Blind Comparison of ^{210}Pb Standards by NIST and NPL

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The two laboratories involved in this exercise were the National Institute of Standards and Technology (NIST) of the USA and the National Physical Laboratory (NPL) of the UK. The principals from each laboratory were Ron Collé and Lena Johansson, respectively.

Standardized solutions of ^{210}Pb (in flame-sealed glass ampoules) were prepared by each laboratory and exchanged as "blinds."

To preserve the "blindness" of the exercise, the results from each laboratory, prior to joint disclosure, were sent to Philippe Cassette at the Laboratoire National Henri Becquerel (LNHB) in France.

The NIST solution, labeled 4337DIL, was shipped to NPL on 4 November 2008.

The NPL solution, labeled A08876, sent to NIST was received on 20 November 2008.

The reference time was chosen to be 0000 UTC 15 December 2008 (1900 EST 14 December 2008).

The NIST solution that was sent to NPL was gravimetrically linked to a previously standardized NIST solution; viz., Standard Reference Material SRM 4337[1], whose 2006 standardization was previously reported on by Laureano-Perez, Collé, et al.[2] Dilution factors linking solution 4337DIL to SRM 4337, derived from dispensed masses and contained masses, were in agreement to better than 0.004 %.

It may be of interest to note that SRM 4337 was also compared in 2007 to a previously-acquired NPL standard.[3] This NPL standard was based on a gravimetric dilution of a standardized solution that had been obtained from the Physikalisch-Technische Bundesanstalt (PTB) in Germany,[4] with confirmatory measurements by NPL using the

[1] National Institute of Standards and Technology (NIST), *Certificate for Standard Reference Material 4337, Lead-210 Radioactivity Standard*, NIST, Gaithersburg, MD USA , issued November 2006.

[2] L. Laureano-Perez, R. Collé, R. Fitzgerald, I. Outola, L. Pibida, A liquid scintillation-based primary standardization of ^{210}Pb, *Appl. Radiat. Isot.* **65**, 1368-1380 (2007).

[3] National Physical Laboratory (NPL), *Certificate of Calibration, Lead-210 Standard A051087 (ref. E06100080)*, NPL, Teddington, UK, 2007.

[4] Physikalisch-Technische Bundesanstalt (PTB), *Calibration Certificate Lead-210 Activity Standard (Serial no. 15523)*, PTB, Braunschweig, Germany, 2005.

^{210}Bi-ingrowth Cerenkov counting method.[5] The NIST standard SRM 4337 and NPL standard were compared by five methods and were shown to agree to within 0.3 %, which was well within the 1.5 % propagated standard uncertainty assigned to both standards.[6]

Table 1 summarizes the properties of the two exchanged solutions as reported by NIST and NPL.

The NIST results for the massic activity of each solution, as of the 0000 UTC 15 December 2008 reference time, are:

NIST 4337DIL: **(7.718 ± 0.062) kBq·g^{-1}**

NPL A08876: **(45.01 ± 0.36) kBq·g^{-1}**

where the cited uncertainty intervals correspond to combined standard uncertainties with a coverage factor of k = 1.

The value for NIST 4337DIL was based on the gravimetric dilution of SRM 4337 (decay corrected to the reference time using an assumed half-life of (22.20 ± 0.22) a) and on a liquid scintillation (LS) assay performed in December, 2008, whose results are 7.715 kBq·g^{-1} for the SRM dilution and 7.718 kBq·g^{-1} for the LS assay. The former result was used only as a confirmation.

The value for NPL A08876 was obtained from a LS assay that was performed simultaneously with a re-standardization of SRM 4337 and from relative measurements of gamma-ray emission rates with a NaI(Tl) sandwich detector using ampoules of dilutions of NPL A08876 that were composition matched to ampoules of NIST SRM 4337. Additional photonic emission rate measurements of both point sources and ampoules with a windowless Si(Li) detector were also performed. Those with the point sources were unsuccessful, having results with unsatisfactorily large uncertainties due to large positioning viabilities and inconsistencies.

