RADIOANALYTICAL CHEMISTRY

Radionuclidic standardization by primary methods: An overview

R. Collé*

Physics Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899-8466, USA

Primary methods of radionuclidic standardization serve as the underlying basis of the physical measurement standards of activity that are needed in virtually every sub-discipline of radioanalytical and nuclear chemistry. Primary methods refer to the direct measurement of the number of nuclear transformations that occur per unit time, without recourse to other calibrations or standards. Such measurements, leading to the development and dissemination of radioactivity standards, are primarily performed under the purview of national metrology laboratories, like the National Institute of Standards and Technology (NIST) in the USA. This paper briefly reviews some of the various primary methods that have been developed by many such laboratories over many years. Their features and their role in ensuring the quality of radioactivity measurements are highlighted by several primary standardizations that have been recently performed at NIST.

Introduction

The availability of radionuclidic standards, through development and dissemination, is essential for performing accurate measurements in many application areas and disciplines involving radioactivity. These include, amongst others, the measurements needed and used for pure research on nuclear decay and reactions, for radioecological and geochemical studies, for environmental monitoring, for quality control of radiopharmaceuticals in production and administration, and for the assay of special nuclear materials in the nuclear-power and -weapons industries. These measurement standards are principally used for calibrating instruments that are used to measure radioactivity and for the monitoring of radiochemical procedures. Most standards are (or at least should be) traceably linked to national standards and to international measurement compatibilities. As a result, primary methods of standardization[1] are at the summit of the traceability hierarchy that is needed to ensure that all radioactivity measurements performed worldwide are compatible and accurate. Within the United States of America (USA), the National Institute of Standards and Technology (NIST) is the nation's metrology laboratory and is the highest authority within the USA for assuring the compatibility and quality of physical measurements. The national basis for accurate radioactivity measurements is established by NIST through a variety of mechanisms, all of which relate back to our ability to perform primary radionuclidic standardizations; namely, the realization of the becquerel for specific radionuclides. This in turn requires traceability to the System International (SI)[2] units of frequency, time, mass (and sometimes length).[3] The mechanisms utilized by NIST to assure high quality radioactivity measurements in the USA include: developing unique national standards and primary measurement methods; disseminating suitable transfer standards, e.g., the present suite of Standard Reference Materials (SRMs)[4] that are linked to national standards; establishing and providing calibration services; conducting measurement proficiency and traceability testing programs; and participating in measurement comparisons with the national metrology laboratories of other nations to ensure international consistency, often organized under the aegis of the International Bureau des Poids et Mesures (BIPM).

The national metrology laboratories of other nations use very similar mechanisms. There are approximately thirty such laboratories and institutes world-wide that routinely perform primary radionuclidic standardizations. Most of these National Metrology Institutes (NMI) participate in the activities of the International Committee for Radionuclide Metrology (ICRM).

Standardization needs

It is important to recognize the great diversity of radionuclides that require standardization because calibration standards are needed for many different purposes. COLLÉ[5] recently gave a brief historical overview of the vast changes that have occurred over the past decades.

NIST was involved in making radioactivity standardization measurements and calibrations since 1914, on the arrival of the first international radium standard.[6] Over the following years, NIST prepared, calibrated, and disseminated standards of nuclides in the three naturally-occurring series (headed by ^{238}U, ^{235}U, and ^{232}Th) in the form of various materials, minerals, ores, and solutions.

* E-mail: rcolle@nist.gov

With the advent of controlled nuclear fission in the late 1940s and early 1950s, the need for many other radioactivity standards became manifest because of the consequential production and widespread use of man-made radioactive materials from both reactor and accelerator operations.[7] The availability of suitable standards for industry, medicine, and research became essential for these increasingly important applications of radioactive materials. The first of these standards were for radionuclides that for the most part are obvious and familiar: ^{3}H, ^{14}C, ^{22}Na, ^{24}Na, ^{32}P, ^{55}Fe, ^{60}Co, ^{65}Zn, ^{90}Sr, ^{131}I, ^{137}Cs, ^{198}Au, ^{204}Tl, and ^{210}Po. During this period, only two laboratories in the world, the National Physical Laboratory (NPL) in the UK and NIST in the USA, were producing and distributing radioactivity standards in quantity and in variety. These two laboratories, under the aegis of the International Commission on Radiological Units (ICRU) and along with the Canadian National Research Council laboratory at Chalk River prepared the necessary samples and began to conduct informal measurement comparisons with the metrology laboratories of all interested countries, in which standardization activities soon proliferated. This was the start of radioactivity measurement comparisons on an international basis for radionuclides other than radium. The success of the effort for over a decade led to recognition, in 1963, that the comparisons should be more formalized and that the proper repository for coordination of these international activities was the BIPM in Sèvres, France.

