

**BIPM comparison BIPM.RI(II)-K1.Ce-141**  
**of activity measurements of the radionuclide Ce-141**

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**Abstract**

Since 1979, five national metrology institutes have submitted six samples of known activity of  $^{141}\text{Ce}$  to the International Reference System (SIR) for activity comparison at the Bureau International des Poids et Mesures. The activities ranged from about 3 MBq to 23 MBq. The degrees of equivalence between each equivalent activity measured in the SIR and the key comparison reference value (KCRV) have been calculated and the results are given in the form of a matrix. A graphical presentation is also given. The results of this comparison have been approved by Section II of the Consultative Committee for Ionizing Radiation (CCRI(II)), comparison identifier BIPM.RI(II)-K1.Ce-141.

**1. Introduction**

The SIR for activity measurements of  $\gamma$ -ray-emitting radionuclides was established in 1976. Each national metrology institute (NMI) may request a standard ampoule from the BIPM that is then filled (3.6 g) with the radionuclide in liquid (or gaseous) form. The NMI completes a submission form that details the standardization method used to determine the absolute activity of the radionuclide and the full uncertainty budget for the evaluation. The ampoules are sent to the BIPM where they are compared with standard sources of  $^{226}\text{Ra}$  using pressurized ionization chambers. Details of the SIR method, experimental set-up and the determination of the equivalent activity are all given in [1].

Since its inception, the SIR has measured over 818 ampoules to give 590 independent results for 62 different radionuclides. The SIR makes it possible for national laboratories to check the reliability of their activity measurements at any time. This is achieved by the determination of the equivalent activity of the radionuclide and by comparison of the result with the key comparison reference value determined from the results of primary realizations. These comparisons are described as BIPM ongoing comparisons and the results form the basis of the BIPM key comparison database (KCDB) that was set up under the Mutual Recognition Arrangement (MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Ce-141 key comparison.

## 2. Participants

Five NMIs have submitted six ampoules for the comparison of  $^{141}\text{Ce}$  activity measurements since 1979. The laboratory details are given in Table 1. In cases where the laboratory has changed its name since the original submission, both the earlier and the current acronyms are given, as it is the latter that are used in the KCDB.

**Table 1. Details of the participants in the BIPM.RI(II)-K1.Ce-141**

Original acronym	NMI	Full name	Country	Regional metrology organization	Date of measurement at the BIPM
AAEC	ANSTO	Australian Nuclear Science and Technology Organisation	Australia	APMP	1979-05-16
UVVVR	ČMI-IIR	Český Metrologický Institut/Czech Metrological Institute, Inspectorate for Ionizing Radiation	Czech Republic	EUROMET	1979-07-06
–	PTB	Physikalisch-Technische Bundesanstalt	Germany	EUROMET	1992-04-02
LPRI	BNM-LNHB	Bureau national de métrologie-Laboratoire national Henri Becquerel	France	EUROMET	1994-07-08
–	NIST	National Institute of Standards and Technology	United States	SIM	1999-05-04

## 3. NMI standardization methods

Each NMI that submits ampoules to the SIR has measured the activity either by a primary standardization method or by using a secondary method, for example a calibrated ionization chamber. In the latter case, the traceability of the calibration needs to be clearly identified to ensure that any correlations are taken into account.

A brief description of the standardization methods for each laboratory, the activities submitted and the relative uncertainties are given in Table 2. Full uncertainty budgets have been requested as part of the comparison protocol only since 1998. When submitted by the NMIs, the uncertainty budgets are given in Appendix 1 attached to this report, as is the case for the NIST.

The half-life used by the BIPM is 32.51 (0.02) days [3].

**Table 2. Standardization methods of the participants for  $^{141}\text{Ce}$**

NMI	Method used	Half-life / d	Activity / kBq	Reference date	Relative uncertainty $\times 100$	
					Type A	Type B
ANSTO	$4\pi\beta\text{-}\gamma$ coincidence	–	2858	1979-05-15	0.03	0.10
ČMI-IIR	$4\pi\beta\text{-}\gamma$ coincidence	32.5	6594	1979-06-14 10:00 GMT	0.10	0.67
PTB	High pressure ionization chamber calibrated by $4\pi\beta\text{-}\gamma$ coincidence*	–	9368	1992-03-01	0.04	0.31
BNM-LNHB	$4\pi\beta\text{-}\gamma$ coincidence	32.50 (1) [4]	19814 19877	1994-06-27	0.05	0.07
NIST	High pressure ionization chamber calibrated by $4\pi(e+x)$ anti-coincidence	32.50 (1)	22682	1999-04-22 19:00 UTC	0.05	0.37

\*Also measured by liquid scintillation counting (CIEMAT-NIST method).

