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RESEARCH ARTICLE

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The ITS-90 after definition of neon isotopic reference composition: extent of the isotopic effect tested on previous inter-comparison results

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Abstract. Starting from the end of the past century, the importance has been recognised of the effect of isotopic composition on some of the temperature fixed points for the most accurate realisations of the ITS-90. In the original definition of the latter, dating back to 1990, only a generic reference was made to “natural” composition of the substances used for the realisation of the fixed points, except for helium. The definition of a reference isotopic composition for three fixed points, e -H₂, Ne and H₂O, while eliminating the non-uniqueness of the Scale in this respect, induced detectable differences in the present and future realisations of the Scale, at the highest accuracy level, with respect to the previous realisations, when they affected the results of past MRA key comparisons, namely the CCT K1 (and K1.1) and CCT K2 (and K2.1–K2.5) and the related regional and supplementary ones. The paper provides evidence of the extent of this effect by using the results of the relevant key comparisons for neon archived in the BIPM KCDB, and of other comparisons existing in the literature (1979–1984, 2007–2012 and 2009–2010 sealed cell comparisons), and discusses the meaning and the outcomes of this evaluation.

Keywords: isotopes / isotopic correction / chemical corrections / neon / triple point / intercomparisons / ITS-90

1 Introductory notes

When the current version of the International Temperature Scale, the ITS-90 [1], was promulgated in 1990, the isotopic effect on the Scale was basically ignored, except originally for helium. The Scale definition only made generic reference to a “natural” composition of the substances used for the realisation of the fixed points.

Since the end of the past century, also thanks to the decreased uncertainty of the best realisations of the ITS-90, the effect of the natural variability of the isotopic composition of some of these substances was recognised as an appreciable contribution to the total uncertainty budget of the realisations of those fixed points, in some cases being the largest single contribution [2,3]. In Table 1 this fact is clearly shown. The goal of a total uncertainty budget of 30 μ K for a measurement on a single cell was reached around 2010 at INRIM [4], PTB and NMIJ.

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1.1 State of the art

Isotopic studies were undertaken, initially on e -H₂ (HD in H₂) [5,6] and H₂O (D₂ and ¹⁸O₂) [7–10], and later also on Ne [4,11–15].

They are relevant to ITS-90, since the triple points of e -H₂ and Ne are required in SPRT subrange 2 (25–273.16) K. The vapour pressure points at \approx 17 and \approx 20.3 K of e -H₂ are required in the range (13.8–273.16) K. The use of the triple point of water (TPW), which can presently be realised also in small metallic sealed cells [16,17], is prescribed for the whole part of the ITS-90 that is based on resistance-thermometer ratios, extending below 273.16 K down to 13.8 K and above 273.16 K up to the silver point, so affecting also all comparisons including these ranges, based on the resistance ratios $W = R(T_{90})/R(\text{TPW})$.

In addition, the triple points of e -H₂ and Ne also affect the range covered by the interpolating gas thermometer (ICVGT), being two of the three fixed points of the ICVGT defined by the ITS-90 in the range 3–25 K – the third being the boiling point of ⁴He (or ³He).

At the time when the key comparisons (KC) CCT-K1 “Realisations of the ITS-90, 0.65 K to 24.5561 K, using rhodium–iron resistance thermometers” (1997–2001) [18], CCT-K2 “Key “Comparison of capsule-type standard

Table 1. Typical and aimed uncertainty budget for cryogenic fixed point measurements [3].

#	Item	Typical 1975-2000 (μK)	Available in 2006 (μK)	Aimed in future (μK)
1	Non-isotopic impurities	$50 \Rightarrow 2000^4$	40	10
2	Isotopic composition	U_p to 700^5	30^6	20
3	Induced by R_{cs}	50–200	30	10
4	Induced by τ	<100	20	10
5	Cryostat other effects ¹	20–300	10	10
6	Resistance measurement ²	30–200	30	10^7
7	T_{tp} definition ³	20–300	20	0
	Total	150–1000	70	30

Legend: R_{cs} = static thermal resistance; τ = cell dynamic time constant; T_{tp} = triple point temperature.

¹ For meltings lasting less than ≈ 12 h. ² Except with $e\text{-H}_2$ when measuring a CSPRT. ³ For $\Delta T_{\text{melt}(20-80\%)} < \approx 0.1$ mK. ⁴ For Ar in O_2 or HD in D_2 . ⁵ For D in H. ⁶ For the best assay uncertainty only. ⁷ Equivalent to $\approx 1 \mu\Omega$ for a SPRT above 40 K.

platinum resistance thermometers from 13.8 K to 273.16 K” (1997–1999) [19] and CCT-K7 “Key comparison of water triple point cells” (2002–04) [20], were organised and completed, the above issue was not yet recognised as important, so not yet formally included in the protocols. Subsequent CCT-K1.1 (2006–14, results available in the BIPM KCDB only recently) [21] and EUROMET.T-K1 (2008–12, similarly) [22] *did not* take the isotopic effect into account, except for INRIM. CCT-K2.1 (2003) [23] and CCT-K2.4 (2006) [24] did not take the isotopic effect into account; CCT-K2.3 (2006) [25] *did* take the isotopic effects into account (official correction for $e\text{-H}_2$ and H_2O ; VSL unofficial evaluation for Ne, see the *separate file* of the Online Supplementary Information (OSI)); also CCT-K2.5 (2015) [26] *did* take the isotopic effects into account; CCT-K2.2 (2014) [27], not yet completed, will also take the isotopic effects into account. The EUROMET.T-K7.1 (2008–2009) [28] and APMP.T-K7 [29] included (optionally in the former) the isotopic issue in the comparisons for water.

For water, the issue also involves the present definition of the kelvin, modified in 2005 to include a reference isotopic composition [30]. In the ITS-90, for $e\text{-H}_2$ and H_2O , corrections to a reference composition were made formally available since the first version of the Technical Annex to the *Mise en pratique* of the kelvin in 2006; for neon it was since its 2014 version [31].

At present, several cases are known of ITS-90 national realisations having adopted, at least partially, isotopic reference compositions: for example, NIST for the all ranges between 4 and 273.16 K only for $e\text{-H}_2$ and of H_2O [32]; INRIM for both $e\text{-H}_2$ and Ne affecting the ICVGT [33].

1.2 Aim of this paper

The study in this paper intends to provide evidence of the consequences of taking the isotopic effect into account. This is best done by using the outcomes of inter-comparisons, because one can also understand to which extent such a correction have affected, and will possibly affect, the differences between laboratories, when they were obtained in studies not having taken that effect into account. In particular, the scrutiny of key comparisons already available

from the BIPM KCDB is important, because that MRA exercise provides to metrology the most valuable results, also in respect to the CMC declarations. However, this paper does not intend to tackle any formal consequence that may arise from, or be related to, the isotopic corrections.

