PAPER

Nickel-63 Standardization: 1968-1995

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The radionuclide ^{63}Ni is widely employed as a relatively long-lived (101.1 ± 1.4 a half-life), low-energy (66.945 ± 0.004 keV maximum β$^-$ energy) beta-particle-emitting calibration standard. Between 1968 and 1995, the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), actively engaged in the preparation and calibration of ^{63}Ni solution standards. Three series of standards, all of which are gravimetrically related to identical stock material, have been disseminated during this time interval. Initial standardization of ^{63}Ni at NBS was based on microcalorimetry using an assumed mean β$^-$ energy per decay for the ^{63}Ni β$^-$ spectrum. This has more recently been supplanted with 4πβ liquid scintillation spectrometry with ^{3}H-standard efficiency tracing. The chronicle given here summarizes these NIST/NBS standardization activities and, moreover, highlights the remarkably consistent measurement results obtained on the standards over the past 27 years.

Introduction

The radionuclide ^{63}Ni with an evaluated half-life of $T = 101.1 \pm 1.4$ a[1] and well-known maximum β$^-$ endpoint energy of $E_{\beta(max)} = 66.945 \pm 0.004$ keV[2-4] (having a calculated number-weighted mean energy of $E_{\beta(mean)} = 17.426 \pm 0.013$ keV[4] for the β$^-$ spectrum of its allowed $J^\pi = \frac{1}{2}^- \rightarrow \frac{3}{2}^-$ transition[5]) has great utility as a relatively long-lived, low-energy β$^-$ calibration standard. Its standardization by our and other national metrological laboratories has been actively pursued for nearly the past third of a century.

This paper chronicles the preparation and calibration of ^{63}Ni solution standards over this period, particularly with emphasis on the standardization activities of the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), and on the three series of ^{63}Ni Standard Reference Materials (SRM) disseminated by this laboratory: SRM 4226 in 1968, SRM 4226B in 1984, and SRM 4226C in 1995.

Pre-1968 2π and 4π beta-particle counting of ^{63}Ni

From the 1950s through about the early to mid-1960s, the method most commonly used to standardize β-emitting radionuclides was based on "absolute" 2π or 4π GM or proportional counting.[6] This methodology is exceedingly troublesome for a low-energy β emitter like ^{63}Ni because of the horrendously difficult energy-dependent absorption and scattering corrections and source preparation requirements.[6-9] As a result, although NBS[10-13] had adopted 4π proportional flow

counting as a primary standardization method as early as 1949, and had calibrated a variety of β emitters (such as ^{32}P, ^{35}S, ^{60}Co, ^{90}Sr-^{90}Y, ^{131}I, ^{198}Au and ^{204}Tl, all of which have substantially greater $E_{\beta(max)}$ than ^{63}Ni) with it, the laboratory never attempted (or at least never reported an attempt at) a similar ^{63}Ni standardization. Difficulties with the standardization of even ^{14}C with an $E_{\beta(max)} \cong 154$ keV were described at the time with the decidedly judicious phrase: "accuracy appears to be in doubt by 5% to 10%"![12]

The fruitlessness of ^{63}Ni standardization by conventional β counting methods may inferentially be appreciated by consideration of several ^{63}Ni activity measurements that had been reported up to 1968. Collé and Zimmerman[1] recently critically reviewed and evaluated all past determinations of the ^{63}Ni half-life T. Of the six determinations reported upon therein, three were derived from specific activity measurements of ^{63}Ni that employed 2πβ or 4πβ counting. In these determinations, T was derived from independent determinations of the number of ^{63}Ni atoms (N) and ^{63}Ni activity (A) – i.e., from $T = (\ln 2)N/A$ – using one of two methodological approaches: (1) estimation of N from neutron activation yields using an assumed neutron-capture cross section σ for the ^{62}Ni(n, γ)^{63}Ni reaction at thermal neutron energies and evaluations of the integral neutron flux either directly or by use of monitor reaction cross sections, followed by either 2πβ GM or proportional-counting activity measurements; and (2) determinations of N by mass spectrometry, and A by more sophisticated 4πβ pro-

portional counting. All three of these early ^{63}Ni half-life determinations were found to be in substantial disagreement with the presently accepted T =101.1 a value. The first two, by Wilson[14] and Brosi et al.,[15] derived T from approach (1) above, and obtained results that disagreed with the present T by about -70% and -20%, respectively. The third result, by McMullen, et al.,[16] was based on approach (2) and disagrees with the current T value by roughly 25%. These disagreements can not be solely attributed to unaccountable errors in the ^{63}Ni assays as has been pointed out and more thoroughly discussed by Collé and Zimmerman.[1] Nevertheless, the combined findings either are suggestive of the inherent difficulties in obtaining accurate measurements of ^{63}Ni by these early $2\pi\beta$ and $4\pi\beta$ counting methods, or are the result of some inexplicable coincidence.

The third T result by McMullen et al.[16] is the most unsettling of these determinations considering the excruciatingly careful source preparations and source self-absorption corrections employed by these researchers.[17-21] It was this same research group with

Figure 1 Schema of the origin and devolution of the gravimetrically-related ^{63}Ni solution standards issued by NBS/NIST in 1968 (SRM 4226), in 1984 (SRM 4226B), and in 1995 (SRM 4226C). The points of various independent standardization measurements are also illustrated.

the same actors at roughly the same time that was largely responsible for establishing the definitive state of the art for $4\pi\beta$ counting. They also specifically addressed applying their method to the measurement of ^{63}Ni.[21] The methodology employed by them was successfully used for the standardization of many other, albeit higher-energy, β emitters, and remained a primary standardization method until the advent of efficiency tracing by $4\pi\beta$-γ coincidence counting.[22]

Parenthetically, one may note that the subsequent three determinations of the ^{63}Ni half-life, upon which the presently adopted T is largely based, utilized the decidedly more reliable techniques of microcalorimetry and liquid scintillation (LS) spectrometry for measurement of the ^{63}Ni activity.

1968 microcalorimetry and SRM 4226

A great leap forward in the standardization of ^{63}Ni was obtained in 1968 when Barnes et al.[23] at NBS performed an elegant microcalorimetry-based calibration of SRM 4226 using a Peltier-effect, Callendar-type, "radiation balance" calorimeter.[24-26] This standardization still remains almost unrivaled in its apparent accuracy, and its ability to withstand the proverbial "test of time".

The preparation of the solution standards SRM 4226 from the gravimetrically-determined dissolution and dilution of one of two irradiated ^{62}Ni-enriched target pellets is schematically illustrated in the upper portions of Figure 1. The microcalorimetry results for the massic power C_W, in units of mi-

crowatts per gram of nickel for the irradiated pellets [then termed an "energy emission rate"], as reported by Barnes et al.[23] is shown in Figure 2. These data, along with the mass spectrometry that was conducted as part of this work, also allowed a new precise determination of the ^{63}Ni half-life T. There was an approximate 0.3% difference in the mean massic power for the two capsules. Only the data obtained for pellet #2 were used for the SRM 4226 calibration.

The C_W results for the irradiated pellet or for the gravimetrically-related solution standard (Figure 1 and Table 1) were converted to massic activity C_A, in units of Bq·g^{-1}, using the mean β$^-$-particle energy $E_{β(mean)}$ for the ^{63}Ni β spectrum; i.e., $C_A = (6.239·10^9$ keV·μW^{-1}·s^{-1})·$C_W/E_{β(mean)}$. At the time, the ^{63}Ni β$^-$ endpoint energy was taken as $E_{β(max)} = 65.87 \pm 0.15$ keV[29] from which Schima[30] calculated $E_{β(mean)} = 17.23 \pm 0.04$ keV. The ^{63}Ni massic activity for the solution standard was thus certified (at a presumed 99% confidence level) as $C_A = (1.501 \pm 0.014)·10^6$ Bq·g^{-1} as of 27 May 1968.[23,31] The ^{63}Ni half-life T, as derived from their activity A measurements and with N from the mass spectrometric data, was given as $T = 100.07$ a $\pm 2.0\%$.

Curiously, the calorimetry data were not corrected for radioactive decay over the three month measurement interval. Even without relying upon an assumed ^{63}Ni half-life T, the corrections would have been rather easy to achieve using an iterative approach to derive their final T and C_A values. The magnitude of the neglected decay corrections, however, is relatively negligible inasmuch as the chosen reference time of 27 May 1968 (Julian day 148) for SRM 4226[31] was near the midpoint of the measurement interval. Subsequent calculations by the present authors indicate that decay corrections of the data would decrease the mean massic power for pellet #2 by 0.012%.

Since the time of the 1968 calorimetry measurements, two very precise measurements of the ^{63}Ni β spectrum endpoint energy have been reported.[2,3] These independent measurements were performed with the Chalk River (Atomic Energy Commission of Canada Limited) and University of Tokyo ironfree π√2 electron spectrometers. Their measurements for $E_{β(max)}$ had reported precision of 1 part in 3400 and 1 part in 22000, respectively; and resulted in newly evaluated[4] and presently "accepted" values of $E_{β(max)} = 66.945 \pm 0.004$ keV and $E_{β(mean)} = 17.426 \pm 0.013$ keV.

Any change in the assumed $E_{β(mean)}$ value for ^{63}Ni necessitates a revision in C_A for SRM 4226 since the original certified value was inversely proportional to an assumed $E_{β(mean)}$. The ^{63}Ni half-life T derived by Barnes et al.[23] from the ^{63}Ni activity determination (along with N from mass spectrometry) must likewise be revised. With $E_{β(mean)} = 17.426 \pm 0.013$ keV, the revised value of C_A at the initial reference time must be decreased by the $E_{β(mean)}$ ratio 17.23/17.426 to give $C_{A(4226)} = 1.484·10^6$ Bq·g^{-1} as of 27 May 1968; and T must be increased by the factor 17.426/17.23 to give $T = 101.21$ a.

