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Report on the second small comparison of activity measurements of a solution of ^{133}Ba

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Abstract

Six laboratories compared for the second time their activity measurements of a ^{133}Ba solution, in order to study adsorption and stability problems. Despite a certain progress, the agreement of the results is still unsatisfactory, and the interpretation is further obscured by inconsistencies in the determination of the mass contained in the ampoules.

1. Introduction

The results of the trial comparison [1] of ^{133}Ba showed a spread similar to that observed in the international reference system (SIR) for the same radionuclide, which clearly exceeds the usual value. As no obvious reason for these discrepancies could be found, Section II (Mesure des Radionucléides) of the Comité Consultatif pour les Etalons de Mesure des Rayonnements Ionisants decided, in May 1981, that the same laboratories (see Table 1) undertake a new comparison, paying special attention to adsorption and stability of the solution. PTB volunteered for the preparation and distribution of the solution and proposed to carry out additional studies regarding the chemical behaviour of the barium solution.

Table 1

List of the participants

AECL	Atomic Energy of Canada Limited, Chalk River, Canada
BCMN	Bureau Central de Mesures Nucléaires, Euratom, Geel, Belgium
BIPM	Bureau International des Poids et Mesures, Sèvres, France
LMRI	Laboratoire de Métrologie des Rayonnements Ionisants, Saclay, France
OMH	Orszagos Mérésügyi Hivatal, Budapest, Hungary
PTB	Physikalisch-Technische Bundesanstalt, Braunschweig, Federal Republic of Germany

In October 1981, each participant received one ampoule (NBS type) containing about 3.6 g of an aqueous solution of HCl (1 mol per dm^3) with 23 μg of $BaCl_2$ per gram of solution. An additional ampoule was supplied for the SIR. The activity concentration was about 1.2 MBq g^{-1}, and the mass of the solution was stated for each ampoule. No γ-ray-emitting impurities had been detected by the supplier, the detection limit of relative activity being 2×10^{-4} for energies below 356 keV and 3×10^{-5} for higher energies. LMRI reported later that a similar analysis had also failed to show any impurity in excess of about 10^{-5} of the main activity.

A new reporting form for coincidence measurements has been distributed, and it was recommended to use a value of (3 846 ± 15) d for the ^{133}Ba half-life, which is the arithmetical mean of four recent measurements quoted in ref. [2]. The reference date for the activity measurements was 1981-11-15, 0 h UT.

2. Mass of solution contained in the ampoules; activity concentration from ionization-chamber measurements

The participants were asked to measure first the activity concentration by a calibrated ionization chamber either by using the original ampoule and the mass value given by the PTB (provided the chamber was calibrated for NBS ampoules), or after transfer of the solution into their own ampoules with its own mass determination.

In transferring the solution into a new ampoule PTB observed a higher mass value than that measured for the original ampoule and a lower activity concentration. The participants were informed of this discrepancy and asked - as far as they had not yet started their measurements - to redetermine the mass in the original ampoule as accurately as possible. In all cases higher values were found. Up to now these differences could not be explained satisfactorily.

It can be seen in Table 2 that, on the one hand, the activity concentrations as derived from ionization-chamber measurements agree rather well with each other when the PTB masses are used. On the other hand, when the participants apply their own mass values, the activity concentrations get very close to the absolute results obtained by coincidence measurements (see Table 6).

3. Adsorption tests

It was considered important that each participant carry out adsorption measurements following a well defined procedure and using a calibrated ionization chamber. Table 3 explains the method proposed and gives the results obtained. As can be seen from the figures, the amount of activity sticking to the walls, after a first rinse, varied widely from ampoule to ampoule. Also, further rinsings did not always have the same effect. However, the fractional activities involved (less than 10^{-3}) could not explain the observed differences in concentration.