In general, a study on the effect that the correction for the isotopic composition may have on the realisation of the ITS-90 in each laboratory is worthwhile if three conditions are met:

- the isotopic composition of the samples used in a comparison are known;
- the equation to compute the temperature correction is included in the current Annex to the MeP of the kelvin;
- the correction can be applied to the results of a substantial number of participants to the comparison.

In addition, no significant effect due to possible remaining chemical impurities should exists, or it has to be taken in account (see for neon the OSI).

Hydrogen. The present information concerning the isotopic correction for hydrogen in CCT-K1 and K1.1 comparisons is quite limited, so the third condition is not met. In addition, the effect of the correction on the latter is almost irrelevant with respect to the comparison uncertainty. Similarly, for the CCT-K2. x the third condition is not met.

Water. The effect of water isotopic composition will not be analysed in this paper, being minimal in the temperature range below 25 K.

Neon. For neon it is possible to assign the isotopic composition to the gas samples used in a few open-cell realisations or contained, in most cases, in permanently-sealed cryogenic metal cells [13]. In these cases, it is possible to apply the equations in the ITS-90 Technical Annex [31] and compute the results at the reference composition. For neon all the above conditions are met for the CCT-K2, K2.1, K2.3–K2.5 (for the chemical impurity corrections see later Tab. 3 and the OSI).

In addition, some data are also traceable to the first International Inter-comparison of sealed cells performed in 1978–84 [34] or also ensures traceability for several results of the 1997–2005 Star Inter-comparison [12].

Table 2. Data used in this study from comparisons involving the Neon triple point, $T_{90p} = 25.5661$ K. Basic data.

#	Data from comparison ^a	Sample fabricated (owned by)	Year (S = sealed)	Cell # ^b	Gas (assay #) ^c	Purity, nom. (measured)	Set #1, CCT-K2.x comparison results ^d , Set #2			
							$\Delta T_{\text{original}}/\text{mK}$	U/mK	$\Delta T_{\text{original}}/\text{mK}$	U/mK
1	K2, Star	BNM-INM	1985 (S)	BCM2H2O	AL	4N	-0.02	1.08	-1.88	2.8
2	K2, Int84, Star	CNR-IMGC	1979 (S)	3Ne	M-b (#2)	4N5 (>4N5)	0.11	0.28	0.11	0.28
3	K2	KRISS	<1997	Open ^e	M	4N4	0.01	0.4	-0.15	0.4
4	K2	NIST	1979	Open	M (#8)	>5N5	-0.13	0.32	0.04	0.32
5	K2, Star, INRIM	NPL	1993 (S)	Ne2	AP (#18)	>5N	-0.10	0.44	-0.19	0.38
6	K2, K2.1	NRC	1985 (S)	F15	AP (#17)	5N	-0.06	0.44	-0.12	0.44
7	K2, Star, INRIM	PTB	1995 (S)	Ne-7	L (#10)	5N	-	-	0.26	0.4
8	K2.1	VNIFTRI	-	Open	-	-	0.28	0.67	0.22	0.67
9	K2.3, Star	INRIM (VSL)	1999 (S)	12Ne	MG (#11)	5N	-0.645	0.66	-0.71	0.66
10	K2.4, Star	INM	2002 (S)	Ne02/1	AL (#14)	5N (4N2)	-0.625	0.78	-0.685	0.78
11	K2.4	INRIM (INTIBS)	2000 (S)	E3Ne	MG (#11)	5N	-0.245	0.64	-0.305	0.64
12	K2.3, K2.4, K2.5	NRC	2004 (S)	Cu-M-1	P (#9)	5N	-0.225	0.20	-0.285	0.20
13	K2.3, K2.4, K2.5, Star	NRC	1985 (S)	F17	AP (#17)	5N	-0.133	0.20	-0.173	0.20
14	K2.5, INRIM	NMIJ-AIST	2006 (S)	Ne-5	AW (#7)	5N (4N2)	-0.54 ^f	0.60	-0.60 ^f	0.61
15	K2.5, (K2.2), INRIM	INRIM	2002 (S)	Ec2Ne	MG (#11)	5N	-0.69	0.68	-0.75	0.68
16	(K2.2), Star	INRIM (NIM)	2000 (S)	E2Ne	MG (#11)	5N	K2.2 not yet completed			
17	Int84, Star, INRIM	CNR-IMGC	1977 (S)	1Ne	M-a (#3)	4N5				
18	Star	INRIM (PTB)	1999 (S)	E1Ne	MG (#11)	5N				
19	Star	INRIM (DSIR)	1986 (S)	11Ne	S (#13)	4N				
20	Star	INRIM (INTIBS)	2002 (S)	7Ne	S (#13)	4N				
21	INRIM	NMIJ	2005 (S)	Ne-2	IB (#5)	5N				
22	INRIM	INRIM	1999 (S)	15Ne	MG (#11)	5N				
23	INRIM	INRIM	2000 (S)	E4Ne	MG (#11)	5N				
24	INRIM	INRIM	2001 (S)	Ec1Ne	MG (#11)	5N				
25	Int84, Star	VNIFTRI	1997 (S)	MC-897	own	5N				
26	Int84	NRC	1979 (S)	Cell 12	M	4N5				
27	Int84	INM	1982 (S)	BCM4	AL	4N				
28	Int84	NRLM	1978 (S)	1Ne	J	4N				
29	Int84	NRLM	1978 (S)	2Ne	J	4N				

^a K2 = CCT-K2 (NRC Pilot, 1997–99) [19]; K2.1–K2.5 = bi- and tri-lateral CCT-K2.x (NRC Pilot, 2003–2015) [24–26]; Star = Comparison (PTB Co-ordinator, 2007–2012) [12]; Int84 = International Intercomparison (IMGCC-CNR Pilot, 1978–84) [34]; INRIM = Comparison at INRIM (INRIM Co-ordinator, 2008–2009) [37,38].

^b Samples measured.

^c Assays reported in [15].

^d Original differences with respect to the KCRV from [19]. Set#:# indicates thermometers set.

^e Mean of results.

^f Measurements repeated in 2013 with the isotopic composition known and corrected for it; the same thermometer has measured samples from two other bottles.

Table 3. Data for neon used in this study and isotopic correction for CCT-K2.x.

