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An inter-comparison of isotopic composition of neon via chemical assays and thermal analyses (IUPAC Technical Report)

(Article begins on next page)

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IUPAC Technical Report

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and Franco Pavese*

An inter-comparison of isotopic composition of neon *via* chemical assays and thermal analyses (IUPAC Technical Report)

Abstract: In 2003–2014, a study on the effect of isotopic composition on the triple point temperature of neon was conducted under the framework of a Project involving laboratories from 11 countries. Natural neon from commercial sources of different isotopic composition, high-purity ^{20}Ne and ^{22}Ne isotopes, and certified artificial isotopic mixtures were used. The thermometric studies comprised: a) a total of 131 analytical assays from 3 laboratories on the isotopic composition of samples taken from 31 different bottles of neon with chemical gas purity 99.99 mol % to 99.9995+ mol %, including chemical impurities for some samples, with up to 12 assays per sample; b) multi-laboratory thermal analyses, with accuracies ranging up to better than 50 μK ($k \approx 2$), on 39 samples, almost all permanently sealed in metal cells, for the determination of the liquidus-point temperature of the triple point as a function of isotopic composition. The thermometric studies also constitute an international inter-comparison of thermal and analytical assays on the isotopic composition— and occasionally of the chemical impurities—of neon. These tests are critically needed for top-accuracy thermometry. The main results of the inter-comparison of the various chemical assays, and of the comparisons between the assays and the results of thermal analyses, are reported. They show discrepancies in $x(^{20,21,22}$Ne$)$, especially for $x(^{22}$Ne$)$, in 'natural' neon, for the same gas bottle, equivalent to an uncertainty of up to 165 μK ($k = 1$) in the triple point temperature, as measured by all testing laboratories, and of about 100 μK ($k = 1$) as measured from a single testing laboratory. This is an unsatisfactory situation for thermometry, since it is difficult to obtain a reliable and accurate isotopic assay for neon, thus limiting the accuracy of the realisation of the neon triple point temperature as a ITS-90 reference point to well above 50 μK. However, it also discloses a strong limitation in the relevant analytical chemistry.

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1 Introduction

In comprehensive studies lasting from 2003 to 2014 the effect of isotopic composition on the triple point temperature was tested on neon of different isotopic compositions obtained from commercial sources [12]. These studies involved 10 National Metrology Institutes (NMIs) and three chemical-assay laboratories [1–11]. The relevance of the isotopic effects in thermometry has already been discussed in depth in [8] and references therein. Analytical assays and thermal analyses were also conducted on high-purity isotopes of ^{20}Ne and ^{22}Ne from commercial bottles, but are not directly relevant to this paper.

The isotopic composition studies comprised:

– Analytical assays from 3 laboratories on the isotopic composition of samples from 31 bottles of high chemical purity commercial neon, as well as on the chemical impurities of some of these samples [1, 11, 13–15];
– Thermal analyses from 9 laboratories on 39 samples, almost all permanently sealed in metal cells (ensuring full physical-chemical sample stability), for the determination of the liquidus-point temperature of the triple point [8]. The sealing is so far tested to perform up to and over 40 years [16], with an accuracy up to or better than about 50 μK; Analytical assays and thermal analyses from bottles of artificial mixtures of high-purity ^{22}Ne in ^{20}Ne, certified by the gravimetric method (only the mixture with 10 % ^{22}Ne relative amount fraction is included here) [13].

Note: *This Report is based on a comparison of physical-chemical and thermal measurements. Therefore, the Authors preferred to make the distinction clearer by using the now obsolete term "assay" for the former and "thermal analysis" for the latter, though they are obviously all "measurements".*

The main final results of the inter-comparisons of chemical assays, and of the final results of thermal analyses, are reported, discussed, and compared with each other. In order to limit the length of the body of this Report, the discussion regarding tests on the assays reproducibility, along with Tables 4 to 9, Figs. 11 to 15, is given in the Online Appendix (italics is used to refer to these Tables and Figures, and the numbering follows that of the main text without starting ahead from Online Appendix A1).