The scheme used to compare the NIST and NPL ^{210}Pb solution is shown in Figure 1. As indicated, two sets of dilution ampoules of NPL A08876 were prepared. The first set (NPL-A, -B, and -C) were deemed to be insufficiently matched in composition to those of SRM 4337 so they were in turn further adjusted, which resulted in ampoules NPL-E, -F, and -G. Table 2 shows the composition matches between these ampoules and ampoules of SRM 4337.

Aliquants from ampoules NPL-G and NIST SRM-4337 were used to prepare LS counting sources. The LS-based measurements followed a protocol that was essentially identical to that used for the original standardization of NIST SRM 4337, which has been described by Laureano-Perez, et al. (cited previously). Two different commercial scintillation fluids (PCS, a xylene-based scintillator; and Ultimagold AB) were used were used to prepare two sets of matched cocktails. Three counting sources of each cocktail composition were made from the NPL-G and NIST SRM-4337 solutions along with a set of three from a NIST ^{3}H standard and matched blanks for background subtraction. The two sets of cocktails were counted for three measurement cycles in each of three different LS counters. Table 3 summarizes the individual trial results for this LS standardization. Table 4 shows

[5] C. Gilligan, private communication on NPL lead-210 standard certification, National Physical Laboratory, Teddington, UK, 2007.

[6] R. Collé and L. Laureano-Perez, On the standardization of ^{209}Po and ^{210}Pb, *Advances in Liquid Scintillation Spectrometry, LSC 2008*, in print, Radiocarbon, Tucson, AZ USA, 2008

the results for the massic activity ratio in the original ampoules (NPL A08876 / NIST 4337DIL) after applying the gravimetric dilution factors given in Table 2. The massic activities in the two ampoules, as obtained from the LS standardization, are summarized in Table 5. The table also shows the excellent agreement (< 0.04 % difference) between the decay-corrected certified value for SRM 4337 and the present re-standardization. The uncertainty analyses for the massic activities are given in Table 6. The major difference between the uncertainty values given here and the previous assessment for the certification of SRM 4337 is that the ^{210}Pb LS efficiency was revisited and its estimated relative standard uncertainty was decreased from 1.1 % to 0.6 %.

The four matched ampoules (NPL-E, NPL-F, NIST-A, and NIST-B) shown in Figure 1 and described in Table 2 were directly intercompared in a $4\pi\gamma$ NaI sandwich detector. The sandwich detector, consisting of two large 20-cm NaI(Tl) scintillation crystals, was used to measure each of the four ampoules by integrating the spectra over the ^{210}Pb 46.539-keV γ-ray photopeak. The lower discriminator setting was located in the minimum valley between the L x-ray and γ-ray peaks. For these measurements, the ampoules laid sideways in a 3.8-cm deep cavity between the crystals and were in a fixed geometry as constrained by an aerated-polystyrene jig. The spectrum from each detector (top and bottom) was collected independently and simultaneously. Seven to ten spectra were collected for each of the four ampoules, with interspersed backgrounds and alternating ampoule sequencing. The pairwise ratios of the massic rates for any two ampoules as obtained from any one detector (with the identical background subtraction) could be compared to the massic activity ratios. The rates were not obtained by peak fitting, but instead were obtained by integrating a fixed region of the spectra, corresponding to the 46.539-kev photopeak. The results of these direct ampoule comparisons is summarized in Table 7. As indicated, the ratio of the mean massic activities for NPL A08876 / NIST 4337DIL is in excellent agreement with that obtained from the LS counting (Table 4), differing by - 0.21 %.

