

Independent Assay of the ^{60}Co Solution Ampoule Used for the SIR Submission

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This work was undertaken as a result of notification by BIPM¹ that a 2007 NIST² submission of ^{60}Co to the SIR³ had a result that differed "significantly" from the KCRV⁴. The magnitude of the significant difference is unknown.

The submitted ampoule (now labeled "S") was returned to NIST in March 2009, at our request, for a re-evaluation.

This ampoule S was independently assayed for the massic activity of the contained solution by ionization chamber measurements (using our extant K value) and by LS⁵ spectrometry (using both the CNET⁶ and TDCR⁷ methods), and by two different methods for the total solution mass contained in the ampoule. The product of the two is, of course, the total activity, which is what is used for comparison to the KCRV.

An overview of the procedures used for these determinations is schematically outlined in Figure 1. All of the ampoules used for this work were NBS/SIR style standard ampoules. Descriptions of the procedure and methods follow.

All results reported herein have been decay corrected to a reference time of 1200 EST (1700 UT) 1 January 2007 using a ^{60}Co half-life of (5.2710 ± 0.0008) a. Unless specifically noted otherwise, all uncertainties given here correspond to appropriate standard deviations, standard uncertainties, or combined standard uncertainties with a coverage factor of $k = 1$.

Ampoule S was measured in our ionization chamber "A" against RRS20⁸ on two separate measurement occasions (24 and 27 March 2009) prior to opening it and removing its solution contents. Following this, Ampoule S was opened and its contents were transferred with an aspirating polyethylene pycnometer to dilution vial M. Both the "picked up" and "dispensed" masses were determined. Based on later mass-loss corrections it was apparent that 99.47 % of the mass was picked up with the pycnometer and removed from the ampoule, with 19.4 mg remaining on the wetted glass. After transfer to vial M, another 22.2 mg remained in the pycnometer. The dilution of S to M was made with a carefully prepared carrier solution that perfectly matched the known solution contents of ampoule S. The carrier solution consisted of (1.07 ± 0.06) mol·L⁻¹ HCl with (59.94 ± 0.09) µg Co⁺² per gram of solution, having a density of (1.017 ± 0.001) g·mL at 20 °C. The dilution factor for the massic activity in solution M and ampoule S was gravimetrically determined by both contained and dispensed mass differences. The dilution factors were found to be in agreement to within 0.007 %. Solution M was used to prepare three ampoules (called I1, I2, and I3) for subsequent ionization chamber measurements, with masses ranging from 4.75 g to 5.13 g.

Ampoule **I1**, following ion chamber measurements on 7 April 2009, was opened and used to gravimetrically prepare another 3.6 g ampoule (called **SSS**) and another 4.1 g ampoule (**I1RR**) of diluted solution **S**. These two new ampoules were also measured on the ion chamber, along with re-measurements of **I2** and **I3**, on two separate occasions (9 and 14 April 2009) for comparisons against the previous ion chamber measurements of ampoules **S** and **I1-I3**.

Figure 2 shows the results for all of the ionization chamber measurements in terms of the massic ionization current ratio (with respect to RRS20) as a function of solution mass in the ampoules. The four independent measurements from the nominal 5.0 g ampoules (from **I1** and **I2**) had a massic ratio of 0.090639 g^{-1} , with a relative standard deviation of the mean of 0.016 % ($n = 4$). The internal relative standard deviation of the mean on each of the four results ranged from 0.083 % to 0.098 %. Using the extant decay-corrected K value and on invoking the known dilution factors (see Figure 1), the corresponding massic activity for solution **S** is

$$(49.98 \pm 0.15) \text{ kBq} \cdot \text{g}^{-1},$$

whose uncertainty is largely dominated by the uncertainty in the K -value calibration. As indicated in Figure 2, there is an approximate -0.33 % volume effect in the ion chamber response between 5.0 g and 3.6 g. This corresponds reasonably well with the -0.45 % value that previously observed by Fitzgerald.⁹

Ampoule **I1** was also used to prepare sources that were used for the LS-based CNET and TDCR assays. One LS vial, labeled **NC**, was used to link solution **M** to the residual activity in vial **N** (see below for details).