2 Summary of the inter-comparison of analytical assays

The studies comprised:

– 31 different bottles of commercial Neon of nominal chemical purity 99.99 mol % to 99.9995+ mol %;
– Assays from 3 laboratories: IRMM (2003–2010), KRISS (2009–2013), University of Tokyo (2011–2014);
– A total of 131 isotopic assays on natural neon, with up to 12 assays per sample over a time span of up to 10 years, of which 118 are analyzed in this paper;
– Three artificial isotopic mixtures of ^{22}Ne in ^{20}Ne (^{21}Ne in trace only) were prepared by KRISS, with relative ^{22}Ne amount fractions of 6.6 %, 10 % (close to 'natural' composition [1]), and 20 %;
– Calibration of apparatuses by means of gravimetrically-certified mixtures (KRISS, University of Tokyo)
– Additional chemical purity assays on some of the neon bottles or samples.

All the outcomes of the Project are now published, as far as the thermal studies are concerned, including evidence of perfect ideality of the isotopic mixture up to the composition of natural neon. As a final outcome, the Bureau International des Poids et Mesures (BIPM) endorsed, by formal inclusion in the Mise en Pratique (MeP) of the kelvin, the proposed equation for the correction of the measured neon triple point temperature for the actual isotopic composition of the sample used, when known [8, 10, 17]. The main object of the Project was the determination of isotopic effects on the neon triple point temperature. Thus, in order to reduce the uncertainty in the measured triple point temperature, in the following all errors and uncertainties are also expressed in temperature units and related to the temperature of the triple point of neon, be it ^{20}Ne or ^{22}Ne.

Table 1: Origin of the neon bottles/samples analyzed more than once in these studies, with chemical impurities N_2 and H_2 [18] and equivalent temperature corrections.

Bottle/ sample #	Gas producer[a]	Bottle date	Nom. impurity, x/µmol mol^{-1} [b]	N_2 /µmol mol^{-1}	H_2 /µmol mol^{-1}	Correction N_2/µK[c]	Correction H_2/µK[c]	Tot. corr./µK[c,d]
2	M-b	1979	50, >50	5.5	—	44	—	44
3	M-a	1977	50, >50	11.3	25	90	125	215
5/#B, #C[f,g]	IB	2003	10, >50	<2	<1	<18	<16	<34
6	AG	2006	10	—	—	—	—	—
7/#A[f,g]	AW	2006	10, 80	<0.5	<0.3	<1	<1	<1
8	M	1979	>5, >5	—	—	—	—	—
9	P	2002	10	—	—	—	—	—
10[f,j]	L	1995	10	<2	—	16	—	16
11[f]	MG	1999	10	<2	<1	<18	<16	<34
12	TNS	2006[h]	10	<2	<1	<18	<16	<34
13	S	1986	100, 50	15	3	120	21	141
14[f,j]	AG	2002	10, 80	<0.1	<0.1	<1	<1	—
16[f,j]	PTB-3	2002	10	—	—	—	—	—
17	AP	1985	10	—	—	—	—	—
18	AP	1989	>10	—	—	—	—	—
24[f]	L	1989	10	—	—	—	—	—
26(12)/#0[f,g]	TNS	2006	10	<2	<1	<18	<16	<34
28(12)/#00[g]	TNS	2006	10	<2	<1	<18	<16	<34
29[i]#X, #XB[g]	TNS	2013	10	<2	<1	<18	<16	<34
27[e]	A(^{20}Ne) + 10 % IB2(^{22}Ne)	2011	30 & 30[k]	10	11	80	77	157