Uncertainty analyses on the massic activity C_A for SRM 4226 as both originally certified and as revised for the change in $E_{β(mean)}$ are worth considering in detail. The exercise may serve to be instructive.

The relative uncertainty in the certified C_A value was originally cited to be $\pm 0.95\%$[23,31] which was said to correspond to a
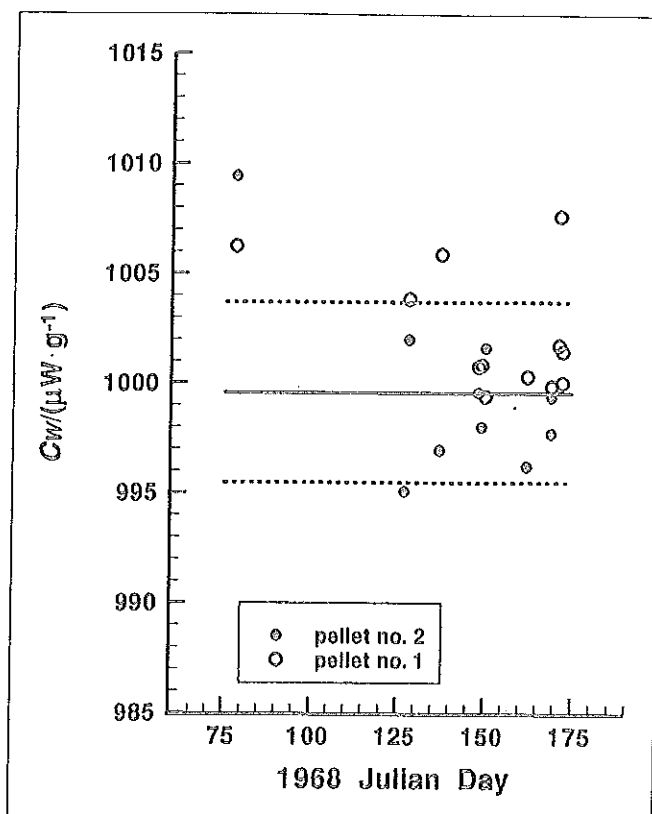
Figure 2   The 1968 microcalorimetry data of Barnes et al.[23] as used for the standardization of ^{63}Ni solution standard SRM 4226[31] in terms of the massic power C_W of two irradiated ^{62}Ni-enriched target pellets at various measurement times. The solid and broken lines correspond to the mean $C_W = 999.57$ μW·g^{-1} and the one standard deviation uncertainty intervals (± 4.11 μW·g^{-1}) obtained for pellet #2, respectively. The apparent difference between the results for pellet #1 and pellet #2 has a mean C_W offset of 0.3%. The datum for pellet #2 at Julian day 78 is an obvious statistical outlier, but was incorporated into the mean C_W used to compute C_A for SRM 4226. No decay corrections were made to the data.

linear addition of three components: (i) 0.42% for the "random error" at the 99% confidence level; (ii) 0.30% for the "maximum uncertainty due to the estimated systematic errors in the measurements"; and 0.23% for the uncertainty in the assumed $E_{β(mean)}$. This combination method and analysis was considered to be a very conservative estimate of the uncertainty on C_A with a very high ≥ 3 σ degree of confidence. Current retrospection indicates that this is not necessarily so, and that the statistical treatment used for the analysis can not fully withstand critical scrutiny.

The so-called "random error" was obtained from $t_{v(p)}s_m$ where $s_m = 0.13\%$ is the relative standard deviation of the mean computed from 10 calorimetry measurements on pellet #2 and $t_{v(p)} = 3.25$ is the standardized deviate of the Student-t distribution for a confidence coefficient $p = 1$-$\alpha = 0.99$ and $v = 9$ degrees of freedom.[32] One may firstly observe that the use of the standard deviation of the mean in this case may not be

Standard	SRM 4226	SRM 4226B	SRM 4226C
Solution composition [a]	84 mg Ni^{+2} per L of 1 mol·L⁻¹ HCl	83 µg Ni^{+2} per g of 1 mol·L⁻¹ HCl	97.8 µg Ni^{+2} per g of 1.1 mol·L⁻¹ HCl
Solution mass [b]	nominal 4.1 g	nominal 4.1 g	5.0804 ± 0.0007 g
Solution density [b]	not reported	not reported	1.016 ± 0.002 g·mL⁻¹
Reference time	27 May 1968	1 December 1984	15 August 1995
Massic activity	$1.501 \cdot 10^6$ Bq·g⁻¹	$1.346 \cdot 10^6$ Bq·g⁻¹	$5.053 \cdot 10^4$ Bq·g⁻¹
Relative uncertainty	0.95 %	1.1 %	0.92 %
Assumed confidence level (CL) and uncertainty basis [c]	assumed 99% CL; linear addition of "random error" at 99% level and "maximum" uncertainty due to "systematic errors"	assumed 95% to 99% CL; three times the quadratic combination of standard uncertainties	assumed 90% to 95% CL; two times the quadratic combination of standard uncertainties
Half-life [b]	100.07 ± 2.0 a	99.49 ± 2.0 a	101.1 ± 1.4 a
Maximum β⁻ energy [b]	65.87 ± 0.15 keV	65.88 ± 0.15 keV	66.945 ± 0.004 keV
Calibration method	microcalorimetry assuming $E_{\beta(mean)} = 17.23$ keV	1968 microcalorimetry results assuming $E_{\beta(mean)} = 17.13$ keV and decay correction for 16.5 a; confirmatory measurements by 4πβ LS spectrometry	4πβ LS spectrometry with ³H-standard efficiency tracing; confirmation from 1968 microcalorimetry results assuming $E_{\beta(mean)} = 17.426$ keV and decay correction for 27.2 a

[a] All standard solutions are contained within 5-mL, flame-sealed, borosilicate-glass ampoules.

[b] The uncertainty intervals given here correspond to that for a one standard uncertainty (or standard deviation) interval.

[c] The differing uncertainty treatments reflect the various historically-rooted error models and prevalent practices at the time of issuance of the three SRMs. That for SRM 4226C (in 1995) reflects those currently employed by the NIST Radioactivity Group, which for the most part are wholly compatible with internationally accepted conventions as adopted by the principal international standardization bodies.[27,28]

Table 1   Properties of the ⁶³Ni solution standards issued by NBS/NIST in 1968 (SRM 4226), in 1984 (SRM 4226B), and in 1995 (SRM 4226C).

statistically legitimate; and secondly note, for the record, that the 99% confidence interval given here is not statistically equivalent to a ±3 σ interval for the normal distribution as is often supposed (particularly for linear combination with so-called "maximum" estimates of "systematic errors").

The latter point can be easily addressed first. For the given $t_{v=9(p=0.99)} = 3.25$, the corresponding normal deviate z is between and closer to z = 2 (with a probability p = 0.9545) than z =3 (with p = 0.9973). The required deviate to obtain an equivalent ±3σ interval for the normal distribution is $t_{v=9(p=0.9973)} = 4.094$[33] whose use would result in a 26% larger value for the first "random" uncertainty component.

The issue regarding the use of the standard deviation of the mean s_m for the random dispersion in C_A is of greater concern. The 10-measurement data set for C_W on pellet #2 is clearly not homogeneous because the datum at Julian day 78 is an obvious substantial outlier to the set (Figure 2). Omission of this datum (having a value of 1009.4 µW·g⁻¹ results in a new mean C_W = 998.48 µW·g⁻¹ for the remaining 9 values with a standard deviation of the mean of 0.78 µW·g⁻¹. Clearly, the value 1009.4 µW·g⁻¹ is outside any confidence interval 998.48 ± k_α(0.78) for any reasonable standardized variate k_α. In fact k_α would have to exceed 12 to achieve consistency between the value 1009.4 and the 999.48 ± k_α(0.78) interval. There is nothing inherently wrong about using the entire 10-value data set to estimate C_W. The choice is arbitrary, and largely dwells within the domain of any metrologist's judgment. However, the appropriateness of

the s_m dispersion measure about the mean in this case is negated because an important assumption regarding its use is violated. The measurements in the data set are not independent (in the statistical sense) and do not constitute a random distribution characterized by a single standard deviation s_w for within-measurement variability. Beyond any variability in the measurements, which might be given by the 9-value s_m = 0.78 µW·g⁻¹, there must be some other component of variability, call it s_b, for the large difference between measurements (as seen in the difference between 998.48 µW·g⁻¹ and 1009.4 µW·g⁻¹ at various times). This temporal correlation violates the assumption of statistical independence. The use of the divisor $\sqrt{n}$ (for n = 10 measurements) is erroneous because n must be the *number of randomly-distributed, statistically-independent measurements* (of which all 10 are clearly not). The use of s_m thereby results in an underestimate of the true variability in the measurements. In fact, a more appropriate estimate of the standard deviation of the mean in this case would be $s_m = (s_b^2 + s_w^2/n)^{1/2}$ where s_b^2 is the component of variance for the between-measurement variability and where s_w^2 is that for the within-measurement variability.[34,35]

As noted, the quantity s_w^2/n could have been taken as the square of s_m for the 9-value data set [i.e., $s_w^2/n = (0.78 \text{ µW·g}^{-1})^2$] since these measurement values were approximately normally distributed (whereas the 10-value set was not). This estimate of $s_w/\sqrt{n}$ for pellet #2, 0.078% on a relative basis, also comports excellently with that for the 12-value data set for pellet #1 in

which $s_w/\sqrt{n} = 0.081\%$.