The efficiency tracing was performed¹⁰ with six varyingly-quenched LS vials that were traced against composition-matched ^3H standard cocktails.¹¹ The cocktails were prepared with "Ultima Gold AB"¹² to an aqueous fraction of about 0.07 using the previously noted carrier solution and were quenched with a ethanol-diluted nitromethane solution. Efficiency calculations for the CNET assays were performed with the CN2003 code of Gunther¹³ using evaluated nuclear and atomic data from Helmer.¹⁴ The LS sources were counted in each of our three LS counters¹⁵ for three cycles. The internal relative standard deviation of the mean ($n = 6$) for the six traced activity values for any one cycle with any one counter ranged from 0.04 % to 0.08 %. The relative standard deviation of the mean across the three cycles for any one counter was typically 0.03 % ($n = 18$). The between-counter relative standard deviation (equivalent to a relative standard deviation of the mean) was 0.054 %. All of the data sets and subsets were tested for normality with DATAPLOT¹⁶ and could accept the normality assumption at the 95 % and 99 % levels. The CNET assay results obtained from the three counters are:

WALLAC	$49.565 \text{ kBq} \cdot \text{g}^{-1} \quad s_m = 0.026 \% (n = 18);$
BECKMAN	$49.611 \text{ kBq} \cdot \text{g}^{-1} \quad s_m = 0.031 \% (n = 18);$ and
PACKARD	$49.564 \text{ kBq} \cdot \text{g}^{-1} \quad s_m = 0.036 \% (n = 18),$

whose average is

MEAN	$49.580 \text{ kBq} \cdot \text{g}^{-1} \quad s = 0.055 \% (n = 3).$
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The values of s_m given here correspond to only the standard deviations of the mean for the internal variation within each data set. The mean value's standard deviation s is equivalent to a standard deviation of the mean since it is derived from the average of three mean values.

This average LS CNET value differs from the ion chamber result by -0.81 %. A combined standard uncertainty in this value has not been evaluated because of the incertitude in the model assumptions and ignorance as to how to assign an uncertainty for the efficiency calculations. The relative combined standard uncertainty is assumed to be not better than 0.4 %, so the LS CNET value can be taken as

$$(49.58 \pm 0.20) \text{ kBq} \cdot \text{g}^{-1}$$

The LS-based TDCR assay result, based on measurement of one source at six efficiency values, is

$$(49.76 \pm 0.25) \text{ kBq} \cdot \text{g}^{-1},$$

with a relative combined standard uncertainty that has been estimated to be ≤ 0.5 %.¹⁷ This value differs from the ion chamber result by -0.45 %.

The total mass of solution contained in ampoule **S** was independently determined by two gravimetric methods. The first method uses a LS-based residual activity correction, and the other method is based on using relative ionization currents from two 3.6 g ampoules prepared from the identical solution and normalized to a known mass in one of the ampoules.

For the LS-based method (see Figure 1), the bottom of the opened ampoule and transfer pycnometer were rinsed with a well-determined mass of carrier solution, and were contained as solution **N**. Aliquants of this solution were used to prepare two LS counting sources (**RN1** and **RN2**). These two sources were assayed relative to an aliquant from ampoule **I1** that was in turn obtained from solution **M**. In addition, the ampoule top (unrinsed) and ampoule bottom (after rinses) were placed into LS counting vials (**TOP** and **BOT**), immersed in LS scintillation fluid, and assayed with respect to LS vial **NC**. The pycnometer was also filled with scintillation fluid, placed in another vial (**PYC**) and surrounded by cocktail for counting. The two vials carrying small remainders of the diluting and rinsing carrier solution (**DIL**) and scintillation fluid (**UGAB**), which had been in contact with the pycnometer in picking up the liquids, were also filled with scintillant and made into suitable counting sources. These additional vials were also measured relative to **NC**. With this, the total mass of solution m_S in ampoule **S** could be obtained by relative LS counting of the various vials by accounting for the activity not contained in **M**; viz.,

$$m_S = m_d \left(1 + \frac{R_L}{R_L + R_M} \right)$$

where $R_L/(R_L + R_M)$ is the fractional mass loss. The loss in rinse solution **N**, the major component of residual activity, was obtained from counting **RN1** and **RN2**:

$$R_N = \frac{1}{2} \left(\frac{R_{RN1}}{m_{RN1}} + \frac{R_{RN2}}{m_{RN2}} \right) m_N$$

where R_{RN1}/m_{RN1} and R_{RN2}/m_{RN2} are the massic LS counting rates and where m_N is the total solution mass in N. The total residual loss R_L was then obtained by summing the relative residual activities (normalized LS counting rates) in all of the residual activity vials;

$$R_L = R_N + \sum_i R_i.$$

The relative activity contained in solution **M** was obtained from the massic counting rate of **NC**, R_{NC}/m_{NC} , multiplied by the total mass of solution in **M**; i.e.,