The 1970s ushered in what can be thought to be a modern era for standards, which followed a number of systematic "needs" studies[8–10] that identified the increasing demand for standards in more and more rapidly growing areas of application – particularly for radiopharmaceutical and environmental measurements. This resulted in collaborations between NIST and users in various measurement communities in establishing "traceable" measurement systems, involving secondary laboratories, measurement quality assurance (MQA) programs, proficiency testing, and the development of a wider array of SRMs. A joint program[11] with the forerunners of the Nuclear Energy Institute (NEI) is the oldest and perhaps the most important of these inasmuch as it became a NIST hallmark MQA program upon which many others were modeled. This program provides SRMs of very short-lived nuclides for nuclear medicine quality control that are not likely to be otherwise available. These radiopharmaceutical standards are distributed not only to NEI participants, but are also made available at select announced times to the general public. They (with their approximate half-lifes) include: ^{125}I (59 d); ^{131}I (8.0 d); ^{133}Xe (5.2 d); ^{67}Ga (3.3 d); ^{201}Tl (3.0 d); ^{111}In (2.8 d); ^{99}Mo (2.7 d); ^{90}Y (2.7 d); and ^{99m}Tc (0.25 d).[4]

The emergence of another new and novel aspect of radioactivity standards occurred in the late 1970s, viz., the development of natural matrix SRMs.[12] Based on an evident need, identified by the worldwide low-level environmental measurement community, NIST initiated a program to produce standards of radionuclide-bearing sediments, soils, and biological materials that were collected from natural sites. These natural matrix SRMs consist of ground, homogenized powders that are characterized for as many as 20 radionuclides at environmental activity levels. They are intended to be used as "real" samples that can evaluate radioanalytical methods and test a laboratory's capability of performing environmental radioactivity measurements in similar matrices at low levels. Uniquely, the calibration measurements leading to certification for these standards are obtained in cooperation with other highly experienced national and international environmental measurements laboratories. The natural matrix SRMs currently or soon to be available are: Columbia River Sediment; Human Lung; Human Liver; Rock Flats Soil #2; Freshwater Lake Sediment; Peruvian Soil; Ashed Bone; Ocean Sediment; Ocean Shellfish; and Seaweed.[4]

As reflected in these developments, there are many needs for radionuclidic calibration standards that require primary standardizations.

Methods of primary standardization

The distinction between primary, or direct, methods of radioactivity standardization and other measurement methods has been previously addressed and clarified.[13,14] As noted above, the main idea is that, generally, no other radioactivity standard or calibration is used to determine the "efficiency" for a detection instrument. Rather, a direct measurement is made by relating a determined number of radioactive transformations to the absolute unit of time, without recourse to the use of another radioactivity calibration or standard. The methods, of necessity, generally involve assumptions and model dependencies, as well as corrections of some sort.

A large variety of different and very specific methods have been developed over the past 60 years. The choice of method is often dictated by the decay scheme of the nuclide of interest and the emitted radiations that are to be detected. The proceedings of the biennial meetings[15] of the ICRM (the 16th of which was held in 2007) are filled with papers devoted to the development of these primary standardization methods by many international laboratories. One of the best and most recent reviews of primary methods of activity standardization is that of POMMÉ.[16] An earlier work by HOPPES[17] reviewed and gave short descriptions of the various methods in use at NIST, which involved the use

of nearly twenty different detection systems that were employed for the primary standardization of 79 different radionuclides.

In most texts covering radioactivity measurements, the methods are usually divided and discussed in terms of the detection method or type of detector and the kinds of radiation to be measured (e.g., alphas, betas and electrons, gammas and other photons, etc.). Primary methods, in contradistinction, – largely following POMMÉ[16] – can be divided into three main classes, irrespective of the detector type, radiations detected, or the detection method. These are:

(1) *high-geometry methods*, e.g., 4π or 2π proportional counting of particles,[18–20] internal gas counting with length-compensated tubes,[21–23] $4\pi\gamma$ counting with large NaI(Tl) or CsI(Tl) sandwich detectors,[24–26] liquid scintillation (LS) counting,[27,28] and both classical[29,30] and cryogenic[31,32] calorimetry;

(2) *defined-solid-angle methods*[33,34,20] that use strictly controlled geometric constructions incorporating a large variety of detectors with known detection efficiencies, e.g., the 0.8π Robinson counter;[35] and

(3) the classical *coincidence counting methods*,[36–38] including the variants of anticoincidence, sum-peak, and correlation counting, and the LS-based triple-to-double-coincidence ratio (TDCR) method.[28]

Time and space restrictions on this paper preclude the inclusion of a more complete bibliography and limit the details that can be given on the principles and practices involved with the various methods. Most of these can be found in the previously cited works of MANN et al.,[14] POMMÉ,[16] and the NCRP handbook.[13] It is equally important to recognize how diverse and specialized many of the methods are, as noted by HOPPES.[17]

The principles behind the high geometry methods are fairly self-explanatory. If one counts with high geometry, without any substantial losses, then the detection efficiency is very close to 100%. The small differences from 100% are usually accounted for by appropriate loss corrections. The corrections are often based on empirical extrapolations or on the use of Monte-Carlo-based radiation transport codes.