Details regarding the solution submitted are shown in Table 3, including any impurities, when present, as identified by the laboratories. The main impurity is indicated in the heading; and others are listed within the table.

Recently the BIPM has developed a standard method for evaluating the activity of impurities using a calibrated Ge(Li) spectrometer [5]. The CCRI(II) agreed in 1999 [6] that this method should be followed according to the protocol described in [7] when an NMI makes such a request or when there appear to be discrepancies in the measured SIR values with time.

#### 4. Results

All the submissions to the SIR since its inception in 1976 are maintained in a database known as the "mother-file". The activity measurements for  $^{141}\text{Ce}$  arise from six ampoules and the SIR equivalent activity for each ampoule is given in Table 4. The dates of measurement in the SIR are given in Table 1. The relative standard uncertainties arising from the measurements in the SIR are also shown. This uncertainty is additional to that declared by the NMI for the activity measurement shown in Table 2. Although activities submitted are compared with a given source of  $^{226}\text{Ra}$ , all the SIR results are normalized to the radium source number 5 [1].

Following the recommendations of the CCRI(II), no measurements were deemed necessary at the BIPM concerning the impurities noted by the NIST.

**Table 3. Details of the solution of  $^{141}\text{Ce}$  submitted**

NMI	Chemical composition	Solvent conc. / (mol dm <sup>-3</sup> )	Carrier: conc. / (μg g <sup>-1</sup> )	Density / (g cm <sup>-3</sup> )	Relative activity of impurity <sup>†</sup> $^{139}\text{Ce}$
ANSTO	CeCl <sub>3</sub> in HCl	0.1	–	1.00	0.6 (0.1) %*
ČMI-IIR	CeCl <sub>3</sub> in HCl	0.1	CeCl <sub>3</sub> :170	–	0.92 (0.06) %
PTB	CeCl <sub>3</sub> in HCl	1.0	CeCl <sub>3</sub> :35	1	$^{152}\text{Eu}$ : 0.226 (0.012) % $^{154}\text{Eu}$ : 0.088 (0.007) % $^{192}\text{Ir}$ : 0.007 (0.003) %
BNM-LNHB	CeCl <sub>3</sub> in HCl	1.0	CeCl <sub>3</sub> :100	1.016	0.115 (0.001) % $^{124}\text{Sb}$ : 0.020 (0.001) %
NIST	CeCl <sub>3</sub> in HCl	1.0	CeCl <sub>3</sub> :900	1.018	0.07 (0.01) %

<sup>†</sup> the ratio of the activity of the impurity to the activity of  $^{141}\text{Ce}$  at the reference date

\* Not taken into account in the submitted activity value.

As no submissions were withdrawn and no recent submission has been identified as a pilot study, the results of each NMI are eligible for Appendix B of the MRA

No international or regional comparison for this radionuclide has been held to date so no linking data are identified.

#### 4.1 The key comparison reference value

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

- only primary standardized solutions are accepted, or ionization chamber measurements that are directly traceable to a primary measurement in the laboratory;
- each NMI has only one result (normally the most recent result or the mean if more than one ampoule is submitted);
- any outliers are identified using a reduced chi-squared test and excluded from the KCRV, if necessary using the normalized error test with a test value of four;
- exclusions must be approved by the CCRI(II).

**Table 4. Results of SIR measurements of  $^{141}\text{Ce}$**

NMI	Mass of solution /g	Activity submitted/ kBq	N° of Ra source used	SIR $A_e$ /kBq	Relative uncertainty from SIR	Total uncertainty $u_i$ / kBq
ANSTO	3.594 34	2 858	1	266 200	$26 \times 10^{-4}$	700
ČMI-IIR	3.612 99	6 594	2	264 200	$22 \times 10^{-4}$	1900
PTB	3.612 8	9 368	2	267 589	$54 \times 10^{-4}$	1659
BNM-LNHB†	3.544 5	19 814	3	266 048	$11 \times 10^{-4}$	383
	3.555 8	19 877		265 833		380
NIST	3.729 4	22 682	3	266 115	$11 \times 10^{-4}$	1036

† the mean of the two  $A_e$  values is used.