Chemical assays are from the commercial producer. Effect of chemical impurities at the triple point: N_2, (-8 ± 2) µK/10^{-6}; H_2, (-7 ± 3) µK/10^{-6}; He, none. [a]Gas assays: #1, #4, #15 IRMM gas references, not reported here. #19–#24, #28 and #31 single assay, therefore omitted here. Gas producer acronyms: A = Aldrich; AG = Alpha Gaz; AL = Air Liquide; AP = Air Products; AW = Air Water; IB, IB2 = IceBlick; L = Linde; M = Matheson; MG = Messer Griesheim; P = Praxair; S = SIO-Air Liquide; TNS = Taiyo Nippon Sanso. [b]IRMM isotopic assays in italics. [c]Correction on the neon triple point temperature. [d]In italics when a H_2 impurity value is unavailable. [e]Certified KRISS mixture (10 % ^{22}Ne). [f]From cylinder sampling by filling a valve (see Figs. 11, 12 in Online Appendix A1). [g]NMIJ #0, #00, #A, #B and #C are samples drawn from the gas handling system. [h]No thermal measurements with this gas, but various samples from this bottle. [i]#29 then at INRIM for making sealed cells Ec24Ne and Ec25Ne for NMIJ in 2014. [j]Not original bottle (large sampling cylinder). [k]Nominal; overall: 100 & 1000 µmol mol^{-1}.

The results of the IRMM assays were all provided for uncorrected ionic current. IRMM discontinued this type of assays in 2010. Assays at IRMM were performed by drawing samples from the original bottles.

After the preparation of the three artificial mixtures in 2011, KRISS assays were performed with a calibrated mass spectrometer [9], basically since 2012. The ratios cal/uncal for some samples were also provided for some assays as additional information about the effect of calibration. These data are presented and discussed in Online Appendix A4.

The University of Tokyo assays were also initially supplied using an un-calibrated mass spectrometer. The assays of 2012 and later were performed with their spectrometer calibrated by means of the KRISS 10 % mixture, and were reported using the IUPAC recommended value as the reference composition. Using Bottomley's reference composition instead, the maximum computed differences were: $46 \cdot 10^{-6}$ for $x(^{21}$Ne) and $35 \cdot 10^{-6}$ for $x(^{22}$Ne). Assays in Japan and at KRISS were performed on small samples drawn at NMIJ and INRIM from the original bottles and sealed in ultraclean, carefully conditioned, Nupro valves, mod. SS4H-V51 (high-pressure, all metal except Vespel gaskets—see Fig. 12 in Online Appendix A1 supplied by NMIJ). Some of these were found by KRISS to be contaminated with air, as illustrated later.

NMIJ also supplied some samples drawn from different places in their gas handling system. A lower-precision single assay was obtained from one laboratory in Canada and another in Russia (not included here).

Figure 1 shows the wide range of $x(^{22}$Ne) (0.0009 for the fit, equivalent to ±129 µK) and the narrower range of $x(^{21}$Ne) (range 0.000 07, equivalent to ±3 µK) of the samples analyzed, and the IUPAC recommended
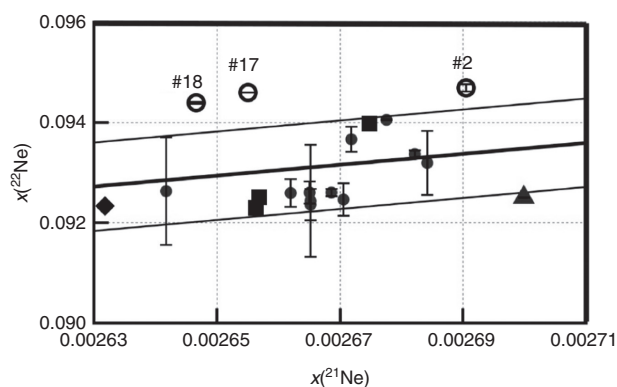
Fig. 1: Overall ^{22}Ne and ^{21}Ne sample dispersion in isotopic composition. The hyphens indicate the measurement uncertainties ($k = 1$) of each datum. Thin lines: $\pm 1\sigma$ of fit: #2, #17, #18 exceeding it. Triangle: IUPAC recommended reference composition. Since the IUPAC composition is used as a reference, the experimental uncertainty in that value can be omitted; x is given in mol mol^{-1}.

composition used as a reference in the following. The hyphens, where visible, indicate the uncertainty on $x(^{22}$Ne$)$ associated with each composition by these studies; where these are not visible, the uncertainty is within the size of the symbol. Temperature indications refer to the effect on the temperature of the triple point.