The defined solid-angle techniques are similar to the high-geometry methods, except that the fraction of detected events is largely determined by the use of restricting apertures to accurately define the solid angle for detection. There are restrictions on the use of the method, particularly for electron counting, as noted in the references cited above.

The various coincidence counting techniques employed for measuring cascade radiations are probably the most powerful and often used standardization methods. Which particular technique is used and what types of detectors are employed wholly depends on the decay scheme of the radionuclide of interest. Many

variations, using coincidence, anticoincidence, and summing of the cascades, have been successfully performed. As covered simply in many texts, the method relies upon detecting two cascade radiations (e.g, β-γ, γ-γ, x-γ, γ-e, etc.) each with some unknown efficiency, and with a simultaneous (coincident) measurement of both radiations (having a coincident efficiency that is the product of the two separate efficiencies), the activity can be inferred from the solution of the equations with three unknowns (the two efficiencies and the activity). This is a very simplistic picture and most realistic measurements require various kinds of corrections and extrapolations to 100% efficiency.

There are two well known special exceptions when other standards are used in what are still considered to be primary methods. The first is the use of another well-characterized nuclide (e.g., ^{60}Co to standardize ^{99}Tc)[39] that is measured simultaneously with the one of interest. In this case, the ^{60}Co is calibrated by $4\pi\beta$-γ anticoincidence counting to trace the self-absorption of ^{99}Tc in the same system with the same mixed sources. The second is the use of ^3H standards in the "primary" LS-based method known as the CIEMAT/NIST efficiency tracing (CNET) method,[28] in which the beta detection efficiency of some other radionuclide of interest, under known, varying quench conditions, is obtained by following the efficiency of closely-matched ^3H standard cocktails. The underlying model used for the CNET method is similar to that used for the LS-based TDCR method, in which the detection efficiency for some radionuclide is calculated from the measured triple- and double-coincidence count rates.[28,40] Both the CNET and TDCR methods require use of beta spectra and efficiency calculations. Computer codes used to perform these calculations have been developed by many laboratories.

Highlights of some recent standardizations (as examples)

Features of some of these methods can be highlighted through several recent primary standardizations that have been performed over the past three years (2005–2008) at NIST. The examples were chosen to reflect different situations and varying levels of complexity.

Determinations of the activity for low and medium energy beta emitters and for nuclides that decay by pure, low-Z (atomic number) electron capture (EC) to the ground state of their daughters are amongst the most difficult within the realm of radionuclidic standardization. These nuclides are often used as test cases for evaluating measurement proficiency in international comparisons.[41] Primary standardizations for four such nuclides, ^{63}Ni, ^{55}Fe, ^{210}Pb, ^{241}Pu, have recently been completed.

Nickel-63

The results for ^{63}Ni, a pure medium-energy beta emitter, have been reported by COLLÉ et al.[42] Two independent LS-based standardization techniques were performed, viz. the CNET and TDCR methods (see above). The latter method was used by both NIST as well as another collaborating metrology laboratory, the Laboratoire National Henri Becquerel (LNHB) in Saclay, France. The measurements were performed on ^{63}Ni solutions linked to NIST standards (SRM 4226D).[4] The CNET measurements were performed at NIST using three different commercial LS counters and a tracing protocol identical to that used for many previous standardizations.[41] The three LS counters have considerably different operating characteristics which help to ensure that any standardization results are independent of the instrumental conditions. The TDCR measurements were made using custom-built TDCR spectrometers at NIST[43] and at LNHB.[44] All three results, as seen in Table 1, were in good agreement within their measurement uncertainties (typically having a $k = 1$ relative combined standard uncertainty of 0.3% for the TDCR values and 0.6% for the CNET). This work not only demonstrated that the two primary standardizing laboratories were in excellent agreement, but also that both primary methods were comparable, although the CNET method had larger uncertainty and was considered to be inherently inferior. This work was part of a nearly 40-year effort to verify the consistency of the ^{63}Ni half-life obtained from decay with a half-life value obtained from earlier specific activity measurements. It was also used to confirm that all of the various series of ^{63}Ni solution standards disseminated by NIST over the past 40 years are internally consistent with past and recent standardizations.

