Update of KCRVs for the BIPM.RI(II)-K1 key comparison series

C. Michotte, BIPM

The rules for the selection of data for the KCRV, originally defined by the CCRI(II) in 2001, are as follows:

The key comparison reference value is derived from the unweighted mean of all the results submitted to the SIR with the following provisions:

- a) only primary standardized solutions are accepted¹, with the exception of radioactive gas standards, for which results from transfer instrument measurements that are directly traceable to a primary measurement in the laboratory may be included;
- b) each NMI or other laboratory has only one result (normally the most recent result or the mean if more than one ampoule is submitted);
- c) any outliers are identified using a reduced chi-squared test and, if necessary, excluded from the KCRV using the normalized error test with a test value of four;
- d) exclusions must be approved by the CCRI(II).

1. KCRV updates published since the last CCRI(II) meeting

Since the last CCRI(II) meeting in 2005, seven key comparison reference values have been updated. In most cases, the update followed the decision taken by the CCRI(II) in 2005 and some more recent SIR results for the same radionuclides that fulfilled the criteria above were also included at the same time. In addition, for two radionuclides for which the KCRV was based on only a few results (¹⁸F and ⁹⁹Tc^m), the decision to update the KCRV was approved by e-mail. Finally, for ²²²Rn, a KCRV has been published for the first time because a second result, from the PTB, became available. These updates are described in Table 1.

The LNE-LNHB ⁶⁷Ga result is the lowest value for this radionuclide. However, it was included in the KCRV because it passed the normalized error (NE k = 4) exclusion test. It is interesting to note that the three lowest ⁶⁷Ga degrees of equivalence are those based on anticoincidence counting. Differences depending on the standardization method and type of deadtime used may be related to the ⁶⁷Zn meta-stable state (9 µs) populated by the ⁶⁷Ga decay². In addition, the decay scheme of this radionuclide shows discrepancies. It should be noted that, in this case, the SIR efficiency curve does not help in discriminating in favour of any particular measurement method as the ⁶⁷Ga decay scheme, taking into account the Bobin et al 2007 publication, would be very useful.

In 2005, the CCRI(II) agreed to update the KCRV for ¹³¹I and ²²Na to include results from the PTB and the BARC respectively. However, as other NMIs later submitted ampoules to the

¹ Ionization chamber measurements that are directly traceable to a primary measurement in the laboratory were included in KCRVs up to December 2005.

² Bobin et al., 2007, Standardization of ⁶⁷Ga using a 4π (LS)- γ anti-coincidence system, *Appl. Radiat. Isotop.*, in press.

SIR for these radionuclides (IFIN, KRISS and CMI-IIR for ¹³¹I; CIEMAT and PTB for ²²Na), the updates have been postponed to incorporate the new values for which the criteria are fulfilled. In addition, it appeared necessary to update the ¹³¹I half-life used in the SIR from 8.021 (1) d to 8.0233 (19) d.

In November 2006, the KCWG discussed the case of ¹³¹I. Considering that the IFIN and the KRISS are planning to submit new ¹³¹I ampoules in 2007 to supersede their 2005 results, the KCWG recommended postponing the inclusion of additional results in the KCRV for this radionuclide and to maintain the decision made by the CCRI(II) in 2005.

Radionuclide	Old KCRV / kBq	<i>u</i> (KCRV) / kBq	New KCRV published /	<i>u</i> (KCRV) / kBq	Year	NMI included
			kBq			
¹⁸ F	15 245	32	15 259	29	2005	PTB
⁶⁷ Ga	116 040	520	116 190	560	2006	CIEMAT
						LNE-LNHB [#]
⁶⁰ Co	7 064.6	3.8	7 061.3	3.5	2006	CNEA
						RC
						NIST(1980)*
						IRMM [#]
⁹⁹ Tc ^m	153 070	460	153 140	330	2005	NPL [#]
¹³⁷ Cs	27 549	44	27 534	42	2005	IRMM
						NMIJ
¹³⁹ Ce	132 870	170	132 740	100	2005	NMIJ
²²² Rn	_	_	9 961	53	2006	IRA [#]
						$\mathrm{PTB}^{\#}$

Table 1 k	CRV II	ndates 1	nublished	since	last	CCRI	II)	meeting
	NCK V U	puales p	Juonsneu	since	last		II)	meeting

[#] inclusion approved by CCRI(II) by e-mail

* to replace NIST (1997) ionization chamber result

2. Proposals for KCRV updates

New proposals for updating the KCRVs are summarized in Table 2. All these updates are based on recently published SIR results except for ¹³³Ba and ¹³⁴Cs for which the latest reports are not yet published.

