REPORT OF THE CCRI(II) KEY COMPARISON WORKING GROUP

2005 – 2007

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The purpose of the Key Comparison Working Group (KCWG) is to support and aid the CCRI(II) and BIPM in meeting obligations arising from the CIPM Mutual Recognition Arrangement, and to identify areas of radionuclide metrology that require further attention in the pursuit of improved standards, key comparison reference values and degrees of equivalence. The KCWG has met at approximately six-month intervals since its inception with individual members, either singly or in collaboration, taking forward the various items of the WG agenda. The Chairman retired during this period and the KCWG appointed Dr Lisa Karam as his replacement; the CCRI(II) is asked to ratify this appointment. The KCWG continues to provide advice to both the BIPM and the CCRI(II) on the many reports arising from the SIR and various comparisons. Specific items that have been considered, and progress on them, are detailed below.

Status on Generic Groupings Table

At the CCRI section II meeting in 2005, the concept of using a generic grouping of radionuclides, based on radiation emission and consequently on method of analysis, was determined to be a viable means by which the number of radionuclide-measurement comparisons to be carried out would be manageable. In fact, the principal driving force for these tables is to enable the entries (the CMCs) in Appendix C of the CIPM MRA to have supporting comparisons. The consolidated, approved tables were posted on the CCRI(II) website for accessibility to the radionuclide metrology community. At the most recent inter-RMO WG meeting (November 2006), a request was made that these tables be used to aid RMO reviewers when considering entries to Appendix C of the CIPM MRA. Specific guidance on the application of these tables for comparisons to support CMCs have been developed and made available to the community as the first page of the tables. The general guidance is outlined here and attached to this report:

- *Radionuclides have been categorized by the measurement methods appropriate to the specific nuclide. The relative difficulty of measuring a specific nuclide by the indicated method is denoted by a color-coded system: "red" for the most difficult, "yellow" for the moderately difficult, and "green" for the least difficult. It should be noted that a "red" nuclide by one method may be indicated as "green" by another.*

- *In general, results from a comparison of a radionuclide indicated as red for a given primary measurement method may be used to support the calibration and measurement capability claims for all other nuclides of the same energy type by that measurement method (i.e., all other red, yellow and green-indicated nuclides for that method). Results from a comparison of a nuclide indicated as yellow will support claims for the yellow and green-indicated nuclides, and that of a green-indicated nuclide will support CMCs of only green-indicated nuclides by the same method.*
- *A comparison result from a radionuclide measured by a specific primary method generally will not be supportive of claims for that radionuclide measured by other primary methods. However, laboratories are encouraged to use any and various methods appropriate to measuring the radionuclide while participating in a comparison.*
- *Secondary methods of measurement, and the expected associated uncertainties for radionuclides measured by them, are not listed in the final table. As comparisons are generally not done for these methods specifically, no grouping of nuclides is feasible. When such a method is used in the context of a comparison, the results for that comparison can support the CMCs of only that nuclide as measured by that method.*

In terms of application of the Table, the KCWG feels that it is important to remind users that

- they should be aware that using a particular method with a particular radionuclide allows claims only for radionuclides *in the same column* that are marked with *the same or "easier" color*, and
- if a laboratory submits a result with a lower uncertainty than indicated in the table, they may be asked to provide justification.

A considerable amount of time has been spent reviewing the status of the "Generic Groupings" Table over the last two years, and relevant documents have been available directly from the CCRI(II) website for comments for nearly a year. The original list of acronyms that was agreed by the CCRI(II) has been monitored regularly in order to ensure that it keeps abreast of the developments in standardization techniques and allows suitable levels of discrimination among them. The Table is considered to be an active and evolving document, and updates are encouraged as new measurements and comparisons are completed. Specific updates and changes to the original table have been made since 2005 to further completion of the Table and to make it internally consistent:

Issue	Recommended Change	Change Made
Notations and instructions	IC (ionization chamber) and GC (grid ionization chamber) methods are not addressed by the generic tables as they are considered secondary methods	A note to this effect has been added to IC and GC on acronyms page
New column (method)	Prof. Winkler proposed the inclusion of high efficiency 4 pi gamma NaI(Tl) (generally well-type) photon counting as a method for the measurement of selected nuclides for which the it can be considered as near to primary	A new column, 4P-PH-NA-00-00-HE, has been added to the table and populated with appropriate radionuclides.
Correctness of entries in Columns 3	Changes to Columns 3 and 4 are necessary to be as inclusive as possible and to separate out the	A new heading, 4P-AP-LS-00-00-HE, has been given to Column 3 and all non-pure alpha emitters have been greyed out and