Table 2

Mass measurements and ionization-chamber results

Laboratory	Ampoule number	Mass of solution (in g) indicated by PTB	Mass of solution (in g) determined by lab.	Mass difference (mg)	Activity concentration at reference date (Bq mg^{-1}) using m_{PTB}	Activity concentration at reference date (Bq mg^{-1}) using m_{lab}
AECL	7173	3.675 0	-	(+ 74)*	-	-
BCMN	7176	3.659 5	-	(+ 95)*	-	-
BIPM	7175	3.648 6	3.659 4	+ 11	1 252.0	1 230.4
	7177	3.629 0	3.697 0	+ 68	1 252.1	1 224.6
LMRI	7178	3.653 1	3.747 2	+ 94	1 259	1 225
OMH	7174	3.645 6	3.700 1	+ 54	1 253	1 234.4
PTB	7179	3.638 8	3.698 8	+ 60	1 252.2	1 221.0
	7180	3.675 5	3.691 5	+ 16	1 252.0	1 225.3

* according to the activity concentration found by the participant

Table 3

Results of the adsorption tests

Laboratory	Activity remaining in the "empty" ampoule after 2 rinsings with 4 cm^3 of distilled water (Bq)	Number of additional rinsings	Final residual activity (Bq)	Remarks
AECL	2 900	2	2 900	a rinse with dilute HCl removed most
BCMN	2 300	2	1 000	
BIPM	706	5	656	
	676	5	357	
LMRI	1 200	3	520	
OMH	38	1	39	± 4 Bq
PTB	34	2	11	NaI(Tl) well crystal

4. Activity measurements by coincidence counting

A summary of technical details reported in the forms is presented on Table 5. All the participants applied the 4π (proportional counter)-γ coincidence technique with efficiency extrapolation and calculated the results using the formulae published by Cox and Isham [3] and by Smith [4]. In addition, LMRI carried out coincidence measurements with a liquid-scintillation detector in the β channel.

5. Activity measurements by 4πγ counting with a large NaI(Tl) well-crystal detector

The efficiency of the detector which LMRI used already in the first comparison [1] has been recalculated with improved values for some of the decay data of ^{133}Ba. The new value is 0.991 2 ± 0.000 6 (1σ). The activity concentration based on sixteen sources turned out to be 1 220.0 Bq mg^{-1} with a standard deviation of 0.4 Bq mg^{-1} and a combined uncertainty of 0.9 Bq mg^{-1}.

Similar measurements have been reported by the Studiecentrum voor Kernenergie, Mol, Belgium, using three sources prepared by BCMN and a recalculated efficiency value. The result was (1 220.3 ± 6.0) Bq mg^{-1}.

6. Activity measurements by the method of selective sampling [5]

BIPM measured some of the sources from each ampoule by means of the recently improved equipment for this new method. The results, summarized in Table 4, are in excellent agreement with the respective coincidence results (see Table 6).

Table 4

Measurements by the selective sampling method

Ampoule number	7175	7177
Number of sources measured	5	4
Number of data points	18	30
Order of fitted polynomial	1	1
Intercept on reference date (Bq mg^{-1})	1 231.0	1 223.1
Standard deviation (")	0.4	0.3

7. Uncertainties - Final results

As in the previous comparison, the uncertainty statements were presented according to the draft recommendation issued by the BIPM [6]. The combined uncertainties and their components are summarized in Table 5. As far as the selective sampling method is concerned, the main contribution seems to be that due to the fitting procedure.

Figure 1 gives a survey of all the results with their uncertainties and includes also the SIR measurements and the 1981 comparison. The link between the three groups is established by the SIR, assuming common values for A_e, the activity needed to produce the same ionization current as the radium reference source. By using this value, the activities contained in the ampoules nos. 7175 and 7177 were calculated. The concentrations were obtained by dividing these activities by the respective solution masses as given by PTB; they agreed with each other and with similar results reported by OMH and PTB.

After transferring the content of the ampoules to new ones, the masses and the ionization currents were measured again. Sources were prepared and the absolute activity concentration was determined. This time, different results were found for the two ampoules, but in each case, the absolute and relative values agreed to better than 2×10^{-3}. These values and those measured before transfer define a scale for the activity concentration which is also shown in Fig. 1. It should be noted, however, that no similar scale applies to the 1981 comparison where the solutions were not transferred subsequently to other ampoules.

