ^{63}Ni master solution. The solution is identified as “M3”, which is also equivalent to SRM 4226C, and consists of 0.9 mol L^{-1} HCl with $98\text{ }\mu\text{g Ni}^{2+}$ per gram of solution. The measurements were either based on the CIEMAT/NIST ^3H -standard efficiency tracing (CNET) method³, obtained with either the

CIEMAT-developed *EFFY4* code⁴ or with the *CN2003* code of Gunther (2003), or on a triple-to-double coincidence ratio (TDCR) method. Features of the former method have been described in numerous publications by the CIEMAT/NIST originators (Grau Malonda and Garcia-Torano, 1982; Coursey et al., 1985, 1986). The method, as currently employed at NIST, is based on well-established procedures, which are somewhat routine for this laboratory (cf., Collé and Zimmerman (1997) and Zimmerman and Collé (1997).) Cassette and Vatin (1992) and Broda (2003) have treated the TDCR method. The implementation of the TDCR method at NIST has been described by Zimmerman et al. (2004a, b). Unless stated otherwise, all uncertainties quoted within this paper correspond to combined standard uncertainties with a coverage factor of $k = 1$, and are calculated and reported according to International Organization for Standardization (ISO) (1993) and NIST (Taylor and Kuyatt, 1994) guidelines.

2.1. CNET at NIST

The CNET measurements at NIST were performed on two occasions: from 21 July to 17 August with a midpoint time of 3 August 2006, and from 31 October to 15 November with a midpoint time of 7 November 2006. Three series of LS cocktails were prepared with PCS⁵ (Amersham Biosciences, Sweden), a xylene-based scintillation fluid, as shown in Table 1. The first and third series used high aqueous fractions (about 7%) obtained by the addition of Ni^{2+} carrier and 1 mol L^{-1} HCl for series I and by adding just blank water for Series III. Series II was made with a low water fraction. The cocktails, as shown in Table 1, were characterized in terms of the aqueous mass fraction f_w , the HCl acid concentration in the aqueous part C_a , and the Ni^{2+} concentration C_n in the aqueous part. Two other series of cocktails—one made with OptiPhase HiSafe3 (Perkin-Elmer, formerly Wallac, Finland), a diisopropylnaphthalene-based scintillation fluid, and another made with PCS and with a very low water fraction ($f_w < 0.005$)—were discounted because of apparent cocktail instabilities. The imposed quenching agent for each series consisted of varying masses m_Q of a 10% solution (by volume) of CH_3NO_2 in ethanol. An equal number of composition-matched ^3H cocktails were prepared using a NIST tritiated-water standard, SRM 4927F (National Institute of Standards and Technology (NIST), 2000).

(footnote continued)

Technologicas (CIEMAT) and the National Institute of Standards and Technology (NIST).

⁴This is an updated and revised version of the *EFFY* code. Refer to Garcia-Torano and Grau Malonda (1985), Grau Malonda et al. (1985), and Garcia-Torano (1993).

⁵Certain commercial equipment, instruments, and materials are identified in this paper to foster understanding. Such an identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials are the best available for the purpose.

³The acronym CIEMAT/NIST refers to the two laboratories that collaborated in developing the protocol for this LS-tracing methodology; viz., the Centro de Investigaciones Energéticas, Medioambientales y

The LS measurements were performed using three different instruments: Packard Tri-Carb A2500TR (Perkin-Elmer, Wesley, MA, USA); Beckman LS 6500 (Beckman Coulter, Fullerton, CA, USA); and Wallac 1414 Winspectral (Perkin-Elmer). They are designated as P, B, and W, respectively (see Table 2). The first of these was also used in earlier 1995 ^{63}Ni measurements, which will be referred to later in Section 3. All three spectrometers have different operating characteristics (e.g., low-energy threshold, dead-time, linear versus logarithmic amplification and ADC, etc.), which helps to ensure that any standardization results are independent of the instrumental conditions. The employed CNET analysis procedure was identical to that used for the previous ^{63}Ni standardization in 1995

(Zimmerman and Collé, 1997; Collé and Zimmerman, 1996a, b, 1997).