From all the recently published SIR results eligible to be included in the KCRV, none has been excluded. In the case of ¹³⁴Cs, the latest CNEA result is in much better agreement with the other participants. Consequently, applying the NE k = 4 exclusion test on all the ¹³⁴Cs results enables the LNMRI to be identified as a third outlier (in addition to KRISS and CIEMAT). The new KCRV seems now more robust as it is based on less scattered data (see Figure 1). In addition, it is now in close agreement with the SIRIC efficiency curve value (10 120 (10) kBq).

Radionuclide	Old KCRV /	u(KCRV)	NMI to be	Year	Proposed	<i>u</i> (KCRV) /
	kBq	/ kBq	included		KCRV / kBq	kBq
²² Na	7 526	5	BARC §	2004	7530	6
			ANSTO §	1981		
			CIEMAT #	2006		
			PTB [#]	2006		
⁵¹ Cr	487 440	540	NPL	2004	487 540	470
			NMIJ	2004	487 920*	320*
⁵⁷ Co	168 700	400	PTB	2005	168 740	400
⁹⁹ Tc ^m	153 140	330	РТВ	2005	153 <mark>000</mark>	340
¹⁰⁹ Cd	$8\ 136 \times 10^3$	14×10^3	РТВ	2004	8.141×10^{3}	13×10^3
			NIST	2004		
¹¹¹ In	43 000	120	РТВ	2005	43 070	130
¹³¹ I	40 390	40	PTB	2004	40 387 ^{§§}	43 ^{§§}
¹³³ Ba	43 965	68	IFIN [#]	2005	43 932	67
			NMIJ [#]	2006		
¹³⁴ Cs	10 096	16	IRMM	2004	10 116 **	13 **
			PTB	2004		
			MKEH	2004		
			LNE-LNHB	2005		
			NMIJ	2005		
			BARC [#]	2005		
			CNEA #	2005		
²³⁷ Np	—	—	РТВ	2006	74 850	110
			IRMM	2006		
²⁴¹ Am	$2\ 053.7 \times 10^3$	3.3×10^3	NPL	2002	$2.054.3 \times 10^3$	2.8×10^{3}
			VNIIM	2006	$2.055.8 \times 10^{3.44}$	$2.8 imes 10^3$ ##

Table 2. Proposals for KCRV updates

[§] already agreed by CCRI(II) in 2005.

^{§§} already agreed by CCRI(II) in 2005; ¹³¹I half-life updated. See text.

* if IRMM is not selected for the KCRV. See text.

** LNMRI excluded. See text.

[#]results not yet published.

^{##} if MKEH (1979) is not selected for the KCRV. See text.

The use in the KCRV of the 1981 result of the IRMM for 51 Cr seems questionable because the ampoule contained a mass of solution (ca 2.87 g) significantly lower than the 3.6 g requested. In addition, the IRMM result is the lowest value for that radionuclide. Consequently, it is proposed to exclude this result from the KCRV which then becomes 487.92 (32) MBq (see Figure 2). It should be noted that, in this case, the SIR efficiency curve does not help in discriminating in favour of any proposed KCRV as the 51 Cr photon emission probabilities have uncertainties that are too large.



Figure 1. ¹³⁴Cs SIR results eligible for the KCRV. Uncertainties shown are at k = 1.



Figure 2. ⁵¹Cr SIR results eligible for the KCRV. Uncertainties shown are at k = 1.

For ²⁴¹Am, the correction for density applied to the SIR results seems not to be applicable in the case of the 1979 MKEH ampoule that contains only 3.28 cm³ of solution (see the <u>BIPM.RI(II)-K1.Am-241 2007 update report</u>). Indeed, the 1979 MKEH result is the lowest value for that radionuclide (see Figure 3) while the MKEH result in the recent CCRI(II)-K2 comparison is much closer to the KCRV. Consequently, it is proposed to exclude this result from the KCRV, which then becomes 2 055.8 (2.8) × 10³ kBq. Again in this case, the SIR efficiency curve does not help in discriminating in favour of any proposed KCRV as the ²⁴¹Am photon emission probabilities have uncertainties that are too large.



Figure 3. ²⁴¹Am SIR results eligible for the KCRV. Uncertainties shown are at k = 1.