Iron-55

Another difficult nuclide to standardize is ^{55}Fe, which decays by pure EC and emits only very low energy X-rays and Auger electrons (<6.5 keV). A primary standardization of it by isothermal microcalorimetry, initiated in 2004, was completed in 2006. A detailed monograph on calorimetry that includes the results of this standardization is still in preparation.[45] For this work, a specially-fabricated solid 30 GBq source of ^{55}Fe was prepared and gravimetrically linked to an ^{55}Fe master solution. Refer to Fig. 1. The calorimeter and the standardization procedures used for these measurements are described in detail by COLLÉ.[30] Many replicate trials of coupled background baseline and inserted source determinations were required to obtain a precise average power. Thirteen independent insertion trials were performed, and independent SI-traceable power (energy per unit time) calibrations were performed for each trial. The calorimetric power result was converted into an ^{55}Fe activity through use of an assumed average energy per decay. This activity for the source was in turn linked to the master solutions. This standardization was used as a basis for certifying a new ^{55}Fe solution standard (SRM 4929F)[4] as well as for measurements of a BIPM-distributed ^{55}Fe solution that was part of an international measurement comparison. The calorimetrically-standardized master solution was linked to the SRM and BIPM-intercomparison solutions by comparative LS measurements (Fig. 1), which involved the determination of 776 activity ratios as obtained with 44 matched cocktails using three different scintillators and as measured in three LS counters over a period of 97 days. This level of effort is typical. The calorimetric master solution was also compared to standardizations by LS TDCR methods performed at both LNHB and at the Polatom laboratory in Otwock-Swierk, Poland (Table 1). The combined standard uncertainty ($k = 1$) on the primary calorimetric-based standardization is 0.39%. The overall expanded uncertainty ($k = 2$) on the recently issued SRM is 1.7%, whereas that reported for the measurements on the BIPM-intercomparison solution was 0.68% (at $k = 1$). The relatively larger uncertainties were due to the LS imprecision that resulted from the low ^{55}Fe LS efficiency. The calorimetrically-based standardization of the BIPM solution was in agreement (Table 1) with the weighted mean value obtained from 15 other metrology laboratories to within 0.4% and differed from the unweighted mean by less than 0.1%.[46] Prior to this standardization, recent calibrations of ^{55}Fe performed by NIST had uncertainties ($k = 2$) in excess of 4%.

Table 1. Summary of some recent NIST primary standardizations and comparison to confirmatory measurements

Nuclide	Method	Relative standard uncertainty, %	Confirmatory measurement	Difference, %
^{63}Ni	4πβ LS TDCR (NIST)	0.16	4πβ LS TDCR (LNHB)	−0.31
			4πβ LS CNET (NIST)	−0.77
^{55}Fe (NIST)	4π calorimetry (linked by LS)	0.39	4π LS TDCR (Polatom)	−0.87
			4π LS TDCR (LNHB)	−0.43
^{55}Fe (BIPM)	4π calorimetry (linked by LS)	0.39	Weighted mean value of 15 NMI labs	−0.37
^{210}Pb	4παβ LS CNET	1.2	4παβ(LS)-γ(NaI) anticoin. counting	+0.7
			^{210}Po a spect. (102 a ^{209}Po tracer)	−3.0
			^{210}Po a spect. (^{128} a ^{209}Po tracer)	−1.3
			HPGe photon spect.	+4.7
^{241}Pu	4πβ LS CNET	1.9	LS (^{241}Am ingrowth)	+1.2
			4πβ LS TDCR (NIST)	−7.9*
			4πβ LS TDCR (LNHB)	−7.7*
^{210}Pb	4παβ LS CNET	1.2	Compare to NPL standard (5 methods) see Table2	−0.3
^{90}Sr	4πβ LS TDCR	0.51	4πβ LS CNET	+0.09
^{241}Am	4πα LS	0.22	4πα LS (independent)	−0.05
			4πα LS (independent)	−0.01
				−0.15
^{229}Th	4παβ(LS)-γ(NaI) anticoincidence counting	0.28	4παβ LS CNET	−0.09
			4παβ LS TDCR	−1.7
			2πα proportional counting	−0.09
			HPGe photon spectrometry	+2.1