8. Conclusion

The results of this second minicomparison show a total spread of 1.4% and are slightly better than those of the first one, but still far from being satisfactory.

Various experiments and checks carried out later by PTB showed that the discrepancies in the mass determinations are unlikely to be due to simple (trivial) weighing errors or balance malfunctioning and that dissolution of glass can be ruled out completely.

On the other hand, the rather disparate findings concerning wall adsorption (see Table 3) might be linked to the observed lack of uniformity of activity concentration.

It is felt that it would be too risky to embark on a full-scale comparison before the reasons of the large spread in the results are known.

Table 5

$4\pi(PC)-\gamma$ and $4\pi(LS)-\gamma$ measurements

			AECL	BCMN	BIPM	IMRI	OMH	PTB
Dilution factor(s)			6.876 97	-	-	-	2.003 8 ± 0.000 2	-
Source preparation								
Substrate; metal coating			VYNS Au-Pd	VYNS Au/Al	VYNS Au	Cellulose Au	VYNS-3 Au-Pd	VYNS Au-Pd
Total mass of source backing before adding further foils		($\mu g\ cm^{-2}$)	30	50	60	40 to 50	30 ± 5	60
Wetting agent			Catanac or Ludox	Ludox (10^{-2})	Ludox SM 10^{-4}	Insulin - Catanac	Ludox + Teepol	Ludox
Drying method			Warm box, dry air	Infrared lamp	open air	-	Infrared lamp	air
Special treatment			NH_3 or $BaSO_4$ precip.	none	none	-	none	disp. on ion-exch. resin
Range of source mass		(mg)	18 to 60	10 to 12	8 to 36	18 to 20	9 to 27	14 to 16
Dead times	τ_β	(μs)	1.925 ± 0.017	3.98 ± 0.02	4.425 ± 0.005	7.22 ± 0.01	3.043 ± 0.005	5.06 ± 0.05
and uncertainties	τ_γ	(μs)	1.992 ± 0.017	4.08 ± 0.02	4.421 ± 0.005	3.74 ± 0.01	3.014 ± 0.005	5.01(5.02)± 0.05
Coinc. resolv. time	τ_r	(μs)	0.689 ± 0.003	1.35 ± 0.08	1.065 ± 0.005	0.973 ± 0.005	1.025 ± 0.010	1.10(1.01)± 0.02
Gandy effect; delay mismatch		(μs)	$\leqslant$ 0.080 ± 0.005	0.00 ± 0.05	0.000 ± 0.010	0.00 ± 0.01	+0.035 ± 0.015	0
correction of intercepts		(%)	$\leqslant$ 0.2	0	0	0	+0.03 to 0.10	0

Table 5 (cont'd)