The four matched ampoules were also directly intercompared by high-resolution γ-ray spectrometry, using a windowless Si(Li) detector in a vacuum chamber. The ampoules were mounted in a rigidly fixed vertical position such that the gravimetric center of the solutions was on the center axis of the detector and located at a distance of about 2 cm. The repositioning was very reproducible, in contradistinction to the evident non-centering difficulties that were encountered with the point sources. A spectrum of each ampoule was collected and the integrated counts under the 46-kev photopeak were used to obtain a decay-corrected massic emission rate. The results are given in Table 8, which are used to obtain the NPL A08876 / NIST 4337DIL ratio in Table 9.

Table 10 compares the NPL A08876 / NIST 4337DIL massic activity ratio as obtained by the three methods. It may be useful to recall that solution NIST 4337DIL was gravimetrically linked to NIST SRM 4337 and its independent LS assay was in excellent agreement with the decay-corrected massic activity for SRM 4337 as originally certified and with the independent re-standardization of SRM 4337.

Figure 2 illustrates all of the linkages between the NPL and NIST ^{210}Pb solutions that have been compared in 2006 and 2008. There are linkages by NIST for all of the solutions shown in the figure. It is not known what linkage NPL has between NPL standard A051087 (from October 2006) and NPL solution A08875 (from November 2008).

Table 1. Properties of the exchanged NIST 4337DIL and NPL A08876 ^{210}Pb solutions

Laboratory of origin	**NIST**	**NPL**
Recipient laboratory	NPL	NIST
source identification	4337DIL	A08876
containment	NIST-style (BIPM) 5-mL standard ampoule, flame sealed	5-mL glass ampoule, flame sealed
mass of solution in ampoule	(4.9512 ±0.0004) g [1]	(3.0062 ± 0.0004) g [1]
solution composition	nominal 1 $mol \cdot L^{-1}$ HNO_3 34 μg Pb^{+2} per gram of solution 44 μg Bi^{+3} per gram of solution	nominal 2 $mol \cdot L^{-1}$ HNO_3 10 μg Pb^{+2} per gram of solution 10 μg Bi^{+3} per gram of solution
solution density	(1.028 ± 0.001) $g \cdot mL^{-1}$ at 20 °C [a]	(1.066 ± 0.005) $g \cdot mL^{-1}$ at 20 °C [a]
nominal total activity	40 kBq	150 kBq

[a] Cited uncertainty intervals correspond to that for a standard uncertainty with $k = 1$.

Table 2. Properties of the composition matched ampoules used for the relative photonic emission rate measurements, based on the original solution properties given in Table 1 and dilution with well-characterized carrier solutions of HNO_3/ Pb^{+2}/Bi^{+3}.

	NPL-E	**NPL-F**	**NPL-G**	**SRM 4337**
ampoule type	NIST std	NIST std	NIST std	NIST std
total mass of solution (g)	5.1393	5.1218	5.1155	5.133 ± 0.002 [a]
solution density ($g \cdot mL^{-1}$) [b]	1.031	1.031	1.031	1.028 ± 0.002 [a]
Pb^{+2} ($\mu g \cdot g^{-1}$) [b]	9.5	9.5	9.4	11
Bi^{+3} ($\mu g \cdot g^{-1}$) [b]	17	16	17	21
HNO_3 ($mol \cdot L^{-1}$) [b]	1.0_3	1.0_6	1.0_4	1.0_0
overall dilution factor [c]	6.20499	5.56820	6.01664	0.922992
nominal massic activity ($kBq \cdot g^{-1}$)	8.0	9.0	8.3	9.0

[a] Cited uncertainty intervals correspond to that for a standard uncertainty with $k = 1$.

[b] Derived values from dilutions assuming that the HNO_3, Pb^{+2}, and Bi^{+3} concentrations and densities given in Table 1 are exact.

[c] Gravimetric dilution factor (multiplicative) used to relate ampoule's massic activity to that for NPL A08876 or NIST 4337DIL.

Table 3. Results for the LS re-standardization of NIST SRM 4337 and assay of NPL-G.