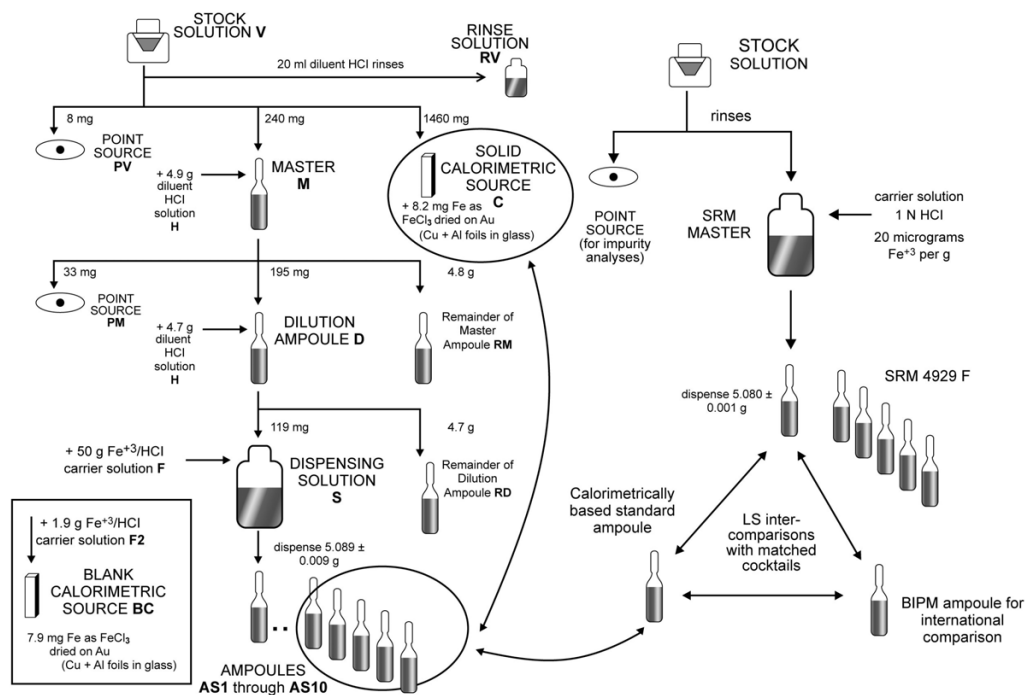* Values are discrepant, and not considered to have confirmed.

Fig. 1. Scheme for the primary calorimetric standardization of ^{55}Fe as used for SRM 4927 and for the BIPM international measurement comparison, showing the gravimetric links between the solid calorimetric source and the various ^{55}Fe solution ampoules

Lead-210

Radionuclidic standards of ^{210}Pb are amongst the most important of those needed by the worldwide environmental radioactivity measurement community. Its standardization, however, is exceedingly difficult because of its particular decay modes, and has rarely been attempted by the national metrology institutes of other countries. The first primary standardization of ^{210}Pb performed by NIST was recently reported on by LAUREANO-PEREZ et al.,[47] and lead to the development and dissemination of another new standard (SRM 4337).[4] The standardization leading to certification was based on $4\pi\alpha\beta$ liquid scintillation (LS) spectrometry with ^{3}H-standard efficiency tracing using the CNET method. Many trials were performed, varying the composition for the matched cocktail sets, LS counters used, quench range, timing and sequencing of measurements, etc. Confirmatory measurements were also performed by three alternative methods: (1) $4\pi\alpha\beta$(LS)-γ(NaI) live-timed anticoincidence counting (LTAC), a primary method; assay of ^{210}Po (the grand-daughter of ^{210}Pb) ingrowth by $2\pi\alpha$ spectrometry with silicon surface barrier detectors; and high-resolution photonic-emission spectrometry with high purity germanium (HPGe) detectors (Table 1). The ^{210}Po assays used a ^{209}Po standard as a tracer. The results were therefore confounded because the currently accepted ^{209}Po half-life (102 a) is suspected to be in error by about 25%.[48] The somewhat low decay probability (4.25%) and low energy of the sole ^{210}Pb (46.54 keV) γ-ray (located on the steep upward side of an HPGe efficiency curve) precluded a more accurate determination by photon spectrometry. The combined standard ($k=1$) uncertainties on the three confirmatory results were estimated to be 1.7%, approximately 1%, and 2.9%, respectively. Considering the large uncertainties associated with the latter two confirmatory results, they are nevertheless consistent with that obtained by the two primary methods. The expanded ($k=2$) combined standard uncertainty, as certified, for the CNET result was conservatively estimated to be 2.4%, which is atypically large compared to most primary radioactivity standardizations that are performed by NIST. This larger-than-usual uncertainty (and our desire to insure the standard's consistency with other national metrology laboratories) lead us to perform a direct measurement comparison with a UK national standard of ^{210}Pb that was obtained from the National Physical Laboratory (NPL), and which was also known to have direct links to a primary standardization

performed by the Physikalisch-Technische Bundes-anstalt (PTB) in Germany. The NIST and NPL solution standards were directly compared with five measurement methods (Table 2). The ratio of the measured activities for the two standards compared to their certified values agreed to within 0.3%, which was well within the 1.5% propagated standard uncertainty assigned to both standards. This finding suggests that the originally assigned uncertainty on the ^{210}Pb standard may have been overestimated.