Table 2 shows the results of 14 counting trials on the three cocktail series, resulting in 336 determinations of the massic activity for the ^{63}Ni SRM 4226C solution. The results were obtained using the *EFFY4* code (Garcia-Torano, 1993). The β -spectra maximum energies $E_{\beta(\text{max})}$ used in the *EFFY4* computations were 66.945 ± 0.004 keV for ^{63}Ni and 18.594 ± 0.008 keV for ^3H (see National Institute of Standards and Technology (NIST) (1995) and references therein). All the results given in Table 2 were decay-corrected to a reference time of 3 August 2006 using a half-life of 101.1 ± 1.4 a for ^{63}Ni and 12.32 ± 0.02 a for ^3H . All these half-life and $E_{\beta(\text{max})}$ values were identical to those used for the earlier 1995 ^{63}Ni standardization on the same solution (Zimmerman and Collé, 1997; Collé and Zimmerman, 1996a, b, 1997). The results obtained with series I cocktails in July–August 2006 and those obtained with series II and III in October–November 2006 were invariant of this choice of half-lives. The mean value of Table 2 ($46,654 \text{ Bq g}^{-1}$) can be compared to the results from just series I ($46,569 \text{ Bq g}^{-1}$ on 3 August 2006) and that from series II and III ($46,633 \text{ Bq g}^{-1}$ at its midpoint time of 7 November 2006). A more recent precise determination of the ^{63}Ni endpoint energy has been given as $E_{\beta(\text{max})} = 66.980 \pm 0.015$ keV (Holzschuh et al., 1999), which is believed to be more accurate than earlier results because the previous work failed to account for the excitation of atomic electrons. The small energy difference (65 eV), however, makes only insignificant changes in the *EFFY4* efficiency computations.

The identical counting data from all 14 trials were also analyzed using the *CN2003* code (Gunther, 2003).

Table 1
LS cocktails used for the CNET and TDCR measurements at NIST

Series	N_c	V (mL)	f_w	C_a (mol L $^{-1}$)	C_n ($\mu\text{g g}^{-1}$)	m_Q (g)
I	8	9.5	0.07	1	24	0.03–0.23
II	6	9.5	0.01	0.55	55	0.05–0.36
III	6	9.5	0.07	0.06	6	0.05–0.37
IV	2	8.9	0.07	0.06	6	–
V	2	9.5	0.004	1	98	–

Series I, II, and III were used for the CNET measurements; series I, III, IV, and V were used for the TDCR measurements.

N_c , number of cocktails in the imposed-quench series; V , volume of PCS scintillation fluid in each cocktail in units of mL; f_w , aqueous mass fraction of each cocktail, i.e., mass of aqueous components to total; C_a , HCl acid content in aqueous fraction in units of mol L $^{-1}$; C_n , Ni^{2+} concentration in aqueous fraction of the cocktail in units of $\mu\text{g g}^{-1}$; m_Q , mass range for the imposed quenching agent (10% CH_3NO_2 in ethanol) in grams.

Table 2
Results for the massic activity for SRM 4226C (master solution M3), at a reference time of 3 August 2006, as obtained from the CNET measurements at NIST

Series	Instrument	Age (d)	N_d	ε_3 (%)	ε_{63} (%)	A (Bq g^{-1})	s (%)
I	W	1	40	21–34	58–70	46,461	0.13
	W	12	40	20–33	57–69	46,622	0.12
	W	24	16	20–33	57–69	46,746	0.02
	B	6	24	27–41	64–74	46,475	0.06
	P	8	24	21–34	58–70	46,489	0.03
	P	26	24	20–33	57–69	46,623	0.03
II	B	2	30	22–48	59–78	46,681	0.08
	B	14	18	22–46	59–77	46,833	0.02
	P	7	18	17–39	54–73	46,672	0.07
	W	12	18	16–39	52–73	46,890	0.07
III	B	2	30	21–42	58–75	46,561	0.06
	B	14	18	21–42	58–75	46,650	0.02
	P	7	18	16–34	52–70	46,616	0.02
	W	12	18	15–34	51–70	46,830	0.06
All	Unweighted mean and relative standard deviation of mean ($n = 14$)					46,654	0.29

Series—refer to Table 1 for LS cocktail compositions. Instrument: LS counter used: W, Wallac; B, Beckman; P, Packard. See the text. Age, approximate time between LS cocktail preparation and the middle of the counting cycles in days; N_d , number of determinations = number of LS cocktails \times number of counting cycles; ε_3 , range of values for the ^3H LS efficiency in the series of quenched cocktails in percent; ε_{63} , range of values for the ^{63}Ni LS efficiency in the series of quenched cocktails in percent; A , massic activity in units of Bq g^{-1} at reference time of 3 August 2006; s , relative standard deviation (for N_d determinations) in percent.

