

## On the evidence of the contamination of argon in oxygen, and its effects at its triple point temperature arising from a 50 years-long database of measurements.

Franco Pavese, Peter P.M. Steur

### 1. Introduction

Since the introduction of the IPTS68, and a consequence of the (recent) fast development of the cryogenic field, especially below 50 K [Pavese, 1994; Pavese, 2006; Pavese and Steur, 2019; Steur and Pavese, 2007] the triple point temperature (TP) of substances that are gaseous at room temperature are being measured accurately, among them oxygen (TPO<sub>2</sub>). Such measurements require accurate calorimetry and a pure substance, since the TP temperature is affected by impurities. In the 70's-80's the available purity of oxygen was limited to 20-50·10<sup>-6</sup> amount concentrations of impurities (pioneered by [Muijlwijk, 1968; Ancsin 1970,1973, 1978; Furukawa, 1986]).

Such measurements in the '70s and early '80s resulted in two inter-comparisons. The first one was performed at NPL (1979) [Ward and Compton, 1979] comparing calibrated thermometers (SPRT), with 10 national labs, 23 thermometers + 14 from NPL, and 7 fixed points of IPTS-68. The second (IntInt) was performed in the period 1978-84 at IMGC-CNR [Pavese, 1984; Pavese, 1983; Pavese *et al.*, 1984] derived from measurements on samples in *sealed metal cells* as reported from SPRTs, with 11 national labs, 7 gases, 31 cells, and 200 meltings (on the IPTS-68 scale). Indeed, it was in the middle '70s that IMGC-CNR initiated the sealed-cell technique [Pavese, 1975; Pavese *et al.*, 1976], which then propagated to several other countries (INM, ASMW (PTB), NPL, NRC, NRLM (now NMIJ), PRMI (now VNIIFTRI)), allowing to repeat measurements for subsequent decades on the same stable samples, due to the absence of further manipulation and contamination.

Another summary of the state-of-the-art situation became available in 1999–2002 with the CCT-K2 Key Comparison (and following bi/tri-laterals until 2014), still obtained by comparing calibrated thermometers at NRC in a copper block [Steele, 2002]. With comparison CCT-K2, 9 national labs participated with 18 SPRTs + others from NRC, using 8 fixed points, on the ITS-90 scale. Comparison K2.1 was between VNIIFTRI, NRC, K2.3 between VSL-Nmi and NRC, K2.4 between INTiBS, INM and, NRC and finally K2.5 between NMIJ, INRiM and NRC.

In 1999, IMGC-CNR started the *production* of many sealed cells for several gases, including pure oxygen: 23 O<sub>2</sub> cells were made and tested, of which 15 were then provided to laboratories of 8 countries worldwide.

In 1997-2005 a further STAR intercomparison was made at PTB by directly measuring *sealed cells* supplied to PTB [Fellmuth *et al.*, 2005] by 10 laboratories, with 4 fixed points and 14 cells—2 cells from VNIIFTRI, 2 cells from INM and 6 cells of IMGC-CNR, of which 4 then owned by other laboratories.

In total, it is now possible to analyse together the results of **51 samples**, from 1970 to 2014 (only a few of them from open-cell measurements) with the nominal purity of the gases ranging from 4N5 to 6N. In the case of the NPL comparison, the differences between national realizations of 10 NMIs were found as registered on SPRTs.

### 2. Data and possible information sources for the effect of chemical impurities on the TPO<sub>2</sub>

The effects of chemical impurities on the oxygen triple point temperature have been studied since the 70's, see at least [Mujilwijk, 1968; Ancsin, 1973; Pavese, 1975]. A summary on this subject is published in [Pavese, 2009], as reported here in Table A1, and more recently in [Steur *et al.*, 2020] where is given,

for Ar: @ TP = +11.75 K mol<sup>-1</sup>; @  $\beta$ - $\gamma$  = -13.9 K mol<sup>-1</sup>; @  $\alpha$ - $\beta$  = -133.9 K mol<sup>-1</sup>. A comprehensive summary of the effects on measurements in the last 50 years is reported in the following.

The presence of N<sub>2</sub> may be significant and is not supposed to be altered by normal accurate manipulation of the sample; after that it remains stable in time in each sealed cell. In addition, the presence of noble gases such as Kr, Xe may be significant, but only Kr is likely to be contained in O<sub>2</sub>. All these impurities have the effect to increase the melting range of the TPO2.

The most insidious impurity is the presence of Ar, because it is undetectable by thermal analysis on the TP, since Ar forms a peritectic with O<sub>2</sub>, so it does not alter the melting slope, but only the liquidus temperature. With normal gas chromatography, its peak coincides with that of the prevalent O<sub>2</sub>, so a special procedure is required for their separation.<sup>1</sup> However, its presence in O<sub>2</sub> is irrelevant for the majority of the users, therefore producers very often *omit* this test, even in recent times [Nasso *et al.*, 2009, Shimosaka, 2017]: in most cases only a “batch value” is provided, when at all. Specific studies on the unreliability of analyses regarding Ar contamination were done since 1988 [Pavese *et al.*, 1988,], showing that the error in Ar content can be quite relevant on the measured temperature of the TPO2. More recently, it was found that the Ar effect can be evaluated instead by measuring the solid-to-solid transitions of O<sub>2</sub>, where it *lowers* the correct temperature value. In [Kang, 1996; Kang, 2001] the  $\beta$ - $\gamma$  transition was studied and more recently [Steur *et al.* 2017; Steur *et al.*, 2020; Steur *et al.*, 2020b] studied both the  $\alpha$ - $\beta$  and  $\beta$ - $\gamma$  transitions by using calibrated Ar-in-O<sub>2</sub> mixtures at INRiM (formerly IMGCCNR), supplied by KRISS [Yang *et al.*, 2017], where the  $\alpha$ - $\beta$  s.s.t. was found to provide a much lower uncertainty in determining the amount concentration  $x(\text{Ar})$ .

In Table 1 a summary of the samples on which the triple point of oxygen was published in International Intercomparisons and at IMGCC (later INRiM) is reported. Effect on TPO2 from analysed samples: Argon: +11.75 K mol<sup>-1</sup>. Nitrogen: -22 K mol<sup>-1</sup>.

**Table 1.** Overview of the inclusion of oxygen triple-point cells in International Intercomparisons and in comparisons performed at IMGCC (later INRiM).

1	2	3	4	5	6	7	8	9
No.	Cell	Sealed	Producer	Measured by	Gas data			Comparison
			(to Owner)		(...) batch; certified $x(\text{Ar})$	(...) batch; certified $x(\text{N}_2)$	Gas	
0	<b>Long stem</b>	(1973) <sup>b</sup> 1975 <sup>c</sup>	IMGCC	IMGCC, NPL	(N5); 10, 5	8, 5 <sup>a</sup>	AP&C	Internal, NPL
1	O200/2	2000	INM	INM, PTB, NRC	(5N5)	(<4)	Air Liquide1	K2, STAR
2	O202/1	2002	INM	INM, PTB	(N6)	—	Air Liquide2	STAR
3	<b>1O2</b> (b1)	1976	<b>IMGCC</b> <sup>^</sup>	IMGCC, PTB	(4N8, <10); 10	8	SIO4	IntInt (Ref), K2, STAR
4	2O2 (b1)	1976	IMGCC (to INTiBS)	IMGCC, PTB	(4N8, <10); 10	8	SIO4	STAR
			(at INTiBS)	INTiBS, NRC				
5	9O2 (b4)	1986	IMGCC (to PTB)	IMGCC, PTB	(5N5, <0.5); 5	0.5	SIAD1	STAR
6	10O2 (b4)	1986	(IMGCC (to PTB))	IMGCC, PTB, NPL	(5N5, <0.5); 5	0.5	SIAD1	NPL, STAR
7	11O2 (b4)		IMGCC (to DSIR)					
8	12O2 (b4)		IMGCC					
9	13O2 (b5)	1999	IMGCC (to VSL)	IMGCC, PTB	(5N5, <10); 3	5	Messer1	K2.3, STAR
10	E1O2 (b6)	1999	IMGCC (to PTB)	IMGCC, PTB	(5N5, <10); 3	5	Messer1	STAR
11	<b>O2-4</b>	1996	PTB	NPL, PTB, NRC	(5N5) $\leq 1$	$\leq 0.5$	AGA	NPL, K2, STAR (Ref)
12	O2-M2-1	1983	NIST	NIST, PTB	—	—	KMnO <sub>4</sub>	IntInt, STAR

<sup>1</sup> In the past, the only safe way to measure Ar impurity in O<sub>2</sub> was the concentration of Ar by adsorption of most O<sub>2</sub> on getters of various sorts [Roboz, 1967; Yamaguchi, 1967; Karlsson, 1975; De Paz *et al.*, 1974].

13	<b>O2-2</b>	1995	NPL	NPL, PTB	(4N8, < 8)	(<5)	Air Liquide	NPL (Ref), K2, STAR
14	O2-F10	1985	NRC	NRC, PTB	(4N8)	—	Air Products	IntInt, STAR
15	MC-495	1995	VNIIFTRI	VNIIFTRI, PTB	(N5)	—	—	NPL, IntInt, STAR
16	MC 897	1997	VNIIFTRI (to PTB)	VNIIFTRI, PTB	(N5); 0.06	2.9	—	NPL, IntInt, K2.1, STAR
17,18, 19	(6O2 to 8O2 (b3))	1978	IMGC	IMGC, NRC	(4N8, <3); 65	1.8	SIO5	Internal, K2
20	3O2 (b1)	1976	IMGC	IMGC	(4N8, <10); 10	8	SIO4	Internal
21	4O2 (b2)	1978	IMGC	IMGC	—	—	O-Math1	Internal
22	5O2(b2.1)	1978	IMGC (to LakeShore Inc.)	IMGC	—	(<5)	O-Math1	—
23 24	14O2 (b5) (16O2 (b5))	1999	IMGC (to KRISS) IMGC (to TIPC)	IMGC	(5N5, <10); <3	(<5)	Messer1	Internal
25 26 27	E2O2 (b7) E3O2 (b7) E4O2 (b7)	1999	IMGC (to NIM) IMGC (to INTiBS) IMGC (to TIPC)	IMGC	(5N5, <10); <3		Messer1	Internal
28	Eb1O2 (b8)	2001	IMGC (to INTiBS)	IMGC, INTiBS	(5N5, <10); <3	(<5)	Messer1	Internal
29	Eb2O2 (b8)	2001	IMGC (to PTB)	IMGC	(5N5, <10); <3	(<5)	Messer1	Internal
30	Ec1O2 (b9)	2002	IMGC	IMGC, INTiBS, NRC	(5N5, <10); <3	(<5)	Messer1	K2.5
31,32	Ec26O2 (b10) Ec27O2 (b10)	2014	IMGC	IMGC	(5N5, <10); <3	(<5)	Messer1	Internal
33	7801	1978	NMIJ	NMIJ, IMGC, NRC	(N4)		—	IntInt
34	CO-7	1984	NBS	NBS, IMGC, NRC	—		KMnO <sub>4</sub>	NPL, K2
35	8O2 INM	1976	INM	INM, IMGC	(5N8, <12)	<5	Air Liquide	IntInt
36	BCM4	1982	INM	INM, IMGC	(5N8, <12)	<5	—	K2.4, IntInt
37	PP07	1981	NIM (Mod. INM)	NIM	(5N8); 0.15	3.1	—	IntInt
38	PP11	1981	NIM (Mod. INM)	NIM	(N5); 0.8	4.2	—	IntInt
39	MC <sup>d</sup>	1973	PRMI	PRMI			—	NPL, IntInt
40	15	1979	NRC	NRC, IMGC			Matheson	IntInt
41 42	M1 M2	1983	NBS	NBS, PTB			KMnO <sub>4</sub>	IntInt, STAR
43	O-2	2015	NMIJ	NMIJ, INRiM				K2.5
44	Cu-M-3	2008	NRC	NRC				K2.3—K2.5
45	<b>Open cell</b>	1974	NML	NML, NPL			—	NPL
46	<b>Open cell</b>	(1970)	NRC	NRC, IMGC			—	IntInt, K2
47	<b>Open cell</b>	(1983)	NRC	NRC, IMGC	—		KIO <sub>4</sub>	IntInt
48	<b>Open cell</b>	(≈1999)	KRISS	KRISS, NRC			—	K2
49	<b>Open cell</b>	1974	KOL	KOL, NPL			—	NPL
50	<b>Cell ???</b>	1974	AMSW	AMSW, NPL			—	NPL, IntInt

**Comparisons:** NPL (1973-75) [Ward and Compton, 1979]; IntInt (1978-84) [Pavese, 1984; Pavese,1983; Pavese *et al.*, 1984]; K2.1-5 (1998-2015) [K2.1 2005; K2.3 2008; K2.4 2012; K2.5 2015]; STAR (1997-2005) [Fellmuth *et al.*, 2005].

<sup>^</sup> At INTiBS from 1982 to 1992.

<sup>a</sup> Kr: 5 K mol<sup>-1</sup>

<sup>b</sup> IMGC thermometer REC 626 on TPW and O<sub>2</sub> measurements in 1973-74 with gases: SIO-1 (Ar: 3 K mol<sup>-1</sup>; N<sub>2</sub>: (11-14) K mol<sup>-1</sup>) and SIO-2 (Ar: <8 K mol<sup>-1</sup>; N<sub>2</sub>: 1 K mol<sup>-1</sup>) [Pavese, 1975]. Lab – NPL = +0.54 mK (**see Section 8**).

<sup>c</sup> Sealed in 1975: SIO-1 (Ar 3: K mol<sup>-1</sup>; N<sub>2</sub>: (11-14) K mol<sup>-1</sup>) and SIO-2 (Ar: < 8 K mol<sup>-1</sup>; N<sub>2</sub>: 1 K mol<sup>-1</sup>) [Pavese, 1975]. T-NPL = +0.54 mK (**see Section 8**). Measured with thermometer LN172205, found to be close to REC 646 within 0.1 mK (see Section 4.2 below).

<sup>d</sup> [Razhba *et al.*, 1973].

### 3. Further information sources for the detection of quantitative effects on TPO2 temperature due to argon impurity

For most of the samples, no *specific analysis* for the Ar contents is provided, but only, at best, a batch analysis. Thus, the information obtained investigating the following cells or looking at the results of the listed comparisons can yield primarily only the order of magnitude of the possible effects.

#### **IMGC Cell #0 (Italian standard 1973-77)**

Contained several gases at different times, whose impurities are listed in Table 3 below [Pavese, 1978]. It was eventually sealed with gas AP&C-5.