Evaluation of the other component of variance s_b^2 is intimately, and strangely, tied to the original estimation of the "systematic errors" in the measurements. Detailed examinations of the original laboratory records[36] by the present authors revealed that the 0.30% "maximum uncertainty" for the "systematic errors" in the measurements was derived exclusively from the linear sum of 0.07% for the uncertainty in the gravimetrically-determined dilution factor and 0.23% for the difference in the mean C_W values for pellet #2 and pellet #1. To us, the difference in calorimetry measurements *between pellets* is rather (and should be) reflective of yet one more component of variance s_x^2 that should be combined in the estimate of s_m; i.e., $s_m = (s_x^2 + s_b^2 + s_w^2/n)^{1/2}$.

The s_b^2 and s_x^2 components could be evaluated as follows. The noted difference between the homogeneous 9-value C_W mean for pellet #2 (998.48 $\mu W \cdot g^{-1}$) and the Julian day 78 datum (1009.4 $\mu W \cdot g^{-1}$) is reflective of the between measurement variability on a single pellet. Therefore, the relative range of these values (1.1%), multiplied by a normalizing factor of 0.886 for the correspondence between the range of two sampled values from a normal distribution and the estimated standard deviation of the normal distribution,[37] can be used to estimate a relative $s_b = 0.97\%$. The relative 0.38% difference between the homogeneous 9-value C_W mean for pellet #2 and homogeneous 12-value C_W mean for pellet #1 can similarly estimate the between-pellet variability $s_x = 0.34\%$. Hence, a more realistic relative standard deviation of the mean for the calorimetry measurements would consist of $s_m = (s_x^2 + s_b^2 + s_w^2/n)^{1/2} \cong 1.0\%$. The above analysis presumes, of course, that the Julian day 78 datum, which largely dominates this result, can not be "rejected" on the basis of some experimental justification. Such justification is not apparent. The datum was included by Barnes, et al.[23] in averaging the results for pellet #2 as used for SRM 4226. It therefore should also have been included in the statistical uncertainty treatment, but not simply as part of a computed standard deviation of the mean since the Julian day 78 datum is a statistical outlier. If the datum is rejected from consideration however, then $s_m = (s_x^2 + s_w^2/n)^{1/2} = 0.35\%$ which, coincidentally, is in reasonable agreement with the original estimate of $t_v(p)s_m$ in the certificate for SRM 4226 (which employed a very different and evidently flawed error-model analysis). It would appear then that the statistical component alone was underestimated by a factor of about 3.

Excepting the bizarre treatment of the between-pellet measurement variability (as mistakenly attributed to "systematic errors"), any uncertainties due to possible calorimetry instabilities or associated thermodynamic and electrical-network considerations were not overtly addressed in the original SRM 4226 certificate.[31] This is indeed curious in that the authors of the work conducted and reported on several independent evaluations of the radiation balance stability,[23] and made earlier systematic studies on the performance of the calorimeter.[24,25] The first such evaluation involved a comparison of calorimetry results obtained with two nominal 5-mg ^{226}Ra sources. From 1968 calorimetry, the two sources were found to have a average ratio of 1.00855 (from two ratio determinations of 1.0099 and

1.0072) compared to a certified ratio of 1.0098 (which was obtained from measurements in the early 1950s using the identical calorimeter). The difference in the two ratios (0.12% on a relative basis) could be invoked as some crude estimate of the calorimeter's stability. The second evaluation consisted of a comparison of the measured power for one of the 5-mg sources as obtained in 1968 and earlier in 1954. The relative difference in the two power measurements, after corrections for decay and ingrowth of the ^{226}Ra daughters was about 0.4%. The third check on stability involved determinations of the resistance difference of calibration coils that were used to reconfirm the extant Peltier coefficient for the balance. The resulting coil resistance differences as measured with the radiation balance and with a standard resistor were in relative agreement to about 0.01%. From the above considerations, one might suppose that a calorimeter instability uncertainty component of 0.1 to 0.2% or so would be in order.

None of the above, however, addresses the inherent uncertainties in the Peltier coefficient itself, in the measurement of the current flowing through the Peltier junctions, or in the standard resistor used to evaluate the Peltier coefficient or to calibrate the current measurements. Again, these uncertainty components may be estimated from published reports[24-26] and internal laboratory records.[36] From data given by Mann,[24,25] it is evident that the standard deviation of the mean for replicate determinations of the Peltier coefficient of typical calorimeter junctions was in the range 0.02 to 0.15% for one set of calibration experiments[24] and about 0.2% for another.[25] The uncertainty in current measurements (from the voltage drop across standard resistors) can similarly be estimated from the information given by Mann and Unterweger.[26] Relative uncertainties in potentiometer readings, as checked by two potentiometers against two calibrated standard voltage cells, were at least of magnitude 0.01 to 0.03%.

Consideration of the last remaining uncertainty component, that for the uncertainty in $E_{\beta(mean)}$ is straightforward. The value of $E_{\beta(mean)}$ is presently considered to be very precisely known, having a relative uncertainty of 0.075%.[4] The relative uncertainty in $E_{\beta(mean)}$ was originally taken to be 0.23%,[23,31] and its contribution to the overall propagated uncertainty may now be substantially reduced. Comparison of the present $E_{\beta(mean)}$ value and its associated uncertainty with those used in 1968, indicates that the original uncertainty component for $E_{\beta(mean)}$ was clearly underestimated.

As an aside, one may note that the presently "accepted" ^{63}Ni $E_{\beta(mean)} = 17.426 \pm 0.013$ keV[4] value is unlikely to significantly change in the reasonably-distant future since it was derived from two wholly independent, unbelievably precise, and exceedingly difficult to replicate, measurements of the ^{63}Ni β spectrum endpoint energy.[2,3] Thus, the revised microcalorimetry result given here for $C_{A(4226)}$ is equally unlikely to undergo any significant future revision due to changes in the assumed ^{63}Ni $E_{\beta(mean)}$. If anything, the cited uncertainty in $E_{\beta(mean)}$ may at later times be adjusted to a more realistic, larger value.

Table 2 summarizes the above re-analysis of the uncertainty on the ^{63}Ni massic activity $C_{A(4226)} = 1.484 \cdot 10^6$ Bq$\cdot$g^{-1} (as of 27 May 1968), as revised here for the change in the assumed

Uncertainty component and descriptor, followed by propagated uncertainties [a]	Uncertainty type (A or B) [a] and comments	Relative uncertainty (%)
s_1, calorimetry within-measurement variability	A; standard deviation of the mean $s_w/\sqrt{n}$ for repeatability on one pellet; $s_m = 0.078\%$ for $n = 9$ measurements on pellet #2; $s_m = 0.081\%$ for $n = 12$ on pellet #1	0.08
s_2, calorimetry between-measurement variability	A; standard deviation s_b based on range between outlier at Julian day 78 and 9-value mean for pellet #2; $s_b = 0.886 \cdot (\text{range})$	0.97 [b]
s_3, calorimetry between-sample variability	A; standard deviation s_x based on range between pellet #2 and pellet #1 means; $s_x = 0.886 \cdot (\text{range})$	0.34
s_4, Peltier coefficient calibration	A; typical standard deviation of the mean from several independent determinations	0.15
u_5, current measurements	B; estimated standard uncertainty due to potentiometer variability and uncertainty in standard resistor	0.02
u_6, calorimetry instability	B; estimated standard uncertainty based on three evaluations	0.15
u_7, gravimetric dilution	B; estimated standard uncertainty in gravimetrically-determined dilution factor	0.04
u_8, decay corrections	B; for an estimated standard uncertainty in the ^{63}Ni half-life of 1.4%; uncertainty in timing is negligible	0.01
u_9, assumed mean β^- energy	B; estimated standard uncertainty	0.075
u_c, combined standard uncertainty [a]	quadratic combination of all component uncertainties; $u_c = (\Sigma_i u_i)^{1/2}$ for $I = 1$ to 9 with $u_i = s_i$ for type A components	1.1 [b]
$U = k \cdot u_c$, expanded uncertainty [a]	for $k=2$, which is assumed to correspond to a confidence level of about 90 to 95%	2.1 [b]

[a] Refer to accompanying text and references 27 and 28 for definition of terms.

[b] If the statistical outlier of Julian day 78 is excluded from the analysis, then component s_2 may be neglected which would result in $u_c = 0.42\%$ and $U = 0.84\%$. For consistency, the datum of Julian day 78 must then also be excluded from the computed mean C_W used to derive C_A for SRM 4226, and the revised value of $C_{A(4226)}$ should be reduced by 0.1% to 1.482 MBq·g^{-1} as of 27 May 1968.

Table 2   Re-analysis of the uncertainty on the 1968 calorimetry-based standardization of the ^{63}Ni massic activity C_A for SRM 4226 as revised in 1995 by the present authors.

$E_{\beta(\text{mean})}$. This treatment may be considered to be a more realistic assessment of the uncertainty on the revised $C_{A(4226)}$, and follows the normal conventions of the NIST Radioactivity Group. By these currently-invoked conventions, which for the most part are wholly compatible with those adopted by the principal international metrology standardization bodies,[27,28] all individual uncertainty components are expressed in terms of experimental standard deviations (or experimental standard deviations of the mean where appropriate) or quantities assumed to correspond to standard deviations irrespective of the method used to evaluate their magnitude. All of the uncertainty component estimators are termed "standard uncertainties", and are classified into two categories depending on their method of evaluation: type A standard uncertainties are evaluated by statistical methods; and type B standard uncertainties are evaluated by other means.[27,28] A propagated uncertainty, termed a "combined standard uncertainty" is expressed at what is assumed to be an estimated standard deviation which is equal to the positive square root of the total variance obtained by summing all variance (square of the standard uncertainty) and covariance components, however evaluated, using the law of propagation of uncertainty for the specific mathematical function given by the model of the measurement procedure.[27] By recently established NIST policy,[28] the combined standard uncertainty is multiplied by a "coverage factor" of $k = 2$ to obtain an "expanded uncertainty" which is assumed to provide an uncertainty interval having a level of confidence of roughly 90 to 95%.