The reduced data set used for the evaluation of the KCRVs is known as the KCRV file and is the reduced data set from the SIR mother-file. Although the KCRV may be modified when other NMIs participate, on the advice of the Key Comparison Working Group of the CCRI(II), such modifications are only made by the CCRI(II), normally during one of its biennial meetings.

Consequently, the KCRV for  $^{141}\text{Ce}$  has been identified as 266 000 (540) kBq using the results from the ANSTO, BNM-LNHB, ČMI-IIR, NIST and the PTB.

#### 4.2 Degrees of equivalence

Every NMI that has submitted ampoules to the SIR is entitled to have one result included in Appendix B of the KCDB as long as the NMI is a signatory or designated institute listed in the MRA. Normally, the most recent result is the one included. Any NMI may withdraw its result only if all the participants agree.

The degree of equivalence of a given measurement standard is the degree to which this standard is consistent with the key comparison reference value [2]. The degree of equivalence is expressed quantitatively in terms of the deviation from the key comparison reference value and the expanded uncertainty of this deviation ( $k = 2$ ). The degree of equivalence between any pair of national measurement standards is expressed in terms of their difference and the expanded uncertainty of this difference and is independent of the choice of key comparison reference value.

#### 4.2.1 Comparison of a given NMI with the KCRV

The degree of equivalence of a particular NMI,  $i$ , with the key comparison reference value is expressed as the difference between the results

$$D_i = A_{ei} - \text{KCRV} \quad (1)$$

and the expanded uncertainty ( $k = 2$ ) of this difference,  $U_i$ , known as the equivalence uncertainty, hence

$$U_i = 2u_{D_i}, \quad (2)$$

taking correlations into account as appropriate (see Appendix 2).

#### 4.2.2 Comparison of any two NMIs with each other

The degree of equivalence,  $D_{ij}$ , between any pair of NMIs,  $i$  and  $j$ , is expressed as the difference in their results

$$D_{ij} = D_i - D_j = A_{ei} - A_{ej} \quad (3)$$

and the expanded uncertainty of this difference  $U_{ij}$  where

$$u_{D_{ij}}^2 = u_i^2 + u_j^2 - \sum_k (f_k u_{k,\text{corr}})_i^2 - \sum_k (f_k u_{k,\text{corr}})_j^2 \quad (4)$$

and any obvious correlations between the NMIs (such as a traceable calibration) are subtracted as are normally those correlations coming from the SIR.

The uncertainties of the differences between the values assigned by individual NMIs and the key comparison reference value (KCRV) are not necessarily the same uncertainties that enter into the calculation of the uncertainties in the degrees of equivalence between a pair of participants. Consequently, the uncertainties in the table of degrees of equivalence cannot be generated from the column in the table that gives the uncertainty of each participant with respect to the KCRV. However, the effects of correlations have been treated in a simplified way as the degree of confidence in the uncertainties themselves does not warrant a more rigorous approach.

Table 5 shows the matrix of all the degrees of equivalence as they will appear in Appendix B of the KCDB. It should be noted that for consistency within the KCDB, a simplified level of nomenclature is used with  $A_{ei}$  replaced by  $x_i$ . The introductory text is that agreed for the comparison. The graph of the first column of results in Table 5, corresponding to the degrees of equivalence with respect to the KCRV, is shown in Figure 1. This representation indicates in part the degree of equivalence between the NMIs but does not take into account the correlations

between the different NMIs. However, the matrix of degrees of equivalence shown in yellow in Table 5 does take the correlations into account.

## Conclusion

The BIPM ongoing key comparison for  $^{141}\text{Ce}$ , BIPM.RI(II)-K1.Ce-141 currently comprises five results. These have been analysed with respect to the KCRV determined for this radionuclide, and with respect to each other. The matrix of degrees of equivalence has been approved by the CCRI(II) and will be published in the BIPM key comparison database. Other results may be added as and when other NMIs contribute  $^{141}\text{Ce}$  activity measurements to this comparison.

## Acknowledgements

The authors would like to thank the NMIs for their participation in this comparison, Mr Christian Colas of the BIPM for his dedicated work in maintaining the SIR since its inception and for the thousands of measurements he has made over the years and Dr P J Allisy-Roberts for editorial assistance.

## References

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- [6] CCRI *Rapport de la 16<sup>e</sup> session* (June 1999), CCRI(II) 81-82. (Paris: Off. Lib.)
- [7] Michotte C., Protocol on the use of the calibrated spectrometer of the BIPM for the measurement of impurities in ampoules submitted to the SIR, *CCRI(II)/01-01*, 2001, 2p.