The basic outcomes of these studies are summarized in Table 2 (and Tables 4, 5 in Online Appendices A2, A3), and in Figs. 3, 4 (and Figs. 11–13 in Online Appendices A2, A3)—see [2] for some preliminary comments.

3 Comments on the data

Figure 2 visually represents the variation of the assay results on replication for the same sample, either by the same laboratory or in different laboratories.

In Table 2, the value or range of the uncertainties of the assays results, as *declared* by each laboratory, is shown in the column labeled $u_{\text{decl}}(x(^{22}$Ne$)) \times 10^{-6}$. The temperature-equivalent of the uncertainty is shown for ^{22}Ne. The uncertainty of the assay results for the greyed cases is higher than the uncertainties supplied by the assay laboratories: the darker the gray, the larger the discrepancy. The table data are for ionic currents, except when calibration is indicated. There may also be a contribution to reproducibility from the variability of the underlying calibration factors (see Online Appendix A3). The number in parenthesis in the assay column indicates the number of assays forming the mean (from 2 to 12). In the last column, the equivalent uncertainty on the triple point temperature of neon is shown (best state-of-the art total budget of thermal analyses below about 50 µK): it arises principally from $x(^{22}$Ne$)$, the effect for $x(^{21}$Ne$)$ being smaller than 10 µK.

In Fig. 3 two examples are reported of the assays' reproducibility, bad and good, respectively.

Additionally, Tables 5 and 6 of Online Appendix A3 report and discuss the analyses of the effect of the calibration factors.

In Table 5, the ratios of results from assays made by pairs of laboratories for the same gas sample are shown. Though different for different pairs, one would expect them to be consistent within the uncertainties as reported by each laboratory or, at least, within the reproducibility in the row, irrespective of the value of the calibration factor. The two before-last columns report the mean of the values in each row and its standard deviation, u_{row}. The ratios exceeding u ($k = 1$) or U ($k \approx 2$) are indicated in italics or boldface, respectively.

In Table 6, conversely, the ratios of the results from assays on a sample and on a reference sample made by the same laboratory are shown. In this case, one would expect them to be consistent within the uncertainties as reported by each laboratory or, at least, within the dispersion in the row, irrespective of the value of the calibration factor. Three different references are used, since the effect may also depend on the chosen reference. In the last three rows the column (sample) mean value, the standard deviation, and the temperature

Table 2: Mean values and u ($k = 1$) of the assays for each of the bottles when more assays are available.

