



⁶³Ni Half-Life: a New Experimental Determination and Critical Review

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The ⁶³Ni half-life has been determined to be 101.06 ± 1.97 a based on three independent measurements, conducted over the past 27 years, of the massic activity of gravimetrically-related ⁶³Ni sources. The ⁶³Ni assays were performed initially (in 1968) by microcalorimetry using an assumed mean β^- energy per decay, and subsequently (in 1984 and 1995) by $4\pi\beta$ liquid scintillation spectrometry with ³H-standard efficiency tracing. The present result is the first and only determination of the ⁶³Ni half-life which is based on actually following the radioactive decay of ⁶³Ni. All previously reported determinations were derived from specific activity evaluations. These earlier determinations have been scrutinizingly reviewed as part of this work. Some of these previous values can be revised in lieu of more recent nuclear data and on consideration of the experimental details. Based on a critical evaluation of the extant data set, a ⁶³Ni half-life value of $T = 101.1 \pm 1.4$ a is recommended. Copyright © 1996 Elsevier Science Ltd

Introduction

A well-known and uniformly accepted value of the half-life for the ground-state β^- decay of ⁶³Ni is of considerable interest and importance in radionuclidic metrology as well as for radiation protection surveillance around nuclear facilities. Generally, ⁶³Ni has great utility as a low-energy β^- calibration standard [1] because of the favorable combination of long half-life ($T \approx 100$ a) and low β^- endpoint energy ($E_{\beta(\max)} \approx 67$ keV). For example, ⁶³Ni was recently selected [2], for use in an international intercomparison, to evaluate liquid scintillation spectrometry techniques among principal national standardization laboratories. In more routine practicality, assays of ⁶³Ni are often performed because ⁶³Ni is a principal neutron-activation product of nickel, found at nuclear-power reactors and their environments. It is also one of the radioactive and chemically corrosive contaminants in high-level liquid-waste at nuclear-fuel storage and reprocessing facilities [3].

Unfortunately, the ⁶³Ni half-life has historically been very poorly known. Reported determinations over the past 45 years, have ranged over more than a factor of two ($T = 60$ a to $T \geq 125$ a). This disparity has been difficult to reconcile considering the presumed measurement uncertainties. Even the more recent 'precise' mass spectrometry-based, specific activity† measurements exhibit scant convergence to a central value, and have reported uncertainties that virtually do not overlap each other.

A critical review of the original determinations reveals that some of the earlier values can be revised in lieu of more recent nuclear data and on considering their experimental details. The revised values form a somewhat more consistent data set.

All previously reported ⁶³Ni half-life values were based on deriving the half-life T from independent determinations of the number of ⁶³Ni atoms (N) and ⁶³Ni 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 for the ⁶²Ni(n, γ)⁶³Ni 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 $2\pi\beta$ GM or proportional-counting activity measurements; and (2) determinations of N by mass spectrometry, and A by more sophisticated $4\pi\beta$ proportional counting, microcalorimetry, or $4\pi\beta$ liquid scintillation (LS) counting methods. None of the previously reported values is based on following the actual decay of ⁶³Ni by sequential activity measurements over time.

*The National Institute of Standards and Technology is an agency of the Technology Administration, U.S. Department of Commerce.

†The term 'specific activity', always given as an activity divided by a mass, is used in many contexts, ranging from the activity of a radionuclide per unit mass of the whole source material, to the activity per unit mass of the element, to the activity per unit mass of the radionuclide itself. This last definition is used throughout this paper so that the ⁶³Ni activity per unit mass of ⁶³Ni can be directly related to the ratio of the ⁶³Ni activity to the number of ⁶³Ni atoms.

Table 1. Previously reported determinations of the ⁶³Ni half-life *T* and revisions in units of years (a)

| Reference | Originally reported <i>T</i> /a | Method to determine ⁶³ Ni activity <i>A</i> | Method to determine ⁶³ Ni atoms <i>N</i> | Revised <i>T</i> /a | Revision basis |
|-----------------------------|---------------------------------|--|---|---------------------|---|
| Wilson [6] | 61 | 2πβ GM counting | neutron activation assuming σ = 14.8 b | 60 | σ = 14.5 b |
| Brosi <i>et al.</i> [7] | 85 ± 20 | 2πβ GM and proportional counting | neutron activation assuming σ = 14.8 b | 83 ± 20 | σ = 14.5 b |
| McMullen <i>et al.</i> [10] | 125 ± 6 | 4πβ proportional counting | mass spectrometry | 86 ± 9 | conjecture, mass spectrometry by 14.5/21 ^(a) |
| Horrocks and Harkness [17] | 91 ± 1.7 ^(b) | 4πβ liquid scintillation counting | mass spectrometry | 93.9 ± 2.0 | LS detection efficiency calculations (<i>E</i> _{β(max)} = 66.945 keV) |
| Barnes <i>et al.</i> [40] | 100.07 ± 2.0 ^(c) | microcalorimetry assuming <i>E</i> _{β(mean)} = 17.23 ± 0.04 keV | mass spectrometry | 101.21 ± 2.0 | <i>E</i> _{β(mean)} = 17.426 keV |

^(a)Revision most probably overcompensates. Refer to the text for discussion. The midpoint between the upper uncertainty limit on the originally reported *T* and lower uncertainty limit on the revised *T* is 104 a.
^(b)The uncertainty was originally reported as ± 3.1 a at a ‘95% confidence level’, and was reduced here by a factor of two to place it on a common (and presumed) one standard deviation uncertainty interval.
^(c)The uncertainty in *T* was originally reported as ± 2%, but its meaning is unclear (and unstated) as to whether this is a one standard deviation interval or some larger interval. The uncertainty in the activity *A* was reported to be ± 0.95% at a 99% confidence level (with a linear addition of ‘estimated systematic’ uncertainty components) which would correspond to a standard deviation of about ± 0.4% (with all uncertainty components combined in quadrature). The uncertainty in determining *N* was unreported.

Review of Previous ⁶³Ni Half-life Determinations

Early determinations

The earliest report of the ⁶³Ni half-life was given by Friedlander [4] in 1949 as ‘several hundred years’. This semi-quantitative estimate was part of work used to establish the original ⁶³Ni mass assignment from neutron-capture reactions on isotopically-enriched nickel sources, and was derived from rudimentary 2πβ activity measurements and an assumed 14.8 b cross-section [5] for the ⁶²Ni(n, γ)⁶³Ni reaction.

This, shortly thereafter in 1951, was followed by the determinations of Wilson [6] and Brosi *et al.* [9] (see Table 1). These were similarly derived from 2πβ activity measurements [6–9] and used an identical σ = 14.8 b cross-section. The cross-section may now be taken as σ = 14.5 ± 0.6 b.* Using this, the *T* = 61 a value of Wilson [6] may be trivially revised by the cross-section ratio 14.5/14.8 to give *T* = 60 a (see Table 1). The measurement uncertainty in the original *T* = 61 a value of Wilson [6] was unreported. Few details on the activity measurement conditions are available [7, 8]. Similarly, the Brosi *et al.* [9] value of *T* = 85 ± 20 a may be revised to 83 ± 30 a (see

Table 1). The ± 25 % or so uncertainty assessment of Brosi *et al.* [9] seems reasonable given the σ assumption, likely knowledge of the integrated neutron flux as determined from the ⁵⁹Co(n,γ)⁶⁰Co monitor reaction, and 2πβ GM counting [12] for the activity measurements.

Compared to subsequent determinations of *T*, both the Wilson [6] and Brosi *et al.* [9] values appear to be strikingly low which implies that their evaluations of *N* were underestimated or that their measurement results for *A* were too large. Reconstruction of sufficient experimental detail to account for possible under-evaluations of *N* is an unlikely enterprise. Any counting loss *per se* (such as those arising from counter dead time, source self-absorption and absorption by counter windows and air spaces, scattering from air and detector components, backscattering from source mounts, detection geometry, etc.) would have the opposite effect on *A*. Overcorrection for counting losses, however, which would result in a lower apparent overall detection efficiency, would certainly be possible and would account for a larger *A* value. Backscattering corrections alone, such as for the ‘weightless samples mounted on infinitely thick’ source mounts used by Brosi *et al.* [7], may range from 10 % to over 70 % [13, 14] and could have been seriously under- or over-estimated. The myriad of difficulties in low-energy 2πβ counting are such that accurate overall detection efficiencies were [13] and are very difficult to obtain.