#### **IMGC Cell 1O2 (Italian standard 1978-2000)**

1O2 (batch #1), sealed in April 1976, Gas: SIO4 (4N8, <10),  $x(\text{Ar}) = 10 \cdot 10^{-6}$ ,  $x(\text{N}_2)$  batch  $< 14 \cdot 10^{-6}$ , IntInt (Ref).

Internal comparisons:  $(+0.2 \pm 0.15)$  mK to previous standard, Cell #0.

NRC(F10) – 1O2 =  $(<+0.10 \pm 0.10)$  mK (2002).

#### **IMGC Cell 8O2 (Italian standard 2001-2014)**

(batch #3) Internal comparisons:  $(+0.48 \pm 0.10)$  mK to previous standard, Cell 1O2.

#### **IMGC Cell Ec1O2 (Italian standard since 2015)**

Ec1O2 (batch #9–same gas as batches #5–#8), sealed in 2002, gas: Messer Greisheim (5N5, <10),  $x(\text{Ar}) = 3 \cdot 10^{-6}$ ,  $x(\text{N}_2) 5 \cdot 10^{-6}$ .

#### **IMGC cells internal comparisons (1973-78)**

Figure A1 shows the results of an internal IMGC comparison of oxygen cells from the long-stem Cell #0 to cell 8O2, taking the former as the reference. [Pavese and Ferri, 1983].

Most IMGC/INRiM cells were sealed in batches (indicated in parenthesis as (bxx) in Table 2) for a group of cells already mounted on the manipulation system. Therefore, they were pre-conditioned in the same way and using the same gas bottle within the same day, according to IMGC procedure. The samples in each batch are thus assumed to have exactly the same impurity content, making their results interchangeable (e.g. see Fig. 1 below). The cells analysed in the following are 32 out of the total 51 listed in Table 2.

#### **NPL intercomparison (1973-75)**

(NPL-ASMW-IMGC-INM-KOL-NML-NRC-NRLM-PRMI-PTB) No information on the gas used is available, neither for the NMI calibrations, except for the case of IMGC.

#### **International Intercomparison of fixed points by means of sealed cells (IntInt) (1978-84)**

(IMGC-ASMW-BIPM-INM-NBS-NIM-NML-NPL-NRC-NRLM-PRMI-VSL-INTiBS-NMIJ)

No information on the gas used is available from the Final Report.

#### **CCT-K2.x (1998- 200X-2008-2012-2015)**

K2 and K2.1-5 NRC (INM-IMGC-NBS-NIM-NML-NPL-NRC-NRLM-PRMI), purity: N5 ( $10^{-5}$ )

K2 and K2.4. INM-BNM: purity: 5N5

K2 and K2.5. IMGC/INRiM: 4N8 (and Ec1O2: 5N5. For K2.5 – with NMIJ and NRC)

KRISS: purity: 4N8

NIST purity n.a. (from  $\text{KMnO}_4$  decomposition)

NPL: purity: 4N8 (unchecked)

PTB: purity: N6

K2.1.VNIIFTRI: purity: 6N

K2.3. NMI-VSL: purity: 5N5 (cell Eb2O2 from IMGC)

K2.4. INTiBS purity 4N8 (cell 2O2 and Eb1O2 from IMGC)

K2.5. NMIJ (cell O-2; impurities effect  $u = 9 \mu\text{K}$ )

K2.2 NIM, INRiM (with IMGC cell E2O2, not yet completed; 2016: measured also at NIM (unpublished))

See Table A4 and also Table 1.

In Table A4, the **orange results** are *inconsistent* with others (see also Section 8b) to d)).

**International STAR intercomparison of low temperature fixed points using sealed triple-point cells (1997-2005) (PTB-INM-NIST-NPL-NRC-VNIIFTRI)**

See Tables A5 and A6.

The analyses of the measured samples are reported in Table 1.

**Recent INRiM papers**

See the References and Tables 1-2.

**4. Results**

**Table 2.** Overview of comparisons of oxygen triple-point cells. Deviations of the TP temperatures from those of the reference cells are given in mK.

The estimates for the Ar content ( $x(\text{Ar})$ ) are based on the assumption that  $x(\text{Ar})$  of the **reference** is zero: PTB cell O2-4 in columns #5-6; IMGC cell 1O2 in #9-11; NPL in #12; KCRV in #13-14; KCRV in #15-16.

1	2	3	5	6	7	8	9	10	11	12	13	14	15	16
N°	Cell	Sealed	STAR 1997-2005 [Fellmuth, 2012]				Measurements at IMGC			NPL 1973- 1975	IntInt 1978-84		CCT-K2.x 1998-2014	
			PTB ref O2-4		with ref 1O2		IMGC ref 1O2		IMGC $x(\text{Ar})/10^{-6}$ (ref 1O2) <sup>a</sup>	Lab – NPL <sup>u</sup>	Lab – KCRV 1O2–KCRV= 0.01 mK		Lab – KCRV <sup>e</sup> 1O2–KCRV= –0.18 mK	
			dT/μK	u/ μK	μK	$x(\text{Ar})/10^{-6}$	dT/μK	u/ μK	mK	mK	u/ mK	mK <sup>e</sup>	u/ mK	
0	Long stem *	1975 <sup>p, q</sup>					–200 <sup>r</sup>	150	17 <sup>r</sup>	–1.0 <sup>m</sup> 0.2 <sup>p, s</sup>			–0.02	(0.15)
1	O200/2	2000	–49	40	+150	13	—	—	(30)				+0.20	0.25
2	O202/1	2002	–65	36	+134	11			(28)					
3	1O2* <sup>^</sup>	1976	–199	35	0**	(0)	0**	(0)	0	–1.0 <sup>o</sup>	0** <sup>s</sup>	(0)	+0.18 <sup>e</sup>	(0.15)
4	2O2	1976	–101	35	+98	8	0	150	(0)					
5	9O2	1986	–58	36	+141	12	+100	150	26 (29)					
6	11O2	1986	–118	35	+81	7	+100	150	26 (29)	–0.1 <sup>m, s</sup>			0	
9	13O2	1999	–16	36	+183	16	—	—	4 (33)				+0.24	0.15
10	E1O2	1999	5	36	+204	17	—	—	4 (34)				(+0.49) <sup>f</sup>	
11	O2-4	1996	0	0	+199	17				+0.3 <sup>s</sup> +0.6 <sup>s</sup>			+0.4	0.25
12	O2-M2-1	1983	–27	35	+172	15			(36)		–0.19	0.15	+0.15	0.25
13	O2-2	1995	–109	35	+90	8			(25)	0 <sup>g</sup>			+0.2	0.18
14	O2-F10	1985	–281	36	–82	—			—	–0.2 <sup>s</sup>			(+0.21) <0.10 <sup>d</sup>	0.22 0.10
15	MC-495	1995	–117	46	+82	7			(24)				+0.05	0.3
16	MC 897	1997	–26	38	+173	15			(32)				+0.1	0.3
19	8O2	1978					+480	150	57		+0.47	0.15	+0.66	0.15
20	3O2	1976					0							
21	4O2	1978					+250	150	38					
22	5O2	1978					+250	150	38					
23	14O2	1999					+60	30	5					
25	E2O2	1999					+190	50	15		–0.12	0.15		
28	Eb1O2	2001							4					

29	Eb2O2	2001		(+60)	30	4 (5)					(+0.48) <sup>f</sup>	0.35	
30	Ec1O2*	2002		+25	30	2							
31	Ec26O2	2014		+40	30	4 <sup>c</sup>							
33	7801	1978				170 <sup>h</sup>	+0.1 <sup>s</sup>	+2.01	0.15	(+0.51) <sup>f</sup>	0.27		
34	CO-7	1984					16 <sup>h</sup>		+0.19	0.15	+0.3	0.1	
35	8O2 INM	1976							-0.15	0.15			
36	BCM4	1982							-0.16	0.15	-0.15	0.15	
37	PP07	1981							-0.02	0.15			
38	PP11	1981							-0.13	0.15			
39	MC	1978					7 <sup>h</sup>	-0.1 <sup>s</sup> -0.3 <sup>s</sup>	+0.09	0.15			
40	15	1979					23 <sup>h</sup>	-0.7 <sup>s</sup>	+0.28	0.15			
41	M1	1983					7 <sup>h</sup>	+0.2 <sup>s</sup>	+0.09	0.15			
42	M2												
43	O-2	2014									(+0.45) <sup>f</sup>	0.24	
44	Cu-M-3	2008									+0.30	0.25	
45	Open cell	1974						-0.1 <sup>s</sup>					
46	Open cell	(1970)			+2300 <sup>h</sup>		215		+0.29	0.15	+0.4	0.25	
47	Open cell	(1983)		<100 <sup>d</sup>	100	<8	-0.2 <sup>s</sup>						
48	Open cell	(≈1999)								+0.28	0.15		
49	Open cell	1974					+0.1 -0.5						
50	Cell ???	1974					-2.1	+0.21					

\* Italian Standards in subsequent times. \*\* Estimated at IMGIC to be  $(+200 \pm 150) \mu\text{K}$ , i.e.,  $x(\text{Ar}) = 17 \cdot 10^{-6}$ , reference cell being the O<sub>2</sub> long-stem sealed Cell #0 [Pavese and Ferri, 1983] §  $T - \text{KCRV}(\text{IntInt}) = (-0.01 \pm 0.22) \text{ mK}$ . ^ At INTiBS from 1982 to 1992.

<sup>a</sup> According to  $dT/dx(\text{Ar}) = 11.75 \text{ K/mol}^{-1}$  from [Steur *et al.*, 2017, Steur *et al.*, 2020]. In parenthesis shown with the value in column 8 added.

<sup>b</sup> A comparison [Yang *et al.*, 2014] was performed in 2015 between **KRISS** (using IMGIC cell 14O2) and **NMIJ** (comparison in a block with NMIJ standard realisation of ITS-90) the result was  $(+0.27 \pm 0.5) \text{ mK}$  higher for NMIJ, i.e.,  $x(\text{Ar})/10^{-6} = 28$ , with the KRISS cell having  $x(\text{Ar})/10^{-6} = 5$ —see cell 14O2).

<sup>c</sup> Estimated from fit.

<sup>d</sup> This comparison was performed in 1977 at NRC with IMGIC cell 1O2.

<sup>e</sup> with 8O2 corrected by  $-0.48 \text{ mK}$  to cell **1O2**, such that  $(\text{KCRV}(\text{K2}) - 8\text{O2}) = -0.18 \text{ mK}$ .

<sup>f</sup> With respect to the KCRV(K2): *probably wrong* (see Section 8) **2O2** (INTiBS) – F10 (NRC) =  $-0.04 \text{ mK}$ .

<sup>g</sup> Reference: NPL, thermometer LN 1728839.

<sup>h</sup> From IntInt 1978-84.

<sup>m</sup> On scale IPTS68-NBS.

<sup>o</sup> PRMI – IMGIC as measured at IMGIC [c10].

<sup>p</sup> IMGIC thermometer REC 646 on TPW and O<sub>2</sub> (Cell#0) measurements in 1973-74 with gases: SIO-1 (Ar  $3 \text{ K mol}^{-1}$ ; N<sub>2</sub>  $11\text{--}14 \text{ K mol}^{-1}$ ) and SIO-2 (Ar  $<8 \text{ K mol}^{-1}$ ; N<sub>2</sub>  $1 \text{ K mol}^{-1}$ ) [c1].  $T - \text{NPL} = +0.54 \text{ mK}$  (*probably wrong* (see Section 8 a)). The IMGIC thermometer was REC 646: @54.361 K,  $W_{\text{TPO}_2}(1722205) - W_{\text{TPO}_2}(1728839) = +90 \cdot 10^{-7}$  (scale IPTS68-NPL) with respect to ref NPL:  $W(54.361 \text{ K}) = 0.091 9739$  @273.16 K (IMGIC):  $25.562873 \Omega$  (NPL [b7]) ( $25.56292 \Omega$  in [Ward and Compton, 1979])

<sup>q</sup> Sealed in 1975 and measured with thermometer LN1722205, found to be close to REC 646 within 0.1 mK (see Section 4.2 below).

<sup>r</sup> See Section 4.2 for an estimate of  $T_{\text{O}_2}(\text{Cell #0})$  from [Pavese and Ferri, 1983].

<sup>s</sup> Lab 1975 calibration at local fixed point (no further specification except for IMGIC).

<sup>u</sup> Lab-NPL in the Table is with respect to the Lab fixed points. The NPL comparison standard uncertainty  $u$  at the TPO2 was reported to be  $20 \mu\text{K}$ . The NPL ref thermometer was LN 1728839:  $R(54.361 \text{ K}) = 2.350 582 \Omega$ , @273.16 =  $25.559 56 \Omega$ ,  $W(54.361 \text{ K}) = 0.091 9649$ . The IMGIC thermometer was REC 646:  $R(273.16 \text{ K}) = 25.56292$ .

Then, in Table 2, columns 5–8, first the results of the STAR comparison are reported (with PTB cell O2-4 as the reference cell), in columns 9–11 the same results are recomputed by using instead IMGIC cell 1O2 as the reference. Then, in the same columns other independent measurements are reported, made at IMGIC/INRiM after 2006) on the same IMGIC cells measured at PTB and on other IMGIC/INRiM O<sub>2</sub> cells.

Finally, the results of the international comparisons made since 1975 are also given, using the respective samples as reference: IPTS-68 for NPL (column 12); IPTS-68 (and cell 1O2) for IMGc in the IntInt (column 13-14); ITS-90 and their cell F10 for NRC in the K2 (column 15-16). Notice that the latter was followed in the years by bi/tri-lateral K2 Supplementary comparisons with NRC: K2.1 NRC-VNIIFTRI (2005); K2.2 INRiM-NIM (INRiM only, not completed); K2.3 NRC-VSL; K2.4 (2012); NRC-BNM-INTiBS (2008); K2.5 NRC-INRiM-NMIJ (2015).