#	Assays	u_{decl} ($x(^{22}Ne)$) $\times 10^{-6}$[c]	Mean $x(^{21}Ne)$, $u(x(^{21}Ne))$	Mean $x(^{22}Ne)$, $u(x(^{22}Ne))$	$\Delta T(x(^{22}Ne))$ /μK
1	(2) IRMM (2006, 2009)	3.5	0.002670 0.000010	0.092653 0.000091	—[f]
2	(3) IRMM (2006, 2009(2))	5.6–7.7	0.002690 0.000009	0.094690 0.000076	11
3	(3) IRMM (2006, 2009(2))	3.2–4.1	0.002682 0.000010	0.093370 0.000073	11
4 (15)	(3) IRMM (2003, 2009) IRMM 2008	3.4–4.5	0.002635 0.000001	0.093049 0.000005	—[f]
5/#B, #C	(12)[e] IRMM (2003, 2009(2)), Japan 2011, Japan 2013 (2)[a] KRISS2 2012 (2)[a] Japan 2014(2)[a]	74 3.4–6.4 110–160 65 140 —	0.002662 0.000050	0.0596 0.000280	41
6	(6) IRMM (2006, 2009(2)), KRISS2 2012[a], Japan 2013(2)[a]	2.9–5.1 137 65	0.002684 0.000015	0.093197 0.000640	94
7/#A	(8) IRMM (2006, 2009(2)), Japan 2011 Japan 2013[a] KRISS2 2012[a], Japan 2014[a]	2.9–5.1 100 75 136 —	0.002665 0.000032	0.092359 0.000320	46
8	(3) IRMM (2008, 2009(2))	6.1–8.3	0.002669 0.000008	0.092604 0.000074	11
9	(4) NGL[b], IRMM (2008, 2009(2))	1000 5.2–6.1	0.002671 0.000050	0.092462 0.000320	47
10	(9) IRMM (2003, 2008, 2009(2)) Japan 2011(2), Japan 2013[a], KRISS2 2012[a] Japan 2014[a]	4.8–5.1 160 55 138 —	0.002672 0.000065	0.093666 0.000250	36
11	(9) IRMM (2003, 2006, 2009(2)) Japan 2011, Japan 2013[a], KRISS2 2012[a] Japan 2014[a]	5.1–6.3 3.3–5.9 110 165 60 135	0.002665 0.000027	0.092441 ¶(0.09352) (0.09158) 0.001114 (0.00070) (0.00016)	164[g] (102) (24)
12/#00	(3) IRMM 2008, IRMM (2009(2))	3.7–4.5	0.002684 0.000007	0.093652 0.000730	107
13	(4) IRMM (2006(2)) 2009(2)	3.6–4.8	0.002678 0.000002	0.094055 0.000005	1
14	(8) IRMM (2006, 2009(2)), Japan 2011, KRISS2 2012[a], Japan 2013[a] Japan 2014[a]	2.3–4.1 100 137 63 —	0.002665 0.000051	0.092604 0.000250	36
16	(6) IRMM (2003, 2009(2)), KRISS2 2012[a], Japan 2013(2)[a]	3.9–6.8 135 65	0.002642 0.000020	0.092635 0.001070	157
17	(3) IRMM (2003, 2009(2))	4.8–5.1	0.002655 0.000001	0.094600 0.000002	<1
18	(3) IRMM (2003, 2009(2))	4.1–6.8	0.002647 0.000001	0.094395 0.000019	3
24	(4)KRISS1 2012[a,d], Japan 2013(2)[a], Japan 2014[a]	136 63 —	0.002657 0.000064	0.092512 0.000240	35

Table 2 (continued)

#	Assays	u_{decl} (x(^{22}Ne)) ×10^{-6})^c	Mean x(^{21}Ne), u(x(^{21}Ne))	Mean x(^{22}Ne), u(x(^{22}Ne))	ΔT(x (^{22}Ne)) /μK
26/#0	(5) Japan 2011, KRISS2 2012^a,	—	0.002632	0.092333	42
	Japan 2013(2)^a, Japan 2014^a	182	0.000072	0.000280	
		45			
		—			
27	(3)KRISS2 2012^a, Japan 2013^a,	137	0.000448	0.091744	13
	Japan 2014^a	169	1.0E-04	8.6E-05	
		—			
28	(3) Japan 2013 (2)^a, Japan 2014^a	62	0.002657	0.092642	33
(12)/#00		—	0.000075	0.000220	
29/#X,	(3) Japan 2013 (2)^a, Japan 2014^a	64	0.002673	0.092758	31
#XB		—	0.000110	0.000170	