One may rightfully conclude that these early determinations should carry scant weight in an evaluation of the ⁶³Ni half-life.

McMullen *et al.*

McMullen *et al.* [15] in 1956 were first to report a ⁶³Ni half-life determination based on ‘specific activity’

This σ value was derived by considering the tabulation given by the National Nuclear Data Center (NNDS) [10]. Excluding one value reported by McMullen *et al.* [15] (see subsequent discussion), 10 independently determined σ values were tabulated. They have a range from σ = 14.0 b to σ = 15.9 b (nine of the values ranged from σ = 14.0 b to σ = 14.8 b), a weighted mean of σ_w = 14.3 ± 0.2 b for eight of the values with reported uncertainties, and an unweighted mean of σ_m = 14.5 ± 0.6 b for all ten values. This value (σ = 14.5 b) agrees with that given in the most recent *Chart of the Nuclides* [11].

measurements. In retrospect, their value has the appearance of being a substantial 'outlier', and is the most unsettling value to try to reconcile. If this value is truly in error by perhaps +25 % then there must be a considerable error in either their measurement of A by $4\pi\beta$ proportional counting, or in their mass spectrometry-based measurement of N , or (less likely) in some peculiar combination of error in N or A .*

The activity measurements, particularly for such a low-energy β emitter, may on first appearances, be more suspect. Any unaccounted scattering or source self-absorption losses would, of necessity, have resulted in a smaller apparent activity and a larger apparent T value. However, the $4\pi\beta$ measurement methodology [16–20] used for this work is exemplary. One must recall that in this time frame (mid 1950s) 4π counting was probably the most widely employed method for activity standardization of β -emitting radionuclides [21], and it was this same research group with the same actors at roughly the same time that was largely responsible for establishing the definitive state-of-the-art for this methodology. Nevertheless, the relatively high overall detection efficiencies of about 91–94 % as reported by McMullen *et al.* [15] (obtained here by implication from comments in their paper) may be the culpable factor. In this same context, however, it is difficult to conceive of $4\pi\beta$ proportional counting efficiencies of only 70 % (to account for a hypothetical 25 % error in T) considering the excruciatingly careful source preparations and source self-absorption corrections employed by these researchers [1–20].

A possible clue to the origin of a 25 % error in T (if it exists) lies in their reported evaluation of the $^{62}\text{Ni}(n, \gamma)^{63}\text{Ni}$ cross-section which was also obtained from their mass spectrometric data. They obtained a value of $\sigma = 21 \pm 2$ b.† Inferentially, one could conjecture that their apparent σ substantially disagrees with the presently accepted

$\sigma = 14.5 \pm 0.6$ b (see previous footnote) because of an error in the mass spectrometry. In this case, one could further suppose that their apparent T value could then be revised by the cross-section ratio $14.5/21$ to give $T = 86 \pm 10$ a (see Table 1). The revised uncertainty in T given here (± 10 %) arises (somewhat arbitrarily chosen) from considering the uncertainty in the assumed $\sigma = 14.5 \pm 0.6$ b used for the normalization, and the originally reported uncertainties in the integrated neutron flux (± 9.3 %), activity measurements of A (± 0.7 to ± 1.8 %) and mass spectrometric measurements of N (± 4.6 %).

The above argument is not wholly compelling in as much as their cross-section measurement was dependent on the integrated neutron flux over the course of the irradiation whereas their determination of T was not. Almost any mass spectrometry result would be expected to be more accurate than any neutron flux determination. Nevertheless, the justification for the revision, although conjectural, is within the realm of reasonable feasibility. It can at least possibly account for the large apparent discrepancy in the ^{63}Ni half-life obtained by McMullen *et al.* [15]. The revision, if anything, probably overcompensates for any bias error since it ascribes all of the apparent +25 % error in T to the mass spectrometry result despite the fact that the observed $\sigma = 21$ b cross-section embodies a considerable uncertainty (at least ± 10 % or so) in the integrated neutron flux. Interestingly, the midpoint between the original $T = 125$ a and revised $T = 86$ a values is about $T = 106$ a which is in substantial agreement with subsequent determinations (see also footnote in Table 1). One cannot and should not make too much of this coincidental finding.

Horrocks and Harkness

In 1962, Horrocks and Harkness [22] reported a value of $T = 91.6 \pm 3.1$ a from mass spectrometry to determine N coupled with activity measurements by $4\pi\beta$ LS spectrometry. The reported uncertainty was revised as given in a footnote to Table 1. Based on their observed single to double-coincidence LS counting rates, as obtained with a commercial two-photomultiplier spectrometer, they derived a 'figure of merit' of $FM = 1.5$ keV (i.e. 'the energy required to be dissipated in the scintillator solution to produce on the average one electron at the photocathode' [23]‡; and thereby calculated, for a ^{63}Ni β^- endpoint energy of $E_{\beta(\text{max})} = 67$ keV, detection efficiencies of $\epsilon_s = 0.93$ and $\epsilon_D = 0.81$ for the observed extrapolated zero-bias integral singles and double-coincidence rates, respectively. The methodology used by Horrocks and Harkness [22, 23], although forefront work for its time, is rather simplistic in its treatment of the β spectral shapes to obtain extrapolated non-detection probabilities below any detection thresholds. More recent treatments [26–28] of non-detection probabilities in LS

*The word 'error' as used here does not refer to an estimated measurement uncertainty, but rather is used in the context of a disagreement with a 'true' or canonically known value.

†Curiously, they contended that this σ 'agrees quite well' with that ($\sigma = 14.8$ b) obtained by Pomerance [5] (a 42 % difference and well outside their respective uncertainty intervals), and concluded that the T value reported by Brosi *et al.* [9] could be revised to $T = 120$ a which would then be in 'excellent agreement' with their $T = 125$ a value. In actuality, a revision of Brosi *et al.* [9] using $\sigma = 21$ b would give $T = 121 \pm 28$ a for an increase by the cross section ratio $21/14.8$.

‡The concept of a 'figure of merit' in LS spectrometry is defined and used in a large variety of ways by various authors [24–28]. Great care, therefore, must be exercised in applying or interpreting a given LS figure of merit value. Practically, the figure of merit is a quantitative descriptor that is applicable for a given LS system (spectrometer, scintillator, sample composition, etc.) and that is normally relatable to the some quench indicating parameter of a given spectrometer.

measurements (that more rigorously account for low-energy β^- spectral shapes) demonstrate that the detection efficiencies reported by Horrocks and Harkness [22] may justifiably be revised. A slight digression is necessary to appreciate the revision justification.

The revision applied here is based in part on recent extensive studies of ^{63}Ni LS spectrometry which were carried out by Zimmerman and Collé [29, 30] using the CIEMAT/NIST* method of efficiency tracing with ^3H standards.

The CIEMAT/NIST efficiency tracing method [27, 28, 31–33] 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 (^3H) is selected to serve as the matched (in terms of sample composition and quenching) standard since extrapolations to the low-energy portions of beta spectra are more sensitive than that obtained by using higher β -emitting standards, e.g. ^{14}C [28, 33]. 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. 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

$$n = E \cdot Q(E) \cdot W(E) / M \quad (1)$$

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. (1) 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. (1) 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

$$\epsilon(E) = (1 - e^{-n})^2 \quad (2)$$

which is the product of the definitionally-assumed [27] 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 ^3H standard samples having known overall detection efficiencies and through the use of the code EFFY4 [34]. This program is a more recent and modified version of EFFY2 which has been described [35, 36].

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† $\epsilon(E)$ normalized by the integral of the entire β spectrum from zero energy to the $E_{\beta(\text{max})}$ endpoint energy, i.e.

$$\epsilon = \frac{\int_0^{E_{\beta(\text{max})}} \epsilon(E) \cdot F(Z, E) dE}{\int_0^{E_{\beta(\text{max})}} F(Z, E) dE} \quad (3)$$

*CIEMAT/NIST is an acronym that refers to the two laboratories that collaborated in developing the protocol for this ^3H -standard 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 U.S.A., respectively.

†Or conversely, the efficiency-weighted β spectrum number distribution since the numerator of Eq. (3) is the integral of the convolution of two distributions, that of $\epsilon(E)$ and $F(Z, E)dE$.