$$R_M = \left(\frac{R_{NC}}{m_{NC}} \right) m_M = \left(\frac{R_{NC}}{m_{NC}} \right) \left(\frac{m_d}{D_{SM}} \right)$$

with dispensed mass m_d and the **S** to **M** dilution factor D_{SM} . Table I shows the distribution of activities within the various residual activity components. The ampoule top (**TOP** vial) contained a substantial portion of the residual activity, particularly in comparison to its bottom (**BOT**), because it had not been rinsed by the carrier solution. It is important to appreciate that this residual activity analysis scheme was very comprehensive since it evaluated and accounted for the activity on everything (ampoules, pycnometer, vials, solutions, etc.) touched or in contact with the ampoule **S** solution.

The mass determination obtained with this LS-based residual activity correction resulted in a value of

$$m_S = m_d(1 + 0.011916) = (3.659 \pm 0.015) \text{ g},$$

where the uncertainty is dominated by that due to the mismatch in LS counting efficiency for the various residual activity vials.

The second mass determination was made by relating the mass of solution in ampoule **S** to the mass in ampoule **SSS** through the ion chamber response ratios for the two ampoules; viz.,

$$\frac{R_S}{m_S} = D_{SSS} \left(\frac{R_S}{R_{SSS}} \right),$$

$$m_S = \left(\frac{m_{SSS}}{D_{SSS}} \right) \left(\frac{R_S}{R_{SSS}} \right)$$

where R_S/m_S and R_{SSS}/m_{SSS} are the massic ion chamber response ratios for the two ampoules, and where D_{SSS} is the overall dilution factor between solution **S** and solution **SSS**. This results in a mass determination of

$$m_S = \left(\frac{3.67217 \pm 0.00073}{4.23172 \pm 0.00085} \right) \left(\frac{0.33038 \pm 0.00020}{0.078425 \pm 0.000094} \right) = (3.6557 \pm 0.0088)$$

Table 2 and Figures 3 and 4 show comparisons of the results for the present determinations to the SIR submitted values. The uncertainty bars shown in the figures correspond to $k = 1$ uncertainty intervals. The agreement in massic activity from the ionization chamber measurement is excellent (0.02 % agreement), which is wholly consistent with all previous findings by Fitzgerald. The suggested systematic difference between the submitted result for the massic activity and the LS results may result from method differences arising from the LS model assumptions. In all cases, the present re-determinations are in agreement with the submitted values to within the measurement uncertainties. It is apparent that any "significant" differences are in the range of less than 0.5 % to 1 % for the massic activities and less than 0.1 % for the mass.

Therefore, there are two possibilities: (i) the "significant" difference seen by BIPM is of magnitude of 1 % or less, and our extant 1980 K value has shifted since 1992 and that this shift has coincidentally agreed with Fitzgerald's new 2007 primary standardization; or (ii) BIPM screwed up their measurement of our ampoule.

Table 1. Distribution of the activity in the various components as obtained from the residual activity analysis scheme.

component		fractional relative activity
BOT	ampoule bottom	0.000134
TOP	ampoule top	0.000643
PYC	transfer pycnometer	0.000003
N	rinse solution N (from vials RN1 & RN2)	0.011138
DIL	carrier solution vial	$-6.2 \cdot 10^{-7}$
UGAB	scintillation fluid vial	$-6.9 \cdot 10^{-7}$
total residual	sum of above components	0.011916 ± 0.000039 *
M	in vial M (from NC)	0.98808 ± 0.00036 *
S	in S (sum of M + total residuals)	1

* The uncertainty interval corresponds to only that due to measurement precision (including "counting statistics") and does not include any contribution from differences in the LS counting efficiency for the various vials.

Table 2. Comparison of the SIR submitted values to the results of the present determinations. All uncertainty intervals correspond that for a $k=1$ coverage factor.

Quantity	SIR submitted value	method	present result	method	difference
solution mass (g)	3.65957 ± 0.00070	gravimetric, dispensed mass	3.659 ± 0.015	measured aliquant mass removed from ampoule with LS-based residual activity correction	- 0.02 %
			3.6557 ± 0.0088	measured mass in ampoules normalized by relative ion current measurements	- 0.11 %
massic activity (kBq·g ⁻¹)	50.00 ± 0.10	$4\pi\beta(\text{LS})-\gamma(\text{NaI})$ AC, with 0.04 % agreement with extant K value	49.98 ± 0.15	IC "A" using extant K value	- 0.04 %
			49.58 ± 0.20	LS CNET	- 0.85 %
			49.76 ± 0.25	LS TDCR	- 0.45 %

Figure 1. Experimental scheme used for the determinations of the ^{60}Co massic activity and the total solution mass in ampoule S.