Table 5. Table of degrees of equivalence and introductory text for <sup>141</sup>Ce

Key comparison BIPM.RI(II)-K1.Ce-141

MEASURAND : Equivalent activity of <sup>141</sup>Ce

**Key comparison reference value:** the SIR reference value for this radionuclide is 266.00 MBq, with a standard uncertainty  $u_R$  of 0.54 MBq.

$x_R$  is computed from the mean of the participants results.

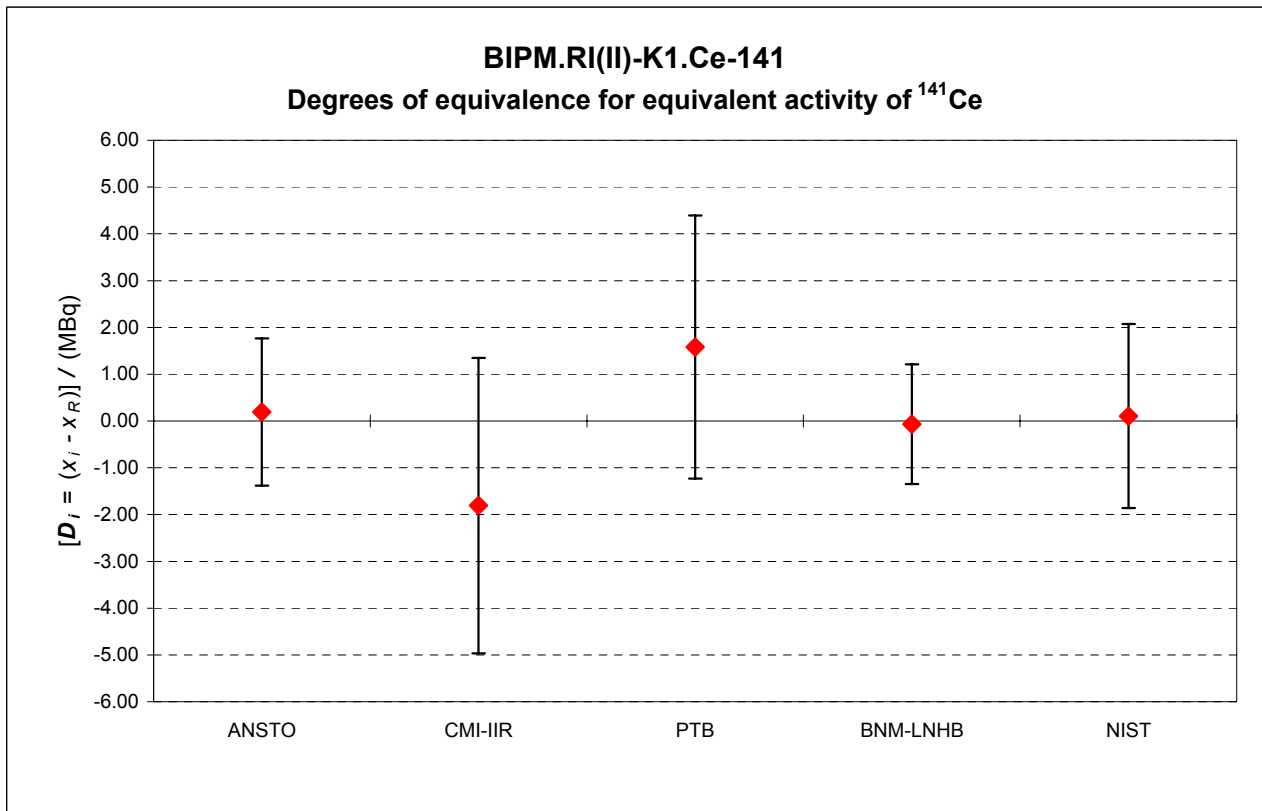
The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms:  $D_i = (x_i - x_R)$  and  $U_i$ , its expanded uncertainty ( $k = 2$ ), both expressed in MBq, with  $n$  the number of laboratories,  $U_i = 2((1-2/n)u_i^2 + (1/n^2)\sum u_i^2)^{1/2}$  when each laboratory has contributed to the calculation of  $x_R$ .

The degree of equivalence between two laboratories is given by a pair of terms:  $D_{ij} = D_i - D_j = (x_i - x_j)$  and  $U_{ij}$ , its expanded uncertainty ( $k = 2$ ), both expressed in MBq. The approximation  $U_{ij} \sim 2(u_i^2 + u_j^2)^{1/2}$  is used in the following table.