and 4	CIEMAT/NIST and TDCR techniques.	moved to columns 12 or 13 as appropriate All entries in Column 4 were moved to column 12 (CN) or 13 (TDCR) as appropriate, and Column 4 has been greyed out (to maintain record).
Correctness of headings in Columns 12 and 13	These headings appear to refer to only pure beta emitters using liquid scintillation counting with either CIEMAT/NIST or TDCR.	Headings were changed to AP/BP/PH/AE/XR-LS-00-00-CN and AP/BP/PH/AE/XR-LS-00-00-TD. Nothing has been deleted from the Table in order to preserve a record of what changes were made.
^{55}Fe	Reports from the recent comparison to be reviewed for additional methods to be included in Table.	An additional entry (4P-XR/AE-PP-00-00-HE, red, 6 %) has been added. Review of reports on-going (comparison recently ended).
^{68}Ge/^{68}Ga	Update on the uncertainty for ??-XR/AE/PO-??-00-00-??	k=2 uncertainty of 6% added
^{87}Sr^{m}	A color assignment for 4P-PH-NA-00-00-HE. CCRI(II) member laboratories that may have measured this nuclide with this technique are asked for their recommendations.	
^{95}Tc^{m}/^{95}Tc	A color assignment for 4P-PH-NA-00-00-HE. CCRI(II) member laboratories that may have measured this nuclide with this technique are asked for their recommendations.	
^{103}Pd	Uncertainties need to be verified.	The UCWG is asked to recommend an uncertainty for 4P-??- PP-00-00-HE (DS) and to ensure that other uncertainties assigned for this radionuclide are reasonable.
^{125}I	Methods, color assignment, and uncertainties needed to be reevaluated for reasonableness.	Current colors remain as originally considered. Additional entries for this radionuclide (4P-BP/AP/XR/AE-NA/CS-00-00-HE, yellow, 2% and ??-XR/AE/PO-??-00-00-??, yellow, 2%) have been added.
^{233}Pa and ^{236}U	Uncertainties are needed	This question is referred to the UCWG; assignment has been made (3 % and 4 %, respectively).

General Issues	
New radionuclides	RMOs and the CCRI(II) are asked if there are new nuclides to be added
Uncertainties	The CCRI(II) is asked to review the uncertainties in the most recent version of the Table.
Additional column headings (methods)	RMOs and the CCRI(II) are asked if there are new primary methods that need to be added

Progress on comparisons arising from generic groupings

To support the CCRI(II) in establishing future comparisons, the KCWG had reviewed the generic groupings tables and identified representative radionuclides (of the medium- to difficult-to-measure categories) in those groupings where there has not been a relevant comparison in the past ten years. If comparisons of these radionuclides continue over the next eight years, this will produce a twenty year period where every generic group has at least one or two comparisons which can be used by the majority of NMIs for the purposes of supporting CMC claims for the measurement of other radionuclides in the same grouping. The proposed comparisons, and their current status as of early 2007, are as follows:

Nuclide	Difficulty	Status 05-2007	Radionuclide type and measurement technique for which a RED (difficult) or YELLOW (medium) nuclide comparison has not been conducted in the last 10 years	
			Acronym	Description
^{3}H	RED	Prep	PB - LSC	Pure beta emitter by liquid scintillation counting
^{35}S	RED		PB - PPC	Pure beta emitter by pressurised proportional counter
^{55}Fe	RED	Report in draft	PEB+	Pure electron capture or positron emitters
^{99}Tc^{m}	RED	Prep LNHB to SIR in 2007	PEB+	Pure electron capture or positron emitters
^{222}Rn	RED	PTB to SIR in 2006	DS - DSA DS - GSC	Delayed state by defined solid angle counting Delayed state by gas counting
^{228}Th	RED		DS - PPC	Delayed state by pressurised proportional counter
^{109}Cd	YELLOW	NIST to SIR in 2005	EG - PPC	Electron capture-gamma emitter by pressurised proportional counter
^{123}Te^{m}	YELLOW		EG - PPC	Electron capture-gamma emitter by pressurised proportional counter
^{131}Cs	YELLOW		PEB+	Pure electron capture or positron emitters
^{133}Xe	YELLOW		BG - GSC	Beta-gamma emitter by gas counting
^{137}Cs	YELLOW		DS – CAC DS - LSC DS - PPC	Delayed state by (anti-) coincidence counting including tracer efficiency Delayed state by liquid scintillation counting Delayed state by pressurised proportional counter

The timing of the tritiated water and gas comparisons is still under discussion between LNHB and NIST, the pilots for the respective comparisons. A call for participants will be sent out after the timeframe and sample compositions are established. Unfortunately, as the LNHB laboratories are now close for renovations, the preparation of the water sources (and the LNHB's participation) will be delayed.