Plutonium-241

A standardization of ^{241}Pu was very recently completed and lead to the development of SRM 4340B.[4] This case was particularly troublesome because it uncovered a major discrepancy, which still remains unresolved. Plutonium-241 is a pure beta emitter whose $E_{\beta(max)}$ endpoint energy is similar to that for ^{3}H (20.8 keV compared to 18.591 keV for ^{3}H). Its daughter is the ^{241}Am alpha-emitter. Initial expectations were that this would be a relatively easy case by $4\pi\beta$ LS counting using either the CNET or TDCR approaches. A large number of standardization measurements were made by the CNET method at NIST and by the TDCR method at both NIST and at LNHB. For example, the CNET results, leading to certification of the SRM, were based on numerous LS cocktails with three different types of scintillator compositions with quench-matched ^{3}H cocktails, each of the series were measured on more than one occasion in each of the three commercial LS counters. The TDCR spectrometers at NIST and at LNHB were the same as those used for the ^{63}Ni standardizations mentioned above. As seen in Table 1, there is a serious method disagreement. This discrepancy is particularly surprising since comparison of the methods, both within laboratories and between laboratories, has shown excellent agreement for many other β-emitting nuclides. The cause of this discrepancy can not be attributed to the underlying model or calculation codes, and doesn't appear to result from uncertainties or inconsistencies in the ^{241}Pu decay scheme. For confirmatory purposes, an additional measurement method was sought. The SRM master solution was insufficiently aged to allow a determination of the ingrowth of ^{241}Am by $2\pi\alpha$ spectrometry. Instead, the LS CNET result was independently confirmed by agreement with ^{241}Am ingrowth measurements ($4\pi\alpha$-LS) that were performed over a period of 31 years on a linked ^{241}Pu solution.

Table 2. Comparison of the NIST and NPL ^{210}Pb standards by five measurement methods

Method	NPL/NIST ratio	Relative standard uncertainty, %
NPL and NIST certified values from primary standardizations	0.037484	1.5
$4\pi\gamma$(NaI) sandwich detector	0.037373	0.56
HPGe spectrometry	0.036542	0.71
$4\pi\alpha\beta$(LS)	0.037249	0.17
^{210}Po assay ($2\pi\alpha$ Si spect.)	0.03736	0.75
Si(Li) low-energy spectrometry	0.0381	1.9

Strontium-90 and Americium-241

The above standardizations are some of the more challenging ones that have been conducted recently. There have been some that were decidedly easier with straightforward results. For example, a ^{90}Sr standardization, for the certification of both SRM 4239 and SRM 4919I,[4] by both LS TDCR and CNET methods showed agreement to better than 0.1% (Table 1), largely as a result of the extremely high beta detection efficiency for ^{90}Sr. This is a case of a high-geometry method with very near 100% detection efficiency, for which only small corrections need to be made for the non-detection efficiency. Similarly, ^{241}Am was independently standardized by both $4\pi\alpha$ LS counting and by $4\pi\alpha$(LS)-γ(NaI) anticoincidence counting, and used to certify the recently issued SRM 4322C.[4] At the same time, these two standardizations could be directly compared to two other independent $4\pi\alpha$ LS standardizations of gravimetrically-linked standard solutions that were used for other purposes at NIST. All of these results were in agreement to less than 0.2% (Table 1). A direct comparative measurement of the new SRM certified value with that from the 1991 ^{241}Am standard (SRM 4332B) by a large (20-cm crystals) $4\pi\gamma$ NaI(Tl) sandwich detector showed that the two SRMs were consistent to within 0.13%.

Thorium-229

The standardization of ^{229}Th is decidedly more complicated. It, as of April 2008, is still ongoing, but is near completion and will lead to the certification of SRM 4328C.[4] Thorium-229 is at the head of a nine-radioactive-member decay chain. Two of the nuclides in the chain (4.2 μs ^{213}Po and 32.4 ms ^{217}At) have half-lifes that interfere with the typical resolving times of counting instruments (1 to 100 μs). The ^{229}Th stock material used to prepare the SRM is also contaminated with a ^{228}Th impurity which requires correction. This impurity, in turn, has eight radioactive members in its decay chain. The primary standardization was based on $4\pi\alpha\beta$(LS)-γ(NaI) anticoincidence counting, and compared with several other confirmatory methods