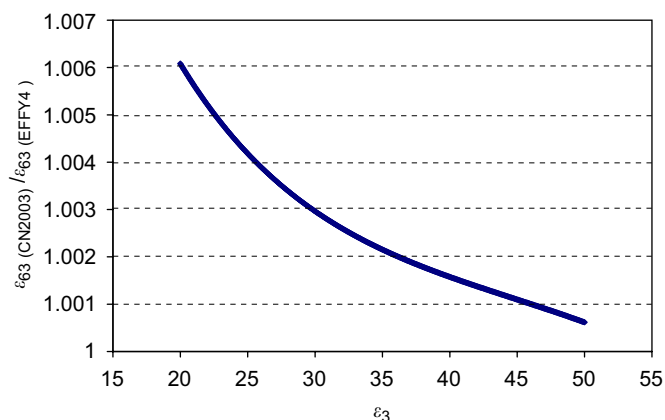


Fig. 2. Ratio of the computed ^{63}Ni efficiencies as obtained with the CN2003 and EFFY4 efficiency tracing codes as a function of the ^3H efficiency obtained with the respective code.

The averaged results were 0.36% lower than that shown in Table 2 as obtained with the EFFY4 code. The discrepancy is due to quench-dependent systematic differences in the two codes computed ^{63}Ni efficiencies compared to the computed ^3H efficiencies. Fig. 2 illustrates the magnitude of the differences as a function of the quench dependence, as reflected in the ^3H efficiency. No differences could be found in the computed ^{63}Ni beta spectra for the two codes. The computed detection efficiency differences were therefore attributed to the use of different ionization quenching functions $Q(E)$ in the two codes. The EFFY4 code used a formula obtained by Los Arcos et al. (1987) for toluene (see also (Grau Malonda, 1999)); whereas our use of the default conditions for the CN2003 code employed a $Q(E)$ approximation of Los Arcos and Ortiz (1997), applicable for a di-isopropylnaphthalene-based scintillation fluid, like Ultima Gold. Neither should be expected to be perfectly correct in the present case because of our current use of xylene-based PCS cocktails. Nevertheless, to ensure calculational consistency with the 1995 standardization results (see Section 3), the EFFY4 code was used exactly as was done previously in 1995.

The relative standard uncertainty ($k = 1$) on the present result for the massic activity is taken to be approximately 0.6%. The uncertainty components are essentially identical to those previously tabulated in great detail (Zimmerman and Collé, 1997; National Institute of Standards and Technology (NIST), 1995).

2.2. TDCR at NIST

The TDCR measurements performed at NIST were carried out during three broadly defined time periods: 13–31 July 2006, 8 August–22 September 2006, and 27 November–19 December 2006. Sources prepared during the earlier time periods were also counted in subsequent ones. The LS cocktails were prepared as described in Table 1. Specifically, three sources from series I, two from series III, and one each from series IV and V were prepared

for the TDCR measurements. With the exception of the sources from series III, to which nominally 0.05 and 0.1 g of the CH_3NO_3 solution were added, the sources that were measured in the TDCR did not contain any added chemical quenching agents. For each counting source, a background blank having an identical cocktail composition (in terms of aqueous fraction, ion content, etc.) was prepared and counted.

Measurements were made using the NIST TDCR spectrometer, which has been previously described (Zimmerman et al., 2004a, b). Each source was measured at least once and as many as seven times over the course of the time periods described above. The longest time between the first and last measurements for any single source was 46 days.

For all experiments except for those performed during the November–December time period, measurements were made at four efficiency points, obtained by varying the voltage on the focusing electrodes of the three photomultiplier tubes. For the experiments performed in November–December, the efficiency was varied using a series of gray filters at two different focusing electrode voltages.

The counting data were analyzed using a program developed in-house for use with the Mathematica (Wolfram Research and Inc., 2001) symbolic mathematics package. The input data consist of a beta spectrum, calculated using the program SPEBETA (Cassette, 1992) with a beta endpoint energy of 66.945 ± 0.004 keV, and the value of the Birks k_B parameter, which was taken to be $0.012 \text{ cm MeV}^{-1}$. The stopping power, dE/dx , for electrons in the LS cocktail was calculated by fitting a function of the form $dE/dx = a + bE + c(\ln E)^2 + d \ln E/E + e/E$ (E is the value of the midpoint energy for each bin the calculated beta spectrum) to data from the NIST ESTAR (National Institute of Standards and Technology (NIST), 2007) database using the compositions given in LNHB (2007) for the LS cocktails. The program calculates the individual phototube efficiencies, thereby allowing for correction due to asymmetry in the counting rates in each of the doubles counting channels.