An important issue arose during the comparison of ^{55}Fe. Because preliminary results had shown two apparently discrepant entries, although the laboratories could not identify any problems, the "closing" of the comparison was delayed. Some participating laboratories that had been waiting some months after the original close-date to be able to continue certain measurements were disappointed by the delay. The KCWG proposes that faster feedback (even before the draft report is prepared) to participants after the close of a comparison would be helpful, and that the BIPM should give an update within a month of the originally announced close of a comparison, regardless of its status. This update could include a scatter plot of results, without identification (or with specific identification for the specific participant; this participant would then be obliged to keep that result), and without questionable results included. At the very least, all participants should be provided with the status of the comparison within a month of the stated end.

Because of the short half-life of $^{99}Tc^{m}$, the BIPM has pursued the development of a travelling standard (e.g. NaI(Tl) plus electronics) to facilitate the comparison on-site. The 3"× 3" NaI(Tl) well detector has been received by the BIPM, and the efficiency curve has been calculated using PENELOPE to correct for impurities (the measured efficiency is nominally 90% from 50 to 150 keV). The electronics continue to be tested; the scalers will be managed using a LabView programme, dead time will be corrected for using the MTR2 live-time correction module donated by LNHB, and gain stability still needs to be checked.

Updates on additional comparisons

SIR Of the 40 SIR submissions received by the end of 2006, 33% are published and results for an additional 38% are in hand. The latest data of ^{131}I results to the SIR were from PTB, IFIN, KRISS, and CMI. The KCWG, as already agreed by CCRI(II), has recommended that the PTB entry, along with a change in the half-life, be used to calculate a new KCRV for publication. The CMI, KRISS and IFIN values will be included in the KCDB but not in the calculation of the KCRV (however, KRISS and IFIN have been encouraged to submit new ampoules when convenient as their results appear to be relatively far away from the others). Several ^{237}Np sources, each having different masses, have been submitted to the BIPM to allow extrapolation of results over a series of masses (from 4 g downward) in the SIR. Little activity has been reported on the extension of the SIR to beta emitters, but the chairman of the Working Group overseeing this effort had called a meeting, for April 2007, for further discussion.

Reference materials Completion of the Draft B report for the seaweed comparison has been delayed, but should be finished in advance of the CCRI(II) meeting (expected distribution to participants in early May). The Draft A report for the Rocky Flats II has been delayed until summer 2007 (pending possible participation by Cuba); the Draft A report for shellfish is planned to be completed in late summer 2007. An IAEA phosphogypsum source is being used in comparisons to measure trace elements, and it has been suggested that it could be used as a model for further chemistry/radioactivity reference materials comparisons. The radioactivity measurements of the NORM content are planned as a supplementary comparison, CCRI(II)-S5, piloted by the IAEA.

An RMO comparison of volume sources containing $^{90}Sr/^{90}Y$, ^{152}Eu, or ^{137}Cs was proposed to the KCWG by COOMET in late 2005 as a possible mechanism to support reference material CMCs of similar density (near to 1). All RMOs are encouraged to ask the working group for this type of technical support when considering potential comparisons. Much discussion has followed concerning various aspects of the proposed artifact (such as the impact of geometry effects). Most recently, the pilot had asked the KCWG to approve the Draft A report submitted in November 2006. The main point of concern remains as to whether good performance with this particular matrix (resin) can give credibility to other matrices. The KCWG feels that under appropriate circumstances, this comparison will be acceptable as support for CMCs that claim capabilities for the radionuclide of interest in similar reference materials as long as the densities are similar (definition of "similar" will be left to the CMC reviewer). The KCWG stresses, however, that the uncertainties on the results are expected to be large. Moreover, there is no possible way to link the results to the SIR and this should not be expected by the participants or the pilot. In terms of reporting, the Supplementary Comparison Defined Values (re: the value accepted as the reference value in the comparison) for the three radionuclides concerned are acceptable for use, but cannot be linked to the KCRV for them. A modified Draft A report was to be received late in 2006, but has not arrived as of this writing. As comparison of these sources, particularly if accepted as a supplementary comparison by the CCRI(II), is expected to support CMCs of reference materials, the appropriate CMCs from COOMET were re-visited. The only applicable CMCs are from VNIIM, and are defined as measurements of radionuclides in "Environmental and Industrial

samples," which do not appear in the official list of media (RI services guide); the CCRI(II) should consider whether a separate classification is needed.