1968-1972 confirmations of SRM 4226 by $4\pi\beta-\gamma$ coincidence counting

The standardized massic activity C_A for SRM 4226 was largely confirmed by several independent determinations that were performed by three sister metrology laboratories during roughly the same time period (1969-1972). The confirmatory results were obtained by the National Research Council (NRC) of Canada,[38] the Atomic Energy of Canada Ltd. (AECL),[39] and the Australian Atomic Energy Agency (AAEC)[40] using $4\pi\beta-\gamma$ coincidence efficiency-tracing methods.

These methods, employed for the standardization of pure β emitters, generally consist of the following sequential steps: (i) standardizing a β^-- and γ-emitting tracer radionuclide, such as ^{54}Mn, ^{60}Co, or ^{134}Cs, using conventional "absolute" $\beta-\gamma$ coincidence counting techniques; (ii) measuring the combined β counting rate from a mixed-radionuclide source of the pure β emitter and the efficiency tracer as a function of the latter's known efficiency; and (iii) extrapolating the resulting count rate vs efficiency function to 100% and subtracting the known activity of the tracer to obtain the activity of the pure β emitter. The efficiency tracing is critically dependent on the choice of tracer radionuclide, on the source-preparation procedure, and on the method used to vary the β efficiency. The principal

Laboratory [a] and reference; method	Measurement method	Time of measurement t_m	$C_A(t_m)$ [b] MBq·g^{-1}	$(t_m\text{-}t_o)$ [c] days	$C_A(t_o)$ [d] MBq·g^{-1}	ratio $C_A(t_o)/C_{A(4226)}$
NBS[23]	calorimetry	27 May 1968	1.4846[e]	0	1.4846	——
NRC[38]	4πβ-γ coincidence efficiency tracing	October 1969	1.487	510	1.501	1.011
AECL[39]	4πβ-γ coincidence efficiency tracing	May 1970	1.502	720	1.522	1.027
AAEC[40]	4πβ-γ coincidence efficiency tracing	April 1972	1.444	1410	1.483	0.9987
NBS[41]	4πβ LS spectrometry efficiency tracing	1 December 1984	1.3297[f]	6032	1.4891	1.0030
NIST[42]	4πβ LS spectrometry efficiency tracing	15 August 1995	1.2305	9941	1.4829	0.9989

(a) Laboratory acronyms are: U.S. National Bureau of Standards (NBS); National Research Council (NRC) of Canada; Atomic Energy of Canada Ltd. (AECL); Australian Atomic Energy Commission (AAEC); U.S. National Institute of Standards and Technology (NIST), formerly NBS.

(b) The ^{63}Ni massic activity of SRM 4226 as measured at time t_m by each respective laboratory. Uncertainties on the values are discussed in the text.

(c) Decay time interval between the reference time t_o and time of measurement t_m. A factor of 365.2422 days per mean solar year is used for conversions.

(d) Decay-corrected ^{63}Ni massic activity of SRM 4226 at the reference time t_o of 27 May 1968 and assuming a half-life of $T = 101.1$ a.

(e) The 1968 NBS calorimetry result, as revised herein for the change in $E_{\beta(mean)}$, is taken as the value of $C_{A(4226)}$ that is used for comparisons.

(f) The 1984 NBS LS spectrometry result was slightly revised, as given herein, from the original report.

Table 3 Confirmatory measurements by 4πβ-γ coincidence efficiency tracing of the revised ^{63}Ni massic activity $C_{A(4226)}$ of SRM 4226 and comparisons to the NBS/NIST calorimetry standardization and subsequent assays by 4πβ LS spectrometry.

criteria are that the pure β and β-γ tracer radionuclides should be chemically compatible,[40] of comparable atomic number,[38] and have similar β-spectrum shapes at the low energy regions.[40] The counting sources, obviously, must consist of a homogeneous and quantitative mix of the two radionuclides. They also should be sufficiently thin with high β detection efficiencies in order to minimize the uncertainty in extrapolating to 100% efficiency.[38-40] Variations in the β detection efficiencies, preferably with very small increments over a relatively small efficiency range,[40] can be achieved by a variety of methods, including use of cover-film absorbers or electronic discrimination on single sources, or source self-absorption with multiple sources. Precision in the extrapolation, which largely dominates the overall measurement uncertainty, can be somewhat controlled by having as many data points as possible in the efficiency curve.

Excepting the use of ^{60}Co as the efficiency tracer in all cases, the methodological details used by the three laboratories to perform the ^{63}Ni assays of SRM 4226 varied considerably. Baerg and Bowes at NRC[38] employed thin, gravimetrically-deposited, freeze-dried sources to achieve quantitative, relatively homogeneously mixed, counting sources of acceptable efficiency. They used discrimination of the β-channel energy threshold to obtain ^{63}Ni efficiency variations over a range of about 50% to 87%. In contradistinction, the counting sources used by Merritt and Taylor at AECL[39] were prepared by electrospraying preconcentrated solutions of the radionuclide mixtures onto gold-coated, insulin-treated, VYNS (a polyvinylchloride - polyvinylacetate copolymer) films. This technique resulted in very thin, very homogeneous sources having efficiencies as high as 92%. The electrospraying procedure, however, is not quantitative

and they therefore had to perform independent determinations of the ^{63}Ni and ^{60}Co yields. They accomplished these yield determinations by relative γ-emission rate measurements, using ^{59}Ni as the yield tracer for ^{63}Ni. Efficiency variations were performed using absorbers of similarly prepared gold-coated VYNS films. Lowenthal, et al. at AAEC[40] employed yet a third variation. Their sources consisted of thin, homogeneous pads of electrosprayed ion-exchange resins. Efficiency variations, ranging from over 60 to nearly 83% for ^{63}Ni, were obtained by source self-absorption using a large number of different sources.

The results of these three confirmatory measurements are summarized in Table 3. As indicated, the agreement with the NBS calorimetry, when the originally reported data are normalized for decay corrections to a common reference time, is within a few percent for all three laboratories: about +1% for NRC; about +3% for AECL; and about -0.1% for AAEC. The relative overall measurement uncertainties on these results, presumably at relatively high confidence levels (i.e., typically with the linear addition of "systematic" effects and three times the "random error"), were reported to be ±1.1, ±1.1, and ±1.4%, respectively.

These three variations on the 4πβ-γ coincidence efficiency tracing technique have comparative advantages and disadvantages which may influence one's judgment on their respective reliability. The NRC method[38] of varying the counting efficiency by electronic discrimination is clearly superior to the other two variations. Unlike this electronic discrimination with a single intact counting source, the use of multiple absorber films to obtain efficiency variations, as done by Merritt and Taylor at AECL,[39] introduces a significant uncertainty component in the measurements. Somewhat similarly, the use of

multiple sources having varying self-absorption, as done by Lowenthal, et al. at AAEC,[40] introduces a between-source component of variability. On the other hand, the freeze-dried source-preparation procedure used by Baerg and Bowes at NRC[38] is probably inferior, in terms of possible inhomogeneity in the mixed sources, to the resin pads used by Lowenthal et al.[40] Lastly, one may note that the AECL electrospraying procedure,[39] although producing very uniform, well-mixed sources, requires independent determinations of the yields for both the pure β and tracer radionuclides. With these criteria in mind, and assuming all other considerations are equal (e.g., that they all were based on employment of sound metrological practices), one might suppose that the AAEC result[40] is more reliable than that of NRC[38] which in turn is slightly more reliable than that AECL.[39] This evaluation is admittedly subjective. Use of other criteria could result in an alternative ranking. Nevertheless, by mere coincidence or not, these laboratories' respective agreement with the NBS microcalorimetry result (Table 3) nicely follows this same relative ordering.

These intercomparison results for SRM 4226 have been previously summarized by Barnes et al.,[23] by Lowenthal et al.,[40] by Coursey et al.,[41] and again by Mann and Unterweger.[26] The summaries of these comparisons, however, are confounded by different reference times used for the comparisons and by subsequent revisions in the microcalorimetry-based massic activity C_A for SRM 4226, and attendant changes in the half-life T, due to changes in the accepted $E_{\beta(mean)}$ for [63]Ni as applied to the original calorimetry data. The present tabulation, which incorporates the originally reported C_A values at their respective original measurement times, should set this record straight (Table 3).

1984 4πβ liquid scintillation spectrometry and SRM 4226B

The initially certified [63]Ni solution standard SRM 4226 was re-issued in 1984 as SRM 4226B with revisions in both the initial C_A and in a recommended T because of a change in the assumed $E_{\beta(mean)}$ (Table 1). A new "accepted" value, from a compiled ENSDF evaluation,[43] was taken to be $E_{\beta(mean)} = 17.13 \pm 0.04$ keV which was computed on the basis of an allowed transition of maximum energy $E_{\beta(max)} = 65.88 \pm 0.15$ keV. Interestingly, this change in $E_{\beta(max)}$ (and hence $E_{\beta(mean)}$) was not based on any new measurements of the [63]Ni endpoint energy beyond that reported by Hsue,[29] but rather was derived from the evaluated 1983 atomic mass table.[44] The revised value of C_A at the initial reference time was thus increased by the $E_{\beta(mean)}$ ratio 17.23/17.13 to give $C_A = 1.510 \cdot 10^6$ Bq·g^{-1} as of 27 May 1968; and T was decreased by 17.13/17.23 to give $T = 99.49 \pm 2.0$ a. The re-issued SRM 4226B was also decay corrected over 16.5 a using the revised $T = 99.49$ a [63]Ni half-life, so that C_A was given as $C_{A(4226B)} = (1.346 \pm 0.015) \cdot 10^6$ Bq·g^{-1} as of 1 December 1984.[45]

The ±1.1% relative uncertainty in $C_{A(4226B)}$ was assumed to correspond to a three standard deviation interval and was obtained by quadratic combination of the relative uncertainties in the calorimetry measurements (0.13%), estimated calorimetry stability (0.15%), assumed $E_{\beta(mean)}$ (0.23%), and [63]Ni decay correction (0.22%).[45] This uncertainty analysis suf-

fers from the same shortcomings that occur, as noted previously, for SRM 4226. The first uncertainty component was the misapplied standard deviation of the mean as invoked originally in the SRM 4226 certificate. The second "calorimetry stability" uncertainty component was taken as one half of the 0.30% "maximum uncertainty" for the "systematic errors" as given in 1968 for SRM 4226 (refer to prior discussion). The more realistic analysis given in Table 2 for SRM 4226 (as revised here), with the inclusion of a 0.15% component for the uncertainty in a decay correction over 16.5 a, would be equally applicable for SRM 4226B.