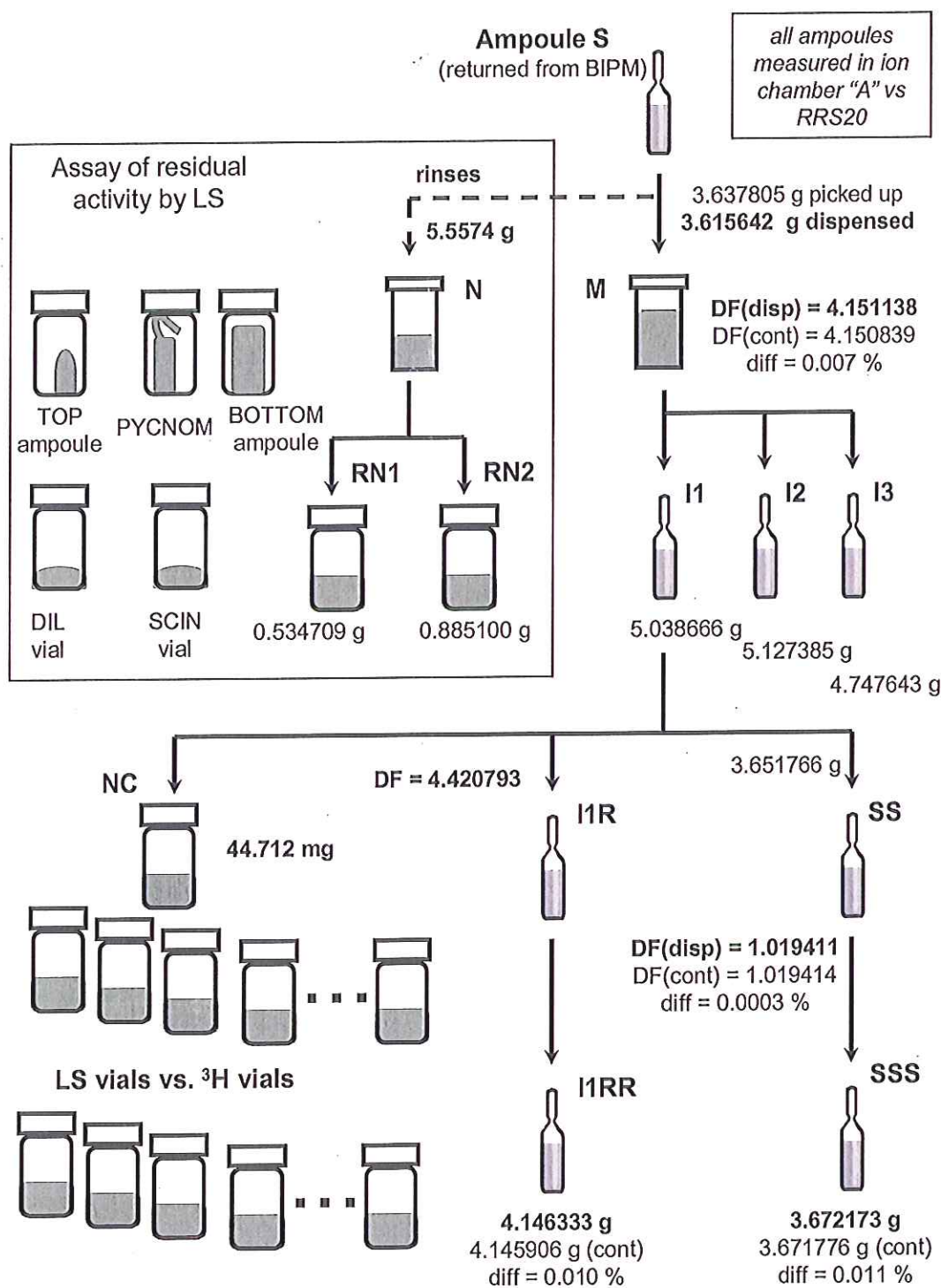


Figure 2.