For these comparisons it is sometimes necessary to obtain the results through *calibrated thermometers* or through the KCRV (the full list of the relevant thermometers is collated in Table 5), as follows for Table 2:

**Cell #0** (Long stem): IMGc thermometer REC 626 on TPW and O<sub>2</sub> measurements in 1973-74 with gases: SIO-1 ( $x(\text{Ar})$  3 (guess);  $x(\text{N}_2)$  (11-14)) and SIO-2 ( $x(\text{Ar})$  <8 (guess);  $x(\text{N}_2)$  1 (guess) [Pavese, 1975].  $T - T(\text{NPL}) = +0.54$  mK (Note p). **Permanently sealed in 1975** and measured with thermometer LN1722205, found to be close to REC 646 within 0.1 mK (see Fig. 2 [Pavese, 1978]) (Table 2, Note q)

**1O2** (batch #1):  $T - \text{KCRV}(\text{IntInt}) = (-0.01 \pm 0.22)$  mK (Note §); NRC(sample #36) – 1O2 = (<100 ± 100) mK (1977, Note d)

**2O2** (batch #1): With respect to the KCRV of K2.4: [2O2 (INTiBS) – F10 (NRC)] = –0.06 mK, Note f).

**8O2** (batch #3) —): 8O2 corrected by –0.48 mK = Cell#0 is such that  $\text{KCRV}(\text{K2}) - 8\text{O2} = -0.18$  mK.

**14O2** (batch #5): 2016 KRISS (IMGc cell) – NMIJ (ITS-90) = –0.27 mK (NMIJ,  $x(\text{Ar})/10^{-6} = 28$ , with KRISS,  $x(\text{Ar})/10^{-6} = 5$ ) [Yang *et al.*, 2015]

**7801, CO-7, Open cell #35**: From Intercomparison IntInt (Note h);  $T(\text{CO-7})$  on Scale IPTS68-NBS.

For **NPL comparison measurements** (IPTS68,  $R_0$  @ 273.15 K, the ice point): NPL – NBS (IPTS68) = +0.5 mK to +0.6 mK. [Pavese, 1975]

**NPL 1728839** in Table 5 of [Ward and Compton, 1979]:  $R(54.361 \text{ K}) = 2.350\,582 \, \Omega$ , @  $T(273.16 \text{ K}) = 25.559\,56 \, \Omega$ ,  $W(54.361 \text{ K}) = 0.091\,9649$ ;  $W_{\text{TPO}_2}(1722203) - W_{\text{TPO}_2}(1728839) = +24 \cdot 10^{-7}$ .

**IMGc, REC 646**: @ 54.361 K,  $W_{\text{TPO}_2}(646) - W_{\text{TPO}_2}(1728839) = +90 \cdot 10^{-7}$  with respect to ref NPL (scale IPTS68-NPL),  $W(54.361 \text{ K}) = 0.091\,9739$ ; @ 273.16 K on IPTS68-NBS = 25.56292  $\Omega$ ; (IMGc): 25.562873  $\Omega$  (NPL [Pavese, 1975]),  $R(54.361 \text{ K}) = 2.351\,117 \, \Omega$   $\Delta R(\text{IMGc}) = +0.000\,54 \, \Omega$ ,  $\Delta T = +0.005 \text{ K}$ .

**VNIIFTRI, PL01-6 (and PL02-6, 45)**. From NPL comparison @ 54.361 K,  $W_{\text{TPO}_2}(\text{PL01-6}) - W_{\text{TPO}_2}(1728839) = -484 \cdot 10^{-7}$ ,  $W_{\text{TPO}_2}(\text{PL02-6}) - W_{\text{TPO}_2}(1728839) = -407 \cdot 10^{-7}$ . @ 273.15 K (PRMI 1974)  $R(\text{PL01-6}) = 25.270\,79 \, \Omega$ ,  $\Delta R = -1223 \, \mu\Omega$ ,  $\Delta T = -12.2 \text{ mK}$ ,  $R_0(\text{NPL}) - R_0(\text{PRMI}) = 240 \, \mu\Omega$ ,  $R_0(\text{NPL}) = 25.271\,03 \, \Omega$  [Ward and Compton, 1979];  $R(\text{PL02-6}) = 25.137\,29 \, \Omega$ ,  $\Delta R = -1023 \, \mu\Omega$ ,  $\Delta T = -10.2 \text{ mK}$ . @ 273.15 K (NPL1976)  $R(\text{PL01-6}) = 25.271\,02 \, \Omega$ .

From **measurements at IMGc** on its fixed points, in the subsequent years 1977–80. [Pavese, 1981]: See Tables 3 and 4.

**Table 3:** Resistance values of the three SPRTs PL01-6, PL02-6, and 45 at the triple points of water and oxygen. Sources of the data: [Pavese, 1981] [Ward and Compton, 1979] The resistance values are given in  $\Omega$ .

Lab	Year	PL01-6	PL02-6	45
<b><math>R_0</math> (273.15 K)</b>				
PRMI	1974	25.270 79	25.137 29	25.679 18
NPL	1976	25.271 02	25.137 49	25.679 38
NPL [W&C]	1976	25.271 03	—	25.679 41

IMGC	1977	25.271 011 <sup>a</sup>	25.137 478	25.679 382
IMGC	1977	25.271 134	25.137 492	25.679 381
IMGC	1978	25.271 136	25.137 500	25.679 412
IMGC	1980	25.271 168	25.137 503	25.679412
<b>O<sub>2</sub> (54.361 K)</b>				
<b>NPL</b>	1978	2.322 781	2.310 725	—
(IPTS68-NPL)	K	54.3622	54.3620	—
PRMI – NPL	mK	<b>+0.1</b>	—	<b>+0.3</b>
<b>IMGC</b>				
Cell 4O2	1977	2.322 833 <sup>a</sup>	—	—
4O2 <sup>b</sup>	1977	2.322 888	2.310 756	2.362 190
8O2 <sup>b</sup>	1978	2.322 916	2.310 789	—
8O2	1980	2.322 917	—	—
5O2 <sup>b</sup>	1980	2.322 881	2.310 733	—
Assigned value	1980	2.322 881	2.310 783	2.362 190
(IPTS68-NPL)	K	54.3620	54.3622	54.3609
PRMI – IMGC	mK	<b>+1.0</b>	<b>+1.2</b>	<b>-0.1</b>

<sup>a</sup> Thermometer changed after this date.  $\Delta T$  value differences may reflect also thermometers' instability with time.

<sup>b</sup> 4O2 and 5O2 from same batch b2, so assumed to realize the same value, +0.25 mK with respect to cell 1O2; 8O2 – 1O2 = +0.48 mK, so 8O2 – 4O2 = +0.23 mK, while here: #PL01-6, 8O2 – 4O2 = 32  $\mu\Omega$   $\Rightarrow$  +0.32 mK; #PL01-6, 8O2 – 4O2 = 33  $\mu\Omega$   $\Rightarrow$  +0.33 mK.

**Table 4:** Resistance values of the three SPRTs PL01-6, PL02-6, and 45 (from IMGC Laboratory book)

from IMGC CALIBRATION Tables @54.361 K		PL01-6		PL02-6		45			
PRMI		2,32279	25,27079	-4,3E-05	2,31062	25,13729	2,362208	25,67918	1,8E-05
	IMGC78		0,091916003	<b>-0,43</b>		0,091920012		0,09198923	<b>0,18</b> mK
	IMGC84			-7,5E-05					
	NPL			<b>-0,75</b>					
				-3,3E-05					
				<b>-0,33</b>					
IMGC78		2,322833	25,271011	-3,2E-05					
	IMGC84		0,0919169	<b>-0,32</b>					
IMGC84		2,322865	25,27114				2,36219	25,679381	
			0,091917697					0,09198781	
NPL		2,322823	25,27103	-1E-05					
	IMGC78		0,091916436	<b>-0,1</b>					
				-4,2E-05					
	PRMI			<b>-0,42</b>					

In Table 5 the **thermometers** used to assess the temperature of oxygen triple point realizations are listed.

**Table 5.** Resistance values of SPRTs at the triple points of water and oxygen (In **bold**: reference thermometers.)

	Exercise:	#1	#2	#3	#5			
		IPTS-68	IPTS-68	ITS-90				
#	Thermometer	<b>NPL</b>	<b>IntInt</b>	<b>K2</b>	<b>Others</b>	$R(TPO_2)/\Omega$ <sup>a</sup>	$R_0/\Omega$ <sup>b</sup>	<b>Scale realisation</b>
1	(217278) 207278	ASMW	ASMW			2.329294	25.346730	NPL
2	217990	ASMW	ASMW			2.314124	25.186290	NPL
3	217977	ASMW	ASMW			2.335410	25.418300	NPL (#1)



						2.335428	25.418580	ASMW(#2) on 1O2
4	REC 646	IMGC				2.351028 2.351114 2.351327	25.562960 25.562910 25.563117 25.563260	NBS NPL IMGC ""1977
5	LN 1812283	INM				2.340650 2.340685	25.494500 25.494711	NPL INM
6	LN43	KOL				2.350014	25.584313	NPL
7	T4	KOL						
8	LN 1812279	NBS				2.346843	25.549790	
9	LN 1812282	NBS	NBS			2.342869 2.342825 2.342918	25.510280 25.510340 25.510280	NBS (#1) NPL NBS (#2) on 8O2
10	LN 1812284	NBS				2.341201	25.496390	
11	LN 1705628	NML				2.351433	25.570230	NPL
12	LN 1731676	NML	NML			2.347185 2.347195 2.347202 2.347228	25.522800 25.522800 25.522800 25.522800	NML 1984 NPL 1984 NPL (#1) NBS (#2) on 8O2
13	LN 1158062	NRC				2.345837 2.345804	25.469660 25.469547	NPL NRC
14	LN 1158066	NRC				2.349702	25.510850	
15	LN 1722203	NRC				2.346279	25.512100	
16	6601	NRLM						
17	6803	NRLM				2.353161	25.558...	
18	<b>LN 1728839</b>	<b>NPL</b>	NPL	NPL		2.350582 2.350556 2.351434 2.345142	25.55956 25.55957 25.560733 25.560733	<b>NPL (#1)</b> <b>NPL (#2) on 1O2</b> <b>NPL (#3)</b> <b>NRC (#3)</b>
19	153374	NPL						
20	LN 1676928	NPL				2.344225	25.53561	NPL
21	PL01-6	PRMI	IMGC		IMGC	2.322790 2.322823 2.322823 2.322833	25.27079 25.271030 25.271140 25.271011	PRMI NPL IMGC IMGC
22	PL02-6	PRMI			IMGC	2.310620 2.310745	25.13729 25.137500	PRMI NPL
23	45	PRMI	IMGC		IMGC	2.362208 2.362255 2.362190	25.67918 25.679390 25.679381	PRMI NPL IMGC
24	170138	PTB						
25	188682	PTB				2.246233	24.366050	NPL
26	LN 1778842	PTB				2.341698	25.52487	NPL
27	226321		BIPM			—	25.369110	from Ar tp
28	188640		NIM			not on O <sub>2</sub>		
29	LN 1521389		NRC			2.344182 2.344137 2.344245 2.344253	25.523050 25.523027 25.523332 25.523332	NPL NRC NRC (#2) on 1O2
30	7681		NRLM			2.333708	25.363060	on 1O2
31	232788		INM			2.306377	25.087300	on 8O2
32	LN 1774095		NBS	NBS		not on O <sub>2</sub> 2.349568 2.349531	25.561811 25.561811	(#2) NBS (#3) NRC(#3)
33	LN 1842381	PRMI	PRMI			2.343744 2.343703	25.544950 25.544950	ASMW(#1) PRMI (#2) on 8O2
34	LN 232788		INM			not on O <sub>2</sub>		
35	LN 1812283		INM			not on O <sub>2</sub>		
36	7703		NIM			not on O <sub>2</sub>		
37	LN 1781356		NRLM			not on O <sub>2</sub>		
38	6601		NRLM			2.308478	25.110420	NRLM

39	7709		NIM			2.328237	25.352963	NIM
40	LN 1872179		NRC			2.349496	25.582650	NRC (unsure)
41	LN 1886904			BNM-INM		2.350042	25.584655	INM
						2.349992	25.584655	NRC
42	1041			BNM-INM		2.347928	25.572698	INM
						2.347999	25.572698	NRC
43	LN 1857277			IMGC & .5 INRiM &.5 NMIJ				<b>IMGC</b>
44	LN 1860951			IMGC & .5 INRiM				<b>IMGC</b>
45	LN 1886906			KRISS		2.345434	25.544273	KRISS
						2.345399	25.544273	NRC
46	1043			KRISS		2.332769	25.410822	KRISS
						2.332850	25.410822	NRC
47	LN 1774092			NIST		2.341603	25.527675	NBS
						2.341668	25.527675	NRC
48	213865			NPL		2.310435	25.164672	NPL
						2,309570	25.163620	NPL 1984
						2.309558	25.164672	NRC
49	<b>LN 1872174</b>			NRC		2.341003	25.499358	<b>NRC</b>
						2.341096	25.499358	<b>NRC</b>
50	LN 1842381			PTB		2.343704	25.54599	
						2.343665	25.54599	NRC
51	LN 1842379			PTB		2.340062	25.50632	
						2.340150	25.50632	NRC
52	346			.1 VNIIFTR				
53	476			.1 VNIIFTR				
54	LN 1820627			.3 VSL-NMI &NRC		2.343107	25.543765	VSL
						2.343121	25.543766	NRC
55	1599			.3 VSL-NMI & NRC		2.345743	25.533513	VSL
						2.345725	25.533508	NRC
56	234721			.4 INTIBS & LNE- CNAM & NRC				
57	LN 1866334			.4 INTIBS & LNE- CNAM & NRC				
58	RS954-7			.5 NMIJ & NRC				
59	RS85A-6			.5 NMIJ & NRC				
60	226322				BIPM	2.290773	24.913330	NPL76
						2.290740	24.913042	IMGC
						2.290740	24.913246	INM
						2.290757	24.913180	NPL
						—	24.913330	BIPM
61	LN 1832685	NPL				2.339780	25.507110	
62	LN 1832689	NPL				2.346380	25.534790	
63	LN 1832691	NPL				2.341410	25.528090	
64	217895	NPL				2.277240	24.817510	
65	217894	NPL				2.320073	25.294540	
66	217890	NPL				2.300590	25.083000	
67	213865	NPL				2.309570	25.163620	
68	221476	NPL				2.259370	24.585370	
69	221420	NPL				2.328070	25.338900	
70	141480	NPL				2.193380	23.837200	
71	1249	NPL				2.344360	25.511800	
72	2 PRMI					2.304044	25.0894	

73	T4 PRMI				2.299499	25.0349	
74	153373			CCT-64	2.296254	24.9830	
75	153374	NPL			2.327288	25.30792	
76	REC 838				2.350380 2.350564	25.565962 25.566498 25.566420	NBS <b>IMGC</b> Same 1977
77	LN 1512846			NBS-55 1959	2.348719	25.547466	NBS
78	LN 1521389	1976		On IMGC cells	2.344110 2.344137 2.344182	25.523027 25.523050	NRC
79	LN 1577530	1961&69			2.350988	25.499961	PSU
80	LN 1577531	1961&69			2.352898	25.538478	PSU
81	LN 1722205	1975		IMGC	2.341179 2.341222	25.459406 25.459272	NBS <b>IMGC</b>
82	LN 1754792			IMGC	2.345143	25.559367	<b>IMGC</b>
83	LN 1761201	1977			2.343794 2.343803	25.522976 25.522799	NBS <b>IMGC</b>
84	LN 1792424			NBS	2.343938	25.502882	IMGC
85	459			NML	2.336506		NBS-55
86	LN 1756761			NML	2.348662		[Kemp, 1976]
87	1284				2.344360	25.511800	NPL
88	5435	2019		INRiM	2.341488	25.493438	INRiM

<sup>a</sup>  $T(\text{tpO}_2) = 54.361 \text{ K @ IPTS68 and } 54.360 \text{ K @ ITS-90.}$

<sup>b</sup>  $T_0 = 273.15 \text{ K @ IPTS68 and previous; } T_0 = 273.16 \text{ K @ ITS-90.}$

## 5 Reference cells

### 5.1 IMGC/INRiM Reference cells

Reminder: The values of the TPO2 temperature,  $T_{\text{TPO2}}$ , and the temperature, at which  $R_0$  has to be given,  $T_0$ , are different for different scales. This is summarised in Table 6.