In retrospect, considering the presently assumed $E_{\beta(mean)}$ value for [63]Ni, this 1984 revision may be considered to have been inadvertently miscorrected. As given previously, with $E_{\beta(mean)} = 17.426 \pm 0.013$ keV, the original [63]Ni half-life from Barnes et al.[23] becomes $T = 101.21 \pm 2.0$ a and the original C_A value for the SRM 4226 must be revised to $C_{A(4226)} = 1.485 \cdot 10^6$ Bq·g^{-1} as of 27 May 1968. Therefore, for consistency, the C_A value for SRM 4226B must be revised to $C_{A(4226B)} = 1.326 \cdot 10^6$ Bq·g^{-1} as of 1 December 1984 for a decay correction over 16.5 years with $T = 101.21$ a. One may note, unsatisfactorily, that the percent differences between the revised C_A values (for both SRM 4226 and SRM 4226B) and the originally reported ones are just outside (-1.1% and -1.5%) the originally reported relative uncertainty intervals (±0.95% and ±1.1%, respectively) despite that these intervals were claimed to be at rather high 99% or so confidence levels. Obviously, the estimated relative uncertainties, particularly on the assumed $E_{\beta(mean)}$ values, were somewhat underestimated.

In 1984, Coursey et al.[41] at NBS performed 4πβ LS spectrometry measurements on gravimetric dilutions of the original SRM 4226 [63]Ni solution standards (Figure 1). They relied upon ^{3}H-standard efficiency tracing using the CIEMAT/NIST EFFY2 calculational protocol[52] (Appendix), and reported an average C_A value that was systematically about 0.8% smaller than the inferred microcalorimetry results as revised (as of 1984) and given in the original SRM 4426B certification.[45] These LS results were largely employed, at the time, for two purposes: to test and verify the CIEMAT/NIST efficiency tracing method for this low-energy β emitter; and to provide a presumably less accurate, but nevertheless independent confirmation of C_A for the revised and re-issued [63]Ni solution standard (NIST SRM 4226B) after the passage of 16.5 a.

This apparent LS measurement result must be re-evaluated, and thereby revised, because of two considerations: the microcalorimetry results, which were used for the comparison, require unfolding for the revisions applied in 1984; and the LS spectrometry results require minor adjustments for changes in the values of $E_{\beta(max)}$ for [63]Ni and ^{3}H used for the CIEMAT/NIST protocol efficiency tracing calculations, as well as differences in the calculations in going from using the EFFY2 code[52] to EFFY4.[51] The change in codes primarily resulted in using improved numerical integration techniques in evaluating the number-weighted efficiency distribution $\varepsilon(E) \cdot F(Z,E) dE$ and Fermi distribution $F(Z,E) dE$ integrals [eq. (A3) in the Appendix].

The LS spectrometry results compared to that for the calorimetry, in terms of the [63]Ni massic activity ratio

$C_{A(LS)}/C_{A(CAL)}$, had a mean ratio of 0.9921 ± 0.0029, as derived from the original tabulation in Coursey et al.[41] The uncertainty cited here is the standard deviation computed for 26 efficiency traced LS determinations of $C_{A(LS)}$. The assumed value of $C_{A(CAL)}$ used for the comparison was $C_{A(4226B)} = (1.346 \pm 0.015) \cdot 10^6$ Bq·g^{-1} as of 1 December 1984 which was obtained from $C_{A(4226B)} = C_{A(4226)} \cdot (\Delta E_{\beta(mean)}) \cdot D$, where $C_{A(4226)} = (1.501 \pm 0.014) \cdot 10^6$ Bq·g^{-1} was the massic activity (as of 27 May 1968) as certified for SRM 4226, $\Delta E_{\beta(mean)} = 17.23/17.13$ was the correction (applied in 1984) in changing the assumed $E_{\beta(mean)}$ from 17.23 keV to 17.13 keV, and $D = 0.89131$ was a ^{63}Ni decay factor using a half-life $T = 99.49 \pm 2.0$ a for the 6032 d decay interval from 27 May 1968 to 1 December 1984. For the present comparison, the revised $C_{A(CAL)} = 1.326 \cdot 10^6$ Bq·g^{-1} is just the 1995 revision of $C_{A(4226B)}$ given above. The LS results can be adjusted by applying a ^{63}Ni LS efficiency correction $\varepsilon_{LS}/\varepsilon_{LS(rev)}$ to each of the reported $C_{A(LS)}/C_{A(CAL)}$ values. The numerator ε_{LS} of this correction represents a given ^{63}Ni LS efficiency as originally calculated by Coursey et al.[33] using the EFFY2 code and an assumed ^{63}Ni $E_{\beta(max)} = 65.88 \pm 0.15$ keV; the denominator $\varepsilon_{LS(rev)}$ represents a corresponding ^{63}Ni LS efficiency as recalculated by the present authors[42,1] using the EFFY4 code and an assumed ^{63}Ni $E_{\beta(max)} = 64.945 \pm 0.004$ keV. Operationally, this correction was effected by relating the reported ε_{LS} to EFFY4-generated figures of merit M which in turn could be used to deduce corresponding $\varepsilon_{LS(rev)}$. These revisions, illustrated in Figure 3, result in a new mean $C_{A(LS)}/C_{A(CAL)}$ ratio of 1.0020 ± 0.0029.

To summarize, one may observe that if the originally reported calorimetry result for $C_{A(4226)} = (1.501 \pm 0.014) \cdot 10^6$ Bq·g^{-1} is corrected for the change in $E_{\beta(mean)}$ from 17.23 keV (in 1968) to the presently assumed value of 17.426 keV, and if corrected for decay over 6032 d (to 1 December 1984) using the revised calorimetry-derived ^{63}Ni half-life $T = 101.21 \pm 2.0$ a; then, the corrected result $C_{A(4226B)} = 1.326 \cdot 10^6$ Bq·g^{-1} is lower than the revised LS measurement result $C_{A(LS)}$ by only 0.2% whereas it was originally reported[41] to be 0.8% higher than $C_{A(LS)}$.

Thus, this LS measurement of the ^{63}Ni massic activity can be taken to be $C_{A(LS)} = 1.3297 \cdot 10^6$ Bq·g^{-1} as of 1 December 1984 (Table 3). Coursey et al.[41] estimated that this LS determination had an "overall uncertainty" (taken to be three times a combined standard uncertainty of 7 component uncertainties) of $\pm 1.1\%$ which was identical to that estimated for the calorimetry standardization of SRM 4226B.

## 1995 $4\pi\beta$ liquid scintillation spectrometry and SRM 4226C

Zimmerman and Collé[42] recently reported on the preparation and calibration of a new series of ^{63}Ni solution standards which will be disseminated by NIST as SRM 4226C[46] (Table 1). The solution standards were prepared from gravimetric dilutions of ^{63}Ni solutions that could be directly related to SRM 4226 and SRM 4226B, and to the calorimetry standardization of Barnes, et al.[23] and $4\pi\beta$ LS spectrometry of Coursey et al.[41] (Figure 1). The recent calibration was also based on $4\pi\beta$ LS spectrometry using the CIEMAT/NIST ^{3}H-standard efficiency tracing protocol

(Appendix), and included rigorous evaluations of multiple variable effects and potential sources of measurement uncertainty.[42]

The LS measurements reported by them for this calibration and evaluation: (i) were performed with two LS spectrometers that employed vastly differing instrument-dependent quench indicating parameters and that had considerably different operating characteristics (e.g., linear versus logarithmic pulse amplification, different coincident pulse resolving times, different detection thresholds); (ii) were made with three commercial scintillation fluids that had different scintillation fluors and solvent compositions; (iii) determined the massic activity C_A of solution M2 through three gravimetric pathways, i.e., with solutions M3 and M4 through M1 to M2, and M5 to M2 (Figure 1); (iv) employed matched ^{3}H and ^{63}Ni samples at two different LS cocktail total volumes, nominally 10 to 11 mL and 15 mL (although other volumes effects on the ^{3}H-standard efficiency tracing method were also independently studied at both smaller and larger cocktail volumes); (v) were made with cocktails having total aqueous content (on a mass fraction basis) that ranged from about 0.01% to 12.5% water, and 30% to 38% water in scintillation gels; (vi) used cocktails with an acidic content in the aqueous portion that ranged from 1 mol·L^{-1} HCl down to less than 0.004 mol·L^{-1} HCl; (vii) were made with cocktails having variable Ni^{+2} carrier ion concentrations in the aqueous portion that ranged from about 0.4 to 100 µg Ni$^+$ per gram of solution; (viii) used cocktails that were quenched with varying quantities of both nitromethane (CH$_3$NO$_2$, or 10% solutions of CH$_3$NO$_2$ in ethanol) and water (or slightly acidic NiCl$_2$ carrier solutions) as imposed quench agents to develop the efficiency tracing curves; (ix) involved a range of LS sample counting rates (for both ^{3}H and ^{63}Ni) from 400 to over 2200 s^{-1}; (x) incorporated measurements on sample cocktails ranging in "age" from to nearly 90 d (where the age is the time difference between sample-preparation and measurement time); (xi) covered efficiency-tracing quenching ranges that corresponded to ^{63}Ni detection efficiencies from 0.60 to 0.81, and ^{3}H efficiencies of 0.17 to 0.56; (xii) involved 34 separate efficiency tracing curves each of which consisted of 4 to 9 samples that had been independently measured 3 to 9 times; and (xiii) included data on a total of 976 sets of measurements on 55 matched ^{63}Ni and ^{3}H LS samples.