Inspection of Eq. (3) reveals that the denominator is just the total number of emitted β particles for the $F(Z, E)dE$ distribution from zero energy to $E_{\beta(\text{max})}$; 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 $\epsilon(E)$ distribution and $F(Z, E)dE$ distribution. The calculated efficiency ϵ is thus

dependent on $E_{\beta(\max)}$, the parameter M , and on the $Q(E)$, $W(E)$, and $F(Z,E)$ functions.*

Given the above, a revision of the Horrocks and Harkness [22] T value may thereby devolve from changing their calculated integral efficiency $\epsilon(^{63}\text{Ni})$ at their $FM = 1.5$ keV to what would be obtained by EFFY4 at this same figure of merit, or at some known ^3H efficiency. The former is hopeless to achieve.† Fortunately, Horrocks and Studier [23] provided an experimentally-determined ^3H efficiency under the same $FM = 1.5$ keV conditions that could be used for normalization. At $FM = 1.5$ keV, they gave an experimental $\epsilon(^3\text{H}) = 0.59$ and a calculated $\epsilon(^{63}\text{Ni}) = 0.81$. For the same $\epsilon(^3\text{H})$, EFFY4

provides $M = 1.040$ and $\epsilon(^{63}\text{Ni}) = 0.830 \pm 0.005$. The EFFY4 results were obtained using $E_{\beta(\max)} = 18.594 \pm 0.008$ keV for ^3H and $E_{\beta(\max)} = 66.945 \pm 0.004$ keV for ^{63}Ni [38]. The $\pm 0.6\%$ relative uncertainty in $\epsilon(^{63}\text{Ni})$ was obtained by assuming a $\pm 1\%$ relative uncertainty in $\epsilon(^3\text{H})$ as it propagated through the $dM/d\epsilon(^3\text{H})$ and $d\epsilon(^{63}\text{Ni})/dM$ sensitivity factors, i.e. $u_\epsilon(^{63}\text{Ni}) = u_\epsilon(^3\text{H}) \cdot [dM/d\epsilon(^3\text{H})] \cdot [d\epsilon(^{63}\text{Ni})/dM]$. The adequacy of the EFFY4 code in generating the $F(Z,E)dE$ β -particle distribution and its integration [whether efficiency-weighted by the $\epsilon(E)$ values or not] may be roughly appreciated by consideration of the code's evaluation of the mean energy $E_{\beta(\text{mean})}$ for the β -particle distributions. For the $E_{\beta(\max)}$ endpoint energies given, the EFFY4 code, after calculation of $F(Z,E)dE$ and applying a Simpson-rule numerical integration provides $E_{\beta(\text{mean})} = 5.71$ keV for ^3H and $E_{\beta(\text{mean})} = 17.43$ keV for ^{63}Ni ; compared to more exactly evaluated and presently 'accepted' values of $E_{\beta(\text{mean})} = 5.69 \pm 0.04$ keV for ^3H [38] and $E_{\beta(\text{mean})} = 17.426 \pm 0.013$ keV for ^{63}Ni [39].

The proposed change in the ^{63}Ni efficiency used by Horrocks and Harkness [22] from 0.81 to 0.830 (based on more rigorous treatment of the non-detection probability as a function of β spectral shape) results in a decrease in their apparent activity A measurement by a factor of $0.81/0.830$, and an increase in their reported half-life T by a factor of $0.830/0.81$ (see Table 1). The revised relative uncertainty in T is $\pm 2\%$, based on propagating in quadrature the relative uncertainty (as revised in Table 1) of $\pm 1.9\%$ in their originally reported T and the $\pm 0.6\%$ for the relative uncertainty $u_\epsilon(^3\text{H})$ in the revised $\epsilon(^{63}\text{Ni})$.

Barnes *et al.*

Barnes *et al.* [40] in 1971 reported on the preparation and calibration of ^{63}Ni solution standards in which the standardization was based on microcalorimetry using the so-called Peltier-effect 'radiation balance' [41]. The solution standards, obtained from a gravimetrically-determined dissolution and dilution of one of two irradiated ^{62}Ni -enriched target pellets, were disseminated by NIST as Standard Reference Material SRM 4226 in August 1969 [42]; and were reissued, with calculational revisions, as SRM 4226B in December 1984 [43]. The calorimetry results obtained from measurements of the two irradiated pellets, along with the mass spectrometry that was conducted as part of the work, allowed a new determination of the ^{63}Ni half-life T . The mass spectrometric data was also used to derive the $^{62}\text{Ni}(n,\gamma)^{63}\text{Ni}$ thermal neutron cross-section σ .‡

The microcalorimetry results for the 'energy emission rates' (*sic*) C_w , in units of microwatts per gram of nickel for the irradiated pellets or microwatts per gram of solution for the gravimetrically-prepared solution standard, were converted to massic activity§

*From a practical standpoint, the procedure consists of executing the EFFY4 code to obtain a table of M vs ϵ for all radionuclides involved in the study, including the ^3H 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, deadtime 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) [37]. The efficiency of the ^3H 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 vs 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 ^3H standards and samples (matched in terms of identical sample compositions), one could obviate the use of any QIP and go directly from the ^3H efficiency to M to the sample efficiency.

†The difficulties in comparing various LS 'figures of merit' become evident in noting that for identical experimentally determined $\epsilon(^3\text{H}) = 0.59$, the value from Horrocks and Studier [23] is $FM = 1.5$ keV; whereas that from Zimmerman and Collé [29] using EFFY4 is $M = 1.040$ keV. This occurs even though their descriptive definitions (energy required to produce one photoelectron at the PMT) are nearly indistinct. The two mathematically-implicit definitions are obviously quite different, and involve different assumptions on the non-detection probability.

‡As reported by Barnes *et al.* [40], the integral neutron flux for the irradiation was not determined in arriving at the $^{63}\text{Ni}(n,\gamma)^{64}\text{Ni}$ cross-section σ . Rather, they relied upon an internal monitor cross-section for the $^{62}\text{Ni}(n,\gamma)^{63}\text{Ni}$ reaction which was stated to be $\sigma_m = 15 \pm 2$ b as obtained from an unpublished communication (their reference number 11). Using this σ_m value and mass spectrometric data, Barnes *et al.* [40] obtained $\sigma = 23 \pm 3$ b which is in excellent agreement with a currently accepted value of $\sigma = 24$ b [10, 11]. As noted previously (see earlier footnote) the $^{62}\text{Ni}(n,\gamma)^{63}\text{Ni}$ monitor reaction cross-section may now be taken as $\sigma_m = 14.5$ b.

§The internationally preferred name for the quantity C_A , which is an activity divided by mass, is 'massic activity', commonly called an activity concentration [44]. By extension, the descriptor for the quantity C_w , which is a power (energy divided by time) divided by mass, is 'massic power'.

C_A , in units of $\text{Bq}\cdot\text{g}^{-1}$, using the mean β^- -particle energy $E_{\beta(\text{mean})}$ for the ^{63}Ni β^- spectrum, i.e. $C_A = (6.239 \cdot 10^9 \text{ keV}\cdot\mu\text{W}^{-1}\cdot\text{s}^{-1}) \cdot C_W/E_{\beta(\text{mean})}$. At the time, the ^{63}Ni β^- endpoint energy was taken as $E_{\beta(\text{max})} = 65.87 \pm 0.15 \text{ keV}$ [45] from which Schima [46] calculated $E_{\beta(\text{mean})} = 17.23 \pm 0.04 \text{ keV}$ for an allowed ($J^\pi = 1/2^- \rightarrow 3/2^-$) ^{63}Ni β^- decay transition. The ^{63}Ni massic activity for the solution standard was thus certified (at a presumed 99 % confidence level) as $C_A = (1.501 \pm 0.014) \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1}$ as of 27 May 1968 [40, 42]. The ^{63}Ni half-life T , as derived from their activity A measurements and with N from the mass spectrometric data, was given as $T = 100.07 \text{ a} \pm 2.0 \%$ [40] (see also footnote in Table 1).