(Table 1). The general approach was to gate the NaI(Tl) detector on some suitable photons (principally the 40 keV γ-rays from ^{225}Ra) and to vary the LS efficiency with a lower level discriminator. The LS rate is then extrapolated to 100% as function of the inefficiency that is reflected in the ratio of the anticoincident to singles photon count rates. Many other tests (e.g., varying instrument dead-times) and multiparameter extrapolations (using other photon energy gates) were made to test the efficacy of the method for this case. The result based on $4\pi\alpha\beta$ LS counting, in which the β-efficiencies were obtained from ^{3}H-standard efficiency tracing with the CNET method, was in excellent agreement. The result obtained from $2\pi\alpha$ proportional counting was equally in excellent agreement. The agreement with the LS TDCR method was surprisingly not as good (Table 1), although this determination is still under investigation. The combined standard uncertainties ($k=1$) for each of these results are approximately 0.3%, 0.6%, 1% and 0.5%, respectively. The HPGe spectrometry with its much larger uncertainties, as seen before, has a consistent result, but is not in very good agreement with the other methods. This standardization is being used as a major test case of our laboratory's methodologies and several other experiments are underway, principally additional proportional counting and high resolution alpha spectrometry using a ^{230}Th standard tracer.

The primary standardizations described here are only those primarily used to support the NIST Radioactivity SRM program. Others, for other programs (such as for radiopharmaceuticals and nuclear medicine) have also been performed during this same period.

General principles underlying primary standardizations

The primary standardization work conducted at NIST can be characterized by several features. The validity of all primary standardizations are generally supported and confirmed by one or more confirmatory measurement methods. This is done to ensure that the standardization result is confirmed by supplementary measurements that are completely independent of the

primary method. The standardization, whenever possible, is also linked back to all previous standardizations, through comparisons with stored standardized solutions, or through use of calibration factors for secondary measurement instruments (e.g., re-entrant ionization chambers or large $4\pi\gamma$ NaI sandwich detectors, etc.). The measurement uncertainty, in terms of a relative standard uncertainty (combined standard uncertainty multiplied by a coverage factor of $k = 2$), for most primary standardizations is generally less than a few tenths of a percent, and is rarely greater than 1% (although it can occur for nuclides with complex decay modes). International consistency is often achieved and demonstrated through both formal (typically organized under the aegis of the BIPM or the IAEA) and informal measurement comparisons with other national metrology institutes, like LNHB in France, Polatom in Poland, NPL in the UK, or PTB in Germany.

Conclusions

Primary methods of standardization lie at the center of the activities that are used by national metrology laboratories to ensure the quality of radioactivity measurements made within their domains and to ensure consistency between nations worldwide.

The national metrology laboratory of the USA, NIST, supports a vigorous applied research program in fundamental radionuclidic metrology. This program includes the capability to perform primary standardizations for many different radionuclides and disseminates these through calibrations and transfer standards, like SRMs. In the past 94 years, approximately 140 radionuclides have been standardized in one form or another at NIST. The work is supported by upwards of 40 unique instruments and methods, which underlies the continued supply of SRMs and the development of new standards. At the present time, there are approximately 65 radioactivity SRMs available from NIST in a number of configurations, although stable solutions of single species of about 45 different alpha, beta, gamma and X-ray emitting nuclides, certified for mass activity, are the most common form.

The artifact transfer standards for radioactivity that are available and distributed by various National Metrology Institutes (NMI), like the SRMs from NIST, are not "national standards," but in principle are directly linked to these. In fact, national standards are not artifacts at all, but rather are the NMI's ability to perform primary standardizations (dependent only on its instruments, its procedures, and its metrologists, etc.). There are no international standards. Instead, international agreement on radioactivity measurements is based on the consensus of the results obtained by primary standardizations from equivalent national laboratories.