	AECL			BCMN	BIPM		IMRI		OMH		PTB	
Counting data					Amp.7175	7177	$4\pi(\mathrm{PC})-\gamma$	$4\pi(\mathrm{LS})-\gamma$				2nd γ detector
γ-channel window limits (keV)	250-490	50-110	249-320	> 250	> 250	> 250	250-512		100-490	240-490	> 250	> 250
Typical count rates N_β (s^{-1})	2 500	10 000	10 700	8 000	18 000	31 000	13 000	18 000	11 500	11 500	9 000	
N_γ	650	600	900	1 400	3 340	6 300	3 300	3 700	2 300	1 600	1 000	1 400
N_c	450	250	700	800	2 120	3 790	1 750	2 960	1 600	1 100	600	830
Background rates B_β (s^{-1})	0.4	0.4	0.4	0.2	1.3	1.1	2.4	30	0.90	0.90	3.5	
B_γ	12	0.6	2.0	4	9.4	9.3	11	18	11.60	7.50	1.2	2.7
B_c	0.05	< 0.01	0.01	0.05	0.5	0.5	0.1	0.08	0.10	0.04	0.007	0.009
Number of measured sources	1	15	16	6	7	4	5	1	22	22	16	16
Number of data points	61	45	64	18*	31	46	10	17	22	22	16	15
Range of N_c/N_γ (%)	74-64	51-35	84-76	65-40	66-20	65-20	70-46	80-53	81-56		73-40	
Method for varying N_c/N_γ	foils	15 sources	sources	foils	Au-plated VYNS		screens	defocussing	conducting films		absorption	
Mean time for one data point (s)	1 000	500	500	1 000	5 000	380	1 000	1 000	1 000 to 1 500		8 000	
Time of the measurements	Jan.20	Nov.06	Nov.17	Jan. 15-28	Dec.1-10	Mar.15-24	Feb.	Feb.	Jan. 04-08		Nov. 16-20	
Efficiency functions												
Order of fitted polynomial	1	1	1	1	1	1	1	1	1	1	1	1
Number of degrees of freedom	59	43	62	16**	29	44	8	15	21	21	14	13
Intercept, $y(x \to o)$ (Bq mg^{-1}) on reference date	1 227.7	1 239.5	1 222.5	1 219.7	1 231.7	1 222.1	1 217.40	1 222.0	1 234.20	1 232.70	1 223.3	1 224.0
Standard deviation (Bq mg^{-1})	1.2	4.3	5.0	1.1	0.4	0.3	0.64	0.29	0.32	0.35	0.7	0.6
Slope-to-intercept ratio	0.040 0	0.496 5	−0.270 8	0.016 3	0.031 2	0.029 9	0.036 4	0.075 0	0.038 8	0.038 0	0.034 7	0.038 9
Standard deviation	0.002 1	0.002 4	0.015 5	0.001 1	0.000 1	0.000 1	0.000 8	0.000 4	0.001 5	0.001 5	0.001 0	0.001 0
Reduced Chi square	1.5	6.22	23.7	1.6	(18.9)	(14.0)	-	-	2.65	2.68	0.48	0.37

* per source

** per fit (a separate fit was made for each source)

Table 6

List of uncertainty components - Final results

	AECL	BCMN	BIPM		IMRI		OMH	PTB
Uncertainty components of the final result (approximations of the corresponding standard deviations, in %)	for $250 < E_\gamma < 490$ keV		coinc.	sel. samp.	$4\pi(PC)-\gamma$	$4\pi(LS)-\gamma$		
due to counting statistics	0.1	(0.2)	0.032	0.14	-	-	0.020	0.02
weighing	0.03	0.09	0.045		0.02	0.02	0.005	0.02
dead time	0.01	< 0.05	0.001	-	0.01	<0.01	0.005	0.01
resolving time	< 0.01	< 0.05	0.018	-	0.015	<0.01	0.010	0.04
delay mismatch	< 0.01	0.06	0.016		-	0.01	0.020	0.01
pile-up	-	-	-		-	-	-	0.01
background	0.04	<0.01	0.050		-	<0.01	0.005	0.02
timing	0.01	-	<0.001		0.01	0.01	0.005	0.01
fitting procedure	0.03	0.05	0.022	0.27	0.05	0.023	0.140	0.10
adsorption	0	⩽ 0.02	0.002		-	0.01	0.001	-
others	0.04	-	0.002		0.01	0.01	0.005	-
Combined uncertainty (square root of summed squares, in %)	0.13	0.14	0.081	0.3	0.06	0.04	0.145	0.11
			7175	7177				
FINAL RESULTS (Bq mg^{-1}) Radioactivity concentration on the reference date (1981-11-15, 0 h UT)	1 227.7	1 220.2	1 231.6	1 222.5	1 217.0	1 222.0	1 233.5	1 223.6
Combined uncertainty (Bq mg^{-1})	1.6	1.7	1.0	1.0	0.7	0.5	1.8	1.3

Weighted mean of 8 results: (1 222.6 ± 1.7) Bq mg^{-1} on 1981-11-05, 0 h UT

Unweighted mean " : (1 224.8 ± 5.7) Bq mg^{-1} "