The certified massic activity for the standard was confirmed by several independent determinations obtained at approximately the same time period (1969–1972) by three other laboratories using a $4\pi\beta$ - γ coincidence efficiency-tracing method [47–49]. The results of these confirmatory intercomparisons of C_A , having values that typically agreed to within ± 1 –2 %, have been summarized by Lowenthal *et al.* [49], Coursey *et al.* [33], and Mann and Unterweger [41]. The summaries of these comparisons, however, are confounded by different reference times used for the comparisons and by subsequent revisions in the microcalorimetry-based C_A for the solution standard, and attendant changes in the half-life T , due to changes in the accepted $E_{\beta(\text{mean})}$ for ^{63}Ni as applied to the original calorimetry data. Collé and Zimmerman [30] have more recently updated this comparison data using a consistent set of $E_{\beta(\text{mean})}$ and T revisions and reference times.

As noted above, 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 $E_{\beta(\text{mean})}$. A new ‘accepted’ value, from a compiled ENSDF evaluation, was taken to be $E_{\beta(\text{mean})} = 17.13 \pm 0.04 \text{ keV}$ which was computed on the basis of an allowed transition of maximum energy $E_{\beta(\text{max})} = 65.88 \pm 0.15 \text{ keV}$ [50]. Interestingly, this change in $E_{\beta(\text{max})}$ (and hence $E_{\beta(\text{mean})}$) was not based on any new measurements of the ^{63}Ni endpoint energy beyond that reported by Hsue [45], but rather was derived from the evaluated 1983 atomic mass table [51]. The revised value of C_A at the initial reference time was thus increased by the $E_{\beta(\text{mean})}$ ratio $17.23/17.13$ to give $C_{A(4226)} = 1.510 \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1}$ as of 27 May 1968; and T was decreased by $17.13/17.23$ to give $T = 99.49 \pm 2.0 \text{ a}$. The re-issued SRM 4226B was also decay corrected over 16.5 years using the revised $T = 99.49 \text{ a}$ ^{63}Ni half-life, so that C_A was given as $C_{A(4226B)} = (1.346 \pm 0.015) \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1}$ as of 1 December 1984 [43]. The $\pm 1.1 \%$ relative uncertainty in $C_{A(4226B)}$ given here 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 $E_{\beta(\text{mean})}$ (0.23 %), and ^{63}Ni decay correction (0.22 %) [43].

At roughly the same time in 1984, Coursey *et al.* [33] performed $4\pi\beta$ LS spectrometry measurements on gravimetric dilutions of the ^{63}Ni solution standards. Using the CIEMAT/NIST protocol for LS efficiency tracing with ^3H standards, they reported average C_A values that were systematically about 0.8 % smaller than that given by the microcalorimetry results (with the comparisons based on decay corrections for 16.5 years using the revised $T = 99.49 \text{ a}$). Appropriate revisions of these LS measurement findings, resulting from even further subsequent changes in $E_{\beta(\text{max})}$, $E_{\beta(\text{mean})}$, and T will be treated in the next section of this paper.

Since this time, two independent high-precision measurements of the ^{63}Ni β spectrum have been reported [52, 53]. These were performed with the Chalk River and University of Tokyo iron-free $\pi\sqrt{2}$ electron spectrometers. Their measurements for $E_{\beta(\text{max})}$ (with reported precisions ranging from 1 part in 3400 to 1 part in 22,000) have resulted in newly evaluated and presently assumed values of $E_{\beta(\text{max})} = 66.945 \pm 0.004 \text{ keV}$ [38] and $E_{\beta(\text{mean})} = 17.426 \pm 0.013 \text{ keV}$ [39].

With these values, the original ^{63}Ni half-life from Barnes *et al.* [40] becomes $T = 101.21 \pm 2.0 \text{ a}$ (see Table 1). Correspondingly, the original C_A value for the SRM 4226 must be revised to $C_{A(4226)} = 1.485 \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1}$ as of 27 May 1968. For consistency, the C_A value for SRM 4226B must be revised to $C_{A(4226B)} = 1.326 \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1}$ as of 1 December 1984 for a decay correction over 16.5 years with $T = 101.21 \text{ a}$. 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 $\pm 1.1 \%$, respectively) despite that these intervals were claimed to be at rather high 99 % or so confidence levels. Obviously, the estimated relative uncertainties on the assumed $E_{\beta(\text{mean})}$ values that were used to derive the C_A were underestimated in all cases.

Present ^{63}Ni Half-life Determination

The previously cited works of Barnes *et al.* [40], Coursey *et al.* [33], and Zimmerman and Collé [29] were used to derive, by inference, the present determination of the ^{63}Ni half-life T . The T value was obtained from their measurements (with appropriate revisions to place them on compatible bases), which virtually followed the decay of the ^{63}Ni massic activity, over the course of 27 years, of gravimetrically-related ^{63}Ni sources. Figure 1 schematically illustrates the various performed measurements and gravimetric relations among the ^{63}Ni sources that were used. The three individual measurement results are given with respect to that for the massic activity $C_{A(M2)}$ of solution M2 (see Fig. 1) at the respective measurement times.

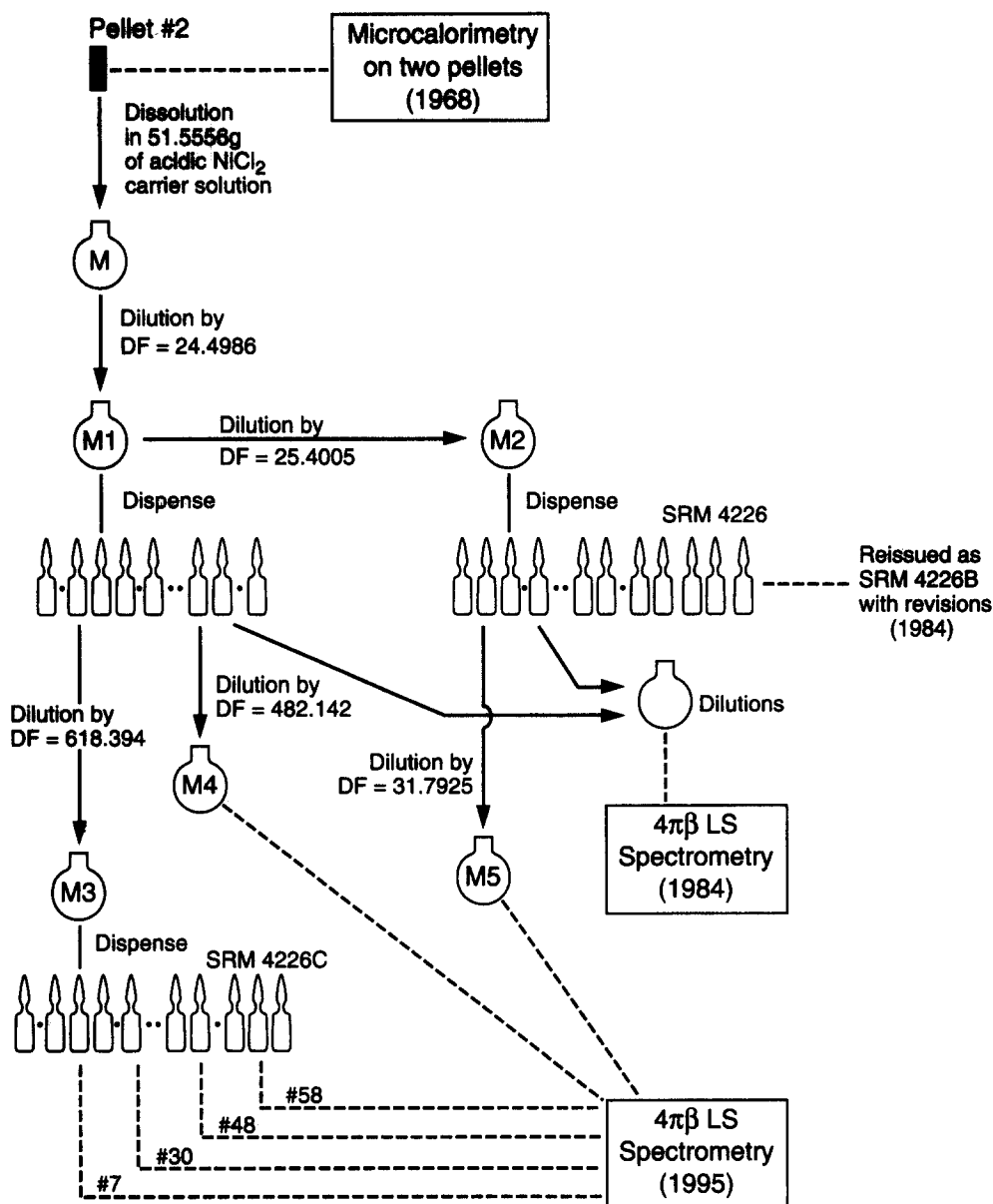


Fig. 1. Schema of the gravimetrically-related sources and measurements used to derive the ^{63}Ni half-life from decay over the course of 27 years of activity measurements. The origin and devolution of the ^{63}Ni solution standards issued by NIST in 1968 (SRM 4226), in 1984 (4226B), and in 1995 (4226C) is also illustrated.