	LS counter [a]	Scintillant [b]	n [c]	massic activity of solution at reference time ($kBq \cdot g^{-1}$)	s (%) [d]
NPL-G	B	PCS	9	7.4891	0.11
	P	UGAB	9	7.4810	0.11
	W	PCS	9	7.4785	0.12
	B	UGAB	9	7.4741	0.13
	P	PCS	9	7.4796	0.10
	W	UGAB	9	7.4786	0.12
	NPL-G grand mean		6 [e]	7.4802	0.066 [f]
NIST SRM 4337	B	PCS	9	8.3590	0.32
	P	UGAB	9	8.3707	0.06
	W	PCS	9	8.3464	0.33
	B	UGAB	9	8.3671	0.06
	P	PCS	9	8.3571	0.31
	W	UGAB	9	8.3690	0.06
	SRM 4337 grand mean		6 [e]	8.3615	0.11 [f]
ratio NPL-G / NIST SRM 4337			0.89459		0.13 [f]

[a] Refers to LS counter used: 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.

[b] Refers to the scintillant used to prepare the counting cocktails: PCS, "PCS, Phase Combining System" (Amersham Biosciences, Sweden); UGAB, "Ultima Gold AB" (Perkin-Elmer, Waltham, MA, USA).

[c] Number of determinations given by the number of measurement cycles (3) and number of LS samples (3).

[d] Relative standard deviation in percent for the mean massic activity .

[e] Number of values in grand mean.

[f] Relative standard deviation on the grand mean; corresponds to a relative standard deviation of the mean for $\nu = 5$ degrees of freedom.

Table 4. LS results for ratio of NPL-G / NIST SRM 4337 computed for each LS Counter / Scintillant trial.

LS counter [a]	Scintillant [a]	*n* [a]	NPL-G / NIST SRM 4337 massic activity ratio	*s* (%) [a]
B	PCS	9	0.89594	0.28
	UGAB	9	0.89371	0.10
P	PCS	9	0.89603	0.25
	UGAB	9	0.89327	0.15
W	PCS	9	0.89501	0.29
	UGAB	9	0.89360	0.15
mean ratio NPL-G / NIST SRM 4337		6 [b]	0.89459	0.14 [c]
ratio NPL A08876 / NIST 4337DIL		**5.8315 (0.14 %, *n* = 6)**		

[a] See corresponding notes in Table 3.

[b] Number of values in grand mean.

[c] Relative standard deviation on the grand mean; corresponds to a relative standard deviation of the mean for $\nu = 5$ degrees of freedom.

Table 5. Summary of LS assay results.

solution	massic activity of solution at reference time (kBq·g^{-1})	u (%) [a]
NIST SRM 4337 2006 certification, decay corrected	8.359	1.2 [b]
NIST SRM 4337 2008 re-standardization	8.362	0.8 [c]
NIST 4337DIL (to NPL)	**7.718**	**0.8**
NPL-G	7.480	0.8
NPL A08876	**45.01**	**0.8** [c]

[a] Relative combined standard uncertainty with $k = 1$.

[b] Refer to prior citations: National Institute of Standards and Technology (op. cit.., 2006); L. Laureano-Perez, Collé, et al. (op cit., 2007).

[c] See Table 6.

Table 6. Uncertainty analysis for the massic activity of NPL-G and NIST 4337DIL, standardized by 4παβ LS counting with ^{3}H-standard efficiency tracing.