Lab <i>i</i> ↓	Lab <i>j</i> →											
			ANSTO		CMI-IIR		PTB		BNM-LNHB		NIST	
	$D_i$	$U_i$	$D_{ij}$	$U_{ij}$	$D_{ij}$	$U_{ij}$	$D_{ij}$	$U_{ij}$	$D_{ij}$	$U_{ij}$	$D_{ij}$	$U_{ij}$
ANSTO	0.19	1.57			2.00	4.05	-1.39	3.60	0.26	1.59	0.09	2.50
CMI-IIR	-1.81	3.16	-2.00	4.05			-3.39	5.04	-1.74	3.88	-1.92	4.33
PTB	1.58	2.81	1.39	3.60	3.39	5.04			1.65	3.40	1.47	3.91
BNM-LNHB	-0.07	1.28	-0.26	1.59	1.74	3.88	-1.65	3.40			-0.17	2.21
NIST	0.11	1.97	-0.09	2.50	1.92	4.33	-1.47	3.91	0.17	2.21		



**Figure 1. Graph of degrees of equivalence with the KCR**  
(as it appears in Appendix B of the MRA)



**Appendix 1. Uncertainty budgets for the activity of  $^{141}\text{Ce}$  submitted to the SIR**

The NIST is the only NMI to have submitted a detailed uncertainty budget according to the MRA as follows:

**Uncertainty evaluation of the massic activity of NIST solution 1287**

Relative standard uncertainties	$u_i \times 10^2$	
	Type A	Type B
PIC A* net response per gram of solution 1287, measured relative to RRS20, 50 100 and 200 $\nu > 100^\dagger$	0.03	–
PIC A net response per Bq of $^{141}\text{Ce}$ in solution, measured relative to RRS20, 50 100 and 200 $\nu > 100^\dagger$	0.03	–
Activity determination used to calibrate PIC A net response per Bq of $^{141}\text{Ce}$ in solution	–	0.35
Half-life of $^{141}\text{Ce}$	0.02	–
Half-life of $^{226}\text{Ra}$	<0.01	
Gravimetric measurements	–	0.05
Live time	–	0.05
PIC A charge collection	–	0.05
Source positioning	–	0.05
Photon emitting impurities	–	0.05
<b>Quadratic summation</b>	<b>0.05</b>	<b>0.37</b>
<b>Total relative combined uncertainty <math>u_c</math></b>	<b>0.37</b>	

$^\dagger$  number of degrees of freedom

\* PIC A, pressurized ionization chamber A

## Appendix 2. Evaluation of the uncertainty of the degree of equivalence

Table 5 indicates for each laboratory the degree of equivalence  $D_i$  with its associated uncertainty  $U_i$ . This appendix presents the procedure used to evaluate these uncertainties.

The degree of equivalence of one laboratory is defined as the difference between the individual value of the equivalent activity  $A_{ei}$  for an NMI  $i$  and a suitable reference value which has been evaluated by the KCDB Working Group and the expanded uncertainty of this difference. Currently, the reference value, KCRV, for a given radionuclide is calculated as the arithmetic mean value of the SIR experimental entries for this radionuclide. Briefly at least four situations can occur depending on the consistency of the experimental SIR data sets :

1. All data are consistent and contribute to the reference value; this is the general case;
2. The value obtained by a laboratory that no longer exists, is used as long as it fits the usual quality criteria; it is taken into account when evaluating the reference value but does not appear in the matrices of results;
3. A value, that has been identified for example as an outlier, is not taken into account for the evaluation of the reference value but, nevertheless, the corresponding laboratory appears in the matrices of results.

The situation where a laboratory that no longer exists but contributes to the reference value and where an outlier has been identified in the data set can occur. This is a combination of both situation 2) and situation 3). The results, deduced from these two preceding cases, are also presented here, case 4.

In the following, the expression of the uncertainty for these four cases is considered on the assumption that the uncertainties of the different equivalent activities  $A_{ei}$  are not correlated. For the sake of coherence with the definition of the variables used in the text, the following notation is used :

$x_i = A_{ei}$  and  $u_i = u_{A_{ei}}$  its uncertainty.