Other A comparison of ^{85}Kr, originally planned to begin in 2006 and piloted by LNHB, has been delayed due to issues in shipping the ampoules to NIST (which is to investigate pressure dependence effects) and ampoule homogeneity (being checked at LNHB). When these various issues have been resolved, ampoules will be sent to the participants (CNEA, CMI, KRISS, NIST, NMIJ, NPL, PTB, SMU, LNE-LNHB) from the BIPM; the deadline for reporting will be 6 months after shipment. A EUROMET comparison of ^{124}Sb began at the end of January 2007 with the distribution of samples to the participants and to the BIPM for measurement in the SIR, with results due by end of October 2007. . Standardization is being carried out using two techniques to check gamma emission probabilities. A proposal made to include a recent inter-laboratory comparison of ^{131}I (carried out by the IAEA as a CCRI Supplementary Comparison) had been incorrectly registered prior to the comparison, but the proper paperwork has now been completed. The draft report is now awaited.

Key Comparison Reports

To address the need for an in-depth review of the details of a comparison (the raw data, equations used, and other details from the participating laboratories) so as to produce a more thorough document which could record and archive the technical details of the comparison, participants have been encouraged to use reporting sheets newly-designed to include more complete information during the recent ^{55}Fe comparison. Although five of the participants used the reporting sheets, not all submitted them electronically and several comments on the sheets were received, including:

- A need for additional macros to be written to extract data from respondents' reports into the Comparison Reports.
- The cells in the spreadsheet should be enlarged to include more complete information.
- The report, when printed out, should represent an archival document for auditing purposes (i.e., complete cells need to be displayed and all relevant information should be printable).
- Space should be provided to indicate traceability to time and mass standards.
- The coverage factor needs to be defined in the form so that the reporting sheet could serve a dual purpose and be useful as an audit document.

A separate comment sheet will be developed in order to address some of the above issues. Further comments should be sent to Carine Michotte of the KCWG.

Additional Topics

The originally-planned Comparison Workshop, to have been held in combination with an Uncertainties Workshop in advance of the CCRI(II) meeting, has been postponed until 2008 for logistical reasons. A proposal to use weighted means in the analysis of comparison data, with an advantage that different weighting factors can be used depending on the confidence of the input data, will be considered in the near future (after the preparation of a review article on the methodology for peer review). The proposed date of the next KCWG meeting is 21 May 2007. Final generic groupings will be expected as the primary output of the meeting. It is hoped that the ICRM LSCWG and LSWG will report on possible comparisons proposed during their meetings in January, 2006.

Lisa Karam
KCWG Coordinator
30 March 2007

Appendix

GROUPING CRITERIA FOR RADIONUCLIDES to SUPPORT CMCs

The CCRI(II) requested that the KCWG(II) and the UCWG(II) produce a table of radionuclides that are grouped generically and for which each has an expected measurement uncertainty. Their work is presented in this paper.

The table contains all the radionuclides that are currently given in the CMC tables of the CIPM MRA Appendix C for activity measurement.

An appropriate measurement method has been allocated to each radionuclide depending on its radiation-type and decay scheme. The relative difficulty of measuring a specific nuclide by the indicated method is denoted by a colour-coded system: "red" for the most difficult, "yellow" for the moderately difficult, and "green" for the least difficult method. It should be noted that a radionuclide measured by a "red" method may be easier to measure by another indicated as "green".

Within each coloured cell is the estimated best relative (%) uncertainty value (k = 2) that can be expected for the measurement of that radionuclide, using the specified measurement method.

In general, participation in a key comparison using a measurement method that is coloured red for a given radionuclide supports the CMCs of all radionuclides in the same measurement group whether the radionuclides are indicated by a red, yellow or green colour.

Participation in a key comparison using a measurement method that is coloured yellow for a given radionuclide generally supports the CMCs of all radionuclides in the same measurement group when the radionuclides are indicated by a yellow or green colour.

Participation in a key comparison using a measurement method that is coloured green for a given radionuclide generally supports the CMCs of all radionuclides in the same measurement group, when they are also indicated by a green colour.

The final column in the table indicates the most recent key comparisons and, in red, those proposed by the KCWG(II) to be undertaken by the CCRI(II) over the next ten years.

Regarding CMC claims in particular, it should be noted that:

- **A comparison result from a radionuclide measured using a specific primary method generally cannot support claims for that radionuclide measured by other primary methods. Consequently, laboratories are encouraged to use every appropriate method to measure the radionuclide while participating in a comparison.**
- **Secondary methods of measurement, and the expected associated uncertainties for radionuclides measured by them, are not listed in the table. Normally, only supplementary comparisons would be made for these methods, so no grouping of nuclides is feasible. When such a method is used in the context of a comparison, the results for that comparison can support the CMCs of only that nuclide as measured by that method.**
- **Users of the generic groupings table should be aware that using a particular method with a particular radionuclide allows claims only for radionuclides in the same column that are marked with the *same or "easier"* colour.**
- **If a laboratory submits a result with a lower uncertainty than indicated in the table, they may be asked to provide justification.**