**Table 6.**  $T_{\text{O2TP}}$  and  $T_0$  on different temperature scales [Pavese, 1970]

<u>Scale</u>	<u><math>T_{\text{O2TP/K}}</math></u>	<u><math>T_0/\text{K}</math></u>
CCT-64	54.352	273.15
NBS-55	54.3528	273.15
NPL-61	54.3647	273.15
PRMI-54	54.3644	273.15
PSU-54	54.3405	273.15
(IPTS68	54.361)	273.15
(ITS-90	54.3584)	273.16

#### 5.1.1 Cell #0

The Cell #0, the long stem cell (made in 1973 and eventually sealed in 1975) served as the IMGC standard until 1977, and its results are shown in Fig. A1 [Pavese, 1978]. The thermometers used in Figure A2 were: REC 646 (●), REC 848 (■) (and LN 1722205 (▲) only since late 1975), having different calibrations corrected to zero current, all originating from the calibration on the IPTS-68-NBS scale obtained in 1969-1971. From the calibration data provided in Table 3 of [Pavese, 1978], one can now compute the differences between the resistance values measured in cell #0 and the calibration values. These differences are shown in Figure A2 for  $F = 1$  [Pavese, 1978], becoming Fig. 1 here, where the mean value, for thermometers REC646 and REC848, was  $\Delta T_{\text{Cell}\#0}(\text{IPTS-68-NBS}) = 54.361 \text{ K}) = (+1.19 \pm 0.06) \text{ mK}$ , so  $T_{\text{Cell}\#0}(\text{IPTS-68-NBS}) = 54.3622 \text{ K}$  (until the cell was permanently sealed).

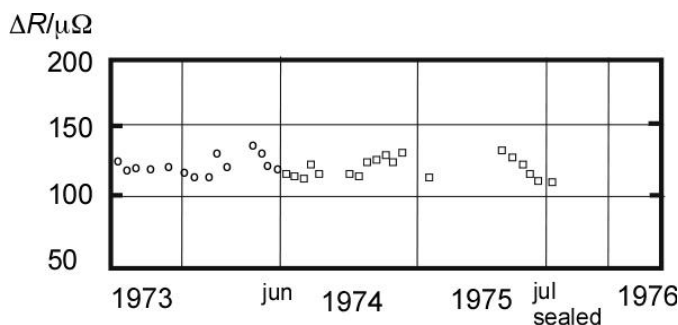


Figure 1. Mean deviation of the resistance values measured for thermometers REC646 and REC848 in cell #0 from the calibration values obtained at NBS using IPTS-68-NBS scale realised in 1969-1971

The thermometers remained stable until April 1975 (then REC 838 became unstable after a new calibration involving—as usual at that date—the tin point). From the NPL comparison, IPTS68-NBS – IPTS68-NPL = -0.5 mK. In IntInt Table VII.4.b, [Pavese, 1984] the value on IPTS68-NBS is 54.3614 K, thus  $T_{O_2,Cell\#0} = 54.3626$  K. On the other hand (see Note p to Table 4),  $T(IMGC) - T(NPL) = +0.2$  mK in 1973-75 (see Table 3 in [Pavese, 1978]), thus, from thermometer REC646 as measured at NPL,  $T_{O_2tp}(Cell\#0) = 54.3620$  K, basically confirming Fig. 1.

On the ITS-90,  $T_{O_2tp} = 54.3584$  K, i.e., 2.6 mK lower with respect to IPTS-68, therefore, from the NBS previous calibration,  $T_{Cell\#0}(ITS-90) = 54.3596$  K.

### 5.1.2 Cell 102

Cell 102 was the first oxygen cell sealed at IMGIC in 1976, and was then compared with Cell#0 and used as IMGIC standard from 1978. See Section 6.1.

### 5.1.3 Cell Ec102

Italian standard since 2015. See Section 6.2.

## 5.2 Non-IMGIC/INRiM Reference cells in other inter-comparisons

5.2.1 **NPL:** (data not available)

5.2.2 **NRC:** F10 then Cu-M-3

5.2.3 **PTB:** O2-4

5.2.4 **NMIJ:** O-2

## 6. Discussion

### 6.1 Observed anomalies in the STAR comparison results

As shown in Table 4, most of the cell differences with the PTB reference cell O2-4 turned out to be significantly *negative*. This may indicate that they are affected by **N<sub>2</sub> impurities** of the order of  $x(N_2) = 5-25 \cdot 10^{-6}$ , more than most (batch) analyses, or that the PTB cell O2-4 is affected instead by argon impurity more than indicated by the AGAgas assay ( $x(Ar) = 1 \cdot 10^{-6}$ ).

In [Fellmuth *et al.*, 2012], the way PTB makes the extrapolation of the melting values to the liquidus point is linear in temperature versus fraction of sample melted, but the melting range of O<sub>2</sub> is so small

that this operation is an unlikely cause for the negative differences. (In reality, the lower temperature value at the middle of the plateau was used. [Fellmuth and Rourke, 2021]. This fact tends to report lower values for the older cells, like, e.g., the 1O2–3O2 are, because of an increase of the melting range with time (see also [Kołodziej *et al.* 2017])) In addition, for samples permanently sealed in a cell, almost 50 years of experience has shown that the samples do not change the original contamination with time.

In the particular case of IMGC cells measured at the STAR comparison, there is a mismatch between the observed depression and the known Ar and N<sub>2</sub> contents in them. Cells 1O2 to 3O2, coming from the same batch, have the same contamination, while the PTB results are different by  $(98 \pm 35) \mu\text{K}$ , equivalent to  $x(\text{Ar}) = 8 \cdot 10^{-6}$ . In addition, their apparent contamination reported by PTB (PTB has reported only temperature differences [Fellmuth and Rourke, 2021]) is inconsistent with IMGC cell differences measured at IMGC in the previous and subsequent years, and in relationship with the cells from other laboratories measured in previous intercomparisons: NPL, IntInt and K2 (and a few during the EU Project MULTICELLS [Pavese, 2003]). Table 4 (and Fig. 2) summarises all of them as available at INRiM.

### 6.1.1 Checks on the STAR comparison (ITS-90, $R_0 = R@273.16 \text{ K}$ )

In Table 2, column 7, the comparison results are recomputed using as a **reference IMGC cell 1O2**, instead, whose contamination was checked at IMGC and in other Labs in several occasions (after filling and sealing IMGC and other Labs could only check the relative contamination by comparison with other cells, except in a few cases where the contamination of the original gas got a new purity assay), and the corresponding Ar contamination computed in column 8. For the IMGC cells, the obtained results have also been compared with other internal measurements performed at IMGC on the same cells, also using cell 1O2 as reference, for comparison with column 7, in column 9 (uncertainty in column 10).

#### A) IMGC cells in the STAR comparison

- cell **1O2**, the discrepancy is larger than the PTB uncertainty
- cell **2O2**, the discrepancy is larger than the PTB uncertainty and than the IMGC-known difference to cell 1O2, of the *same batch #1*
- cell **9O2**, the accordance with columns 7 and 9 is for sign and within the PTB uncertainty
- cell **11O2**, the accordance with columns 7 and 9 is for sign and within the IMGC uncertainty
- cell **11O2–9O2**, difference  $(-60 \pm 35) \mu\text{K}$ : inconsistent, being both from the *same batch #4*
- cells **13O2** the large PTB inconsistency is with the argon content in the bottle Messer1 of  $4 \cdot 10^{-6}$  (as INRiM checked).
- for cell **E1O2** the large PTB inconsistency is with the argon content in the bottle Messer1 (as INRiM checked [Steur *et al.*, 2020]).

#### B) Non-IMGC cells in STAR comparison

- cell **O2-4** (ref PTB) differs from 1O2 by  $+199 \mu\text{K}$  (comparison uncertainty  $\approx 40 \mu\text{K}$ ). Assuming the Ar content of 1O2 to be zero, this difference would mean for O2-4 to contain  $x(\text{Ar}) = 17 \cdot 10^{-6}$  instead of  $x(\text{Ar}) = 1 \cdot 10^{-6}$  according to the AGA assay.
- cell **O2-M2-1** (NBS/NIST) differs from 1O2 by  $(+172 \pm 35) \mu\text{K}$ , corresponding to  $x(\text{Ar}) = 15 \cdot 10^{-6}$  under the same assumption as for O2-4 (such a large Ar content is questionable because the oxygen sample was produced at NBS from  $\text{KMnO}_4$ ).
- cell **O2-2** (NPL, ref in NPL intercomparison) differs from 1O2 by  $(+90 \pm 35) \mu\text{K}$ , corresponding to  $x(\text{Ar}) = 8 \cdot 10^{-6}$ .
- cell **O2-F10** (NRC, reference in K2 and K2.1) differs from 1O2 by  $(-82 \pm 36) \mu\text{K}$ , indicating a dominant N<sub>2</sub> contamination (but see below).

—**cell MC-495** (PRMI/VNIIFTRI) differs from 1O2 by  $(+82 \pm 46) \mu\text{K}$ , corresponding to  $x(\text{Ar}) = 7 \cdot 10^{-6}$ .

—**cell MC-897** (PRMI/VNIIFTRI) differs from 1O2 by  $(+173 \pm 38) \mu\text{K}$ , corresponding to  $x(\text{Ar}) = 15 \cdot 10^{-6}$ .

See Fig. A3.

## 6.2 Results from other comparisons

### 6.2.1 IMG C cells in non-STAR comparisons

—**Cell #0** is of the long stem type made in 1973 (sealed from 1975, still existing but not measured anymore since a long time). The long stem cell was the reference for the IMG C measurements at the NPL comparison, where it was found  $\text{IMG C}(\text{IPTS68-NBS}) - \text{NPL} = +1.0 \text{ mK}$  and  $(+0.2 \pm 0.15) \text{ mK}$  for IMG C thermometer REC 646—see Fig. A1 and Note p to Table 2.

—**Cell 1O2** (batch #1) was the effective IMG C **reference cell** in comparison K2, though the reference cell in the Report was the 8O2, because the latter was corrected for the difference to this one of  $+0.48 \text{ mK}$ , and is therefore linked to K2. The difference with respect to Cell #0 was  $(+0.2 \pm 0.15) \text{ mK}$ . It also participated in the comparison IntInt and was found to differ from the KCRV (differing from 1O2 by  $-0.01 \text{ mK}$ ) by  $(-0.12 \pm 0.15) \text{ mK}$ , compatible with the gas.

—**Cell 2O2** (batch #1), lent to INTiBS for its participation in K2.4, was found to have a difference with respect to the KCRV of K2.4 (where  $2\text{O2}(\text{INTiBS}) - \text{F10}(\text{NRC}) = -0.06 \text{ mK}$ ) of  $(+0.35 \pm 0.34) \text{ mK}$  (*but see Section 8*).

—**Cell 11O2** (batch #4) also *indirectly* participated in the NPL comparison via a thermometer calibrated on the IPTS68-NBS scale, showing a difference of  $(+0.1 \pm 0.1) \text{ mK}$ .

— **Cell 13O2** (batch #5) was sealed in the *same batch* of cells 14O2 (then supplied to KRISS) and 16O2 (then supplied to TIPC). They have therefore the same Ar content as 13O2. Cell 14O2 was measured at IMG C and the difference with 1O2 was found to be  $(+60 \pm 30) \mu\text{K}$ , i.e.  $x(\text{Ar}) = 5 \cdot 10^{-6}$ , thus the contamination of the batch of cells is compatible with the gas assay.

— **Cell E1O2** (batch #6) was sealed in the *same batch* of cells E2O2 (then supplied to NIM), E3O2 (then supplied to INTiBS) and E4O2 (then supplied to TIPC). These have thus the same Ar content as cell E1O2 (and as cells 13O2-16O2). Cell E2O2 was measured at IMG C and the difference with 1O2 was found to be  $(+85 \pm 30) \mu\text{K}$ , i.e.  $x(\text{Ar}) = 7 \cdot 10^{-6}$ , thus compatible with the gas assay.

### 6.2.2 Non-IMG C cells in non-STAR comparisons

a) **NPL comparison** (reference NPL) (IPTS68,  $R_0$  @ 273.15 K)

(Note: In this comparison  $R_0 = R@273.15 \text{ K}$ , the ice point)

— **Cell MC** (PRMI)  $T_{\text{PRMI}} - T_{\text{NPL}} = (+0.1 \pm 1.0) \text{ mK}$ .

— **Cell F15** (NRC)  $T_{\text{NRC}} - T_{\text{NPL}} = (+0.2 \pm 0.7) \text{ mK}$ .

— **Cell M1, M2** (NBS)  $T_{\text{NBS}} - T_{\text{NPL}} = (+0.5 \pm 0.6) \text{ mK}$ .

— **Open cell #43** (Table 4) (NML)  $T_{\text{NML}} - T_{\text{NPL}} = (+0.1 \pm 0.02) \text{ mK}$ .