1968 Microcalorimetry

The first measurement of the massic activity $C_{A(\text{M}2)}$ of solution M2 was obtained from the revised microcalorimetry standardization results of Barnes *et al.* [40] as certified for NIST SRM 4226 [42]. This value of $C_{A(\text{M}2)\text{I}} = 1.485 \cdot 10^6 \text{ Bq} \cdot \text{g}^{-1}$ as of 27 May 1968 was revised (as given herein) from the original reports [40, 43] due to a change in the assumed ^{63}Ni $E_{\beta(\text{mean})}$ from 17.23 to 17.426 keV. The relative uncertainty in this $C_{A(\text{M}2)\text{I}}$, for statistical weighting purposes only, is assumed to be about $\pm 0.5\%$ at a one standard deviation confidence interval [see also note (c) in Table 1].

The presently assumed ^{63}Ni $E_{\beta(\text{mean})} = 17.426 \pm 0.013 \text{ keV}$ [39] 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 [52, 53]. Thus, the revised microcalorimetry result given here for $C_{A(\text{M}2)\text{I}}$ is equally unlikely to undergo any significant future revision due to changes in the assumed ^{63}Ni $E_{\beta(\text{mean})}$. If anything, the cited uncertainty in $E_{\beta(\text{mean})}$ may at later times be adjusted to a more realistic, larger value.

1984 $4\pi\beta$ LS spectrometry

The second measurement of the massic activity $C_{A(\text{M}2)}$ of solution M2 was obtained from the $4\pi\beta$ LS spectrometry results of Coursey *et al.* [33] which

relied upon ^3H -standard efficiency tracing using the CIEMAT/NIST EFFY2 calculational protocol [35] (see prior discussion). 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 years. As noted previously, the LS measurement results of Coursey *et al.* [33], as of 1 December 1984, exhibited an apparent $C_{A(M2)}$ value that was 0.8 % smaller than the inferred microcalorimetry results as revised (as of 1984) and given in the original SRM 4426B certification [43].

This 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 $E_{\beta(\text{max})}$ for ^{63}Ni and ^3H used for the CIEMAT/NIST protocol efficiency tracing calculations, as well as differences in the calculations in going from using the EFFY2 code [35] to EFFY4 [34]. The change in codes primarily resulted in using improved numerical integration techniques in evaluating the number-weighted efficiency distribution $\epsilon(E) \cdot F(Z, E) dE$ and Fermi distribution $F(Z, E) dE$ integrals [see Eq. (3)].

The revision is as follows. We give that

$$C_{A(M2)II} = (0.9920 \pm 0.0029) \cdot C_{A(M2)CAL} \cdot [\Delta\epsilon_{LS}(^{63}\text{Ni})]$$

where $C_{A(M2)II}$ is the revised LS spectrometry result for $C_{A(M2)}$ as of 1 December 1984 (revised from the original $C_{A(M2)LS}$), where $C_{A(M2)CAL}$ is that for the calorimetry result as revised in 1984 for SRM 4226B, where $\Delta\epsilon_{LS}(^{63}\text{Ni})$ is an average correction in the efficiency-traced ^{63}Ni LS efficiency as obtained from recalculations using the EFFY4 code, and where the proportionality constant 0.9920 ± 0.0029 is the mean ratio of $C_{A(M2)LS}/C_{A(M2)CAL}$ from 26 efficiency traced LS sample measurements as originally reported by Coursey *et al.* [33]. The assumed calorimetry result used for the comparison was $C_{A(M2)CAL} = (1.346 \pm 0.015) \cdot 10^6 \text{ Bq} \cdot \text{g}^{-1}$ as of 1 December 1984 which was obtained from $C_{A(M2)CAL} = C_{A(4226)} \cdot (\Delta E_{\beta(\text{mean})}) \cdot D$, where $C_{A(4226)} = (1.501 \pm 0.014) \cdot 10^6 \text{ Bq} \cdot \text{g}^{-1}$ was the massic activity (as of 27 May 1968) as certified for SRM 4226, $\Delta E_{\beta(\text{mean})} = 17.23/17.13$ was the correction (applied in 1984) in changing the assumed $E_{\beta(\text{mean})}$ from 17.23 to 17.13 keV, and $D = 0.89131$ was a ^{63}Ni decay factor using a half-life $T = 99.49 \pm 2.0\text{a}$ for the 6032d decay interval from 27 May 1968 to 1 December 1984. The ^{63}Ni LS efficiency correction $\Delta\epsilon_{LS}(^{63}\text{Ni}) = 0.99582 \pm 0.00016$ was derived from the mean ratio $\epsilon_{LS}/\epsilon_{LS(\text{rev})}$, where the numerator ϵ_{LS} represents a given ^{63}Ni LS efficiency as originally calculated by Coursey *et al.* [33] using the EFFY2 code and an assumed ^{63}Ni $E_{\beta(\text{max})} = 65.88 \pm 0.15 \text{ keV}$, and where the denomi-

nator $\epsilon_{LS(\text{rev})}$ represents a corresponding ^{63}Ni LS efficiency as recalculated by Collé and Zimmerman [30] using the EFFY4 code and an assumed ^{63}Ni $E_{\beta(\text{max})} = 64.945 \pm 0.004 \text{ keV}$. 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 $\epsilon_{LS(\text{rev})}$ values. Further detail on this correction can be found in Collé and Zimmerman [30].

Thus, the second measurement of the massic activity of solution M2 is taken to be $C_{A(M2)II} = 1.3297 \cdot 10^6 \text{ Bq} \cdot \text{g}^{-1}$ as of 1 December 1984 which arises from the above revision of the originally reported $4\pi\beta$ LS spectrometry results of Coursey *et al.* [33]. The relative uncertainty on this measurement of $C_{A(M2)II}$, as will be used here for statistical weighting purposes only, is assumed to be about $\pm 0.7\%$ at a one standard deviation confidence interval.

As an aside, one may note that if the originally reported calorimetry result for $C_{A(4226)} = (1.501 \pm 0.014) \cdot 10^6 \text{ Bq} \cdot \text{g}^{-1}$ is corrected for the change in $E_{\beta(\text{mean})}$ from 17.23 keV (in 1968) to the presently assumed value of 17.426 keV, and if corrected for decay over 6032d (to 1 December 1984) using the revised calorimetry-derived ^{63}Ni half-life $T = 101.2 \pm 2.0\text{a}$; then, the corrected result $C_{A(4226)} = 1.326 \cdot 10^6 \text{ Bq} \cdot \text{g}^{-1}$ is lower than the revised LS measurement result $C_{A(M2)II}$ by only 0.2 % whereas it was originally reported [33] to be 0.8 % higher than $C_{A(M2)LS}$. Details of this finding are also given at length in Collé and Zimmerman [30].

1995 $4\pi\beta$ LS spectrometry

Zimmerman and Collé [29] 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. 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.* [40] and $4\pi\beta$ LS spectrometry of Coursey *et al.* [33] (see Fig. 1). The recent calibration was also based on $4\pi\beta$ LS spectrometry using the CIEMAT/NIST ^3H -standard efficiency tracing protocol, and included rigorous evaluations of multiple variable effects and potential sources of measurement uncertainty [29].

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 vs 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 $C_{A(M2)}$ of solution M2 through three gravimetric pathways, i.e. with solutions M3 and M4 through M1 to M2, and M5 to M2 (see Fig. 1);

(iv) employed matched ^3H and ^{63}Ni samples at two different LS cocktail total volumes, nominally 10–11 and 15 mL (although other volumes effects on the ^3H -standard efficiency tracing method were also independently studied at both smaller and larger cocktail volumes [54]);

(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 $\mu\text{g Ni}^+$ per gram of solution;

(viii) used cocktails that were quenched with varying quantities of both nitromethane (CH_3NO_2 , or 10 % solutions of CH_3NO_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 ^3H and ^{63}Ni) from 400 to over 2200 s⁻¹;

(x) incorporated measurements on sample cocktails ranging in 'age' from < 1 to nearly 90 days (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 ^3H 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 ^3H LS samples.