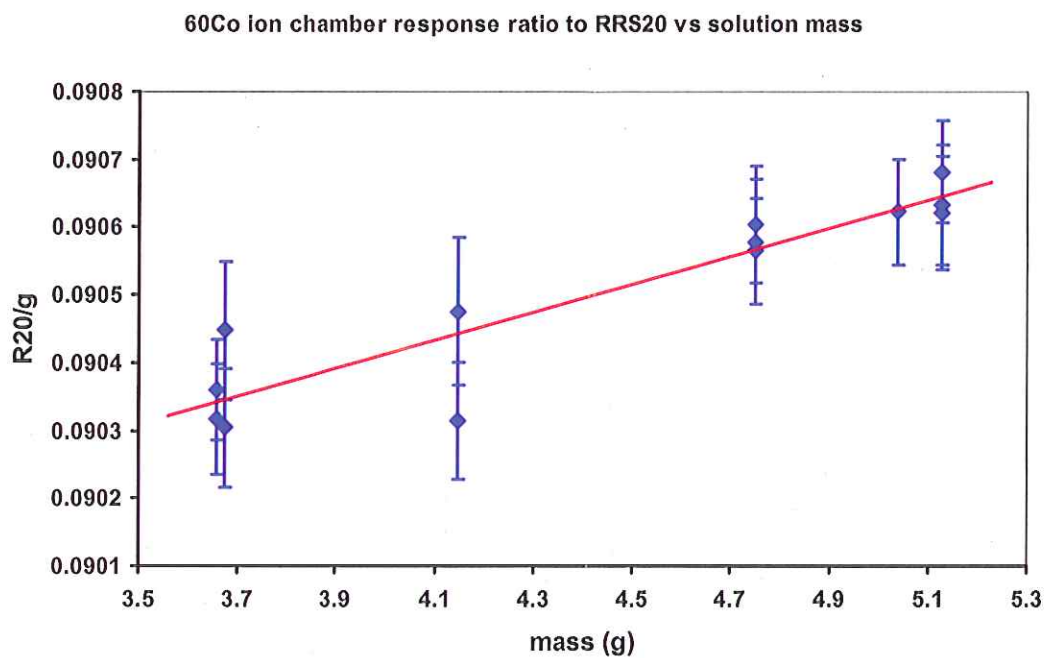


Figure 3.

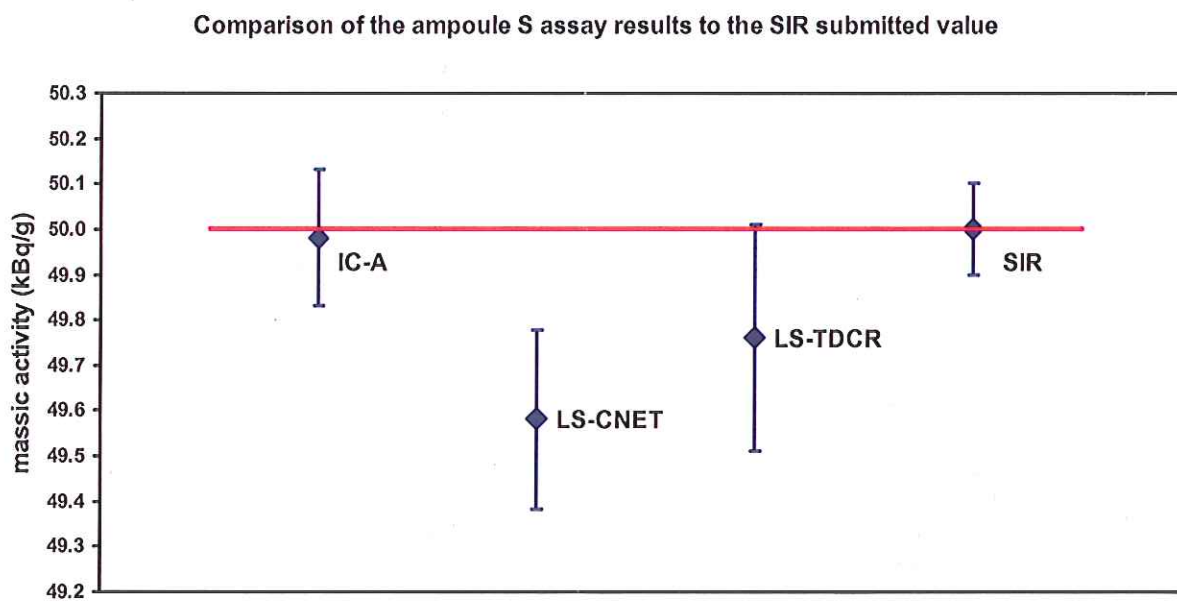
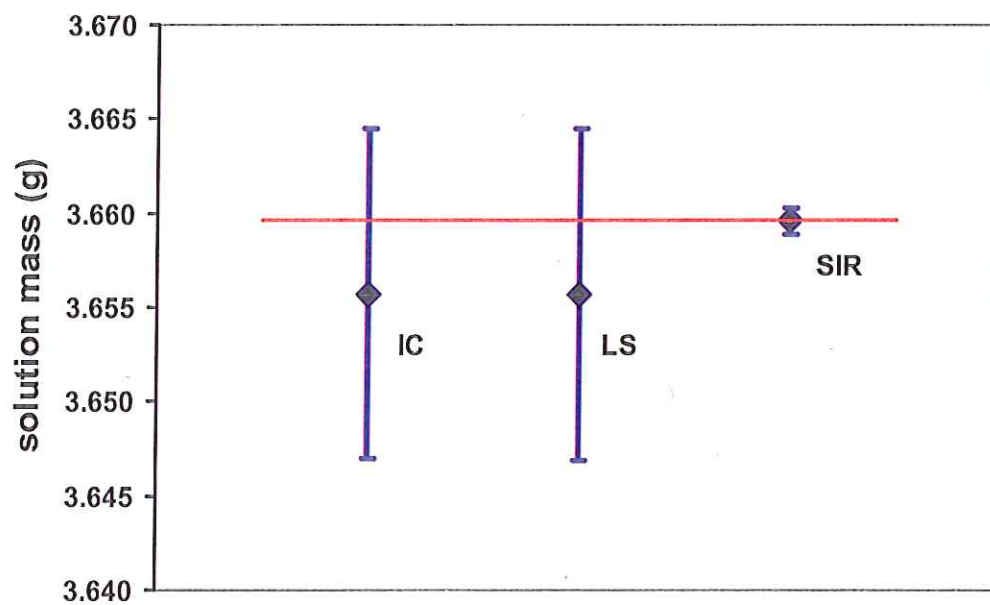