There were no significant differences in the efficiency traced measurements for C_A across many of the variables and conditions given in the above vast array. The results were invariant of the spectrometer used for the measurements, the scintillation fluid employed, the gravimetric pathway to $C_{A(M2)}$, the cocktail volume over the 10- to 15-mL range, the imposed quenching agent, the sample counting rates, the sample ages, and the detection efficiency ranges. The LS cocktail composition (in terms of the relative proportions of water content, acidity and Ni^{+2} carrier concentration in the aqueous portion, and scintillation fluid) was, however, critically important. These findings and the complete measurement results for the calibration of SRM 4226C are treated at length by Zimmerman and Collé.[42]

The ^{63}Ni massic activity of SRM 4226C, as of 15 August 1995, was certified as $C_{A(4226C)} = (5.053 \pm 0.046) \cdot 10^4$ Bq·g^{-1}
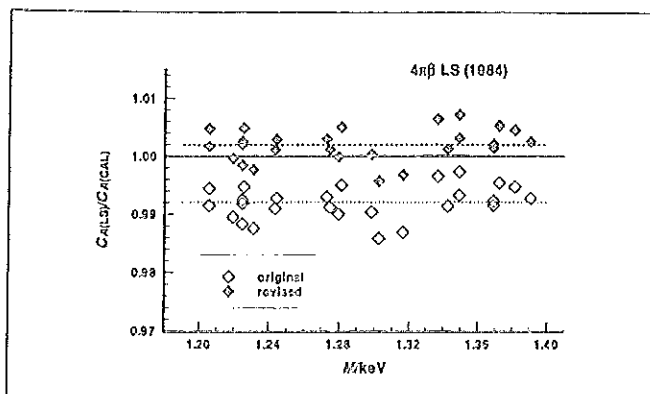
Figure 3 Comparison between the 1984 $4\pi\beta$ LS spectrometry data of Coursey et al.[41] and microcalorimetry-based standardization of ^{63}Ni solution standard SRM 4226B. The ^{63}Ni massic activity ratio as obtained from the LS spectrometry $C_{A(LS)}$ and calorimetry $C_{A(CAL)}$ is plotted against the 1995 calculations of the EFFY4-generated LS figure of merit M (in units of keV). The data for the original ratios $C_{A(LS)}/C_{A(CAL)}$ (open symbols) for the 26 LS samples were those originally reported,[41] and were obtained using $C_{A(CAL)}$ from the 1984 revision of the calorimetry standardization. The mean ratio of the original $C_{A(LS)}/C_{A(CAL)}$ data (0.9921) is shown by the dotted line. The revised ratios (closed symbols) were derived from small adjustments in the LS efficiency-tracing calculations of $C_{A(LS)}$ on each datum and from the 1995 revision of the calorimetry standardization. The mean ratio (1.0020) for the revised data set is shown by the dashed line. Refer to text for details on the revisions.
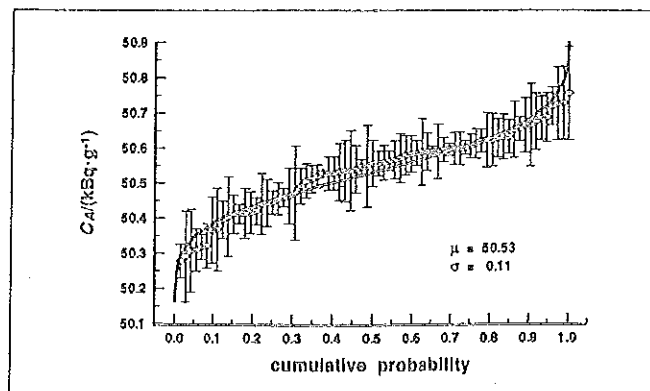
Figure 4 Distribution of 72 determinations of the ^{63}Ni massic activity $C_{A(4226C)}$ of SRM 4226C in units of kBq·g^{-1} as obtained in 1995 from $4\pi\beta$ LS spectrometry with ^{3}H-standard efficiency tracing. The data are averages from efficiency tracing with matched ^{63}Ni and ^{3}H LS samples under a wide variety of measurement and sample conditions. The results were obtained with 18 independent efficiency tracing curves. The uncertainty bars on each datum correspond to a one standard deviation interval for the measurement repeatability of the individual determinations (each based on 3 to 6 replicate measurements). The solid curve is that computed for a normal distribution with a mean of $\mu = 50.53$ kBq·g^{-1} and standard deviation of $\sigma = 0.11$ kBq·g^{-1}.

(Table 1). The cited uncertainty interval, ±0.92% on a relative basis, is presumed to correspond to a 90 to 95% confidence interval (Table 4). The ogive of Figure 4 illustrates the results for $C_{A(4226C)}$ that were obtained from 72 independent LS determinations which were not believed to have been substantially influenced by cocktail composition effects. Each datum in the figure was a mean value obtained with a matched ^{3}H sample using one of 18 efficiency tracing curves. The samples were prepared with one of the three scintillation fluids and measured with one of the two employed spectrometers (each sample being replicately measured about 3 to 6 times over the course of a few days). The results average over a large variety of LS measurement and sample composition variables.

The mean $C_{A(4226C)}$ value for all 72 determinations is $(5.0534 \pm 0.0013) \cdot 10^4$ Bq·g^{-1} (where the cited uncertainty is the standard deviation of the mean s_m for $\nu = 71$ degrees of freedom); whereas the grand mean of the results of aggregated data for the mean values from 18 efficiency curves is $(5.0530 \pm 0.0021) \cdot 10^4$ Bq·g^{-1} (where the uncertainty is the s_m for $\nu = 17$). Neither statistical uncertainty estimator given here is valid however. Although the data of Figure 4 is approximately normally distributed, it is not a homogeneous set. Use of a s_m is thereby precluded. There are in fact three distinct, and evaluatable, components of measurement variability in the data: the LS measurement *repeatability* on a given individual LS sample;

the *reproducibility* among differently-quenched samples (of similar cocktail composition) with a single-efficiency tracing curve; and the *reproducibility* between the data for efficiency tracing curves for samples of differing composition. The uncertainty in $C_{A(4226C)}$ was estimated from an exhaustive analysis that is outlined in Table 4. As indicated, the analysis considers 28 individual uncertainty components. Figure 5, in addition, illustrates the measurement model for this calibration and identifies the uncertainty components as they enter into the model.

The ^{63}Ni massic activity $C_{A(4226C)}$ for SRM 4226 may be directly compared to the decay-corrected results for SRM 4226 and 4226B, as done in Table 3, using the gravimetrically-determined dilution factors (Figure 1).

Discussion and summary

Table 3 summarizes the remarkably excellent agreement among the calorimetry and LS spectrometry standardizations of ^{63}Ni that were performed by NBS/NIST over the past 27 years. All of the NBS/NIST standardizations agree within ±0.5% despite that the comparisons require substantial decay corrections. One may equally conclude that the three ^{63}Ni solution standards, SRM 4226, 4226B, and 4226C, issued by NBS/NIST over this same 27-year period are compatible and consistent. The NBS/NIST standardization results also comport well, within

Uncertainty component and descriptor, followed by propagated uncertainties [a]	Uncertainty type (A or B) [a] and comments	Relative uncertainty (%)
s_1, LS measurement variability	A; standard deviation of the mean s_m in C_A for repeatability of LS measurements on any one LS sample ($v_{eff} = 4$ effective degrees of freedom); typical value obtained from 72 independent determinations of s_m (each with $v = 2$ to 5 degrees of freedom); the "relative uncertainty (Δ) on the uncertainty estimator (relative standard deviation of s_m values is 50%	0.055
s_2, LS sample (quench dependence) variability	A; standard deviation s_2 in C_A for reproducibility among samples (differently quenched) within a single efficiency tracing curve ($v_{eff} = 3$); obtained from 18 independent determinations of s_2 (each with $v = 2$ to 4); Δ (relative standard deviation of s_2 values) is 60%	0.15
s_3, LS efficiency tracing (sample composition) variability	A; standard deviation s_3 in C_A for reproducibility between 18 efficiency tracing curves for samples of differing composition ($v = 17$)	0.18
s_4, background measurement variability	A; standard deviation s_4 (Poisson "counting error") in background from 180 determinations on matched LS blanks (0.22%)	0.0004 (and PE)[b]
u_5, gravimetric (mass) determinations for LS samples	B; estimated standard uncertainty in mass for any one LS sample	0.05 (and PE)[b]
u_6, ^{3}H standard primary calibration	B; for a standard uncertainty of 0.18% from NIST calibration	0.11[c]
u_7, ^{3}H standard gravimetric dilution	B; estimated standard uncertainty in gravimetrically-determined dilution factor	0.03
u_8, ^{3}H standard decay correction	B; for a standard uncertainty in half-life of 0.46% for decay over 16.95 a; uncertainty in timing is negligible	0.27
s_9, LS spectrometer dependence	A; ratio of mean C_A between 13 efficiency tracing curves obtained with one spectrometer and 17 curves with the other was 0.9990 ± 0.0047	WE[b]
s_{10}, scintillator dependence	A; ratio of mean C_A between 15 curves obtained with one scintillator and 11 curves with another was 1.0008 ± 0.0048	WE[b]
u_{11}, LS cocktail stability age dependence	B; estimated standard uncertainty on fit of relation between C_A and sample age (time between sample preparation and measurement)	0.03% (and PE)[b]
u_{12}, LS cocktail composition dependence	B; estimated standard uncertainty on systematic relation between C_A and aqueous mass fraction in LS sample	0.06% (and PE)[b]
u_{13}, LS cocktail mass (volume) dependence	B; estimated standard uncertainty on systematic relation between C_A and sample volume	0.04% (and PE)[b]
u_{14}, mismatch of LS cocktail composition in ^{3}H, ^{63}Ni and blank samples	B; estimated standard uncertainty of about 3 to 4% based on comparison of quench indicating parameters for matched samples	WE[a]
u_{15}, live-time determinations for LS counting time intervals	B; estimated standard uncertainty of 0.1% for each of 2 spectrometers	0.07
u_{16}, uncorrected dead-time counting effects	B; estimated standard uncertainty corresponding to 1% of correction (for each of two spectrometers) divided by $\sqrt{2}$	0.04
u_{17}, decay corrections for ^{63}Ni from measurement time to common reference time	B; for estimated standard uncertainties in timing (0.001%) and ^{63}Ni half-life (1.4%) for decay over intervals <0.2 a	0.001 (and PE)[b]
u_{18}, radionuclidic impurities	B; none detected; estimated standard uncertainty corresponding to the detection limit for the photonic-emission rate	0.004
s_{19}, determination of quench indicating parameter (QIP) for ^{3}H	A; for a relative standard deviation s_{QIP} of 0.34% (based on repeatability with 4 samples each with $v = 2$ to 6); Δ (relative standard deviation on the 4 s_{18} values) is 60%	0.09 (and PE)[b]
s_{20}, determination of QIP for ^{63}Ni	A; for a relative standard deviation s_{QIP} of 0.34% (based on repeatability with 4 samples each with $v = 2$ to 6); Δ (relative standard deviation on the 4 s_{19} values) is 60%	0.09 (and PE)[b]
u_{21}, precision of ^{3}H efficiency versus figure of merit (M) calculations	B; calculational step sizes	0.008
s_{22}, fit of relation between ^{3}H QIP and calculated M	A; for a standard deviation of 0.12% on the fit for 4 independent M versus QIP curves	0.02
u_{23}, precision of ^{63}Ni efficiency versus M calculations	B; calculational step sizes	0.002
s_{24}, fit of relation between calculated M and ^{63}Ni efficiency	A; for a standard deviation of 0.006% on the fit for the relation between the calculated efficiency and M	0.002