#	Comparisons	Cell#	Set#1, K2.x ^a , Set#2		Corrections		Isotopic-corrected K2.x ^b		$T_{\text{meas,ac}} - T_{\text{KCRV,ac}}/\mu\text{K}$		Isotopic-corrected K2.x ^c		$(T_{\text{thermal,ac}} - 24.5561\text{K})/\mu\text{K}$	
			$T_{\text{meas,bc}}/\text{K}$	$T_{\text{KCRV,bc}}$ = 24.55638	D/T (μK)	Isotopic ^d	Chemical ^e	$T_{\text{meas,ac}}/\text{K}$	$T_{\text{KCRV,ac}}$ = 24.55647	$T_{\text{meas,ac}} - T_{\text{KCRV,ac}}/\mu\text{K}$	$T_{\text{th,mean}}$ = 24.56610 K	$T_{\text{th,mean}}$ = 24.56610 K		
1	K2, Star	BCMH2O	24.55630	24.55640	326	150	24.55663	24.55482	155	-1737 ^g	24.55597	24.55417	-166	-2026 ^g
2	K2, Int84, Star	3Ne	24.55643	24.55649	310	47	24.55674	24.55680	269	237	24.55612	24.55618	-20	-20
3	K2	Open ^f	24.55633	24.55623	-34	1058	24.55630	24.55619	-175	-367	24.55636	24.55626	224	64
4	K2	Open	24.55619	24.55642	22	-	24.55621	24.55644	-259	-121	24.55617	24.55639	28	198
5	K2, Star, INRIM	Ne2	24.55622	24.55619	279	-	24.55650	24.55646	28	-94	24.55594	24.55591	-199	-289
6	K2, K2.1	F15	24.55626	24.55626	308	-	24.55657	24.55656	97	5	24.55595	24.55595	-188	-248
7	K2, Star, INRIM	Ne-7	-	24.55664	196	17(1) ^h	-	24.55683	-	273	-	24.55644	-	244
8	K2.1	Open	24.55660	24.55660	289	-	24.55660	24.55660	-	326	-	24.55631	-	111
9	K2.3, Star	12Ne	24.55668	24.55667	123	24(1) ^h	24.55580	24.55579	-673	-770	24.55555	24.55554	-588	-653
10	K2.4, Star	Ne02/1	24.55570	24.55569	-32	2(1) ^h	24.55571	24.55571	-761	-853	24.55568	24.55568	-460	-520
11	K2.4	E3Ne	24.55608	24.55607	123	24(1) ^h	24.55620	24.55619	-273	-365	24.55595	24.55595	-188	-248
12	K2.3, K2.4	Cu-M-1	24.55610	24.55609	-32	-	24.55609	24.55608	-382	-474	24.55610	24.55610	-39	-99
13	K2.3, K2.4, Star	F17	24.55621	24.55620	308	-	24.55652	24.55651	44	-48	24.55590	24.55589	-241	-301
14	K2.5, INRIM	Ne-5	24.55578	24.55578	4	6(5) ^h	24.55578	24.55578	-207	-299	24.55578	24.55578	-364	-419
15	K2.5, (K2.2), INRIM	Ec2Ne	24.55563	24.55563	123	24(1) ^h	24.55575	24.55575	-357	-449	24.55551	24.55551	-633	-688
17	Int84, Star, INRIM	1Ne	24.55643	24.55649	115	272	24.55655	24.55660	74	42	24.55628	24.55407	-218	175
18	Star	E1Ne			123	24(1) ^h								
19	Star	11Ne			230	150								
20	Star	7Ne			230	150								
21	INRIM	Ne-2			23	24(1) ^h								
22	INRIM	15Ne			123	24(1) ^h								
23	INRIM	E4Ne			123	24(1) ^h								
24	INRIM	Ec1Ne			123	24(1) ^h								
25	Int84, Star	MC-897			289	343(1) ^h								

Cell F15 is the reference cell for the CCT-K2.x.

^a Original, with KCRV_{bc} computed as indicated in the text.

^b Using KCRV_{ac} computed as indicated in the text (isotopic correction only).

^c Isotopic-corrected values.

^d From [31]. See uncertainties in column " $U_{\text{iso},f}$ " in Table 4. Mean for cells #2 to #8 is +180 μK . On isotopic assays, see also [15].

^e In italics the assays for only N_2 impurity (not available for H_2 impurity). No uncertainty: no reliable measure available.

^f See (g) in Table 2.

^g Not elaborated, clearly being an outlier.

^h If the impurity is higher than 10 ppm, the uncertainty of the impurity is 5 ppm or 2.5% of the impurity itself, whichever is higher ($k=1$); if the impurity is lower than 10 ppm, the uncertainty of the impurity is 50% of the impurity itself ($k=1$).

Therefore, in this paper the computation of the corrections and the discussion of some consequences is limited to neon, as an example of the complexity of the information needed to perform sound corrections, which may also affect the same type of corrections for other substances. See [35] for the way the information drawn from [31] should be used to take isotopic composition into account in the calibration of SPRTs on the ITS-90, and [15] for details about the needed isotopic-composition assays and their outcomes.

In the OSI, the effects of the chemical impurities in neon are briefly presented, presently *not* subject to correction according to [31] but only considered as an uncertainty component, to compare the importance of their effect with the isotopic effect.

2 Isotopic effects on ITS-90 for the neon triple point temperature (24.5561 K)

During a worldwide study lasted about 10 years, 26 different bottles of high-purity neon of commercial origin obtained from distillation of air, plus three certified reference mixtures, were studied, including isotopic composition and chemical impurities assays; thermal studies were performed on 34 samples drawn from them [13]. These studies and the subsequent ones on pure ^{20}Ne and ^{22}Ne samples [13] led to the equation, now included in [31], relating $T_{90,\text{ref}}$ (ITS-90 defined value) to the value T_{90} for the isotopic composition of the sample used, and allow to compute, from the measured resistance-ratio value, the corresponding value at $T_{90,\text{ref}}$ [35].

In Table 2 the data are reported for the outcomes of several comparisons concerning neon, and in Table 3 the results for the CCT-K2.x of having taken into account the isotopic effect, based on the assay values selected after the critical evaluation of the assays, and their associated uncertainties [13,15].¹ In Table 5 the results of the isotopic corrections for the Star Inter-comparison are reported [12]. For important specific conditions concerning the way the data of each laboratory were obtained, see the OSI associated with this paper.

2.1 Taking the effect of the isotopic composition into account

We recall here that, according to the MRA, the key comparison reference value (KCRV) of the comparison CCT-K2 is common to all the subsequent integrations of its results with the results of the subsequent supplementary comparisons. It is not affected by uncertainty, as indicated in [19].