There were no significant differences in the efficiency traced measurements for $C_{A(M2)}$ 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

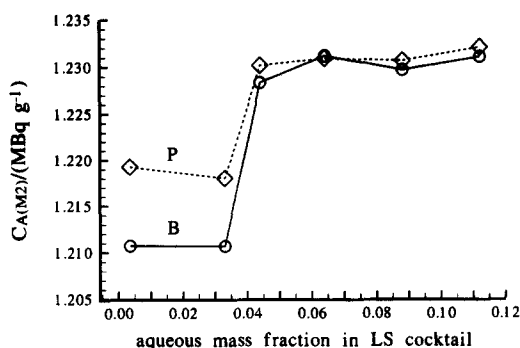


Fig. 2. Illustration of an effect of LS cocktail composition on the apparent ^{63}Ni massic activity of solution M2. The apparent ^{63}Ni massic activity $C_{A(M2)}$ in units of $\text{MBq}\cdot\text{g}^{-1}$ as measured in 1995 by $4\pi\beta$ LS spectrometry with ^3H -standard efficiency tracing is given as a function of the water content (and hence HCl and Ni^{2+} carrier content). The data are averages of results for $C_{A(M2)}$ on each sample of six samples as obtained from two efficiency-tracing curves for each spectrometer (labelled B and P). Refer to text for discussion.

portion, and scintillation fluid) was, however, critically important. Several examples may be invoked to demonstrate the invariance on most of the variables, and the dependence on cocktail composition. The results obtained from 17 efficiency tracing curves as obtained with one spectrometer (called B) with that obtained from 13 efficiency curves with the other (P) spectrometer had a ratio of B to P mean $C_{A(M2)}$ values of 0.9990 ± 0.0047 where the uncertainty here is the propagated standard deviation on the ratio of the two means. Similarly, the ratio mean $C_{A(M2)}$ values obtained using one scintillator (called R) compared to that for another scintillator (U) was found to be 1.0008 ± 0.0048 for 15 efficiency tracing curves with R and 11 curves for U. These two results average over many quenching and sample composition variables. The mean $C_{A(M2)}$ values as obtained from normalized measurements on the three dilutions were:

$$\text{from M3, } C_{A(M2)} = (1.2299 \pm 0.0004) \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1};$$

$$\text{from M4, } C_{A(M2)} = (1.2302 \pm 0.0005) \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1};$$

and

$$\text{from M5, } C_{A(M2)} = (1.2303 \pm 0.0010) \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1};$$

after applying the gravimetrically-determined dilution factors (see Fig. 1) and after normalizations to cocktail-composition-independent measurement results. The cited uncertainties here correspond to only the standard deviations of the mean for $\nu = 41$, 34, and 34 d.f. respectively.*

Sample age comparisons (ranging from ages of less than 1 day to 86 days) gave results that were indistinct (with maximum differences in the means of less than 0.4 %) even though the ^3H and ^{63}Ni LS counting rates over the same period had decreased by substantially greater percentages because of cocktail degradations. The complete measurement results obtained by Zimmerman and Collé [29, 30] for the calibration of SRM 4226C demonstrate many other

*A final certified ^{63}Ni massic activity for solution M3 as used for the standard SRM 4226C [55] and its associated uncertainty is not as yet available inasmuch as the NIST certification process has not been completed as of this date.

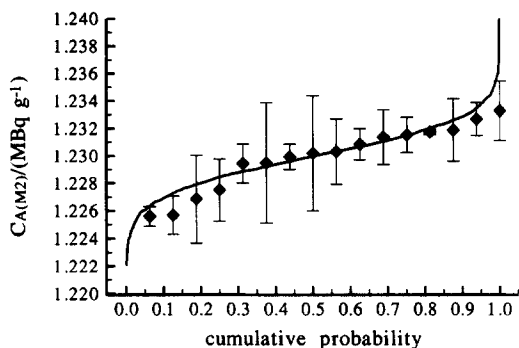


Fig. 3. Distribution of 16 determinations of the ^{63}Ni massic activity $C_{A(M2)}$ in units of $\text{MBq}\cdot\text{g}^{-1}$ as obtained in 1995 from $4\pi\beta$ LS spectrometry with ^3H -standard efficiency tracing. The solid curve is that computed for a normal distribution with $\mu = 1.2299 \text{ MBq}\cdot\text{g}^{-1}$ and $\sigma = 0.0024 \text{ MBq}\cdot\text{g}^{-1}$.

variable and condition invariances, such as for cocktail volume effects, for ^3H efficiency quenching ranges, and for certain select cocktail compositions.

Figure 2 illustrates one example of the effect of LS cocktail composition on $C_{A(M2)}$ as obtained from one sequence of six samples (prepared with varying quantities of water and scintillator to a constant volume of 10 mL) and as obtained from measurements with both the B and P spectrometers. The aqueous mass fraction in the samples range from about 0.35 % water to more than 11 % water. The corresponding acid and Ni^{2+} carrier content in the aqueous portion ranges from 1 to about $0.03 \text{ mol}\cdot\text{L}^{-1}$ HCl, and 100 to $3 \mu\text{g}$ Ni^{2+} per gram of water solution. It is quite evident that there is a relatively abrupt change in the apparent efficiency-traced massic activity at aqueous mass fractions around 4 % water (i.e. with about $0.2 \text{ mol}\cdot\text{L}^{-1}$ HCl and $20 \mu\text{g}$ Ni^{2+} per gram of water solution). The results shown in Fig. 2 were obtained from averaging the results from two efficiency tracing curves for each spectrometer (with 3–5 replicate measurements at sample ages of roughly 4–5 and 7–8 days for B; and 0.2–2 days and 6–7 days for P). For samples below about 4 % water the cocktails were clearly unstable which was evident from large decreases in the ^{63}Ni counting rates as a function of sample age and in large variations in the efficiency-traced massic activity. For samples above about 4 % water the efficiency-traced mean $C_{A(M2)}$ values are relatively constant with much smaller random variations about this constant $C_{A(M2)}$. Similar cocktail composition effects were also systematically studied and observed for other sample compositions [29, 30].

The ogive of Fig. 3 illustrates the results for $C_{A(M2)}$ that were obtained from 16 efficiency tracing curves which were not believed to have been substantially influenced by cocktail composition effects. Each datum in the figure was a grand mean value obtained from efficiency tracing with a series of matched samples prepared with one of the three scintillation fluids and measured with one of the two employed spectrometers (each sample being replicately

measured about 3–6 times over the course of a few days). The uncertainty intervals on the individual values (i.e. for each of the 16 efficiency tracing curves) are standard deviations as calculated from the means for each sample. The large differences in the magnitudes of the standard deviations largely reflect differences in the cocktail stability for the various cocktail compositions used. The unweighted mean of the 16 determinations is $C_{A(M2)} = 1.2299 \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1}$ with a standard deviation of $0.0024 \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1}$. The solid curve of Fig. 3 is a normal distribution computed with these values as estimates of the population mean μ and standard deviation σ . As indicated, the data are slightly skewed to lower values of $C_{A(M2)}$.

A weighted combination of the entire data set across all variables resulted in $C_{A(M2)III} = (1.2305) \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1}$ as of 15 August 1995. This value was taken as the third independent measurement of the massic activity of solution M2 that could be used for the present ^{63}Ni half-life T determination. As for $C_{A(M2)II}$, the relative uncertainty on $C_{A(M2)III}$, for statistical weighting purposes, was assumed to be $\pm 0.7 \%$ at a one standard deviation interval.

Decay of ^{63}Ni massic activity over 27 years

Figure 4 illustrates the decay of the ^{63}Ni massic activity $C_{A(M2)}$ over the course of the 27 year interval. A fitted half-life of $T = 101.06 \pm 1.97 \text{ a}$ was obtained using the following massic activity values, relative statistical weights, and relative decay times:

$$C_{A(M2)I} = (1.4846) \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1} (w_I \simeq 4) \text{ at } t_I = 0$$

$$C_{A(M2)II} = (1.3297) \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1} (w_{II} \simeq 2) \text{ at } t_{II} = 6032 \text{ d}$$

$$C_{A(M2)III} = (1.2305) \cdot 10^6 \text{ Bq}\cdot\text{g}^{-1} (w_{III} \simeq 2) \text{ at } t_{III} = 9941 \text{ d}$$

The statistical weights were obtained from $w = 1/s^2$ where the s values are the assumed relative one standard deviations given previously for each $C_{A(M2)}$ value.