— **Open cell #45** (Table 4) (NRC)  $T_{\text{NRC}} - T_{\text{NPL}} = (+0.2 \pm 0.02) \text{ mK}$ . A comparison was also performed in 1978 [Ancsin, 1978] at NRC with IMG C cell 1O2 and with INM, it was found  $T_{\text{NRC}} - T_{\text{IMG C}} = (<+0.1 \pm 0.1) \text{ mK}$ , while  $T_{\text{NRC}} - T_{\text{INM}} = (-0.4 \pm 0.1) \text{ mK}$ .

— **Open (unsure) cell #47** (Table 4) (ASMW)  $T_{\text{ASMW}} - T_{\text{NPL}} = (-0.1 \text{ \& } +0.5) \text{ mK}$ .

b) **IntInt comparison** (reference cell IMG C 1O2  $\equiv$  KCRV) (IPTS68,  $R_0$  @ 273.15 K, the ice point)

— **Cell 7801** (NRLM) Outlier, with  $T_{\text{Lab}} - T_{\text{KCRV}} = +2.02 \text{ mK}$ , corresponding to  $x(\text{Ar}) = 170 \cdot 10^{-6}$ .

— **Cell CO-7** (NBS) As measured at NBS,  $T_{\text{Lab}} - T_{\text{KCRV}} = +0.19 \text{ mK}$ .

— **Cell 8O2** (INM) As measured at INM,  $T_{\text{Lab}} - T_{\text{KCRV}} = -0.15 \text{ mK}$ . Also measured at NIM ( $+0.02 \text{ mK}$ ), NML ( $+0.24 \text{ mK}$ ) and NRC ( $-0.03 \text{ mK}$ ).

- **Cell BCM4** (INM) As measured at INM,  $T_{\text{Lab}} - T_{\text{KCRV}} = -0.15$  mK. Also measured at NRC ( $-0.01$  mK).
  - **Cell PP07** (NIM) As measured at NIM,  $T_{\text{Lab}} - T_{\text{KCRV}} = -0.02$  mK.
  - **Cell PP11** (NIM) As measured at NIM,  $T_{\text{Lab}} - T_{\text{KCRV}} = -0.13$  mK.
  - **Cell MC** (PRMI) As measured at PRMI,  $T_{\text{Lab}} - T_{\text{KCRV}} = +0.09$  mK, corresponding to  $x(\text{Ar}) = 7 \cdot 10^{-6}$ .
  - **Cell 15** (NRC) measured at NRC,  $T_{\text{Lab}} - T_{\text{KCRV}} = +0.16$  mK, corresponding to  $x(\text{Ar}) = 13 \cdot 10^{-6}$ . Also measured at ASMW ( $+0.15$  mK), IMG C ( $+0.28$  mK), INM ( $-0.12$  mK), NML ( $+0.14$  mK), and NPL ( $+0.08$  mK).
  - **Cells M1, M2** (NBS) As measured at NBS,  $T_{\text{Lab}} - T_{\text{KCRV}} = +0.09$  mK.
- See Fig. A4.**

c) **Comparison CCT-K2.x** (NRC reference thermometer LN 1872174 and cell F10 until K2.1) (ITS-90,  $R_0$  @ 273.16 K)

- **Cell O2-2** (NPL, ref cell in NPL intercomparison). In K2, the cell showed a difference of  $(+0.25 \pm 0.18)$  mK from the KCRV, where the difference with IMG C cell #0 was  $(-0.18 \pm 0.15)$  mK, so that O2-2 is  $(+0.26 \pm 0.25)$  mK with respect to IMG C 1O2.
  - **Cell O2-F10** (NRC, reference in K2 and K2.1). From K2.4, where a difference (2O2 (IMG C/INTiBS) – F10 (NRC) =  $-0.06$  mK) was found, one can get a difference with cell 1O2 of  $(+0.21 \pm 0.22)$  mK.
- See Fig. A5.**

- **Cell Cu-M-3** (NRC, used in K2.3 to K2.5)  $T_{\text{Cu-M-3}} - T_{\text{F10}} = +0.098$  mK.
- **Cell O-2** (NMIJ, used in K2.5). Differences  $T_{\text{NMIJ,O-2}} - T_{\text{INRiM, Ec1O2}} = 0.019$  mK and  $T_{\text{NMIJ,O-2}} - T_{\text{NRC,Cu-M-3}} = 0.212$  mK.

For anomalies see Section 9.

## 6.3 Comparisons during Project **MULTICELLS** (ITS-90, $R_0$ @ 273.16 K)

### 6.3.1 IMG C Cells

**Eb1O2**— (INTiBS Report 5, Nov 2001, Multicell Report AA-INTiBS) Reference Thermometer LN 1866336: **54.358 655 K** ( $\Delta T(\text{ITS-90}) = +0.255$  mK)

**Eb1O2**— (NMI-VSL Report Final, Multicell Report Z-NMi) Thermometer LN1820627: **2.343 1245  $\Omega$**

(INTiBS Report 5, 2001; Multicell Report AA) Thermometer LN1820627: **54.358 66 K**

**Ec1O2**— (INTiBS, March 2002) Thermometer LN 1866336, *calibrated on thermometer 2O2*: **54.358 51 K** ( $\Delta T(\text{ITS-90}) = +0.11$  mK). (INTiBS Report 6, Oct 2002, Multicell Report AM-INTiBS) Thermometer LN 1866336: **54.358 51 K** ( $\Delta T(\text{ITS-90}) = +0.11$  mK).

e) Comparison INRiM – LNE-CNAM (2019)

**Ec1O2** (INRiM) – **O2-01/1** (LNE-CNAM). Thermometer Rosemount 5435 calibrated on both cells:  **$(+0.23 \pm 0.25)$  mK**. [Imbraguglio *et al.*, 2020]

### 6.3.2 Non-IMG C Cells (ITS-90, $R_0$ @ 273.16 K)

**Multicell cell BNM-CNAM, Cell O2-02/1** (VSL Report 5, MULTICELL Report AK, 2002) thermometer LN 1820627,  $R = 2.343\ 107\ \Omega$ . Same thermometer in K2.3, measurements @ VSL ITS-90 scale:  $R_0 = 25.543\ 765\ \Omega$ ,  $W(\text{tpO}_2) = 0.091\ 730\ 333$ ,  $R(\text{tpO}_2) = 2.343\ 138\ \Omega$ ,  $\Delta R_{\text{O2-02/1}} = -31\ \mu\Omega$ ,  $\Delta T_{\text{O2-02/1}} = -0.31\ \text{mK}$ .

Measurements @ NRC **cell Cu-M-3**:  $R_0 = 25.543\ 766\ \Omega$ ,  $W(\text{tpO}_2) = 0.091\ 729\ 674$ ,  $R(\text{tpO}_2) = 2.343\ 121\ \Omega$ ,  $\Delta R_{\text{O2-02/1}} = -14\ \mu\Omega$ ,  $T_{\text{O2-02/1}} - T_{\text{Cu-M-3}} = -0.14\ \text{mK}$ . Finally,  $(T_{\text{VSL(BNM)}} - T_{\text{NRC(K2)}})_{\text{tpO}_2} = +0.27\ \text{mK}$ .

#### f) Other internal comparisons at IMG C/INRiM (ITS-90, $R_0$ @ 273.16 K)

**14O2**— (cell IMG C batch 5, measurement 1999-12-20) Thermometer LN 1722205: **2.341 3049**  $\Omega$ . (**K2**) 2.341 2896  $\Omega$ ,  $T - T(\text{K2}) = +0.15\ \text{mK}$ .

**E2O2**— (cell IMG C batch 7, measurement 2001-02-24) Thermometer LN 1722205: **2.341 308**  $\Omega$ ; (**K2**) 2.341 2896  $\Omega$ ,  $T - T(\text{K2}) = +0.19\ \text{mK}$ .

**Ec1O2**—(cell IMG C batch 9) IMG C measurement for **K2.2**: thermometer LN 1857277: 2006-06-30: **2.346 6044**  $\Omega$  ( $\Delta T(\text{ITS-90}) = +0.078\ \text{mK}$ ); 06-27: **2.346 5994**  $\Omega$  ( $\Delta T(\text{ITS-90}) = +0.16\ \text{mK}$ ); 06-24: **2.346 5966**  $\Omega$  ( $\Delta T(\text{ITS-90}) = +0.18\ \text{mK}$ ).

**Ec26O2**— (cell INRiM batch 10) 2015 comparison of thermometers 1860951 and 1857277, both calibrated on **1O2** at intercomparison **K2**: INRiM (1860951) – 1O2 =  $-0.102\ \text{mK}$ ,  $-0.090\ \text{mK}$ ,  $-0.099\ \text{mK}$ , average  $-0.097\ \text{mK}$ ; INRiM (1857277) – 1O2 =  $-0.050\ \text{mK}$ ,  $-0.042\ \text{mK}$ ,  $-0.049\ \text{mK}$ , average  $-0.047\ \text{mK}$ .

## 7. Overall consistency of IMG C/INRiM reference cells

### 7.1 Consistency of Cell #0 with cell 1O2

—Cell #0 – 1O2 =  $(-0.2 \pm 0.15)\ \text{mK}$  for IMG C thermometer REC 646 (@ < 1980).

### 7.2 Consistency of cell 1O2 (2O2, 3O2) with cell Ec1O2

—Cell O2-2 (NPL, ref in NPL Inter-comparison) differed from 1O2 by  $(+0.090 \pm 0.035)\ \text{mK}$ , corresponding to  $x(\text{Ar}) = 8 \cdot 10^{-6}$ .

— Cell 14O2 was measured at IMG C and the difference with 1O2 found to be  $(+0.060 \pm 0.030)\ \text{mK}$ , i.e.  $x(\text{Ar}) = 5 \cdot 10^{-6}$ , compatible with the gas assay

—Cell E2O2 (mod. a, year 2000), measured at IMG C and the difference with 1O2 found to be  $(+0.085 \pm 0.03)\ \text{mK}$ , i.e.  $x(\text{Ar}) = 7 \cdot 10^{-6}$ , compatible with the gas assay. It also participated in the comparison **IntInt** and was found to differ from the KCRV (differing from 1O2 by  $-0.01\ \text{mK}$ ) by  $(-0.12 \pm 0.15)\ \text{mK}$

—(INTiBS Report 6, Oct 2002, Multicell Report AM-INTiBS) Thermometer LN 1866336: 54.358 51 K ( $\Delta T(\text{ITS-90}) = +0.11\ \text{mK}$ )

— K2.4: Cell 2O2 (batch #1), loaned to INTiBS, was found to have a difference with respect to the KCRV of K2.4 (where 2O2 (INTiBS) – F10 (NRC) =  $-0.06\ \text{mK}$ ) of  $(+0.35 \pm 0.34)\ \text{mK}$  (*but see Section 8 for a possible problem in K2.4*).

### 7.3 Consistency with 1O2 of IMG C/INRiM cells using samples from gas Messer1 ( $x(\text{Ar}) = 4 \cdot 10^{-6}$ )

#9— 13O2: same batch of 14O2

#10— E1O2: same batch of E2O2

#23, #24— 14O2, 15O2:  $(+0.060 \pm 0.030)\ \text{mK}$

#25 - #27— E2O2-E4O2:  $(+0.19 \pm 0.050)\ \text{mK}$

#28— Eb1O2: **+0.15 mK** with respect to cell #30

#29— Eb2O2:  $(+0.060 \pm 0.030)\ \text{mK}$

#30— through **Ec1O2**: *see above*



#31, #32— Ec26O2, Ec27O2: (+**0.040** ± 0.030) mK.

**8. A few misprints and possible inconsistency issues @ TPO2 estimated in previous documents**  
(also after Rourke [Fellmuth and Rourke, 2021])

a) NPL Comparison (Note: In this comparison  $R_0 = R @ 273.15 \text{ K}$ , the ice point)

In the Metrologia paper of the comparison [Ward and Compton, 1979], one finds, in Section VI:

“VI. Analysis of Results

a) *Comparison of R, and Fixed Point Values*

The differences between the  $R$ , as measured in the originating laboratory and the mean  $R$ , measured at

NPL are given in column 3 of Table 3 for each thermometer in the form  $(R_{\text{lab}} - R_{\text{NPL}}) \dots$ , while in the heading of Table 3 it is indicated:

“Differences between the measurements of the originating laboratory and those of NPL. In the fixed point comparisons, a positive entry indicates the **NPL realization is hotter**”,

which has the opposite meaning.

**But, in the footnote:** “The table can also be considered as representing  $(T_{\text{Lab}} - T_{\text{NPL}})$  at the **NPL fixed points**, since if the fixed point of a laboratory IS “hotter” than that of NPL, a thermometer calibrated at that fixed point will indicate a temperature below the defined temperature when at the NPL fixed point.”

*The former has been taken here as the correct one.*

In Table 1 of [Ward and Compton 1979], for the PRMI thermometer 45, the value  $R_0 = 25.66718 \Omega$  is incorrect, the correct one being  $R_0 = 25.67918 \Omega$ , as in [Pavese, 1981].

b) CCT-K2 Report

**Table 5.5**, (IMGC **1O2** (corrected from 8O2))

	<u>LN 1857277</u>	<u>LN 1860951</u>
	$(R_0 = 25.549\ 662 \Omega)$	$R_0 = 25.536\ 5537 \Omega)$
$W(\text{TPO2})_{\text{K2}} =$	0.091 844 64	0.091 811 04
<b><i>Recomputed here ab initio</i></b>		
	<b>0.091 844 634</b>	<b>0.091 811 054</b>
<b><math>R =</math></b>	<b>2.346 5994</b>	<b>2.344 5379</b>
	(−0.15 $\mu\Omega$ )	(+0.35 $\mu\Omega$ )
NRC(K2)	0.091 842 149	0.091 813 149
	2.346 5359	2.344 5914
$T_{\text{NRC,K2}}(\text{F10}) - T_{\text{IMGC,last}}(\text{1O2}):$	<b>−0.635 mK</b>	<b>+0.535 mK</b> (diff. 1.18 mK)

***What is the meaning?***

One has to consider that the results from the laboratories are taken **at** the fixed point temperature (54.3584 K @ IPTS-68), while the NRC measurements were performed **near** the nominal TPO2 temperature value.

In fact, **from CCT-K2draftA.P2** (information not available in the K2 Final Report)

$KCRV$ (K)	Group A	Group B
	<b>54.357 91</b> (−0.49)	<b>54.359 05</b> (+0.65) (diff. 1.14 mK)

**They are different.**

Let us consider the above calculations leading to the corresponding temperature values.