In order to take the effect of the isotopic composition on $T_{\text{tp,Ne}}$ into account, it is useful to summarise the exact meaning of the CCT-K2 results (*not including the CCT-K2.x*), and the procedure for applying the isotopic correction to them

- (a) Each participant used a sample of neon whose effect of the isotopic composition, at that time, was taken into account in the uncertainty budget only. This contribution to uncertainty is reported in Table 4, whose mean value amounts to $305\ \mu\text{K}$ out of $361\ \mu\text{K}$ of the total mean laboratory budget (85%) and out of $517\ \mu\text{K}$ of the total comparison mean budget (59%) – so being the dominant contribution.
- (b) The results of the realisation of the triple point temperatures were compared through exchange of thermometers calibrated without taking into account the isotopic effect. However, being the triple point of neon a fixed point of the ITS-90, each participant laboratory associated to the provided measured value of the resistance ratio $R_{\text{tp,Ne}}/R_{\text{TPW}}$ the ITS-90 temperature value, $24.5561\ \text{K}$, exact. When the thermometers were compared in a comparison block at NRC, the measured resistance ratios did not exactly reproduce the supplied values – being that evidence the very reason of the comparison.
- (c) According to the CCT-K2 protocol, although one cell (NRC F15) was taken as the reference, the value $24.5561\ \text{K}$ was not associated to it as the KCRV of the comparison. Instead, the resulting differences in the results, expressed as ΔT_{meas} , were computed in [19] with respect to a T_{KCRV} being the *weighted mean* of the resulting temperatures.²
- (d) Normally those differences would directly express the difference in the realisations of the fixed point between the participant laboratories, T_{thermal} , due to thermal or technical effects. However, in this case, the measured temperatures were instead $T_{\text{meas}} = T_{\text{thermal}} + DT$, where:
 - a DT_x is the temperature difference due to the isotopic composition of a sample with respect to the reference composition defined after 2014, the $^{\text{IUPAC}}_x$ (Ne) one. Thus the corrections $DT_x = T_{\text{meas},x} - 24.5561\ \text{K}$.
 - all the remaining items of the uncertainty budget that are usual in a comparison, are taken into account for T_{thermal} . Notice that the KCRV_{bc} used in [19] is affected by the DT_x – see item (f) below.³ Thus, $T_{\text{thermal}} = T_{\text{meas}} - DT_x = T_{\text{meas}} - (T_x - 24.5561\ \text{K}) = 24.5561\ \text{K} + (T_{\text{meas}} - T_x)$. However, the final aim of this paper is instead to find $\delta T_{\text{thermal}} = T_{\text{thermal}} - \text{KCRV}_{\text{ac}}$.
- (e) Let us start from the fact that $\Delta T = T_{\text{meas}} - T$ ($\text{KCRV}_{\text{bc}} = T_{\text{meas}} - \text{wmean}(T_{\text{meas}})$). This can be approximated by replacing the *weighted mean* with the *simple mean*:

$$\Delta T = T_{\text{meas}} - \text{mean}(T_{\text{meas}}) = T_{\text{meas}} - \text{mean}(T_{\text{thermal}}) - \text{mean}(DT) = T_{\text{thermal}} + DT - \text{mean}(T_{\text{thermal}}) - \text{mean}(DT).$$

² In this paper, the Greek Δ is used for differences before isotopic correction (e.g., $\Delta T_{\text{meas}} = \Delta_{\text{or}}$ in Table 2), while capital Roman D is used for the isotopic effect – see text in (d). In this paper the differences due to a different amount of chemical impurities is not considered – see the OSI.

³ In this paper subscripts bc – for before correction – and ac – for after correction – are used. Thus the KCRVs are indicated in the following as KCRV_{bc} and KCRV_{ac} , respectively.

¹ All uncertainties u in this paper are the standard deviations ($k=1$); U is the expanded uncertainty ($k \approx 2$).

Table 4. Uncertainties for neon of the inter-comparisons CCT-K2 and CCT-K2.x with and without the contribution of the isotopic factor.

Comparisons	#	Cell fabricated (measured)	Sealing Cell date	$U_{KC,original}^a$		U_{lab}^b mean ^b	U_{NET} without U_{iso}^f	U_{CORR} mean ^c	Better by ^j	
				#1	#2					
K2, Star	1	BNM-INM	1985	BCMH2O	1080 ^j	2800 ^j	–	–	–	
K2, Int84, Star	2	CNR-IMGC	1979	3Ne	280	280	110	130	170	39%
K2	3	KRISS	–	Open	400	400	300 ⁿ	340	100	74%
K2	4	NIST	–	Open	320	320	150	180	170	46%
K2, Star, INRIM	5	NPL	1993	Ne2	440	380	300	190	80	79%
K2, K2.1	6	NRC	1985	F15	440	440	320 ⁿ	360	120	73%
K2, Star, INRIM	7	PTB	1995	Ne-7	400	400	320	340	80	73%
K2.1	8	VNIFTRI	–	Open	670	–	400 ⁿ	–	270	–
K2.3, Star	9	INRIM (VSL)	1999	12Ne	620	620	314	–	392	50%
K2.4, Star	10	INM	2002	Ne02/1	760	760	480	600	280	62%
K2.4	11	INRIM (INTiBS)	2000	E3Ne	640	640	320 ⁿ	–	400	49%
K2.3, K2.4	12	NRC	2004	Cu-M-1	640	640	320	–	400	48%
K2.3, K2.4, Star	13	NRC	1985	F17	640	640	320	–	320	50%
K2.5, INRIM	14	NMIJ-AIST	2006	Ne-5	600	600	280 ^o	–	290	50%
K2.5, (K2.2), INRIM	15	INRIM	2002	Ec2Ne	680	680 ^p	8 ^q	–	110	–

s.d.^kMean^l^a Original uncertainties of the ΔT s (ΔT_{or} in Tab. 2).^b Original laboratory uncertainty budgets from [19]; mean of #1 and #2 sets.^c Uncertainties (a) cleaned up from the isotopic uncertainties (“ U_{iso} only” under (b)); mean on #1 and #2 sets.^d Item for the isotopic effect of the estimated laboratory uncertainty.^e Total laboratory uncertainty budget.^f Uncertainty budget corrected for the isotopic effect contribution.^g Uncertainty of the isotopic corrections taken from [15].^h New total uncertainty budget taking also (f) into account.ⁱ Lowering of (h) with respect to (e).^j Data not elaborated.^k Standard deviation of the column data.^l Mean of the column data.^m Improvement of (h) on (e) in percent.ⁿ Also includes chemical impurities.^o Uncorrected, used in the uncertainty budget.^p For the direct comparison (INRIM – NRC) 300 μ K.^q Uncertainty of the corrected value.

Table 5. Data for neon used in this study: isotopic correction for the Star Cell Intercomparison [6].