The massic activity of the ^{63}Ni solution M3 was calculated from a total of 27 independent measurements and was found to be $47.00 \pm 0.14 \text{ kBq g}^{-1}$ as of the reference time of 18 August 2006, which was the midpoint time of all the TDCR measurements. The 26-value data set can be assumed to be normally distributed. It was tested for a normality distribution assumption using three methods (probability plot correlation coefficient, Wilk-Shapiro, and Anderson-Darling) in Dataplot (2007), which resulted in an acceptance at the 99% level for all three tests.

The uncertainty on the massic activity was calculated from the components listed in Table 3. The largest contribution to the uncertainty comes from the determination of the detection efficiency at each counting point for a given source. This is most likely due to the lack of optimization of the k_B value. Ordinarily, one would expect

Table 3
Uncertainty components for the determination of the ^{63}Ni massic activity from the TDCR measurements at NIST

Component, u_i	Method of evaluation; comments	Relative standard uncertainty (%)
Sample repeatability	A; typical standard deviation of the mean on the determination of massic activity for a single LS cocktail ($n = 2$ –8 determinations of A_{M3} per source); values ranged from 0.02% to 0.12%.	0.05
LS cocktail composition variability	A; standard deviation on determination of A_{M3} for seven cocktails, each having different composition	0.11
Efficiency dependence	A; typical standard deviation on determination of massic activity for a single source at four efficiency values, varied wither by defocusing or by use of grey filters ($n = 26$ independent measurements); values ranged from 0.13% to 0.39%.	0.27
Effect of ^{63}Ni $E_{\beta(\text{max})}$ on efficiency calculations	B; standard uncertainty on determination of A_{M3} due to standard uncertainty of $6 \times 10^{-3}\%$ on the ^{63}Ni endpoint energy.	7×10^{-4}
Composition of LS cocktail	B; standard deviation on A_{M3} determinations using five stopping power data for five different LS cocktail formulations. This was investigated because the exact molecular composition of the cocktails that were used was not known.	0.06
Half-life	B; standard uncertainty on decay correction over typical interval (> 20 d) given a standard uncertainty of 1.38% on the ^{63}Ni half-life.	9×10^{-4}
Mass determinations	B; estimated standard uncertainty of mass for any single LS cocktail.	0.03
Live time	B; standard uncertainty arising from an estimated uncertainty of 0.01% on the determination of the live time	0.01
Background	A; standard deviation on the determination of A_{M3} determined via Monte Carlo simulation. A total of five background data sets were constructed from random data arising from normal distributions defined by the average and standard deviation of experimental backgrounds at four efficiency points having four repetitions each; calculations were carried out with all five background data sets for a single experimental ^{63}Ni data set.	3×10^{-3}
Combined relative standard uncertainty, $u_c = (\sum u_i^2)^{1/2}$		0.30

the optimal value of kB to be that for which the calculated activity is independent of the value of the TDCR. For the present measurements in which only the focusing voltage was varied, the kB value that gave a zero slope for A_{M3} as a function of the experimental TDCR was usually found to be unreasonable (either too large or negative). The reason for this is still under investigation. Adopting a canonical value of $kB = 0.012 \text{ cm MeV}^{-1}$ gave reasonable activity values, but still tended to have a positive slope in the plot of A_{M3} versus TDCR, hence the uncertainty in the A_{M3} values. A subsequent experiment using only gray filters indicated that the adopted canonical value was consistent with the optimal kB value for these cocktails under these specific conditions, giving a value of $0.0124 \pm 0.0015 \text{ cm MeV}^{-1}$. The other dominant uncertainty component was that due to variability in A_{M3} determinations obtained from cocktails having differing compositions. The magnitude of the relative standard uncertainty in this case was 0.11% and is of the same order as is observed in the present CNET measurements and in similar, previous CNET measurements of ^{63}Ni (Zimmerman and Collé, 1997) made at NIST.

2.3. TDCR at LNHB

The TDCR measurements at LNHB were performed between 27 and 31 October 2006. Four series of LS cocktails were prepared with two different scintillators:

Ultima Gold and Ultima Gold LLT (Perkin-Elmer), both di-isopropylnaphthalene-based scintillation fluids. The second and fourth series used the higher aqueous fractions (about 2%) obtained by the addition of 0.1 mol L^{-1} HCl. The cocktails, as shown in Table 4, were characterized in terms of the aqueous mass fraction f_w , the HCl acid concentration in the aqueous part C_a , and the Ni^{2+} concentration C_n in the aqueous part. No chemical quenching agent was added to vary detection efficiency.