uncertainty component	assessment type	relative uncertainty (%)	
		NPL A08876	NIST 4337DIL
1. LS within-measurement precision; typical standard deviation of the mean for 9 measurements (3 sources x 3 cycles) for a given cocktail composition and given counter. See Table 3.	A	0.06	0.17
2. LS between-measurement-occasion precision; reproducibility in 6 determinations (2 cocktail sets x 3 counters); standard deviation in the six values (equivalent to a standard deviation of the mean). See Table 3.	A	0.07	0.11
3. LS background variability; wholly embodied in components 1 and 2.	A	---	---
4. LS cocktail stability and composition mismatch effects; estimated from typical PCS and UGAB differences. See Table 4.	B	0.2	0.2
5. Gravimetric mass measurements and ^{3}H standard dilution	B	0.07	0.07
6. Gravimetric dilution factors (Table 2)	B	0.1	0.07
7. Livetime determinations for Ls counting	B	0.06	0.06
8. decay corrections for ^{210}Pb and ^{3}H standard	B	0.003	0.003
9. Nuclear data; beta endpoint energies and branching ratios for ^{210}Pb and ^{210}Bi	B	0.4	0.4
10. Computed LS detection efficiency for ^{210}Pb	B	0.6	0.6
11. Computed LS detection efficiency for ^{210}Bi	B	0.04	0.04
12. Assumed α LS efficiency for ^{210}Po	B	0.05	0.05
RELATIVE COMBINED STANDARD UNCERTAINTY (k=1)		0.77	0.79

Table 7. Comparative measurements of NIST and NPL ampoules with NaI(Tl) sandwich detectors.

		NIST		NPL	
ampoule		A	B	E	F
Bottom NaI	*n* [a]	7	8	10	7
	γ rate (s^{-1}) [b]	731.10	730.72	635.77	709.23
	s (%) [c]	0.35	0.16	0.21	0.21
Top NaI	*n* [a]	7	10	11	9
	γ rate (s^{-1}) [b]	736.79	734.01	639.01	709.23
	s (%) [c]	0.16	0.21	0.30	0.35
ampoule massic γ rate ($s^{-1}\cdot g^{-1}$) [d]	Bottom	142.43	142.36	123.71	138.52
	Top	143.54	143.00	124.34	138.47
solution massic γ rate ($s^{-1}\cdot g^{-1}$) [e]	Bottom	131.46	131.40	767.61	771.31
	Top	132.49	131.99	771.52	771.05
mean massic γ rate ($s^{-1}\cdot g^{-1}$) [f]	Bottom	131.43 (0.26 %; n = 15)		769.13 (0.32 %; n = 17)	
	Top	132.19 (0.26 %; n = 17)		771.31 (0.33 %; n = 20)	
ratio NPL/NIST massic γ rates [g]	Bottom	5.8520 (0.41 %, ν = 31)			
	Top	5.8349 (0.42 %, ν = 36)			
grand mean ratio NPL A08876 / NIST 4337DIL [g]		**5.8436 (0.29 %, ν = 66)**			

[a] Number of replicate measurements.

[b] Mean γ-ray emission rate obtained from the n measurements.

[c] Relative standard deviation in percent for the mean γ rate.

[d] Massic γ rate for the ampoule obtained from the mean γ rate divided by the mass of solution in the ampoule (see Table 2).

[e] Massic γ rate for the solution NIST 4337DIL or NPL A08876 as obtained from the massic γ rate for the ampoule multiplied by the gravimetric dilution factor (see Table 2).

[f] The mean value of the massic γ rate for the solution, averaged across the two ampoules. The value in parentheses is the relative standard deviation in percent for the n determinations.

[g] The value in parentheses is the relative standard deviation in percent for ν effective degrees of freedom, where ν is derived from the Welch-Satterwaithe formula using the input numbers of determinations and relative standard deviations.