Table 4 Summary of the uncertainty analyses for the ^{63}Ni massic activity C_A of SRM 4426C, calibrated by $4\pi\beta$ LS spectrometry with ^{3}H-standard efficiency tracing.

Uncertainty component and descriptor, followed by propagated uncertainties [a]	Uncertainty type (A or B) [a] and comments	Relative uncertainty (%)
u_{25}, effect of ionization quenching assumptions on efficiency calculations	B; estimated standard uncertainty	0.1
u_{26}, effect of asymmetry in phototube responses on efficiency calculations	B; estimated standard uncertainty of 0.2% effect divided by $\sqrt{2}$ for two spectrometers	0.14
u_{27}, effect of ^{3}H $E_{\beta(max)}$ on efficiency calculations	B; for an estimated standard uncertainty of 0.04% in $E_{\beta(max)}$	0.09
u_{28}, effect of ^{63}Ni $E_{\beta(max)}$ efficiency calculations	B; for an estimated standard uncertainty of 0.006% in $E_{\beta(max)}$	0.0024
u_c, combined standard uncertainty [a]	quadratic combination of all component uncertainties; $u_c = (\Sigma_i u_i)^{1/2}$ for $i = 1$ to 28 with $u_i = s_i$ for type A components	0.46
$U = k \cdot u_c$, expanded uncertainty [a]	for $k=2$, which is assumed to correspond to a confidence level of about 90 to 95%	0.92

[a] Refer to accompanying text and references 27 and 28 for definition of terms.

[b] The relative uncertainty for this component is wholly (WE), or in part (PE), embodied in the relative standard uncertainties of components (1), (2) and (3).

[c] Based on the primary calibration for NIST SRM 4927E (August, 1971).

Table 4 Summary of the uncertainty analyses for the ^{63}Ni massic activity C_A of SRM 4426C, calibrated by $4\pi\beta$ LS spectrometry with ^{3}H-standard efficiency tracing.

3% in a worst case, with that obtained from three other metrology laboratories that used three distinct variations on the $4\pi\beta$-γ coincidence efficiency tracing standardization method. The agreements are more vividly demonstrated in Figure 6 where the individually reported C_A values at both their original measurement times and as decay corrected are plotted against the original time of measurement. A regression of the three NBS/NIST values to an exponential (solid line in Figure 6) reproduces the presently adopted ^{63}Ni $T = 101.1$ a half-life.[1] The three NBS/NIST values have a relative agreement, expressed in terms of the mean $C_{A(0)}/C_{A(4226)}$ ratio (Table 3) of 1.0006.

The validity of the present comparisons is critically dependent on two assumptions: on the stability and integrity of the massic activity in solutions stored over the course of 27 years; and on the absence of any radionuclidic impurities.

The ^{63}Ni solutions are, by all available evidence, of unquestionable stability. The solutions in all cases were stored within flame-sealed glass ampoules so that there were no evaporation or solution transpiration losses. From a chemical viewpoint, the solutions can reasonably be expected to be indefinitely stable since they were maintained at an acidic content of about 1.0 mol·L^{-1} HCl and they contained inactive nickel carrier anions at concentrations in the range of 80 μg to 200 μg Ni^{+2} per gram of solution.[31,45,46] In addition, Zimmerman and Collé[12] performed several experiments to evaluate the quantitative transfer of all ^{63}Ni activity out of the 27-year-old solution storage ampoules, and to evaluate the possible presence of any residual ^{63}Ni in the emptied ampoules. There was no evidence to suggest that there was any "plateout" or adsorption losses onto the glass ampoules, or that the ^{63}Ni massic activity in the solutions was not maintained over the course of the 27-year storage periods.

The ^{63}Ni solutions were also radionuclidically very pure. They were independently examined for possible photon-emit-

ting impurities in both 1968[23,31] and 1984,[45] as well as recently in 1995.[42,45] Excepting a trace quantity of ^{110m}Ag (250-d half-life) observed in 1968,[23] no other impurities were detected. It was estimated that the ^{110m}Ag impurity would have had less than a 0.01% effect on the 1968 microcalorimetry data.[23] With subsequent decay to 1984 and 1995, the effect of this impurity becomes truly negligible. The effect of any other undetected possible impurity (at the lower limit of detection) on the 1995 LS spectrometry was estimated to be less than 0.004% (u_{18} Table 4).[42]

A concluding note on the post-1995 future

Despite the terminal, epitaph-looking title of this paper, the present chronology is not entirely complete. Efforts are currently underway to perform an international ^{63}Ni activity measurement intercomparison, which has a primary focus on the adequacy of LS spectrometry techniques. The participants in this intercomparison are undoubtedly among the premier radionuclidic metrology laboratories in the world. Hence, the findings of this intercomparison should be most interesting. One may reasonably anticipate that the findings will be wholly compatible with the past 27-year history of NBS/NIST calibrations and standards as summarized here. If this is indeed the case, then all surely will be sound within the realm of ^{63}Ni standardization. Should the intercomparison findings, however, be in substantial variance with that presented herein, then we will be faced with a most disconcerting dilemma. Any such dilemma, should it occur, will be exceedingly difficult to reconcile. It will require refuting, and consistently arguing against, at least some parts of the present congruence among: the admirable 1968 calorimetry data for SRM 4226; the results of the subsequent $4\pi\beta$ LS spectrometry on the standards SRM 4226, 4226B and 4226C; the presently accepted $E_{\beta(max)}$ and $E_{\beta(mean)}$ values for ^{63}Ni; the presently recommended $T = 101.1 \pm 1.4$ a