The given T value was determined by fitting the exponential form of the decay equation $C_{A(M2)} = C_{A(M2)}^0 \exp(-\lambda t)$ to the data using a weighted non-linear χ^2 -minimized regression, where $C_{A(M2)}^0$ is

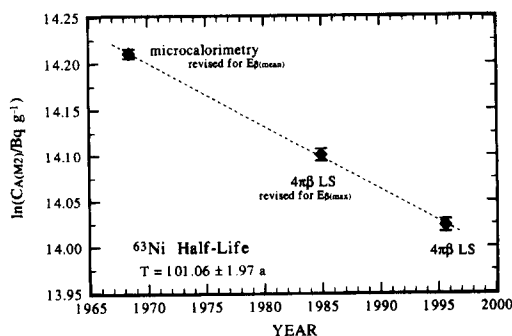


Fig. 4. ^{63}Ni half-life T as determined by three independent measurements of the massic activity C_A of gravimetrically-related sources over the course of 27 years. Refer to text for measurement value revisions and discussion.

the fit-determined intercept at $t = 0$ and where λ is the fitted decay constant given by $\lambda = (\ln 2)/T$. The result for T was converted to units of years using the factor 365.2422 calendar days per mean solar year (which is the conversion factor used throughout this paper). The residuals, on a relative basis, for the weighted fit were -0.12 , $+0.32$ and -0.20 %, respectively. The relative difference in T between the weighted fit given and from an unweighted fit of the exponential to the data was 0.09 %. The residuals for the unweighted fit were nearly comparable, but slightly poorer, than that for the weighted fit.

The validity of the present determination 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 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 $1.0 \text{ mol}\cdot\text{L}^{-1}$ HCl and they contained inactive nickel carrier cations at concentrations in the range of $80\text{--}200 \text{ }\mu\text{g Ni}^{2+}$ per gram of solution [29, 30, 42, 43, 55]. These concentrations correspond to Ni to ^{63}Ni atom ratios of about 6 for solution M1, about 160 for solution M2, and about 4300 for solutions M3, M4, and M5 (see Fig. 1). In addition, Zimmerman and Collé [29, 30] 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. The amount of long-lived ^{59}Ni (with a 76,000 a half-life) produced in the thermal neutron irradiation of the enriched nickel target may be estimated from the mass spectrometric data of Barnes *et al.* [40]. From the change in the ^{59}Ni isotopic abundance and the ^{63}Ni abundance after irradiation, one may infer that the atom ratio of ^{59}Ni to ^{63}Ni in the irradiated nickel was $N(^{59}\text{Ni})/N(^{63}\text{Ni}) = 0.0135$ which corresponds to an activity ratio of $A(^{59}\text{Ni})/A(^{63}\text{Ni}) = 1.8\cdot 10^{-5}$. The only known and observed impurity in the ^{63}Ni solutions was $^{110\text{m}}\text{Ag}$ (with a 250 day half-life). The activity ratio of $^{110\text{m}}\text{Ag}$ to ^{63}Ni was reported to be $A(^{110\text{m}}\text{Ag})/A(^{63}\text{Ni}) = 1.6\cdot 10^{-6}$ as of the 1968 reference time for SRM 4226 [42]. It was estimated that this $A(^{110\text{m}}\text{Ag})$ would have had less than a 0.01 % effect on the microcalorimetry data used to determine $C_{A(M2)}$. With subsequent decay to 1984 and 1995, the impurity ratios become $A(^{110\text{m}}\text{Ag})/A(^{63}\text{Ni}) < 10^{-13}$ for $C_{A(M2)\text{II}}$, and $A(^{110\text{m}}\text{Ag})/A(^{63}\text{Ni}) < 10^{-18}$ for $C_{A(M2)\text{III}}$. The solutions were also

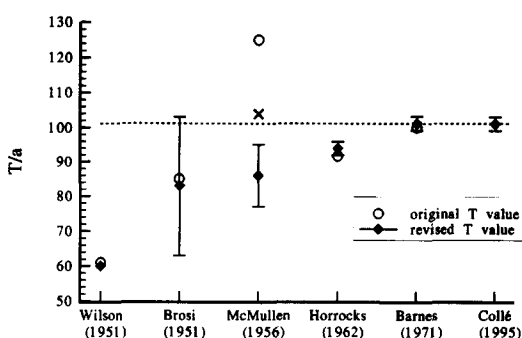


Fig. 5. Original and revised values of the ^{63}Ni half-life T in units of years (a) as obtained by six independent determinations. The revisions are given in Table 1 and discussed in the text. The cross (\times) for the McMullen (1956) result represents the midpoint between the upper limit of the originally reported T and the lower limit of the revised T value. The dashed line corresponds to the recommended value $T = 101.1$ a as given herein.

independently examined for possible photon-emitting impurities in both 1984 [43] and 1995 [29, 30]. None were detected. Lower limits L , in terms of the ratio of the number of photons emitted per second to the ^{63}Ni activity in units of Bq, at various energy regions, from the 1995 analyses [29, 30, 55] using high-resolution intrinsic Ge detectors were:

- in the region $12\text{--}88 \text{ keV}$, $L < 5\cdot 10^{-6}$;
- in the region $96\text{--}507 \text{ keV}$, $L < 2\cdot 10^{-6}$;
- in the region $515\text{--}1456 \text{ keV}$, $L < 8\cdot 10^{-7}$; and
- in the region $1456\text{--}1900 \text{ keV}$, $L < 3\cdot 10^{-7}$.

The reported limits from the 1984 analyses [43] using Ge(Li) and Si(Li) detectors were somewhat smaller, particularly at lower energy regions. These earlier results for the lower limits L , on present reconsideration, are now believed to have been underestimated.

As a final aside to this analysis, it should be noted that the data used for this determination of T could have been supplemented with the $4\pi\beta - \gamma$ efficiency tracing measurements on $C_{A(M2)}$ for SRM 4226 that were performed by Merritt and Taylor [47], Baerg and Bowes [48], and Lowenthal *et al.* [49] in the 1969–1972 time period. These results were not included since the present authors did not have recourse to examine the original measurement data, and since it was felt that their incorporation would unduly influence the decay curve by having a majority of measurements at only the initial few years of the 27 year decay time interval (and which would thereby virtually ‘fix’ the $t_i \simeq 0$ intercept with considerable variability). Nevertheless, it can be demonstrated that the inclusion of these data would have decreased the present fitted T value by less than about 5 % while increasing the uncertainty in the fitted T by over a factor of 3 (i.e. to $T \simeq 95 \pm 6$ a). Unlike other previous summaries of these $4\pi\beta - \gamma$ efficiency tracing results for measurements on SRM 4226 which tabulated the values by making decay corrections to common reference times with various assumed ^{63}Ni

half-life values [49, 33, 41], Collé and Zimmerman [30] tabulated the original values as obtained at their respective measurement times.

Evaluated ⁶³Ni Half-life

A comparison among the original and revised values for the ⁶³Ni half-life *T* that were previously reported (and reviewed herein), and with the new determination given in this work is illustrated in Fig. 5. As indicated, there is a good general convergence in the data, particularly amongst the last three determinations. Although the revisions of the previously reported *T* values form a more consistent data set, the remaining disparity is such that several different measures of central tendency should be considered.

The data naturally divide into two sub-groups: (i) the *first three determinations* which are considerably less reliable in that two of them were based on determinations of *N* by neutron activation yields and in that the third is the subjective and wholly conjectural revision of the McMullen *et al.* [15] result; and (ii) the *last three determinations* which are considerably more reliable in that the earlier two were based on mass spectrometric measurements of *N* and on only small revisions of *A* (which could be unequivocally justified on the basis of new information) and in that the sixth determination was obtained from actually following the radioactive decay of gravimetrically-related sources. The latter sub-group obviously must carry significantly greater weight in any evaluation.