Table 8. Comparative measurements of NPL and NIST ampoules with Si(Li) detector.

measured ampoule	massic emission rate for measured ampoule ($s^{-1}\cdot g^{-1}$)	dilution factor (Table 2)	massic emission rate for distributed ampoule ($s^{-1}\cdot g^{-1}$)	distributed ampoule
NPL-E	0.36443	6.20499	2.2613	NPL A08876
NPL-F	0.40622	5.56820	2.2619	NPL A08876
NIST-A	0.41611	0.922992	0.38407	NIST 4337DIL
NIST-B	0.42159	0.922992	0.38913	NIST 4337DIL

Table 9. Massic emission rate ratio for NPL A08876 / NIST 4337DIL from Si(Li) detector results.

	mean massic emission rate ($s^{-1}\cdot g^{-1}$)	s (%) [a]
NPL A08876	2.2616	0.02 ($\nu = 1$)
NIST 4337DIL	0.3866	0.93 ($\nu = 1$)
Ratio NPL A08876 / NIST 4337DIL	5.8500	0.93 ($\nu = 3$)

[a] relative standard deviation s in percent and the degrees (or effective degrees) of freedom ν.

Table 10. Comparison of the massic emission rate ratio for NPL A08876 / NIST 4337DIL by three methods.

	ratio	s (%) [a]	difference (%)
LS counting (Table 4)	5.8436	0.14 ($\nu = 5$)	----
NaI sandwich detector (Table 7)	5.8315	0.29 ($\nu = 66$)	- 0.21
Si(Li) spectrometer (Table 9)	5.8500	0.93 ($\nu = 3$)	+ 0.11

[a] relative standard deviation s in percent and the degrees (or effective degrees) of freedom ν.

Figure 1. Scheme used to compare the NIST 4337DIL and NPL A08876 ^{210}Pb solutions