[KCRV(K2) – IMG(C2)] (mK)	<b>+0.200</b>	<b>+0.167</b>
[KCRV(K2) – NRC(K2)] (mK)	–0.180	–0.240
$T(\text{IMG(C) K})$	<b>54.357 71</b> (–0.69)	<b>54.358 88</b> (+0.48) (diff. 1.17 mK).
$T(\text{NRC) K})$	54.357 99	54.358 81
and, from <i>the here recomputed data</i>		
(mK)	(+0.200+0.001) = +0.201	(+0.167–0.004) = +0.163
$T(\text{IMG(C) K})$	54.357 51 (–0.79 mK)	54.358 88 (+0.48) (diff. 1.17 mK)

Thus		
$T(\text{IMG(C) K})$	54.357 51 (–0.79 mK)	54.358 88 (+0.48) (diff. 1.17 mK)

The reported temperature differences for both thermometers fully originate from the different values of the two  $T(\text{KCRV})$ . As said above, the NRC  $R$  values are not comparable with the  $R$  values of the Labs. If that is taken into consideration, the results are consistent with the IMG(C) measurements within  $u < 0.10$  mK.

$T(\text{NRC) K})$	54.357 99	54.358 81
[NRC(K2) – IMG(C2)] (mK)	+0.28	+0.04

**Bilateral equivalence (K2 Table B.5)**

[NRC(K2) – IMG(C2)] (mK)	–0,38	–0.40
--------------------------	-------	-------

c) CCT-K2.5 Report

*Directly from the meltings* at INRiM it is possible to obtain the value for the two INRiM thermometers used in the IMG(C)/INRiM cell **Ec1O2**.

	<u>LN 1857277</u>	<u>LN 1860951</u>
$W(\text{TPO2}) =$	0.091 844 639	0.091 810 803
$R(\text{Ec1O2}) =$	2.34659939	2.344531338

In the CCT-K2.5 Report, only data for thermometer LN 1860951 are fully reported. It was provided by INRiM to NRC with the value:

$W(\text{TPO2}) =$	0.091 810 533	<i>incorrect;</i>
the <i>correct</i> one (for the right thermometer) is	0.091 810 803	(+68.9 $\mu\text{K}$ )

The CCT K2.5 does not report any direct new comparison NRC – IMG(C)/INRiM, but only a  $T(\text{INRiM, Ec1O2}) – T(\text{NMIJ})$ .

However, in K2.5, from  $T(\text{NMIJ}) – T(\text{NRC}) = +0.21$  K (mean) and  $T(\text{INRiM}) – T(\text{NMIJ}) = –0.019$  K, for the same NMIJ cell, one gets  $T(\text{INRiM}) – T(\text{NRC}) = +0.19$  K.

Also the difference  $T_{\text{INRiM, Ec1O2}} - T_{\text{KCRV(K2)F10}}$  for the same thermometer is reported in the K2.5 Report, Table 8 Group B,  $(+0.58 \pm 0.28)$  mK, where the KCRV is the same as in K2. The recomputation in K2.4 leads to  $T_{\text{INRiM, Ec1O2}} - T_{\text{KCRV(K2)F10}} = -0.451$  mK (note the different IMGC cell, now an INRiM one).

From this and from  $T_{\text{IMGC, 1O2(K2)}} - T_{\text{KCRV(K2)}} = -0.167$  mK in the above a), one gets  $T_{\text{INRiM, Ec1O2}} - T_{\text{IMGC, 1O2}} = -0.284$  mK.

This value is inconsistent with K2.5 (using  $W(\text{IMGC}_{\text{K2}}) = 0,091811040$ )  $= -0.060$  mK for the same thermometer. this latter being consistent, but only within the uncertainty, with the (INRiM only) K2.2 one,  $+0.024$  mK and the MULTICELLS Report AM, INTiBS,  $+0.11$  mK.

As to NMIIJ, the difference  $T_{\text{NMIIJ, O-2}} - T_{\text{NRC, Cu-M-3}} = +0.212$  mK (mean) is *incorrect* (the correct being  $+0.243$  mK) and the difference  $T_{\text{INRiM, Ec1O2}} - T_{\text{NRC, Cu-M-3}} = +0.019$  mK is consistent with the correct one  $+0.050$  mK. Thus the difference  $T_{\text{INRiM, Ec1O2}} - T_{\text{NRC, Cu-M-3}} = 0.050 - 0.243$  becomes  $-0.193$  mK. Since the NRC cell Cu-M-3 is used, providing a TPO2 higher by  $+0.098$  mK than the NRC cell F10 used in the CCT-K2, the difference  $T_{\text{INRiM, Ec1O2}} - T_{\text{NRC, F10}} = (-0.193 + 0.098)$  mK  $= +0.391$  mK, instead of  $-0.40$  mK in K2, and with a different sign (see above [b\) CCT-K2 Report](#)).

## 9. Conclusions

The chain of IMGC/INRiM cells shows a very good consistency with each other within 0.10 mK (corresponding to a Ar content of  $x(\text{Ar}) \approx 8 \cdot 10^{-6}$ ). The assumption, from the above consistency, that cell 1O2 argon content is almost zero is compatible with the Ar impurity experimentally found—from a deep analysis published about the behaviour of oxygen at its triple point, in the gas Messer 1:  $x(\text{Ar}) = 4 \cdot 10^{-6}$ . Consequently, also their differences with respect to other cells depend basically on the uncertainty of the measurements. With the above consistency, the results of the most recent STAR comparison would be more likely to be the ones reported in column 9 of Table 2, by using cell 1O2 as reference. This would imply that PTB reference cell O2-4 contains about  $17 \cdot 10^{-6}$ , instead of  $1 \cdot 10^{-6}$ , of Ar. That would also mean that other non-IMGC/INRiM cells show a larger Ar contamination, i.e., higher  $T_{\text{TPO2}}$  than assumed so far to have. This is suggested, e.g., in Table A5 from the results of the K2 comparison, where cell IMGC 1O2 was the lowest, consistent with the above assumption concerning the Ar content of cell 1O2. On the other hand, a resulting argon content of 15 ppm of cell O2-M2-1 (NBS/NIST) is questionable because the gas used for filling this cell was produced at NBS from  $\text{KMnO}_4$ .

In addition, during the above analysis, a small number of typos and inconsistencies were found in previously published documents, from IMGC/INRiM, NPL, and NRC. In particular, while the differences between IMGC/INRiM cells with NRC cells were always found consistent, the differences between these cells with the KCRV(K2) started to show increasing dubious high values since comparison K2.3 (evidence here reported only in Table A8 of the Appendix), though within the quite high uncertainty associated with those late measurements. In Table A8 anomalies in some of the results of the CCT.K2 are evident.

We guess that an inconsistent sign might be due to a misunderstanding in the application of the NPL Note reported in 8.a) above.

In conclusion, it looks like, in general, the realisation of the triple point of pure oxygen is affected by a higher argon contamination than expected, which would make some of the national realizations too high by 0.3–0.5 mK, today a significant difference, considering the present state-of-the-art realization uncertainty (0.05–0.15 mK). Consequently, the technique of measuring also the  $\alpha$ – $\beta$  transition as a check and for possible correction for the effective Ar contamination looks like an effective precaution for the future.

## Acknowledgements

The Authors are grateful for the accurate and useful comments and suggestions obtained from Bernd Fellmuth and Patrick Rourke [Fellmuth and Rourke, 2021] and from Aleksandra Kowal [Kowal, 2021]. Some useful INTiBS information became unavailable with the sudden death of Leszek Lipinski in 2019.

## References

- [Ancsin, 1970] J. Ancsin, The Triple Point of Oxygen and its Change by Noble Gas Impurities, *Metrologia* **6** (1970) 53
- [Ancsin, 1973] J. Ancsin, Dew Points, Boiling Points and Triple Points of "Pure" and Impure Oxygen, *Metrologia* **9** (1973) 26
- [Ancsin 1978] J. Ancsin, Intercomparison of Triple Points of Argon and Oxygen of INM, IMGCC and NRC, *Metrologia* **14** (1978) 79
- [De Paz *et al.*, 1974] M. De Paz, F. Pavese, G. Cagna, Analyse de traces d'impuretés dans l'oxygène ultrapur par spectrométrie de masse, dans la réalisation du point triple de l'oxygène à 54.361 K, *Le Vide, Suppl.* 169 (1974) 265–71.
- [Fellmuth *et al.*, 2005] B. Fellmuth, L. Wolber, Y. Hermier, F. Pavese, P.P.M. Steur, I. Peroni, A. Szmyrka-Grzebyk, L. Lipinski, W.L. Tew, T. Nakano, H. Sakurai, O. Tamura, D. Head, K.D. Hill and A.G. Steele, Isotopic and other influences on the realization of the triple point of hydrogen, *Metrologia* **42** (2005), 171-193.
- [Fellmuth *et al.*, 2012] B. Fellmuth, L. Wolber, D. Head, Y. Hermier, K.D. Hill, T. Nakano, F. Pavese, A. Peruzzi, V. Shkraba, A.G. Steele, P.P.M. Steur, A. Szmyrka-Grzebyk, W.L. Tew, L. Wang, D.R. White: Investigation of low-temperature fixed points by an international star intercomparison of sealed-triple point cells, *Metrologia* **49** (2012) 257-265
- [Fellmuth and Rourke, 2021] Private Communications.
- [Furukawa, 1986] Furukawa G.T., The triple point of oxygen in sealed transportable cells, *J. Res. NBS* 1986 **91**, 255–275
- [Hill *et al.*, 2005] K.D. Hill, A.G. Steele, Y.A. Dedikov, V.T. Shkraba, CCT-K2.1: NRC/VNIIFTRI bilateral comparison of capsule-type standard platinum resistance thermometers from 13.8 K to 273.16 K, *Metrologia* 2005 **42**, Technical Supplement 03001
- [Hill *et al.*, 2012] K.D. Hill, A. Peruzzi, R. Bosma, CCT-K2.3: NRC/NMi-VSL bilateral comparison of capsule-type standard platinum resistance thermometers from 13.8 K to 273.16 K, Final Report 2012, *Metrologia* **49** Tech.Suppl. 03004
- [Hill *et al.*, 2012b] K.D. Hill, A. Szmyrka-Grzebyk, L. Lipiński, Y. Hermier, L. Pitre, F. Sparasci, CCT-K2.4: NRC/INTiBS/LNE-Cnam trilateral comparison of capsule-type standard platinum resistance thermometers from 13.8 K to 273.16 K, Final Report, *Metrologia* 2012 **49** Tech.Suppl. 03004
- [Hill *et al.*, 2015] K.D. Hill, T. Nakano, P. Steur, CCT-K2.5: NRC/NMIJ/INRiM comparison of capsule-type standard platinum resistance thermometers from 13.8 K to 273.16 K, Final Report, *Metrologia* 2015 **52** Tech.Suppl. 03003
- [Imbraguglio *et al.*, 2020] D. Imbraguglio, P.P.M Steur, F. Sparasci, Comparison of ITS-90 realisations from 13 K to 273 K between LNE-CNAM and INRiM, *Measurement* **166** (2020) 108225, <https://doi.org/10.1016/j.measurement.2020.108225>
- [INTiBS, 2001] INTiBS-PAN: "Investigation of the IMGCC multicell at INTiBS. Report No 5", 20 November 2001. EU Project "MULTICELLS".
- [Kang *et al.*, 1996] K. H. Kang, K. H. Kim, J.-J. Kim and C. Rhee, Phenomenological interpretation of impurity redistribution effects on the freezing curve of oxygen, *Metrologia* 1996, **33**, 421-425

- [Kang *et al.*, 2001] Kee-Hoon Kang, Chang-Ho Song, Yong-Gyoo Kim, Device and method for measuring argon impurity by utilizing the triple point and the  $\beta$ - $\gamma$  transition temperatures of oxygen, US Patent 6,324,895 B1, 2001
- [Karlsson, 1975] B.M. Karlsson, Determination of argon and nitrogen in oxygen by gas chromatography, *Chromatografia* 8 (1975) 155
- [Kemp *et al.*, 1976] R.C. Kemp, W.R.G. Kemp, J.A. Cowan, The boiling points and triple points of oxygen and argon, *Metrologia* 12 (1976) 93
- [Kowal, 2021] Aleksandra Kowal, private communication.
- [B. Kołodziej *et al.*] B. Kołodziej, A. Kowal, L. Lipiński, H. Manuszkiwicz, A. Szmyrka-Grzebyk, Comparison of the Argon Triple-Point Temperature in Small Cells of Different Construction, *Int J Thermophys* (2017) 38:94 DOI 10.1007/s10765-017-2225-7
- [Muijlwijk, 1968] R. Muijlwijk, Vapour pressures of oxygen and platinum resistance thermometry below 100 K, KOL Thesis, Leiden 1968
- [Nasso *et al.*, 2009] C. Nasso, G. Bissolotti, F. Turra, M. Segal, E. Amico di Meane, F. Rolle, La taratura dei gas: determinazione della purezza, (in Italian) Proc. VI Congress "Metrologia & Qualità", April 7, 2009, Turin, 1-4
- [Pavese, 1970] Confronti di scale termodinamiche e pratiche, II) Campo da 13.81 K a 90.188 K, IMGC Int. Rep. S/71 (in Italian)
- [Pavese, 1975] F. Pavese, Realization of the IPTS68 between 54.361 K and 273.15 K and the triple points of oxygen and argon, *Inst. Phys. Conf. Series (GB)* 26 (1975) 70-79.
- [Pavese *et al.*, 1976] F. Pavese, G. Cagna, D. Ferri, Miniature sealed cells as an easy-to-use temperature calibration device and a precision thermostat for cryogenic temperatures, Proc. 6th Int. Cryo. Engin. Conf. (ICEC6), IPC Science and Tech. Press, Guildford (1976) 205-07.
- [Pavese, 1978] F. Pavese: "The triple point of argon and oxygen", *Metrologia* 14 (1978) 93-103; full Report: F.Pavese, IMGC Int. Report S/161 (in English) (1978).
- [Pavese, 1981] F. Pavese, Intercomparison of the IPTS68 realizations made at PRMI (USSR) and IMGC (Italy) by means of USSR-made cryogenic platinum resistance thermometers, Proc. Conf. on Temperature Measurement in Science and Industry, Dum Techniki CSVTS, Karlovy Vary (1981) 25-31.
- [Pavese, 1983] F. Pavese, On the use of first-generation sealed cells in an international inter-comparison of triple point temperature of gases, *Temperature, Its Measurement and Control in Science and Industry*, J.F.Schooley ed., Amer.Inst.of Phys., New York 5 (1983) 209-13.
- [Pavese and Ferri, 1983] F. Pavese, D. Ferri, Ten years of research on sealed cells for phase transition studies of gases at IMGC, *Temperature, Its Measurement and Control in Science and Industry*, J.F.Schooley ed., Amer.Inst.of Phys., New York 5 (1983) 217-27.
- [Pavese, 1984] F. Pavese, Final Report of the International Intercomparison of fixed points by means of sealed cells: 13.81 K to 90.686 K, Monograph 84/4 of Bureau International des Poids et Mesures, BIPM Sèvres (1984), pp.219.
- [Pavese *et al.*, 1984] F. Pavese, J. Ancsin, D.N. Astrov, J. Bonhoure, G. Bonnier, G.T. Furukawa, R.C. Kemp, H. Maas, R.L. Rusby, H. Sakurai, Ling Shankang, An International Intercomparison of fixed points by means of sealed cells in the range 13.81 K to 90.686 K, *Metrologia* 20 (1984), 127-144.
- [Pavese *et al.*, 1988] F. Pavese, D. Ferri, D. Giraudi, Evidence of unreliability of factory analyses of argon impurity in oxygen, *Adv.Cryo.Engin.*, 33 (1988) 1039-1043.
- [Pavese, 1994] F. Pavese, Gas-based thermometry and thermodynamics below 273.16 K at IMGC, IMEKO World Congress, Book dedicated to A. Bray (Barbato Ed.), 1994, 132-37
- [Pavese, 2003] F. Pavese, B. Fellmuth, D. Head, Y. Hermier, A. Peruzzi, A. Szmyrka Grzebyk, L. Zanin, MULTICELLS: A European Project on Cryogenic Temperature Fixed Points in Sealed Cells, *Temperature, Its Measurement and Control in Science and Industry*, D. Ripple ed., Amer.Inst.of Phys., New York A, 8 (2003), 161-166.