The LS measurements were performed using three different instruments: viz., RCTD1 and RCTD2, two LS triple coincidence counters both of which used Burle⁶ 8850, 5 cm diameter photomultiplier tubes (PMT), but with slightly different bases and optical chambers; and RCTD3, a LNHB LS counter prototype, using C1983P channel photomultiplier tubes (CPM) from Perkin-Elmer (Ivan et al., 2007). The optimum detection efficiencies obtained with these LS counters using sources prepared with Ultima Gold were 0.80, 0.78, and 0.53. The three counters have similar signal processing systems based on the MAC3 coincidence unit (Bouchard and Cassette, 2000) and similar operating characteristics imposed by the use of the TDCR model (e.g., low-energy threshold adjusted under the amplitude of the single photoelectron response, 40 ns coincidence resolving time, and $50 \mu\text{s}$ extending-type dead-time duration). The RCTD3 counter uses photodetectors

⁶Burle Industries, Inc. (Lancaster, PA, USA).

Table 4
LS cocktails used for the TDCR measurements at LNHB

Series	Scintillation fluid	N_c	V (mL)	f_w	C_a (mol L ⁻¹)	C_n (μg g ⁻¹)
F1	UG	5	10	0.005	0.9	98
F2	UG	5	10	0.02	0.3	24
F3	UG-LLT	5	10	0.005	0.9	98
F4	UG-LLT	5	10	0.02	0.3	24

Scintillation fluid: UG, Ultima Gold (regular); UG-LLT, Ultima Gold LLT.

N_c , number of cocktails in the series; V , volume of PCS scintillation fluid in each cocktail in units of mL; f_w , aqueous mass fraction of each cocktail, i.e., mass of aqueous components to total; C_a , HCl acid content in aqueous fraction in units of mol L⁻¹; C_n , Ni²⁺ concentration in aqueous fraction of the cocktail in units of μg g⁻¹.

operating in a saturated mode, with photocathode surfaces that are ten times smaller than that for the 5-cm PMTs.

For each experiment, the detection efficiency was calculated using the LNHB TDCR07 program with a Poisson statistical distribution of the number of photoelectrons in the photodetectors. The scintillator non-linearity is calculated with the Birks formula (Birks, 1964) and the calculation of the electron stopping power in the LS cocktail was obtained using equations (2.16), (2.17), and (2.18) in International Commission on Radiation Units and Measurements (ICRU) (1984). The TDCR07 program derives the detection efficiency for the logical sum of double coincidence from three individual values of triple-to-double coincidence count rate ratios, thus taking into account the individual quantum efficiency of each photodetector.

All the sources were stable over the measuring period, as no apparent counting rate variation was observed using any of the three counters. All sources gave compatible measurement results when using the same calculation parameters in the detection efficiency calculation code.

The optimum value of Birks ionization quenching parameter (kB) was determined by variation of the detection efficiency by defocusing the PMT of RCTD1 and RCTD2 counters and also by comparison with RCTD3 results. As all sources were compatible, this analysis was only made with the first set of sources. Fig. 3 shows the massic activity of a source versus the value of the kB parameter for RCTD2 (PMT) and RCTD3 (CPM). As expected, the slope of the RCTD3 curve is higher than the slope of RCTD1 curve, as the detection efficiency is significantly lower and thus the calculation model has a higher influence on the activity result. It is worth noticing that these curves cross in the 0.009–0.011 cm MeV⁻¹ kB value region. This means that there is only a small kB value range for which the activity of the ⁶³Ni LS sources are independent of the LS counter used. This naively led us to the conclusion that this is the best kB value range to use and to take into account for the uncertainty assessment of this measurement result.