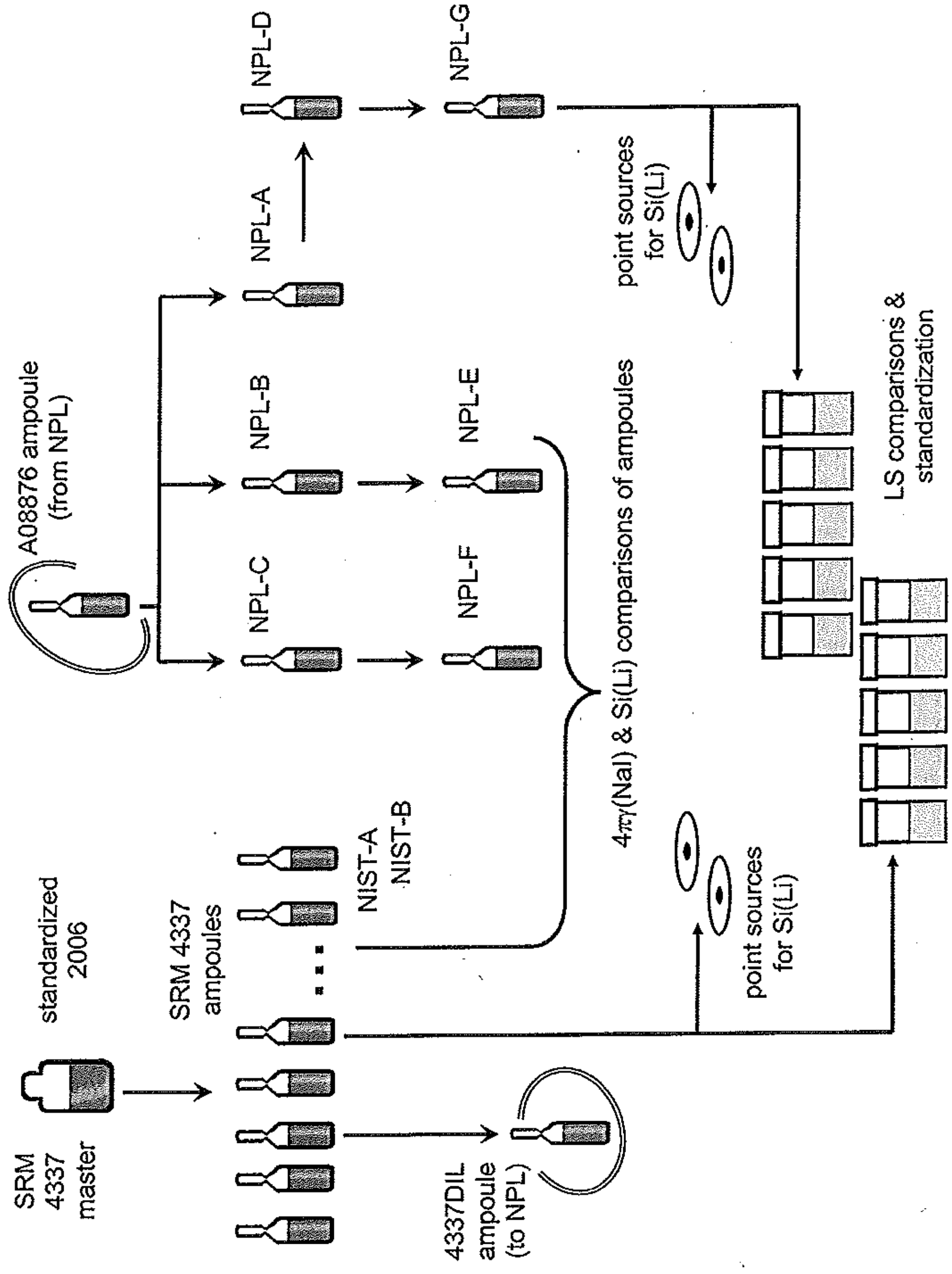
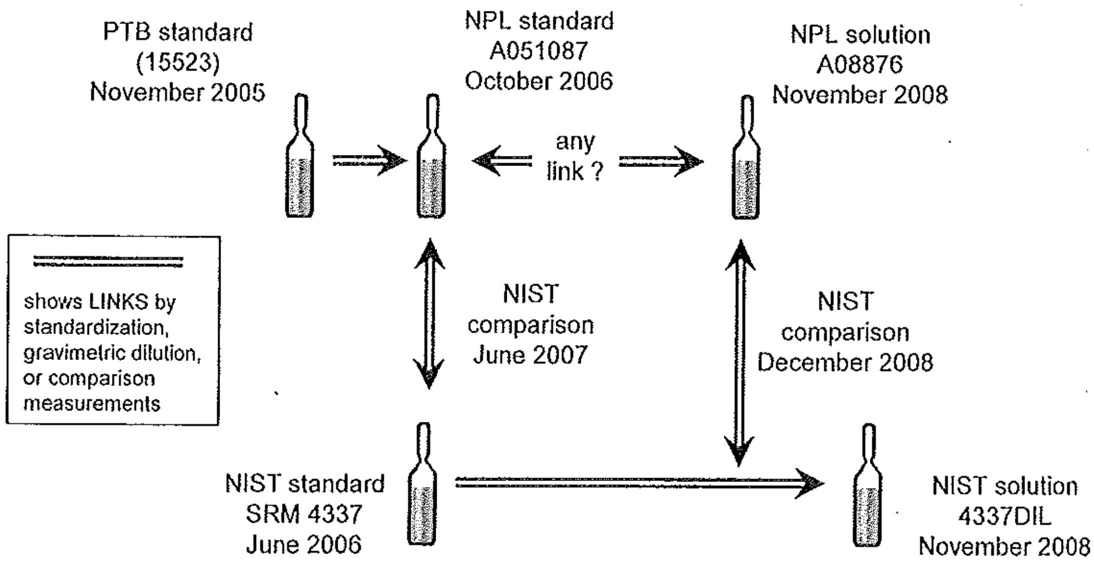


Figure 2. Scheme showing the links between various NPL and NIST 210Pb standards


PTB standard
(15523)
November 2005
NPL standard
A051087
October 2006
NPL solution
A08876
November 2008
any
link ?
shows LINKS by
standardization,
gravimetric dilution,
or comparison
measurements
NIST
comparison
June 2007
NIST
comparison
December 2008
NIST standard
SRM 4337
June 2006
NIST solution
4337DIL
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