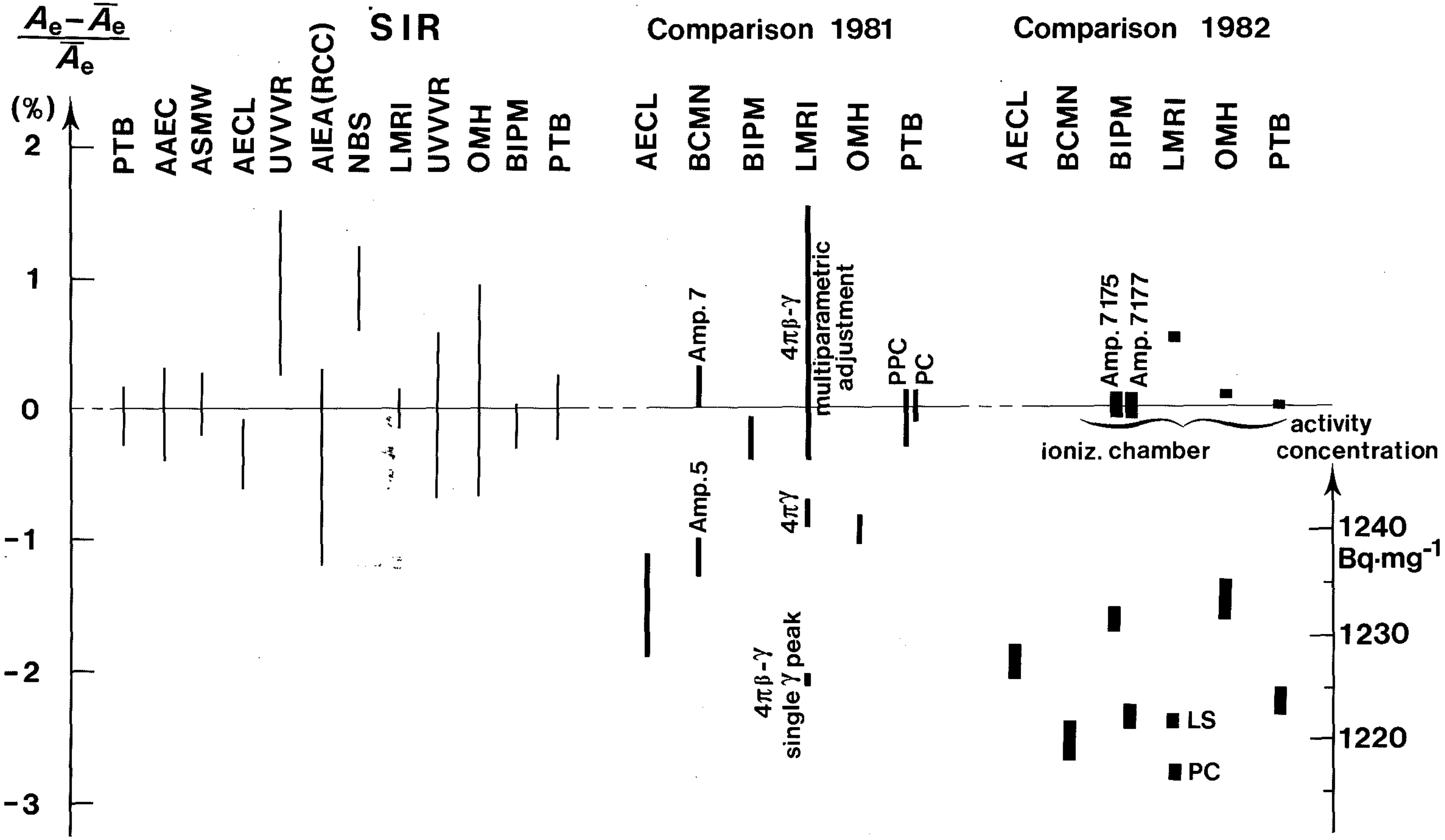

Fig. 1 Graphical representation of the results

References

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