[Pavese, 2006] F. Pavese, Lessons learnt in 50 years of cryogenic thermometry, Chapter in “Cryogenic Engineering: Fifty Years of Progress”, Timmerhaus and Ross eds., Springer, New York, 2006, ch.10, pp. 179-221.

[Pavese, 2009] F. Pavese, Critical review of information relevant to the correction of the effect of chemical impurities in gases used for the realization of ITS-90 fixed points, *Metrologia*, 46 (2009) 47-61 IF 1,780

[Pavese and Steur, 2019] F. Pavese, P.P.M. Steur, 50 years of thermal metrology in cryogenics (1967–2008) at IMGC-CNR/INRiM, TEMPMEKO 2019

[Razhba *et al.*, 1973] Razhba, Ya.E., Belyansky, L.B., Orlova, M.P., Sharevskaya, D.I.: *Meas. Tech.* 16,390 (1973).

[Roboz, 1967] J. Roboz, Mass spectrometric determination of trace impurities in oxygen, *Analytical Chemistry* 39 (1967) 175–178

[Shimosaka, 2017] T. Shimosaka, Development of primary standard gas mixtures containing 10

lmol/mol oxygen in nitrogen with verification by a two-oven GC-TCD system for effective separation of oxygen from argon in presence of plenty of nitrogen, *Accred. Qual. Assur.* 22 (5) (2017) 281–289.

[Steele *et al.*, 2002] Steele A.G., Fellmuth B., Head D.I., Hermier Y., Kang K.H., Steur P.P.M., Tew W.L., CCT-K2: key comparison of capsule-type standard platinum resistance thermometers from 13.8 K to 273.16 K, *Metrologia* 39 (2002) 551–571.

[Steur, 1999] P.P.M. Steur, Correction file sent to NRC.

[Steur and Pavese, 2014] P.P.M. Steur and F. Pavese, 1967-2017, 50 anni di *Metrologia Termica in Criogenia* IMGC/INRiM (50 years of thermal metrology in cryogenics at IMGC/INRiM 1967-2017). Internal Report INRiM (2014) n.20, (partially in Italian), pp 100.

[Steur *et al.*, 2017] P.P.M. Steur, Inseok Yang, F. Pavese, Evidence for argon content in pure oxygen from thermal data, *IJOT* 38(2) 2017 20–32. DOI: 10.1007/s10765-016-2160-z

[Steur and Pavese, 2019] P.P.M. Steur and F. Pavese, 2018-2019: 50 anni di *Metrologia Termica in Criogenia* IMGC/INRiM (50 years of thermal metrology in cryogenics at IMGC/INRiM 1967-2019). Internal Report INRiM (2014) 2019 update (partially in Italian), pp 16

[Steur *et al.*, 2020] P.P.M. Steur, Inseok Yang, F. Pavese, The effect of argon content on the  $\beta$ - $\gamma$  transition of oxygen, *Int. J. Thermophysics* *IJOT* 41 (2020) 7–13, <https://doi.org/10.1007/s10765-019-2582-5>

[Steur *et al.*, 2020b] P.P.M. Steur, Inseok Yang, D. Giraudi, F. Pavese, Amount concentration of Ar in O<sub>2</sub> obtained by means of thermal analysis of certified mixtures at the  $\alpha$ - $\beta$  transition of O<sub>2</sub>, and preliminary confirmation of a new finding, *J. Chem. Thermodynamics* 141 (2020) 7, <https://doi.org/10.1016/j.jct.2019.105934>

[Yamaguchi and Araki, 1967] N. Yamaguchi, S. Araki, Mass spectrometric analysis of impurities in oxygen (in Japanese), *Bunseki Kagaku* 16 (1967) 348–354

[Yang *et al.*, 2017] Inseok Yang, Jin Bok Lee, Dong Min Moon, Jin Seog Kim, Preparation of primary reference material of argon in oxygen by the gravimetric method for application to thermometry, *Metrologia* 54 (2017) 184–192

[Yang *et al.*, 2014] I. Yang, T. Nakano, O. Tamura, Y.-G. Kim, Comparison of realizations of the triple point of oxygen between KRISS and NMIJ, TEMPMEKO 2014, unpublished

[Ward and Compton, 1979] S.D. Ward and J.P. Compton, Intercomparison of Platinum Resistance Thermometers and T<sub>68</sub> Calibrations, *Metrologia* 15 (1979) 31-46

**APPENDIX**  
**Some data from relevant publications**  
 References in Tables are the ones in the original publication)

TABLE A1. [Pavese, 2009]

Effect on  $T_{ip}$  per volume fraction of various gaseous chemical impurities on the indicated pure substances (in bold the principal  $s_L$ ): initial liquidus line slopes  $s_L = dT_{liq}/dc_i$  (in parentheses the initial solidus line slopes  $s_S$ ) and uncertainties  $u(dT_{liq}/dc_i)$ .

Chemical impurity	Effect on $T_{ip}$ per volume fraction/ $\mu\text{K ppm}^{-1}$			
	<i>e</i> -hydrogen	Neon	Oxygen	Argon
He	$-11 \pm 2$ ( $s_S$ n.a.)	None [18]	$+1.5 \pm 0.5^a$ ( $s_S$ n.a.)	n.a. <sup>b</sup>
H <sub>2</sub>	—	$-7 \pm 3^c$ ( $s_S$ n.a.)	n.a. <sup>b</sup>	None [35]
Ne	$-2 \pm 0.5$ ( $s_S$ n.a.)	—	$-1 \pm 0.5^a$ ( $s_S$ n.a.)	None [35]
O <sub>2</sub>	None <sup>d</sup>	n.a. <sup>b</sup>	—	$-22 \pm 3^a$ ( $-35$ ) <sup>e</sup>
N <sub>2</sub>	None <sup>d</sup>	$-8 \pm 2^{a,c}$ ( $-21$ ) <sup>e</sup>	$-22 \pm 3^a$ ( $-35$ ) <sup>e</sup>	$-22 \pm 3^a$ ( $-50$ ) <sup>e</sup>
Ar	n.a. <sup>b</sup>	None [18]	$+12 \pm 3^a$ ( $s_L = s_S$ )	—
CO	—	None [18]	n.a. <sup>b</sup>	$-24 \pm 4^a$ ( $-50$ )
F <sub>2</sub>	—	—	n.a. <sup>b</sup>	$-10 \pm 2$ (‘much larger’)
CH <sub>4</sub>	—	—	$< -30$ ( $s_S$ n.a.)	$-25 \pm 5^a$ ( $-80$ )
Kr	—	—	$-5 \pm 1^a$ ( $-9$ ) <sup>e</sup>	$+5 \pm 3^a$ ( $s_L = s_S$ )
Xe	—	—	$-8 \pm 2$ ( $-30$ ) <sup>e</sup>	$-6 \pm 2$ ( $s_S$ n.a.)

<sup>a</sup> Estimated only from thermal metrology studies.

<sup>b</sup> n.a. = no data available.

<sup>c</sup> Both H<sub>2</sub> and N<sub>2</sub> impurities can easily be removed today to much less than 1 ppm with the use of zirconium-getter based commercial filters.

<sup>d</sup> Estimated from solubility data.

<sup>e</sup>  $s_S$  provided with no uncertainty estimate, to qualitatively evaluate from ( $s_L - s_S$ ) the value of  $k_0$ .

TABLE A2. [Pavese, 1978]

Table 1. Impurity analysis for oxygen and argon  
 Oxygen

Sample Impurity (ppm)	SIO—1 <sup>c</sup>		SIO—2			SIO—3			LIF—4		AP&C—5				
	Feb 74 LAB 3	Feb 74 LAB 3 <sup>a</sup>	Dec 74 LAB 2	Dec 73 LAB 1	Dec 74 LAB 2	May 75 LAB 4	Nov 73 LAB 1	Dec 74 LAB 2	Nov 75 LAB 2 <sup>e</sup>	Nov 69 LAB 5	Dec 74 LAB 2 <sup>f</sup>	1973 LAB 6	Oct 74 NPL	Jul 75 IMGC	Nov 75 LAB 2
	N <sub>2</sub>	11 ± 2	14 ± 4	12	<10	1.1	≤ 2	< 5	1.0	13	5	4300	8	5	—
Ar	<2	2 ± 1	—	< 8	—	—	<12	—	—	<1	70 ± 50	10	5	—	—
CO <sub>2</sub>	11 ± 2	9 ± 2	1	none	1.6	≤20	< 1	2.9	3.4	<5	—	<0.5	—	—	1
CO	—	—	<0.5	—	≤0.5	≤10	—	≤0.5	—	<1	—	<1	—	—	—
H <sub>2</sub> O	1 ± 1	<1	—	< 5	<1.5	—	< 3	1.5	—	<2	10.5	0.15	—	—	—
H <sub>2</sub>	4 ± 2	2 ± 1	—	—	—	<10	—	—	—	—	—	—	—	—	—
Hydroc. (as CH <sub>4</sub> )	none	none	—	< 2	—	< 1	—	≤0.5	—	<0.5	—	0.5	—	—	—
Other <sup>d</sup> noble	none	none	—	< 2	—	< 2	3	—	—	<1	—	10 <sup>(2)</sup>	5 <sup>b</sup>	<2 <sup>b</sup>	—

<sup>a</sup> Sample stored in our sampling cylinder after 4-months use

<sup>b</sup> Krypton

<sup>c</sup> The number indicate the cylinder. SIO = SIO—Air Liquid; LIF = LIF-O-Gen Co.; AP&C = Air Products and Chem. Co.

<sup>d</sup> Note that some manufacturers give krypton figures of 10–15 ppm (see also [1, 3]); they are likely to be sensitivity limits, therefore not to be used for corrections

<sup>e</sup> Cylinder almost empty

<sup>f</sup> It also contained 1.4% of He

TABLE A3. (NPL – Lab) (Table 3 in [Ward and Compton, 1979])

Laboratory	Thermometer No.	$\Delta R_{\theta}$ ( $\mu\Omega$ )	$\Delta W_{4,2K}$ $\times 10^8$	Fixed point differences (mK)						
				e-H <sub>2</sub> t. pt.	e-H <sub>2</sub> "17K"	e-H <sub>2</sub> b. pt.	Ne b. pt.	O <sub>2</sub> t. pt.	O <sub>2</sub> c. pt.	H <sub>2</sub> O b. pt.
ASMW	207278	-40	78	1.3	-1.2	-2.0	-6.3	-2.1	-5.8	0.8
	217990	-140	19							-3.5
	217997	-260	55							-0.8
IMGC	646	0		-0.3	1.7	-0.4	2.0	1.0	3.8	1.0
								-0.2		
INM	1812283	-200								
KOL	T4	20	9	0.5	0.3	0.6	1.6	-0.1	-0.3	-2.4
	LN43	0	-6	0.3	-0.1	0.6	1.3	0.5	-0.2	2.4
NBS	1812279	-60		-4.0	-1.4	-1.7	1.2	0.6	3.1	1.8
	1812282	-50		-4.1	-1.2	-1.7	1.2	0.5	3.1	1.8
	1812284	-60		-3.9	-1.4	-1.8	1.2	0.6	3.0	1.4
NML	1705628	20		-0.3	0.1	-0.6	1.6	0.1	0.3	1.2
	1731676	0	20	-0.3	0.1	-0.6	1.6	0.1	0.3	3.0
NRC	1158062	90	-10	-1.8	2.5	-1.1	1.2	0.2	0.6	0.5
	1158066	-10	70	5.4	6.5	1.1	2.3	0.7	1.2	-0.9
				2.5	1.9	0.5				
NRLM	1722203	0	0	-1.0	2.7	-0.9	1.3	0.4	0.7	-0.5
	6601	10	190	1.9	-2.7	0.8	0.7	-0.1	-0.1	-1.3
	6803									-3.1
PRMI	16	-240		1.2	0	0.3	2.1	0.1	1.5	0.5
	45	-230		1.1	0.2	0.3	2.1	0.3	1.3	2.5
PTB	170138	-150			-3.7	-2.8	-0.1	-0.6	-1.9	-0.8
	188682	-40		-0.6	-0.5	-0.6	0.9	-0.3	-1.7	-0.5
	1778842	0	45							-0.3

TABLE A4. Summary of the K2.1–5 results (as elaborated in the present Report).

Red-evidenced data: inconsistent (see text).