Comparisons	#	Cell, fabricated (measured)	Sealing date	Cell	Gas (#analysis)	Star (Ref: PTB Ne-7)	
						DT = cell-ref	DT corrected
K2, Star	1	BNM-INM	1985	BCMH2O	AL1 (#19)	210	80
Int84, Star	3	CNR-IMGC	1979	3Ne	M-b (#2)	66	-49
K2	4	(KRISS)	Open	Open	M		
K2	5	(NIST)	Open	Open	M (#8)		
K2, Star , INRIM	6	NPL	1993	Ne2	AP (#18)	132	49
K2, K2.1	7	NRC	1985	F15	AP (#17)		
K2, Star , INRIM	8	PTB	1995	Ne-7^a	L (#10)	0 ^a	0
K2.3, Star	10	INRIM (VSL)	1999	12Ne	MG (#11)	-62	9
K2.4, Star	11	INM	2002	Ne02/1	AL2 (#14)	8	236
K2.4	12	INRIM (INTiBS)	2000	E3Ne	MG (#11)		
K2.3, K2.4	13	NRC	2004	Cu-M-1	P (#9)		
K2.3, K2.4, Star	14	NRC	1985	F17	AP (#17)	170	58
(K2.2)	15	INRIM (NIM)	2000	E2Ne	MG (#11)		
K2.5, INRIM	16	NMIJ	2006	Ne-5	AW (#7)		
INRIM	17	NMIJ	2005	Ne-2	IB (#5)		
K2.5, (K2.2), INRIM	18	INRIM	2002	Ec2Ne	MG (#11)		
Int84, Star , INRIM	2	CNR-IMGC	1977	1Ne	M-a (#3)	37	117
Star	19	INRIM (PTB)	1999	E1Ne	MG (#11)	-23	48
Star	20	INRIM	1986	11Ne	S (#13)	55	21
INRIM	21	INRIM	1999	15Ne	MG (#11)		
INRIM	22	INRIM	2000	E4Ne	MG (#11)		
INRIM	23	INRIM	2001	Ec1Ne	MG (#11)		
Star	24	INRIM (INTiBS)	2002	7Ne	S (#13)	77	43
Int84, Star	25	VNIIFTRI	1997	MC-897	Own	156	63
Int84	26	NRC	1979	Cell 12	M		
Int84	27	INM	1982	BCM4	AL		
Int84	28	NRLM	1978	1Ne	J		
Int84	29	NRLM	1978	2Ne	J		
Star	30	INM	1999	Ne99/2	AL2 (#19)	205	75
Star	31	PTB	1995	Ne-12	L (#10)	8	8
Star^b	32	NIST	1998	NIST201	Math (#20) ^b	130	302 ^b

^a Reference cell.

^b Uncertain filling-gas attribution to a bottle. Not elaborated.

(f) Then, one can compute the net contribution for each sample:

$$T_{\text{thermal},x} = \text{mean}_{\text{ac}}(T_{\text{thermal}}) + \Delta T_{\text{meas},x} - DT_x + \text{mean}(DT_x). \quad (1)$$

where the last term takes into account the offset in the original KCRV_{ac} , and finally, $\delta T_{\text{thermal}} = [\text{mean}_{\text{ac}}(T_{\text{thermal}}) + \Delta T_{\text{meas},x} - (DT_x - \text{mean}(DT_x))] - \text{mean}(T_{\text{thermal}})$:

$$\delta T_{\text{thermal}} = \Delta T_{\text{meas},x} + (\text{mean}(DT_x) - DT_x). \quad (2)$$

The method used in this paper aims at implementing the above procedure based on temperature values. First, one needs to compute the value of KCRV_{bc} , not explicitly reported in [19].

2.1.1 Main comparison (CCT-K2)

The comparison did not define a “reference cell” to which assign the ITS-90 value, 24.5561 K but, as recalled above, the temperature value of the KCRV of CCT-K2 was computed as the *weighted mean* of the temperature values measured in the comparison block by each calibrated thermometer participating in the comparison, leading to the $\Delta T_{\text{original}}$ values in Table 2: the value of $T_{90,\text{K2}}$ assigned to the KCRV was *not* indicated in the Final Report.

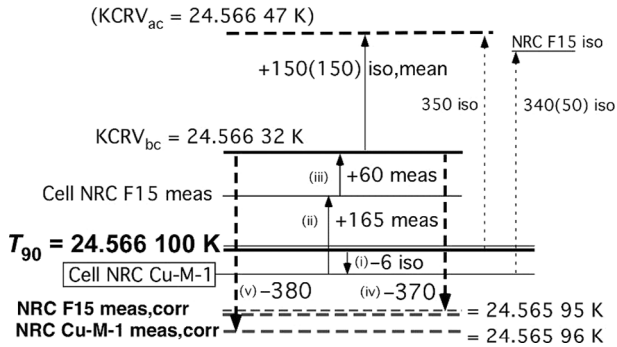


Fig. 1. Graphical representation of the procedure described in Section 2.1.1 for set #1. The procedure starts from cell NRC Cu-M-1, step (i), where $T_{\text{ref}} = T_{90, \text{Ne}} = 24.5561 \text{ K}$. For the KCRV_{ac} see Table 3 and Figure 2. The KCRV_{ac} is 24.56647 K .

When instead the isotopic composition is taken into account, *an arbitrary choice for T_{KCRV} is not allowed anymore*, since the ITS-90 definition was later integrated by attributing the value 24.5561 K to, and only to, neon having the reference isotopic composition, the one recommended by IUPAC, ${}^{\text{IUPAC}}x(\text{Ne})$: ${}^{22}x = 0.0925$; ${}^{21}x = 0.0027$; ${}^{20}x = \text{the rest}$ [36].

This means that, in principle, the CCT-K2 KCRV *after* correction *is unlikely to be equal to* the CCT-K2 KCRV *before* correction, i.e. to the one used to express the differences in Table 2.

The $T_{90}(\text{KCRV}_{\text{ac}})$ and difference ($\text{KCRV}_{\text{ac}} - \text{KCRV}_{\text{bc}}$) can now be evaluated with good approximation. Should the KCRV be the simple mean of the T_{meas} , it would be exact to say that $\text{KCRV}_{\text{ac}} = \text{KCRV}_{\text{bc}} + \text{mean}(DT_x)$; in this case it is a good approximation because the corrections are small with respect to the temperature values. In addition, as illustrated in Section 2.1, one is not interested in the $\text{KCRV}_{\text{ac}}(T_{\text{meas}})$, as it would directly come from the elaboration of the Final Report of CCT-K2, but in the $\text{KCRV}_{\text{ac}}(T_{\text{thermal}})$, i.e. based on the measured values cleaned from the isotopic effect, $T_{\text{thermal}} = T_{\text{meas}} - DT_x$.

Being not all corrections necessarily exactly consistent with each other, the resulting value of the KCRV_{ac} can vary somewhat depending on the correction chosen as the reference (exact) one.