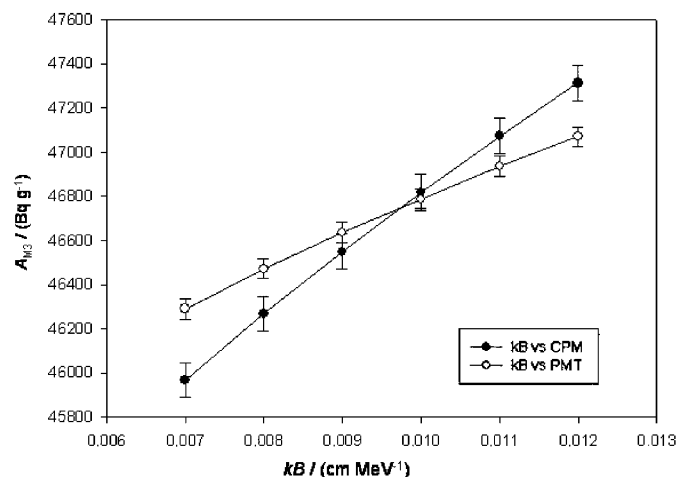


Fig. 3. Massic activity A_{M3} (in units Bq g⁻¹) as a function of the ionization quenching factor, kB (in units of cm MeV⁻¹), for the measurement of ⁶³Ni LS source prepared with Ultima Gold LS cocktail. The open and closed circles are for data obtained with the RCTD3 counter (with CPM) and with the RCTD2 counter (with PMT), respectively (refer to text).

Table 5
Uncertainty components for the determination of the ⁶³Ni massic activity A_{M3} from the TDCR measurements at LNHB

Component, u_i	Relative standard uncertainty (%)
Counting statistics	0.12
Weighing and source variability	0.11
Deadtime	0.02
Background	0.02
Accidental coincidences	0.03
Counting time	<10 ⁻³
Effect ⁶³ Ni $E_{\beta(max)}$ ^a	0.013
Ionization quenching parameter, kB	0.27
Combined relative standard uncertainty, $u_c = (\sum u_i^2)^{1/2}$	0.32

^aBased on a value of 66.980 ± 0.015 keV, as obtained from Holzschuh et al. (1999).

The massic activity of the ⁶³Ni master solution M3, based on the LNHB determination, is 46.79 kBq g⁻¹ with a standard uncertainty of 0.15 kBq g⁻¹ at the reference date of 31 October 2006, 1200 UT. The uncertainty budget for this determination is summarized in Table 5.

3. Findings and discussion

The relation of the current measurements at NIST and LNHB to the previous ⁶³Ni standardization work is illustrated in Fig. 1. One should note that in addition to the present comparison between the two laboratories, there was an earlier direct comparison in 1995 on a EUROMET solution (Cassette et al., 1998; Collé and Zimmerman, 1997). Although the two laboratory results for this earlier comparison were identical to three significant figures, the results were somewhat clouded because of slight differences

Table 6

Results of the current LS measurements on master solution M3 and comparison of the results at a reference time of 3 August 2006 with decay corrections obtained with a half-life of 101.2 a

Measurement	A_{M3} (kBq g ⁻¹) at time T	Reference date T	A_{M3} (kBq g ⁻¹) at 3 August 2006
CNET at NIST	46.57 ± 0.28	3 August 2006	46.57 ± 0.28
CNET at NIST	46.63 ± 0.26	7 November 2006	46.71 ± 0.26
TDCR at NIST	47.00 ± 0.14	18 August 2006	47.01 ± 0.14
TDCR at LNHB	46.79 ± 0.15	31 October 2006	46.87 ± 0.15

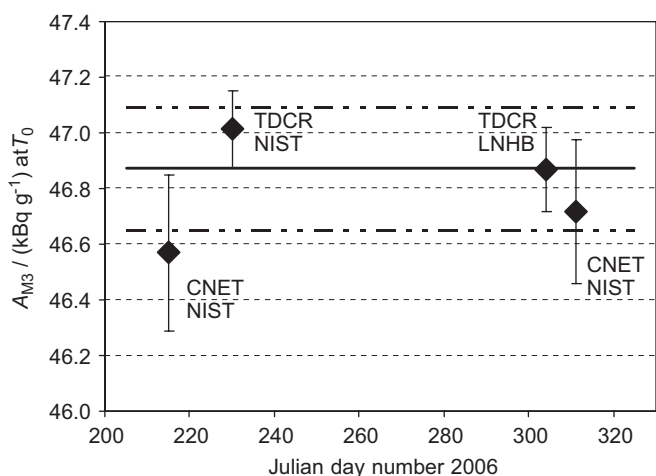


Fig. 4. Comparison of the current 2006 measurements at NIST and LNHB, in terms of the massic activity of master solution M3 in units of kBq g⁻¹, after decay correction to a common reference time of 3 August 2006. The graph abscissa indicates only the reference time for the individual measurement results, usually the midpoint-time interval for the determinations. The solid line corresponds to the decay-corrected value (from 15 August 1995) of the certified value for the massic activity of SRM 4226C (equivalent to master solution M3). The broken lines reflect its $k = 1$ combined standard uncertainty interval as propagated. All decay corrections were obtained using a half-life of 101.2 ± 1.2 a.

in model and nuclear data assumptions, as noted by Collé and Zimmerman (1997).