Figure 4.

Comparison of the ampoule S solution mass determinations to
the SIR submitted value



ENDNOTES

¹ BIPM refers to the Bureau International des Poids et Mesures.

² NIST refers to the National Institute of Standards and Technology. The submission was made by Ryan Fitzgerald in 2007.

³ SIR refers to the International Reference System.

⁴ KCRV refers to the Key Comparison Reference Value.

⁵ LS refers to liquid scintillation counting.

⁶ CNET refers to the LS-based CIEMAT/NIST efficiency tracing method, so named after the two laboratories that collaborated in developing the protocol for this LS tracing methodology. The acronym CIEMAT refers to the Centro de Investigaciones Energeticas, Mediambientales y Tecnologicas laboratory in Spain.

⁷ TDCR refers to the Triple-to-Double Coincidence Ratio method.

⁸ RRS20 refers to the NIST Radium Reference Source "20", which contains a very nominal 20 µg ²²⁶Ra in a standard geometry.

⁹ R. Fitzgerald, NIST Internal Report entitled "NIST ⁶⁰Co Standardizations and SIR Submissions", dated April 2009.

¹⁰ L. Laureano-Perez performed the CNET measurements and data analyses, with a modicum of assistance by R. Collé.

¹¹ The ³H standard used was a dilution of SRM 4927F.

¹² "Ultima Gold AB" is a product of Perkin Elmer, Waltham, Ma, USA.

¹³ E. Gunther, 2003. Private Communications on CN2003 code. Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany.

¹⁴ R.G. Helmer (Jan 2006) in M.M. Bé (ed.), Table of Radionuclides, CEA tabulation of recommended data. Available at http://www.nucleide.org/DDEP_WG/DDEPdata.htm.

¹⁵ The three LS counters are referenced as: B, Beckman LS 6500 (Beckman Coulter, Fullerton, CA USA); P, Packard TriCarb A2500TR (Perkin-Elmer, Wesly, MA USA); W, Wallac 1414Winspectral (Perkin-Elmer, Wesly, MA USA).

¹⁶ DATAPLOT, 2009. Dataplot is a free, public-domain, multiplatform software system for scientific visualization, statistical analysis, and non-linear modeling. It was developed at NIST (Gaithersburg, MD, USA). Available at <http://www.itl.nist.gov/div898/software/dataplot/>.

¹⁷ B.E. Zimmerman performed the TDCR measurement and analyses.