References

1. T. J. QUINN, Metrologia, 34 (1997) 61.
2. B. N. TAYLOR, The International System of Units (SI), NIST Special Publ. 330, Natl. Inst. Stds & Tech., Gaithersburg, MD, USA, 2001.
3. K. DEBERTIN, Appl. Radiation Isotopes, 47 (1996) 423.
4. National Institute of Standards and Technology (NIST), Standard Reference Materials for Radioactivity, NIST, Gaithersburg, 2006. A current, on-line catalog is available at http://ts.nist.gov/measurementservices/referencematerials/index.cfm
5. R. COLLÉ, Trans. Amer. Nucl. Soc., 97 (2007) 355.
6. B. M. COURSEY, R. COLLÉ, J. S. COURSEY, Appl. Radiation Isotopes, 56 (2002) 5.
7. W. B. MANN, Int. J. Appl. Radiation Isotopes, 1 (1956) 3.
8. National Academy of Sciences (NAS), National Uses and Needs for Standard Radioactive Materials, NAS, Washington, DC, 1970.
9. L. M. CAVALLO, B. M. COURSEY, S. B. GARFINKEL, J. M. R. HUTCHINSON, W. B. MANN, Nucl. Instr. Nucl. Meth., 112 (1973) 5.
10. R. COLLÉ, Trans. Amer. Nucl. Soc., 39 (1981) 84.
11. R. COLLÉ, Measurements for the Safe Use of Radiation, National Bureau of Standards (NBS) Special Publ. 456, NBS, Washington, DC, 1976, p. 71.
12. K. G. W. INN, Z. LIN, Z. WU, C. MCMAHON, C. LIU, R. HOLLOWAY, J. HARVEY, I. L. LARSEN, T. BEASLEY, C. A. HUH, S. MORTON, D. MCCURDY, P. GERMAIN, J. HANDL, M. YAMAMOTO, B. WARREN, T. H. BATES, A. HOLMS, B. R. HARVEY, D. S. POPPLEWELL, M. J. WOODS, S. JEROME, K. J. ODELL, P. YOUNG, I. CROUDACE, J. Radioanal. Nucl. Chem., 248 (2001) 227.
13. National Council on Radiation Protection and Measurements (NCRP) A Handbook of Radioactivity Measurements Procedures, Second Ed., NCRP Report No. 58, NCRP, Washington, DC, 1985, p. 17.
14. W. B. MANN, A. RYTZ, A. SPERNOL, Radioactivity Measurements: Principles and Practice, Pergamon Press, 1988, p. 4.
15. M. WOODS, P. DE FELICE, Appl. Radiation Isotopes, 64 (2006) 1091 (Proccedings of the 15th International ICRM Conference; refer to references therein for citations of earlier proceedings).
16. S. POMMÉ, Metrologia, 44 (2007) S17.
17. D. D. HOPPES, Environ. Int., 10 (1984) 99.
18. NCRP, ibid., p. 100.
19. J. M. R. HUTCHINSON, L. L. LUCAS, P. A. MULLEN, Int. J. Appl. Radiation Isotopes, 27 (1976) 43.
20. L. L. LUCAS, Standardization of Alpha-Particle Sources, ASTM Special Technical Publ., 698, American Society for Testing and Materials, Philadelphia, 1980, p. 342.
21. NCRP, ibid., p. 109.
22. S. B. GARFINKEL, W. B. MANN, F. J. SCHIMA, M. P. UNTEWEGER, Nucl. Instr. Meth., 112 (1973) 59.
23. M. P. UNTERWEGER, Metrologia, 44 (2007) S79.
24. J. M. R. HUTCHINSON, J. L. LANTZ, W. B. MANN, P. A. MULLEN, R. H. RODDRIGUEZ-PASQUES, IEEE Trans. Nucl. Sci., NS19 (1972) 117.

25. J. M. R. Hutchinson, W. B. Mann, P. A. Mullen, Nucl. Instr. Meth., 112 (1973) 187.
26. B. Deneke, Nucl. Instr. Meth., A339 (1994) 92.
27. M. F. L'Annunziata, Handbook of Radioactivity Analysis, 2nd Ed., Academic Press, New York, 2003, p. 347; and references therein.
28. R. Broda, P. Cassette, K. Kossert, Metrologia, 44 (2007) S36.
29. W. B. Mann, M. P. Unterweger, Appl. Radiation Isotopes, 46 (1995) 185.
30. R. Collé, Metrologia, 44 (2007) S118.
31. R. Collé, B. E. Zimmerman, Appl. Radiation Isotopes, 56 (2001) 223.
32. E. LeBlanc, P. de Marcillac, N. Coron, J. LeBlanc, M. Loidl, J. F. Metge, J. Bouchard, Appl. Radiation Isotopes, 56 (2002) 245.
33. NCRP, ibid., p. 117.
34. W. Bambynek, Standardization of Radionuclides, International Atomic Energy Commission, Vienna, 1971, p. 373.
35. NCRP, ibid., p. 117.
36. C. Bobin, Metrologia, 44 (2007) S27.
37. NCRP, ibid., p. 75.
38. R. Fitzgerald, Trans. Amer. Nucl. Soc., 97 (2007) 359.
39. L. L. Lucas, Appl. Radiation Isotopes, 49 (1998) 49.
40. R. Broda, Appl. Radiation Isotopes, 58 (2003) 585.
41. R. Collé, B. E. Zimmerman, J. Res. Natl. Inst. Stds. Tech., 102 (1997) 523.
42. R. Collé, B. E. Zimmerman, P. Cassette, L. Laureano-Perez, Appl. Radiation Isotopes, 66 (2008) 60.
43. B. E. Zimmerman, R. Collé, J. T. Cessna, Appl. Radiation Isotopes, 60 (2004) 455.
44. J. Bouchard, P. Cassette, Appl. Radiation Isotopes, 52 (2000) 669.
45. R. Collé, L. Laureano-Perez, P. Volkovitsky, J. Res. Natl. Inst. Stds. Tech., (2008) to be published.