The current experimental results for the massic activity of master solution M3 (equivalent to NIST SRM 4226C) are tabulated in Table 6. The two sets of CNET at NIST measurements are given separately at their midpoint times. All the values in Table 6, after decay correction to a common reference time of 3 August 2006 as obtained with a half-life of 101.2 a, are compared in Fig. 4. The figure also shows the excellent agreement with the decayed value for the massic activity of SRM 4226C as certified by NIST in 1995.

The 38-year measurement history of the linked ⁶³Ni standardizations is compiled in Table 7 and graphed in Fig. 5. The results of all six independent determinations, through comparison of the massic activity for master solution M2 at a common time of 3 August 2006, again shows the excellent consistency in using a ⁶³Ni half-life of 101.2 a.

The measurement data of Table 7 and several subsets were fit to the exponential decay law using weighted

non-linear regressions. The weighting factors were reciprocals of the squared standard uncertainties given in column 2 of Table 7. The regressions were performed using an on-line version of Dataplot (2007). The regression results showing the fitted half-life values are given in Table 8. As indicated, the result for the weighted fit using all six measurement values is 100.7 ± 1.3 a. For comparison, the value from an unweighted fit is 100.1 ± 1.2 a. The effect of the CNET measurements on the fitted half-life was also examined. The reliability of the CNET results can be considered to be more suspect; firstly, because the 1984 CNET value (Coursey et al., 1989) required subsequent adjustment (Collé and Zimmerman, 1996a, b), and secondly because of questions about the adequacy of the quench functions used in the tracing codes for any of the CNET measurements. As seen in Table 8, the CNET measurements did not unduly influence the decay-fitted half-life. In fact, all four of the fitted values given in Table 8 are statistically equivalent. The value obtained with just the 1968 calorimetry result and the two 2006 TDCR determinations, which is essentially a two-point fit over 38.4 a, is 101.2 ± 1.5 a. Based on our subjective judgment, this is probably the most reliable result.

All of the above findings confirm and support both the values previously obtained from decay measurements (Collé and Zimmerman, 1996a, b) and the value originally obtained by Barnes et al. (1971) from a specific activity determination, as revised by Collé and Zimmerman (1996a, b). They were 101.2 ± 2.0 and 101.1 ± 2.0 a, respectively, and served as the basis for the previously “recommended” 101.1 ± 1.4 a value. The former decay measurement value is now updated and replaced with

$$T_{1/2} \text{ (present determination)} = 101.2 \pm 1.5 \text{ a.}$$

The National Nuclear Data Center compilation of Bai and Huo (2001), employing a data cutoff date of March 1999, does not include any revisions or updates for the ⁶³Ni half-life. It did not include a revision in the Barnes et al. (1971) specific activity determination, which is required for the known change in the average energy of the ⁶³Ni beta spectrum. Nor did it include either the previous decay measurement result of Collé and Zimmerman (1996a, b) or their critical evaluation. A more recent evaluation by Lee (2005)⁷ recommended a value of 98.7 ± 2.4 a, based on a

⁷Readers are cautioned to note that this compilation mistakenly tabulates the uncertainty in the Barnes et al. (1971) value as ± 0.2 a, instead of the correct ± 2.0 a.

Table 7

Decay data for the measurements of the ^{63}Ni massic activity of master solution M2 over the past 38 years by all methods

Reference date T	A_{M2} at T (MBq g^{-1})	Measurement	Reference	A_{M2} (MBq g^{-1}) at 3 August 2006
27 May 1968	1.4846 ± 0.0074	NIST calorimetry	Barnes et al. (1971); revised Collé and Zimmerman (1996a, b)	1.1429
1 December 1984	1.3297 ± 0.0093	NIST LS CNET	Coursey et al. (1989); revised Collé and Zimmerman (1996a, b)	1.1463
15 August 1995	1.2305 ± 0.0058	NIST LS CNET	Zimmerman and Collé (1997).	1.1414
3 August 2006	1.1358 ± 0.0068	NIST LS CNET	Present work	1.1358
18 August 2006	1.1442 ± 0.0034	NIST LS TDCR	Present work	1.1445
31 October 2006	1.1391 ± 0.0037	LNHB LS TDCR	Present work	1.1411