In order to first obtain the value of the $\text{KCRV}_{\text{bc}}(T_{\text{meas}})$, the method used in this paper is the following (where #1 and #2 indicate the thermometer set)⁴:

- (i) the value $T_{90}(\text{Ne}) = 24.5561 \text{ K}$, exact, corresponds to ${}^{\text{IUPAC}}x(\text{Ne})$;
- (ii) a *reference sample is chosen*. The choice of the **NRC F15** sample seems the most obvious, since NRC was the pilot in all K2.x comparisons;
- (iii) for NRC's *last* reference cell, Cu-M-1, the isotopic-effect difference to ${}^{\text{IUPAC}}x(\text{Ne})$ is $DT_{\text{Cu-M-1}} = -6(94) \mu\text{K}$;
- (iv) thus, the ITS-90 value of the NRC Cu-M-1 cell is $T_{90}(\text{Cu-M-1})_{\text{ac}} = 24.566 094 \text{ K}$;

- (v) the NRC difference *measured* through cell F17 [$T(\text{Cu-M-1}) - T(\text{F15})$]_{bc} = $-165(200) \mu\text{K}$, so one gets $T_{90}(\text{F15})_{\text{ac}} = 24.566 259 \text{ K}$;
- (vi) the differences ΔT_{F15} indicated in [19, exCCT-K2] are $\Delta T_{\text{F15}\#1} = T(\text{F15} - \text{KCRV})_{\#1} = -0.06(44) \text{ mK}$ and $\Delta T_{\text{F15}\#2} = T(\text{F15} - \text{KCRV})_{\#2} = -0.12(44) \text{ mK}$;
- (vii) thus $T_{90}(\text{KCRV}_{\text{bc}})_{\#1} \approx 24.566 32 \text{ K}$ and $T_{90}(\text{KCRV}_{\text{bc}})_{\#2} \approx 24.566 38 \text{ K}$;
- (viii) incidentally, the isotopic-effect *from the assays* is [$T(\text{Cu-M-1}) - T(\text{F15})$] = $-342(95) \mu\text{K}$: this is not a discrepancy since it is a different component of the cell differences.

Figure 1 depicts graphically the above procedure.

The *temperatures* actually measured during the CCT-K2, T_{meas} , are obtained by adding to $T_{\text{KCRV}_{\text{bc}}}$ the ΔT_{meas} values recorded under “results” in [19] for each sample.

One could then compute the $T_{\text{meas,ac}}$ by simply adding to ΔT_{meas} the DT_x obtained from the ITS-90 Technical Annex of [31], and then compute the weighted mean from the latter set, for both sets #1 and #2: $\delta T_{\text{meas,ac}} = T_{\text{meas,corr}} - T(\text{KCRV}_{\text{ac}})$. The isotopic corrections are reported in Table 3 in the column “Isotopic DT ”. For the isotopic composition of the samples, see [13–15]. The KCRV_{ac} are reported in Table 3: $T_{\text{KCRV}_{\text{ac}}} = 24.566 471 \text{ K}$ for thermometers #1, and $T_{\text{KCRV}_{\text{ac}}} = 24.566 558 \text{ K}$ for thermometers #2, different, as expected, from the KCRVs before correction: notice that these values correspond to the values in item (viii) above well within the uncertainties. That change alone entails changes of $+0.15 \text{ mK}$ and $+0.18 \text{ mK}$, respectively, to all the $\Delta T_{\text{meas}} = T_{90\text{bc}} - T_{\text{KCRV}_{\text{bc}}}$ in Table 3 – and in Sections 2.1.4–2.1.6 – but note that pair differences are unaffected.⁵

However, the above computation is of limited interest, since the T_{meas} are those biased by the isotopic effect through ΔT . They should be transformed into the T_{thermal} , according to the procedure indicated in Section 2.1, approximated by using the simple mean of the T_{meas} .

Starting from equation (1) in Section 2.1(f), the values known in it are those for: all ΔT_x from [19] and all DT_x from [31]. Note that equation (1), *does not contain any absolute value of T* , but only mean or relative values: however, one obtains the temperature values in Table 3 as $T_{\text{thermal}} = 24.566 100 \text{ K} + \delta T_{90, \text{thermal}}$. The $\delta T_{90, \text{thermal}}$ after correction replace the ΔT_{meas} before correction.

The summary of the uncertainties is reported separately in Table 4 – and commented in Section 2.2.

It is interesting to compare the $\delta T_{90, \text{thermal}}$ with the $\delta T_{\text{meas,ac}}$ computed before. Both are approximated: the latter because, as said, they use T_{meas} ; the former because the simple mean replaced the weighted mean and they still use the ΔT . However, the difference between the two is fixed and only $+40 \mu\text{K}$ for #1 and $+95 \mu\text{K}$ for #2. The reason is that $\delta T_{90, \text{thermal}} - \delta T_{\text{meas,ac}} = \text{KCRV}_{\text{bc}} - 24.5661 \text{ K} - \text{mean}(DT_x)$.

⁴ These values, as all the ΔT_{meas} , are affected by the lack of isotopic correction.

⁵ The new KCRVs were obtained by omitting the INM datum, probably already omitted from the KCRV computation by NRC in the Final Report, and by including KRISS, whose datum was not processed in the Final Report [19].

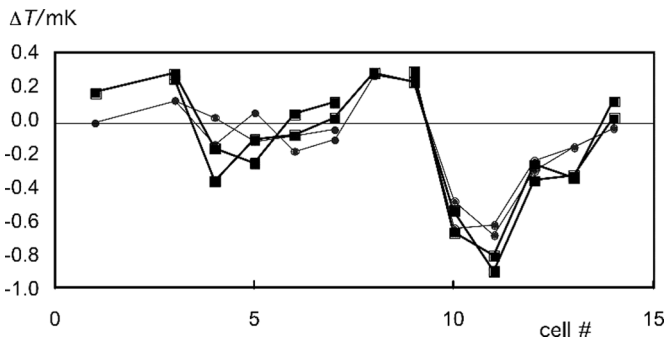


Fig. 2. Graphical representation of the corrected data $\Delta T = (T_{\text{meas,ac}} - T_{\text{KCRV,ac}})$ from Table 3 and the uncorrected data $\Delta T = \Delta T_{\text{original}}$ from Table 2, for cells #1 to #15 and for thermometer sets #1 and #2. Gray dots and lines: uncorrected differences. Black squares and lines: isotopic-corrected differences.

It is to be noticed that, after correction for the isotopic effect, the NRC experimental difference $(\text{Cu-M-1} - \text{F15})_{\text{NRC}} = -165(200) \mu\text{K}$ becomes $(\text{Cu-M-1} - \text{F15})_{\text{thermal}} + 147(220) \mu\text{K}$. However, this change does not require a correction in the procedure Section 2.1.1(v) nor an iteration of the calculations, since in (v) one must use the KCRV based on which the values of the ΔT_{or} in Table 2 were computed, as taken from [19].

2.1.2 Comparison K2.1 (VNIIFTRI, NRC)

In this comparison, the NRC reference cell was still F15. The isotopic composition of the VNIIFTRI sample used in the CCT-K2 is unknown, so no computation is possible to take it into account. Therefore, the measured differences $+0.28 \text{ mK}$ (#1) and $+0.22 \text{ mK}$ (#2) remain unchanged.

Should one assume that the sample in question is from the same bottle that was used for the cell participating to the 1978–84 Inter-comparison [34] and the more recent Star Inter-comparison [12], an isotopic correction of -0.29 mK would apply, leading to a difference of -0.01 mK (#1) and -0.07 mK (#2), respectively.