Table 2 summarizes various measures of central tendency in *T*, for the two sub-groups of data values, as might be considered for an evaluated, and recommended, ⁶³Ni half-life. The uncertainty estimators *u* for the central tendency measures are defined in notes to Table 2. Beyond the obvious unweighted and weighted means, medians are also given to provide more robust estimators [56] for this evidently

Table 2. Various measures of central tendency and their uncertainties for an evaluated ⁶³Ni half-life *T* in units of years (a)

| | <i>T/a</i> | |
|--------------------------------|--------------------------|---------------------------|
| | for all 6 determinations | for last 3 determinations |
| Unweighted mean ^(a) | 87.8 ± 6.3 | 98.7 ± 2.4 |
| Median ^(b) | 90.9 ± 7.5 | 101.1 ± 0.2 |
| Weighted mean ^(c) | 99.4 ± 1.1 | 98.7 ± 1.2 |

^(a)The uncertainties given here for the unweighted means are standard deviations of the mean *s_{um}*. The corresponding standard deviations are $\sqrt{n \cdot s_{um}}$ where *n* is the number of determinations in each mean.

^(b)The uncertainty estimator for the median with *n* determinations $s_{med} = [\pi/2(n - 1)\alpha^2]^{1/2} \cdot MAD$ where *MAD* is the “median of the absolute deviations” from the median and where $[\pi/2(n - 1)\alpha^2]^{1/2} \approx 1.858/(n - 1)^{1/2}$ is a proportionality factor, evaluated by Müller [56], that normalizes the *s_{med}* estimate to that which would be obtained (in the limit of large sample sizes) for sampling from a normally distributed population.

^(c)The weighted means were obtained using weights of $w_i = 1/u_i^2$ where *u_i* is the assigned uncertainty on each of the *n* determinations. The associated weighted uncertainty is $s_{wm} = (1/\sum w_i)^{1/2}$.

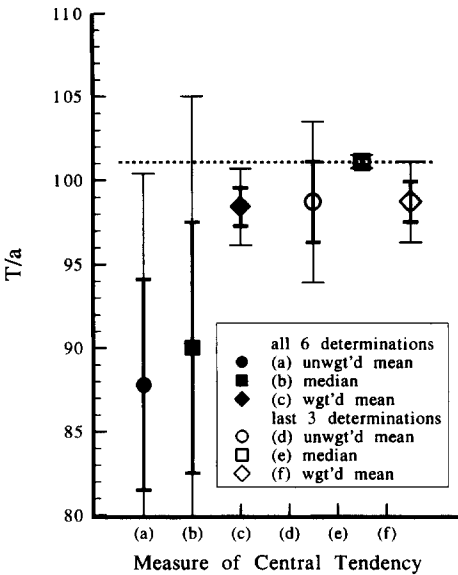


Fig. 6. Evaluated ⁶³Ni half-life *T* in units of years (a) as given by various measures of central tendency for the data set of six independent determinations. The value for the mean of the last two determinations *T* = 101.1 is recommended and is illustrated by the broken horizontal line. The two sets of upper and lower uncertainty interval bars correspond to one standard deviation (*s*) and two standard deviations (*2s*) on the respective measures of central tendency.

inconsistent data set. When the aggregate of these measures of central tendency (Table 2) are viewed in this way, however, they appear remarkably harmonious. This is more vividly demonstrated in Fig. 6. A ‘best available’ estimate of *T* may be taken to be the mean of the last two determinations: *T* = 101.14 a. As shown in Fig. 6, this value lies within the ± 2*u* uncertainty interval for nearly every central tendency measure given in Table 2.

The weighted mean of the Horrocks and Harkness [22] determination (as revised here by 2.5 %), the Barnes *et al.* [40] determination (as revised here by 1.1 %), and the present experimental determination is 98.7 ± 2.1 a (where the cited uncertainty is $\sqrt{3}$ times the associated weighted uncertainty *s_{wm}* = 1.2 given in Table 2). This *T* value is wholly consistent (statistically) with the mean obtained from using just the last two determinations, and could very well equally serve as a recommended, evaluated half-life for ⁶³Ni. We, however, opt to use only the last two determinations since they are in remarkably excellent agreement (considering the vastly different methodologies used for their determinations) and since the revision of the Horrocks and Harkness result was not entirely unequivocal.

Therefore, in consideration of all of the critical analyses given above, we recommend a ⁶³Ni half-life of

$T = 101.1 \pm 1.4$ a.

This value is based on the unweighted mean of the revised Barnes, *et al.* [40] microcalorimetry determi-

nation and the present experimental decay-curve result. The two results have essentially equivalent estimated uncertainties (about $\pm 2\%$) and thereby equal statistical weights. The standard deviation of the mean is 0.08 a (with a standard deviation of 0.11 a). The cited uncertainty on the recommended half-life is derived from the $\pm 2\%$ estimated uncertainty on either value which is reduced by a factor of $\sqrt{2}$ for the two independent determinations.

Discussion and Conclusions

For the past quarter century, virtually all authoritative compilations of radionuclidic half-life data have tabulated the ^{63}Ni half-life on the basis of a very limited evaluation. Invariably, these evaluated compilations have relied on: either some averaging of the originally reported T values of Horrocks and Harkness [22] ($T = 92$ a) and that of Barnes *et al.* [40] ($T = 100$ a); or, more prevalently in recent times, exclusively on the sole value given by the latter. Rarely, have any recent compilations made adjustments to the original findings as might be warranted by subsequent new information, e.g. changes in the ^{63}Ni β spectrum endpoint energy $E_{\beta(\text{max})}$ or its derived $E_{\beta(\text{mean})}$. Going slightly further back in time, one discovers that the ^{63}Ni half-life was usually considered to be whatever value was last reported. Relevant examples include the following evidence. The 1966 revision of the *Chart of the Nuclides* [57] and the 1968 edition of the *Table of Isotopes* of Lederer *et al.* [58] both reported $T = 92$ a which was obviously taken in whole from Horrocks and Harkness [22]. Earlier editions of the *Chart* and *Table* literally tracked the reports of Wilson [6] ($T = 61$ a), Brosi *et al.* [7] ($T = 85$ a), and McMullen *et al.* [10] ($T = 125$ a). Following the reported result of Barnes *et al.* [40] ($T = 100.1$ a) in 1971, tabulations typically used an average of this value and that of Horrocks and Harkness [22]. In 1978, for example, ENSDF [59] tabulated $T = 96 \pm 4$ a which is the exact mean and median of these two reports, and the uncertainty appears to have been chosen to envelope both values. Since then, tabulated values tend to rely more on that given by Barnes *et al.* [40]. Currently compiled values include $T = 100$ a from the currently-available, but now-dated *Table of Isotopes* of Lederer *et al.* [60]; $T = 100$ a from the current *Chart of the Nuclides* [11]; $T = 100.1$ a in the 1991 update of *Nuclear Data Sheets* [61]; and $T = 100.1 \pm 2.0$ a in the French CEA compilation [62]. Up until recent communications of a few weeks ago by Schima [46] and others of this laboratory—who pointed out the inconsistency between using a new ^{63}Ni $E_{\beta(\text{max})}$ (from recent precise electron spectrometer measurements [52, 53]) and retaining the Barnes *et al.* [40] T value (which is directly dependent on the assumed $E_{\beta(\text{mean})}$)—the ENSDF compilation [38, 39] similarly tabulated $T = 100.1 \pm 2.0$ a.

The $T = 101.06 \pm 1.97$ a value, as experimentally determined in this work, is a significant addition to our current knowledge of the ^{63}Ni half-life. It largely confirms the revised values of Horrocks and Harkness [22] and Barnes *et al.* [40] (but only if their values are appropriately revised for current beliefs, e.g. for the ^{63}Ni β spectrum endpoint energy $E_{\beta(\text{max})}$). And secondly, it does so by determining the half-life from radioactive decay data as opposed to relying exclusively on the earlier specific-activity measurement determinations.

It is hoped that the critically evaluated, and recommended, ^{63}Ni value given here

$$T = 101.1 \pm 1.4 \text{ a}$$

which is based on the foregoing exhaustive analyses will be considered and adopted.

This study should also provide sufficient motivations for other researchers to perform more rigorous (and moreover, well documented) 'absolute' (*sic*) determinations of source-tractable radionuclidic activities so that other relatively long-lived radionuclidic half-lives may be revealed by measurements of decay over long time periods. After all, the science of radioactivity is 100 years old!

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