The values are also compared to a common time of 3 August 2006 using a half-life of 101.2 a

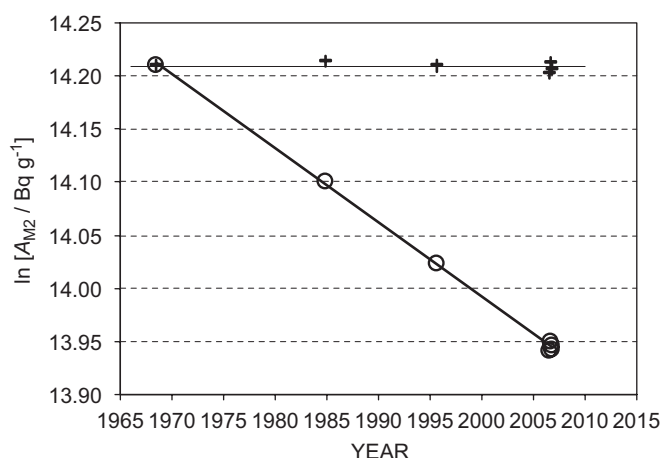


Fig. 5. Measurements of the ^{63}Ni massic activity of master solution M2 (in units of Bq g^{-1} on a logarithmic scale) as a function of time over the past 38 years. A weighted non-linear regression of all six values to the radioactive decay law yields an apparent half-life of 100.7 ± 1.3 a. The influence of the CNET measurement values is shown in Table 8. The crosses (at the averaged upper line) correspond to the decay-corrected measurement values obtained with a half-life of 101.2 a. Refer to the text for details.

Table 8

Fitted values for the ^{63}Ni half-life as obtained from weighted non-linear regressions of the measurement data given in Table 6

Data set used for fit	ν	$T_{1/2}$ (a)	\hat{s}
All six values	4	100.7 ± 1.3	0.65
Excludes 1984 CNET value	3	100.9 ± 1.4	0.70
Excludes both 1984 and 1995 CNET values	2	100.9 ± 1.8	0.85
Excludes all three CNET values	1	101.2 ± 1.5	0.70

ν , degrees of freedom, $n-2$, number of measurement values n minus number of fitted parameters. $T_{1/2}$, fitted parameter for the half-life (in units of years) as obtained from a weighted non-linear regression of the data to the function $y = ae^{bx}$, where $b = -\ln(2)/T_{1/2}$. The cited uncertainty for $T_{1/2}$ is a standard deviation derived from the variance on the fitted parameter b . $\hat{s} = [(\sum_i (f(x_i) - y_i)^2 / s_i^2) / \nu]^{1/2}$ is a goodness-of fit parameter given by the square root of the weighted sum of the residuals divided by the degrees of freedom (Hamilton, 1964).

weighted average that included an older value of Horrocks and Harkness (1962). The present authors do not believe that this recommended value can withstand critical scrutiny.

4. Concluding summary

This work resulted in several important findings.

4.1. ^{63}Ni half-life

The ^{63}Ni half-life, as determined by decay measurements over 38.4 a, is in excellent agreement with the earlier specific activity determination of Barnes et al. (1971). A value of 101.2 ± 1.5 a, as reported here, along with the correctly revised Barnes value should be more seriously considered in subsequent data evaluations.

4.2. NIST ^{63}Ni standards

The solution standards of ^{63}Ni disseminated by NIST for the past 40 years include SRM 4226 in 1968, SRM 4226B in 1984, SRM 4226C in 1995, and a forthcoming SRM 4226D in 2007–08. All these standards are linked gravimetrically and through comparative measurements, and have been shown to be internally consistent with all past and present primary standardizations.

4.3. ^{63}Ni measurement consistency

This work demonstrated that LS-based primary standardizations of ^{63}Ni by the TDCR and CNET methods are in good agreement within their measurement uncertainties. This is consistent with previous findings within NIST (Zimmerman et al., 2004a, b) and from international comparisons (Cassette et al., 1998; Collé and Zimmerman, 1997). Interestingly, the agreement between the two LS methods at NIST appears to be better previously than that observed in the present work. It is also apparent that the primary standardizations of ^{63}Ni by LNHB and by NIST (the national metrology laboratories of

France and USA, respectively) are in excellent agreement, particularly with the TDCR method.

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