2.1.3 Comparison K2.3 (NMI-VSL, NRC)

In this comparison, the NRC reference cell was changed to the newest Cu-M-1, whose *uncorrected* difference from cell F15 has been measured at NRC (though cell F17) to be $[T(\text{Cu-M-1}) - T(\text{F15})]_{\text{bc}} = -165(200) \mu\text{K}$. See Table 3 for the values before and after correction of $T_{90}(\text{12Ne})$, $T_{90}(\text{F15})$ and $T_{90}(\text{Cu-M-1})$.

NMI-VSL used INRIM cell 12Ne (5N gas sample from Messer Griesheim, with assay #11, [15] assigned isotopic correction $123 \mu\text{K}$). Thus, from Table 3 the values after correction are $[T(\text{12Ne}) - T(\text{Cu-M-1})] = -0.00055 \text{ K}$, $[T(\text{12Ne}) - T(\text{F15})] = -0.00040 \text{ K}$ and $[T(\text{12Ne}) - T_{90}] = -0.00055 \text{ K}$.⁶

⁶ The above values derive from considering the NRC F15 as the reference cell for the *original* CCT K2 [19]. The $\text{KCRV}_{\text{K2.3}}$ remains that of the CCT-K2.

2.1.4 Comparison K2.4 (INTiBS, LNE-INM, NRC)

In this comparison, the NRC reference cell was also the newest Cu-M-1—see comparison K2.3.

INTiBS used INRIM cell E3Ne (5N gas sample from Messer Griesheim, with assay #11, [15] assigned isotopic correction $123 \mu\text{K}$). Thus, from Table 3 one gets the value of $T_{90}(\text{E3Ne})$ and the values after correction are $[T(\text{E3Ne}) - T(\text{Cu-M-1})] = -0.00015 \text{ K}$, $[T(\text{E3Ne}) - T(\text{F15})] = 0 \text{ K}$ and $[T(\text{E3Ne}) - T_{\text{KCRV}}] = -0.00015 \text{ K}$.⁷

LNE-INM used cell Ne02/1 (5N gas sample from Air Liquide, with assay #14, [15] assigned isotopic correction $-32 \mu\text{K}$). Thus, from Table 3 one gets the value of $T_{90}(\text{Ne02/1})$ and the values after correction are $[T(\text{Ne02/1}) - T(\text{Cu-M-1})] = -0.00042 \text{ K}$, $[T(\text{Ne02/1}) - T(\text{F15})] = -0.00027 \text{ K}$ and $[T(\text{Ne02/1}) - T_{\text{KCRV}}] = -0.00042 \text{ K}$.⁷

2.1.5 Comparison K2.5 (NMIJ-AIST, INRIM, NRC)

This comparison is the *only one* supplied with the results corrected for the isotopic composition of the samples. This requires an inverse computation in order to get the values before correction. For this comparison, the NRC reference cell was also the newest Cu-M-1—as with comparisons K2.3 and K2.4.

NMIJ-AIST used its cell Ne-5 (5N gas sample from AirWater, with assay #7, [15] assigned isotopic correction $4 \mu\text{K}$). Thus, from Table 3 one gets the value of $T_{90}(\text{Ne-5})$ and the values after correction are $[T(\text{Ne-5}) - T(\text{Cu-M-1})] = -0.00032 \text{ K}$, $[T(\text{Ne-5}) - T(\text{F15})] = -0.00018 \text{ K}$ and $[T(\text{Ne-5}) - T_{\text{KCRV}}] = 0.00032 \text{ K}$.⁷

INRIM used cell Ec2Ne (5N gas sample from Messer Griesheim, with assay #11, [15] assigned isotopic correction $123 \mu\text{K}$). Thus, from Table 3 one gets the value of $T_{90}(\text{Ec2Ne})$ and the values after correction are $[T(\text{Ec2Ne}) - T(\text{Cu-M-1})] = 0.00059 \text{ K}$, $[T(\text{Ec2Ne}) - T(\text{F15})] = 0.00044 \text{ K}$ and $[T(\text{Ec2Ne}) - T_{\text{KCRV}}] = 0.00059 \text{ K}$.⁷

2.2 Uncertainty of the CCT-K2 comparisons

The uncertainty issue has been treated separately in Table 4, since its complex analysis requires a full table.

Table 3 shows an important issue: every comparison exercise adds uncertainty to the previous results, in average a 30% more when comparing U_{KC} to $U_{\text{TOT,Tab}}$. In addition, as expected, the increase is larger for the late K2.1–K2.5 ($\approx 30\%$) than for the original K2 ($\approx 20\%$).

Another very important issue is that, by strongly decreasing the uncertainty on the isotopic composition, one strongly affects the overall *laboratory* uncertainty budget of the comparison of neon samples: in fact the average contribution of the isotopic effect is of $305(97) \mu\text{K}$ out of a total of $361(145) \mu\text{K}$, so accounting for more than half.

Since the isotopic uncertainty drops in average from $305(97)$ to $37(33) \mu\text{K}$, the laboratory differences decrease by about 30% in average after compensating for the isotopic effect, and the comparison uncertainty accordingly: *the benefit of the corrections amounts in average to 60 (15)%, i.e. it cuts the comparison uncertainty by more than half.*

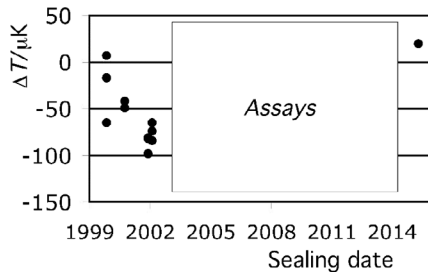


Fig. 3. Differences between samples drawn at INRIM at different times (from left to right) from the same bottle; zero of ΔT arbitrary, hydrostatic head correction applied. Sealing dates of INRIM cells: from left, cell 12Ne–15Ne; cell E2–E4Ne; cell Ec1Ne; cell Ec2Ne; cell Ec29Ne sealed and measured in 2015. Uncertainty of each determination is $\pm \approx 50 \mu\text{K}$.

3 Discussion and final remarks

Figure 2 shows a graphical representation of data reported in Table 3: the mean value of the original deviations ΔT_{or} is $-147(268) \mu\text{K}$ ⁷ for set #1 and $-166(309) \mu\text{K}$ for set #2, while those after correction, $\delta T_{\text{iso}} = (T_{90\text{ac}} - \text{KCRV}_{\text{ac}})$, are $-175(306) \mu\text{K}$ for set #1 and $-187(388) \mu\text{K}$ for set #2, thus basically the same: this only means that the (obviously unknown) thermal contributions to the deviations are dominant.