**Case 1.** All  $n$  laboratories contribute to the reference value, and appear in Table 5. In this case obviously we have

$$x_{\text{ref}} = \bar{x} = \frac{\sum_{j=1}^n x_j}{n} \quad (\text{A-1})$$

$$D_i = x_i - x_{\text{ref}} \quad (\text{A-2})$$

$$D_i = x_i - \frac{\sum_{j=1}^n x_j}{n} = x_i \left(1 - \frac{1}{n}\right) - \frac{\sum_{j \neq i} x_j}{n} \quad (\text{A-3})$$

At this stage the uncertainty of  $D_i$  has to be calculated. Applying the method of Gauß for the propagation of the uncertainties it is necessary to calculate the partial derivatives of  $D_i$  with respect to the  $x_i$ .

$$\text{So } \frac{\partial D_i}{\partial x_i} = \left(1 - \frac{1}{n}\right), \text{ and} \quad (\text{A-4})$$

$$\frac{\partial D_i}{\partial x_j} = -\frac{1}{n}, (j \neq i). \quad (\text{A-5})$$

Then the total combined uncertainty becomes

$$u_{c_i}^2 = \left(\frac{\partial D_i}{\partial x_i}\right)^2 u_i^2 + \sum_{j \neq i} \left(\frac{\partial D_i}{\partial x_j}\right)^2 u_j^2 \quad (\text{A-6})$$

$$= \left(1 - \frac{1}{n}\right)^2 u_i^2 + \frac{1}{n^2} \sum_{j \neq i} u_j^2 \quad (\text{A-7})$$

or, after recombination

$$= \left(1 - \frac{2}{n}\right) u_i^2 + \frac{1}{n^2} \sum_{j=1}^n u_j^2. \quad (\text{A-8})$$

When a coverage factor of 2 is used (A-8) becomes

$$U_i^2 = 2^2 \left[ \left(1 - \frac{2}{n}\right) u_i^2 + \frac{1}{n^2} \sum_{j=1}^n u_j^2 \right]. \quad (\text{A-9})$$

**Case 2.** A laboratory was used to evaluate the reference value but does not appear in Table 5.

Let us assign the subscript  $n$  to the additional laboratory that contributes to the reference value. The uncertainty of this laboratory will appear only in the second part of equation (A-9). Accordingly, equation (A-9) becomes

$$U_i^2 = 2^2 \left[ \left(1 - \frac{2}{n}\right) u_i^2 + \frac{1}{n^2} \left(\sum_{j=1}^n u_j^2\right) \right], \text{ for } i = 1, n-1. \quad (\text{A} - 10)$$

**Case 3.** The reference value was evaluated with all reported values except one.

For the sake of simplicity let us assign the subscript  $n + 1$  to the ineligible laboratory so that the subscript for the other laboratories will run from 1 to  $n$ . Under this assumption the treatment of the ineligible laboratory will be slightly different and two formulae are deduced.

The ineligible laboratory does not contribute to the reference value, so the term  $(1 - 2/n)$  in (A-9) reduces to 1 and the uncertainty is simply given by

$$U_{n+1}^2 = 2^2 \left[ u_{n+1}^2 + \frac{1}{n^2} \sum_{j=1}^n u_j^2 \right]. \quad (\text{A} - 11)$$

In the evaluation of the uncertainty related to the  $n$  other laboratories the contribution from laboratory  $n + 1$  disappears totally and the uncertainty remains given by the expression (A-10) without restriction over the subscript range i.e.

$$U_i^2 = 2^2 \left[ \left(1 - \frac{2}{n}\right) u_i^2 + \frac{1}{n^2} \sum_{j=1}^n u_j^2 \right]. \quad (\text{A} - 12)$$

**Case 4.** A laboratory that no longer exists contributes to the reference value and an outlier has been identified for another laboratory.

Let us assign the subscript  $n$  to the defunct existing laboratory so that the expression for the mean (A-1) remains applicable. In addition the outlier will be labelled by  $n + 1$ . For the  $(n - 1)$  first laboratories which contribute to the mean value and appear in Table 5 the uncertainty of  $D_i$  is given by

$$U_i^2 = 2^2 \left[ \left(1 - \frac{2}{n}\right) u_i^2 + \frac{1}{n^2} \sum_{j=1}^n u_j^2 \right], \text{ for } i = 1, n-1. \quad (\text{A} - 13)$$

For the laboratory  $n + 1$  that is ineligible for the KCRV, its coefficient  $(1 - 2/n)$  in (A-13) reduces to 1 and the expression of the uncertainty in Table 5 becomes

$$U_{n+1}^2 = 2^2 \left[ u_{n+1}^2 + \frac{1}{n^2} \sum_{j=1}^n u_j^2 \right], \quad (\text{A} - 14)$$

similar to (A-11).