OXYGEN				K2										K2.1		K2.3		2012 K2.4		2016 K2.5	
K2		BNM	<i>u</i> /mK	IMGC	KRIS	NBS/NIST		NPL		NRC		PTB		VNIIFTRI		Nmi-VSL Eb202		INTIBS 202		NMJ O-2	
LabGKCRV		-0,07	0,26	-0,2	0,12	0,09	0,17	0,07	0,1	0,02	0,18	0,18	0,22	0,18	0,23						
Lab G NRC(K2)		0,01	0,25	-0,16	0,12	0,1	0,17	-0,05	0,12	0,06	0,15	0,24	0,22								
IMGC/INRIMGLab		0,19 *		N	0,28		0,15		0,2 **		0,05 †		0,36	0,05							-0,02
LabGKCRV	K2.1										F10			-0,13	0,33						
Lab G NRC(K2)														0,34	0,32						
														0,64	0,32						
LabGKCRV	K2.3										Cu-M-3 ‡					0,48	0,36				
Lab G NRC(K2)																0,17	0,28				
LabGKCRV	K2.4										Cu-M-3 ‡								0,35	0,34	
Lab G NRC(K2)														0,36	0,34				0,04	0,33	
LabGKCRV	K2.5			Ec1O2							Cu-M-3 ‡										0,51
Lab G NRC(K2)					0,49	0,57															0,27
INRIMGNMJ				N		0,08															0,22
				-0,019																	0,25
																					0,224
																					0,25

# 802 G 102 = +0,48 mK \* Bonnier private communication (CCT/76-32) \*\* NPL CCT/76-41G0,04 (in Metrologia 76(77)) † Ancsin, Metrologia 76(77) ‡ Cu-M-3 G F10 = +0.098 mK (NRC)

TABLE A5. STAR comparison of cells [Fellmuth *et al.*, 2005].



Cell No	Manufacturer	Owner	Model	Sealing	Gas purity	Gas source*
O200/2	INM	INM	M-cell SS body / Cu tube [9, 23]	2000	5N5 <sup>a</sup>	Air Liquide
O202/1	INM	INM	M-cell SS/Cu [10]	2002	6N <sup>b</sup>	Air Liquide
1O2	INRIM	INTiBS	A SS/Cu / In seal [1, 11, 12, 23]	Sep 76	4N8 <sup>c</sup>	SIO4
2O2	INRIM	INTiBS	A SS/Cu / In seal [1, 11, 12, 23]	Sep 76	4N8 <sup>c</sup>	SIO4
9O2	INRIM	PTB	L SS/Cu [1, 11, 12, 23]	Oct 86	5N5 <sup>d</sup>	SIAD
11O2	INRIM	MSL	Cbis SS/Cu [1, 11, 12, 23]	Oct 86	5N5 <sup>d</sup>	SIAD
13O2	INRIM	VSL	C SS/Cu [1, 11, 12, 23]	Nov 99	5N5 <sup>e</sup>	Messer Griesheim
E1O2	INRIM	PTB	M-cell a SS/Cu [4, 13]	Nov 99	5N5 <sup>e</sup>	Messer Griesheim
O2-M2-1-NIST	NIST	NIST	316LSS [15]	Feb 83		NBS (KMnO <sub>4</sub> )
O2-2-NPL	NPL	NPL	Wide SS/Cu/In seal [20]	Aug 95	4N8 <sup>f</sup>	Air Liquide
O2-F10-NRC	NRC	NRC	Cu / In seal [21]	Oct 85	4N8	Air Products
O2-4	PTB	PTB	C Cu [22]	Mar 96	6N <sup>g</sup>	AGA
O2-MC-495	VNIIFTRI	VNIIFTRI	M-cell Cu tubes [1, 23]	1995		
O2-MC-897	VNIIFTRI	PTB	M-cell Cu tubes [1, 23]	Dec 97	5N <sup>h</sup>	

\* Identification of commercial equipment and materials in this paper does not imply recommendation or endorsement by PTB, nor does it imply that the equipment and materials identified are necessarily the best available for the purpose.

<sup>a</sup> NIC: H<sub>2</sub>, CO, CO<sub>2</sub> 0.1 ppm; N<sub>2</sub> 4 ppm; CH<sub>4</sub> 0.2 ppm; H<sub>2</sub>O 1 ppm.

<sup>b</sup> NIC: H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>n</sub>H<sub>m</sub> < 0.1 ppm; H<sub>2</sub>O < 0.5 ppm.

<sup>c</sup> Analysis results: N<sub>2</sub> ≤ 14 ppm; Ar < 10 ppm; Kr + Xe < 1 ppm; CO<sub>2</sub> 0.4 ppm.

<sup>d</sup> Analysis results: Ar 5 ppm; N<sub>2</sub> < 0.5 ppm.

<sup>e</sup> Analysis results: N<sub>2</sub> < 5 ppm; Ar < 3 ppm; CH<sub>4</sub> < 0.1 ppm.

<sup>f</sup> NIC: Ar < 8 ppm; Kr, Xe < 2 ppm; N<sub>2</sub> < 5 ppm; H<sub>2</sub>O < 3 ppm; other 0.5 ppm.

<sup>g</sup> Analysis results: Ar ≤ 1 ppm; N<sub>2</sub>, H<sub>2</sub>O ≤ 0.5 ppm; CO<sub>2</sub>, C<sub>n</sub>H<sub>m</sub> ≤ 0.1 ppm.

<sup>h</sup> Analysis results: Ar 0.06 ppm; N<sub>2</sub> 2.9 ppm; H<sub>2</sub>O 6 ppm.

TABLE A6. STAR comparison of cells [Fellmuth *et al.*, 2005].

**Table 6.** Differences  $\Delta T_{LP} = T_{LP} - T_{Ref}$  between the liquidus-point temperatures of the investigated oxygen cells,  $T_{LP}$ , and that of the reference cell O<sub>2</sub>-4,  $T_{Ref}$ , together with their standard uncertainties  $u(\Delta T_{LP})$ . The sources and purities of the gases are listed in table 2.

Cell No	Producer	$\Delta T_{LP}/\mu\text{K}$	$u(\Delta T_{LP})/\mu\text{K}$
O200/2	INM	-49	40
O202/1	INM	-165	36
1O2	INRIM	-199	35
2O2	INRIM	-101	35
9O2	INRIM	-58	36
11O2	INRIM	-118	35
13O2	INRIM	-16	36
E1O2	INRIM	5	36
O2-M2-1-NIST	NIST	-27	35
O2-2-NPL	NPL	-109	35
O2-F10-NRC	NRC	-281	36
MC-495	VNIIFTRI	-117	46
MC 897	VNIIFTRI	-26	38

(Table 2 in that paper is Table A5 here above)

TABLE A7. CCT-K2 comparison [Steele, 2002],

misprint in Line O2 1857277:  $W$  [Steur, 1999]

	1857277		1860951	
	$W$	$u_L$	$W$	$u_L$
H <sub>2</sub>	0.001191671	0.11	0.001215794	0.11
17				
20.3				
Ne	0.008495882	0.11	0.008503931	0.11
O <sub>2</sub>	0.09184464	0.09	0.09181104	0.09
Ar	0.21598525	0.05	0.21594546	0.05
Hg	0.84416905	0.04	0.84415967	0.04
H <sub>2</sub> O	25.5496619	0.03	25.5365537	0.03

Table 2.2: Calibration data for IMGC capsule thermometers.

TABLE A8. Summary of CCT-K2.xx comparisons [Steele, 2002; .....].

	BNM	u/mK	IMGC	KRISS	NIST	NPL	NRC	PTB	VNIFTRI	Nmi-VSL Eb202	INTiBS 202	NMIJ O-2		
<b>K2</b>														
Lab ĞKCRV	-0,07	0,26	-0,2	0,12	0,09	0,17	0,07	0,1	0,02	0,18	0,18	0,22		
Lab Ğ NRC(K2)	0,01	0,25	-0,16	0,12	0,1	0,17	-0,05	0,12	0,06	0,15	0,24	0,22		
			-0,38											
			-0,4											
<b>K2.1</b>														
Lab ĞKCRV														
Lab Ğ NRC(K2)										-0,13	0,33			
										0,34	0,32			
										0,64	0,32			
<b>K2.3</b>														
Lab ĞKCRV							<b>Cu-M-3</b>							
Lab Ğ NRC(K2)							0,098 > F10			0,48	0,36			
										0,17	0,28			
<b>K2.4</b>														
Lab ĞKCRV	Multicell improved M-cell						<b>Cu-M-3</b>							
Lab Ğ NRC(K2)	0,036	0,34					0,098 > F10				0,35	0,34		
	0,05	0,33									0,04	0,33		
<b>K2.5</b>														
Lab ĞKCRV			<b>Ec1=2</b>				<b>Cu-M-3</b>							
Lab Ğ NRC(K2)			-0,49	0,57								-0,51	0,27	
			(Ğ316)										-0,53	0,27
			(-240)										-0,22	0,25
INRIMĞNMIJ			-0,019	0,08									-0,224	0,25

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of numbers:

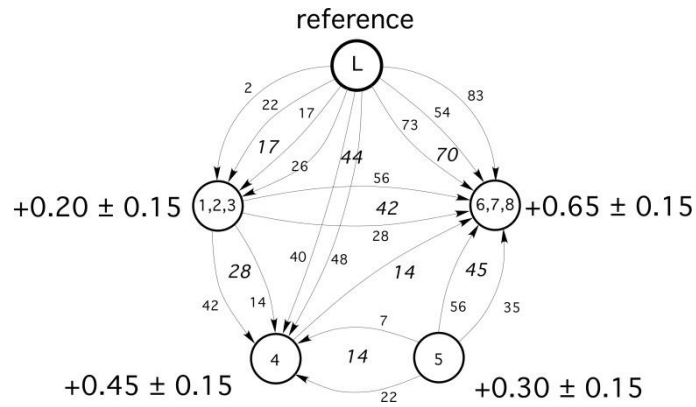


Figure A1. [Pavese and Ferri, 1983]

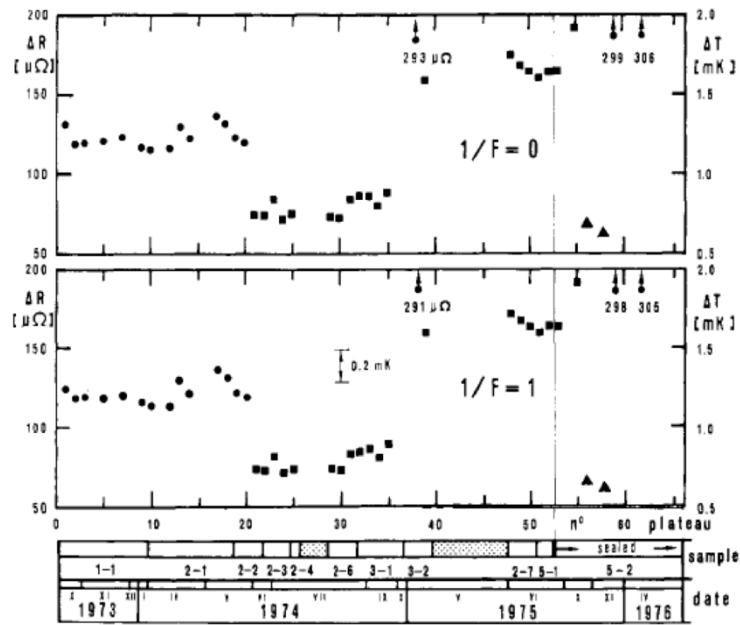


Figure A2. [Pavese, 1978]

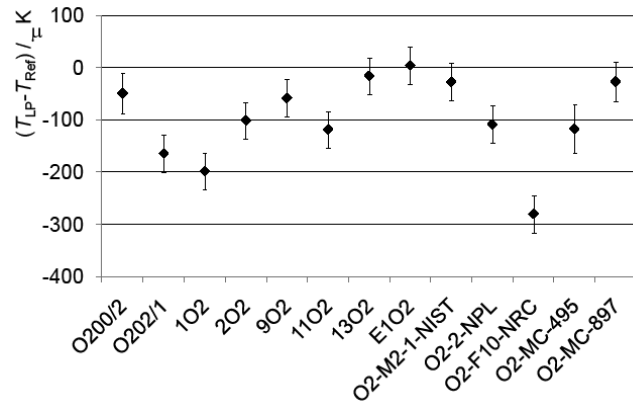


Figure A3. STAR Cells comparison (see differences in this Report). [Fellmuth *et al.*, 2011]

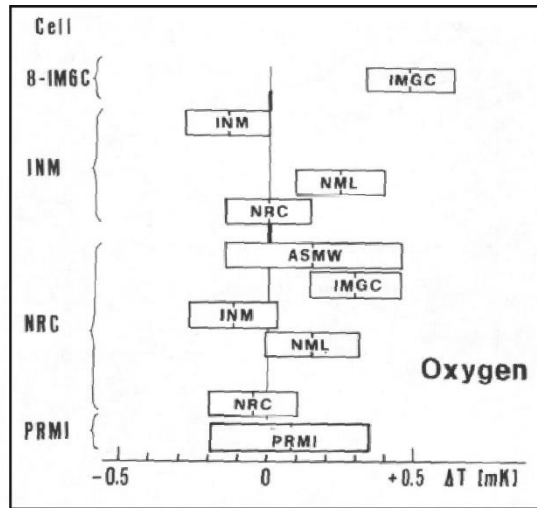


Figure A4. IntInt: Lab<sub>cell</sub> – KCRV(≡ 102), as measured by different Labs [Pavese, 1984].

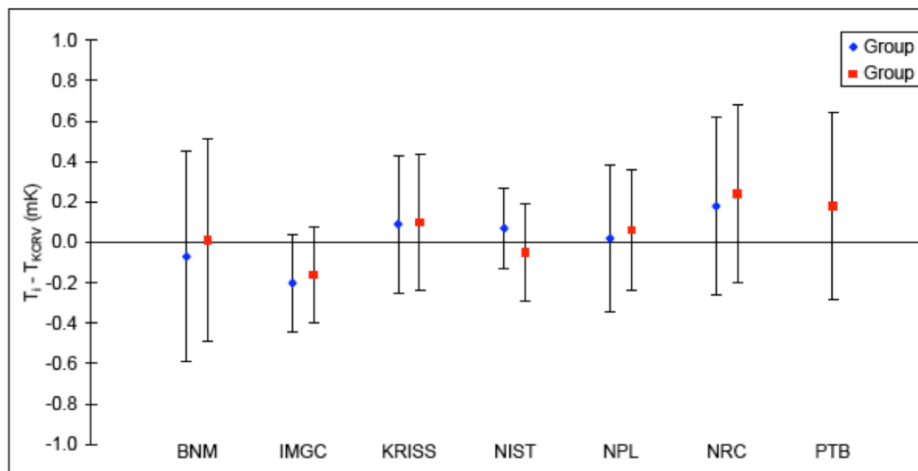


Figure. A5. CCT-K2.