However, when subtracting from the original differences the contribution of the isotopic effect, in Figure 4 one gets for $\delta T_{\text{thermal,ac}}$ $-167(233) \mu\text{K}$ for set #1 and $-147(240) \mu\text{K}$ for set #2, where the uncertainty is reduced by 60% in average, as already observed in Table 4. In addition, apart for two samples, the deviations after correction are within the interval $(+0.3, -0.2) \text{mK}$, while in Figure 2 they were in the wider interval $(+0.4, -0.8) \text{mK}$.

Therefore, by taking into account the isotopic effect, one can have a substantial improvement in the quality of the comparison results of the CCT-K2.x, though the uncertainty will necessarily increase progressively by adding up new comparisons, as it happened for the supplementary comparisons on the same fixed point – see Table 4 and Section 2.2.

In some cases, it is also possible to compare cell differences of INRIM production or of cells of other NMIs directly measured also at INRIM [4] with the values obtained from the K2.x ones.

In Figure 3 the following cells are shown, all sealed with gas taken from the same bottle of gas (Messer Greisheim, analysis #11 [15]): from the left, 2000: INTiBS (INRIM) cell 15Ne; 2000: VSL (INRIM) cell 12Ne [25] that was made in the same batch (21 Oct 1999) of cell 15Ne; 2001: INRIM cell E3Ne [24], that was made in the same batch (24 Aug 2000) of cell E4Ne; 2001: PTB (INRIM) E1Ne (12 Dec 1999) [12] that was sealed two months before the E2Ne to E4Ne batch; 2002: INRIM Ec1Ne and Ec2Ne (reference cell) [4]; finally, 2015: INRIM Ec29Ne that was sealed from the same bottle of gas after its return back to INRIM after the assays at IRMM, and measured in 2015. All results are compatible with each other except the last one with respect

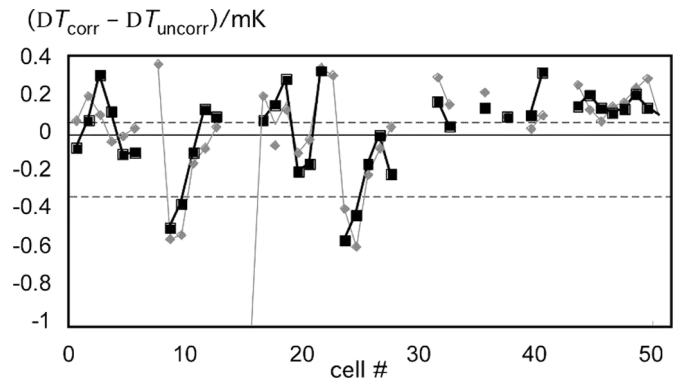


Fig. 4. Graphical representation of differences from the KCRV of K2-xx and Star direct-cell Inter-comparison, uncorrected (gray dots and lines) and corrected (black squares and lines): $(T - \text{KCRV}_{\text{K2ac}}) = \Delta T_{\text{thermal,ac}}$ (Tab. 2); $(T - \text{KCRV}_{\text{K2bc}}) = \Delta T_{\text{original}}$ (Fig. 1). On the left until #28: K2-xx differences for cells #1 to #15 and thermometer sets #1 and #2. $\Delta T_{\text{original, \#1}} = -147(268) \mu\text{K}$, $\Delta T_{\text{original, \#2}} = -166(309) \mu\text{K}$; $\Delta T_{\text{thermal,ac, \#1}} = -167(233) \mu\text{K}$, $\Delta T_{\text{thermal,ac, \#2}} = -147(240) \mu\text{K}$. On the right from #30 to end: Star differences ($56(68) \mu\text{K}$; $74(87) \mu\text{K}$ before isotopic correction), $u = 47 \mu\text{K}$ [12]. The dotted lines indicate the range of the isotopic effect for the studied samples, as obtained from the MeP [31] in Table 3.

to the 2002 ones. The $+94 \mu\text{K}$ increase of T_{tp} in 2015 is attributed in [15] to a possible change for unknown reasons of gas isotopic composition within the bottle during the years.

The results of the CCT-K2.x can also be compared in Figure 4 with the results of the largest direct comparison of samples in sealed cells made after the Int84 [34]: the Star Inter-comparison [12], whose data are compared in Table 5 using the data of Table 2.

Figure 4 (right part) makes self-evident the improvement of the Star data (right part) with respect to the K2.x data (left part). Only two samples are outlying: INM Ne02/1 and NIST 201. The latter is greyed in Table 5 because traceability back to the right filling gas is unsure. With its exclusion, the mean of the corrected differences is $56(68) \mu\text{K}$ (compared with $74(87) \mu\text{K}$ before isotopic correction), thus basically not significant at the U level being the measurement uncertainty ($k = 1$) of $\approx 47 \mu\text{K}$. Except one, all deviations are now within $\pm 50 \mu\text{K}$.

4 Conclusions

The inter-comparisons were taken as the main basis of the analysis in this paper because, in order to evaluate the importance of the effect of the isotopic correction, one needs to have a number of “comparable” data.

This does not necessarily mean that the authors suggest to always “correct” previous data, e.g. due to uncorrected significant chemical-impurity effects. However, in this way, one can get the correct understanding of the often-complex procedure to be used for performing the isotopic correction. Originally, that study was undertaken mainly for the latter purpose, then we considered it worth also for comparing different types of inter-comparisons.

⁷ In parentheses the standard deviation.

The technical conclusions are as follows.

- The exercise made on the KC2 has shown that the total *uncertainty* of the results for neon can be reduced to less than half by making the isotopic correction, because up to 80% of the original uncertainty budget was due to the contribution of the unknown isotopic compositions (Tab. 3).
- Being the original KC2 uncertainty budget made of two main components – the isotopic one and the instrumental one – the results of the corrected data show instead that the resulting inter-comparison *dispersion* of the degrees of equivalence (DoE) for the corrected data is basically the same, though the values are obviously different. This means that the instrumental and thermal uncertainty components (including the not-small comparison contribution) is of the same order of magnitude of the isotopic corrections. So one gets basically the same size of the DoEs, but less uncertain.
- The same exercise made on other types of inter-comparisons have shown the *superiority of the direct-cell comparison*, especially clear for the Star Inter-comparison (Tab. 4 and related figure) – see also the OSI.
- Concerning the effect of the chemical impurities (see the OSI), there is not yet, at present, a formal obligation from CCT to make a correction, at least for the cryogenic range: nothing on this matter is included yet in the Technical Annexe to the ITS-90 [31], though CCT documents of the Working Groups already exist. Therefore that Section is placed in the OSI, together with more information on direct-cell inter-comparisons. However, the contribution to the final values and uncertainties of the chemical impurities, though variable depending on their level, in the worst cases can be substantial and even larger than the isotopic effect.

Supplementary Material

Supplementary Material supplied by the authors.

The Supplementary Material is available at <https://www.metrology-journal.org/10.1051/ijmqe/2017022/olm>.

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