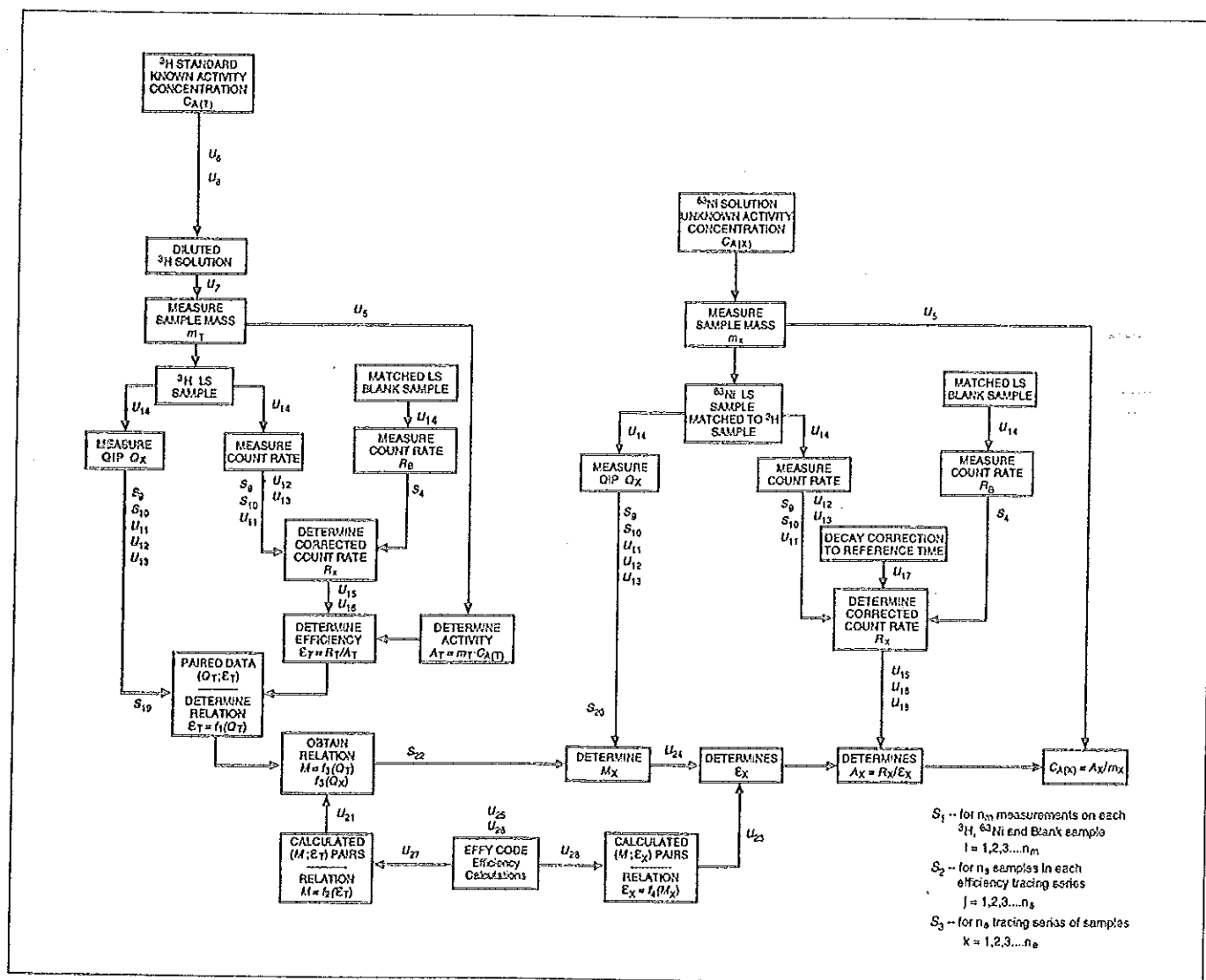**Figure 5** Schematic representation of the measurement process for $4\pi\beta$ LS spectrometry of ^{63}Ni with ^{3}H-standard efficiency tracing using the CIEMAT/NIST protocol, and component uncertainties (identified as the s_i and u_i quantities given in Table 4).

^{63}Ni half-life; and the extant protocol for $4\pi\beta$ LS spectrometry with ^{3}H-standard efficiency tracing as applied to the assay of ^{63}Ni. The above conditionals are obviously all highly interrelated and correlated as demonstrated herein.

Appendix

The CIEMAT/NIST efficiency tracing method for $4\pi\beta$ LS spectrometry

The acronym CIEMAT/NIST refers to the two laboratories that collaborated in developing the protocol for this LS spectrometry tracing methodology; *viz.*, the Centro de Investigaciones Energeticas, Medioambientales y Technologicas (CIEMAT) and the National Institute of Standards and Technology (NIST) which are the national metrological standards laboratories of Spain and the United States, respectively.

The CIEMAT/NIST method[47-50] is a protocol by which the $4\pi\beta$ LS counting efficiency for a sample of interest under known, varying quenching conditions is obtained by following

the efficiency of a closely-matched standard. Tritium (^{3}H) is selected to serve as the matched (in terms of sample composition and quenching) standard since extrapolations to the low-energy portions of beta-particle spectra are more sensitive than that obtained by using higher-energy β-emitting standards, e.g., ^{14}C.[41,48] As in other LS measurement procedures, the CIEMAT/NIST method also invokes a "figure of merit" parameter M to characterize the quenching and overall detection efficiency of the counting system. Despite that the quantity M has a unit of energy (keV), one must not erroneously interpret M to be the energy required to produce one photoelectron. Rather, the reciprocal quantity $1/M$ (in units of keV^{-1}) describes the number of photoelectrons striking the first dynode of the photomultiplier tube (PMT) per keV of a detected β^- particle.

For a given single β particle of energy E, the mean number n of photoelectrons striking the PMT is

$$n = E \cdot Q(E) \cdot W(E)/M \qquad (A1)$$

where $Q(E)$ and $W(E)$ are functions that give the fractional energies of E that are *not* lost due to secondary interactions (quenching) within the scintillator and to absorption losses outside the scintillator (i.e., in the LS vial walls), respectively. The numerator of eq. (A1) corresponds to the amount of the original energy E that is still available to produce photoelectrons, and represents the unquenched energy of that single decay event. Division of this remaining energy [eq. (A1) numerator] by M gives the mean number n, from which the LS detection efficiency for the single β of energy E may be derived.

The coincidence counting efficiency for the single β of energy E *above* some largely unknown detection threshold, for a two-PMT LS system, may be approximated by

$$\varepsilon(E) = (1 - e^{-n})^2 \qquad (A2)$$

which is the product of the definitionally-assumed[47] detection probabilities $(1 - e^{-n})$ for detection by each of the two individual PMT, assuming that the two PMTs are matched and have nearly identical "singles" efficiencies. This efficiency, however, still only applies to β events at energies greater than the apparent detection threshold. Extrapolations down to zero β energy are achieved in the CIEMAT/NIST method by employing matched ^{3}H standard samples having known overall detection efficiencies and through the use of the code EFFY4.[51] This program is a more recent and modified version of EFFY2 which has been described.[52,53]

The program, in addition to calculating approximations of the $Q(E)$ and $W(E)$ functions, calculates an overall, integral detection efficiency ε for a given M by first evaluating the number distribution (by energy) of β particles for a particular radionuclide (i.e., the shape of the β spectrum) by using the well-known differential Fermi distribution function $F(Z,E)dE$ (with appropriate shape factor corrections) for that radionuclide. This overall, integral detection efficiency for the given β emitter and for M is then simply the integral of the number-weighted efficiencies $\varepsilon(E)$ [Or conversely, the efficiency-weighted β spectrum number distribution since the numerator of eq. (A3) is the integral of the convolution of two distributions, that of $\varepsilon(E)$ and $F(Z,E)dE$.] normalized by the integral of the entire β spectrum from zero energy to the $E_{\beta(max)}$ endpoint energy, i.e.,

$$\varepsilon = \frac{\displaystyle\int_0^{E_{\beta(max)}} \varepsilon(E) \cdot F(Z,E)dE}{\displaystyle\int_0^{E_{\beta(max)}} F(Z,E)dE} \qquad (A3)$$

Inspection of eq. (A3) reveals that the denominator is just the total number of emitted β particles for the $F(Z,E)dE$ distribution from zero energy to $E_{\beta(max)}$; whereas the numerator corresponds to the probable number of β particles that are detected over the same energy interval and for the convolution of the detection efficiency $\varepsilon(E)$ distribution and $F(Z,E)dE$ dis-
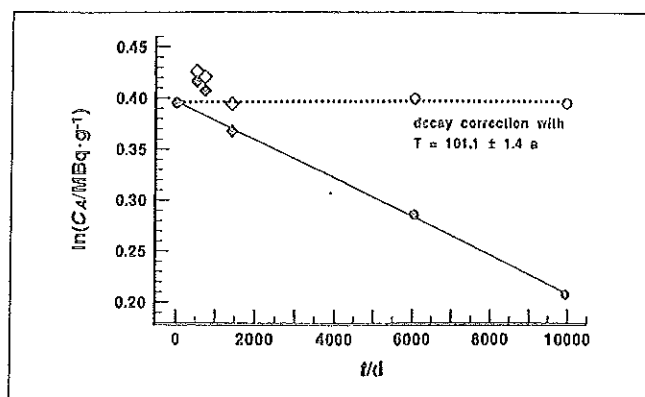
Figure 6 Comparison of all reported independent determinations of the ^{63}Ni massic activity C_A of solutions gravimetrically related to SRM 4426, 4426B and 4426C in units of MBq·g^{-1} as a function of the time of measurement t in units of days. The reference time $t = 0$ corresponds to that for SRM 4226 (27 May 1968). The closed and open symbols represent, respectively, the C_A values at their respective measurement times t and decay-corrected values obtained with an assumed half-life of $T = 101.1$ a. The horizontal broken line is the decay-corrected mean of the three NBS/NIST values (open circles). The solid curve is an exponential regression of the three NBS/NIST values and reveals a fitted ^{63}Ni half-life of $T = 101.06 \pm 1.97$ a.[1] The closed and open diamonds represent, respectively, the original and decay-corrected confirmation measurements by $4\pi\beta$-γ coincidence efficiency tracing.

tribution. The calculated efficiency ε is thus dependent on $E_{\beta(max)}$, the parameter M, and on the $Q(E)$, $W(E)$, and $P(Z,E)$ functions.

From a practical standpoint, the procedure consists of executing the EFFY4 code to obtain a table of M versus ε for all radionuclides involved in the study, including the ^{3}H standard used for tracing. For a series of samples and matched standards with varying quenching (and hence varying efficiency), one then experimentally determines the sample and standard counting rates (appropriately corrected for background, radioactive decay, dead-time losses, etc.) and some measure of the quenching conditions for each sample, typically through use of a given commercial LS spectrometer's "quench indicating parameter" *(QIP)*.[54] The efficiency of the ^{3}H standards is obtained from the observed counting rates and known activities, and corresponding values of M are obtained from the EFFY4-generated table. A functional fit of M versus *QIP* for the standards is then obtained. Since this $M = f(QIP)$ relationship is assumed to be independent of the radionuclide, it can be used to generate a set of M values for the samples using the sample *QIP* values. The efficiencies ε for the samples are then obtained from these M values using the EFFY4 table. For perfectly matched series of ^{3}H standards and samples (matched in terms of identical sample compositions), one could obviate the use of any *QIP* and go directly from the ^{3}H efficiency to M to the sample efficiency. In performing the EFFY4 calculations one

must be wary of the precision in the chosen calculational step sizes. Substantial interpolation errors (approaching several tenths of a percent on a relative basis) can occur, for example, if one interpolates by polynomial-functional regressions of ε versus M for insufficiently precise EFFY4-generated tables of data.

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