Note: Total 131 assays. For the sample number in column # refer to Table 1. *The deeper a cell gray filling the higher the value of u.* ΔT(x(^{22}Ne)) = triple-point temperature equivalent of u: best total uncertainty budget for thermal measurements ΔT_{tp} less than about 50 μK.
^{a}Calibrated. ^{b}Canadian laboratory (low precision). ^{c}Reported for each assay. ^{d}KRISS1: Bottle calibrated against a mixture of 3.3 % ^{22}Ne in ^{20}Ne. ^{e}Including NMIJ #28 and #29. ^{f}IRMM reference gas. ^{g}In parentheses: first, mean of only early assays; second, mean of only late assays (see the bottle/sample assay changes in Fig. 3).
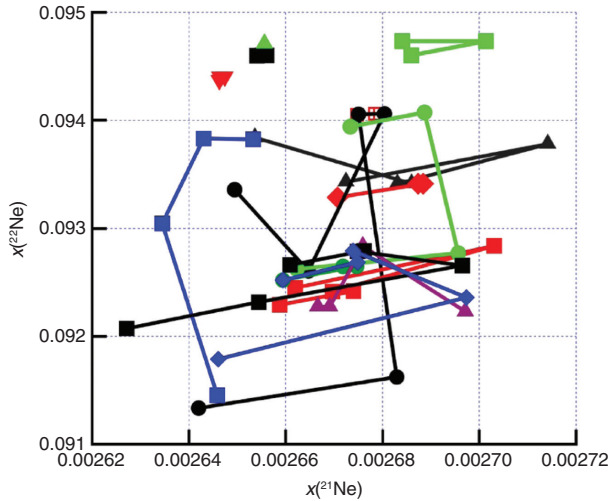
Fig. 2: Irreproducibility of subsequent assays for each of the gas samples in Table 1. Identical symbols of the same colour (or gray tone) indicate replicated analyses *of the same bottle*, either by the same laboratory or in different laboratories; amount fraction x is given in mol mol^{-1}.

equivalent in microkelvin (effect on the neon triple-point temperature) are reported. The ratios exceeding u ($k = 1$) or U ($k \approx 2$) are indicated in italics or boldface, respectively.

In Fig. 13 of Online Appendix A3, a third way to evaluate the quality of the assays is shown and discussed by means of the correlation between pairs of laboratory data or, for all with respect to the fractionation line.

4 Discussion of overall results on the assays

The total number of assays per sample was variable for contingent reasons, but also because it was decided to measure samples with the widest discrepancy among the initial assay results again. Consequently, samples with only two assays do not necessarily indicate that the statistical dispersion of the assays is much narrower.
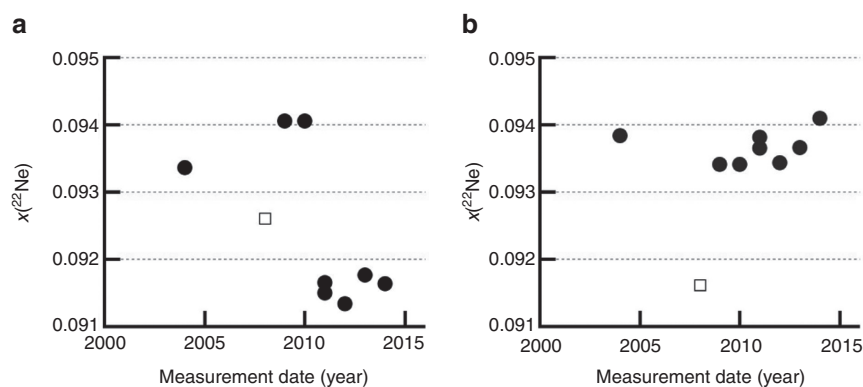
Fig. 3: Extreme examples of reproducibility with time of $x(^{22}Ne)$ in repeated assays. (a) Bottle #11: $u(T_{tp}) = 161\,\mu K$, inconsistent results (Mean 2004-2009: 0.093 520 $u(T_{tp}) = 102\,\mu K$; Mean 2010-2013: 0.091 593 $u(T_{tp}) = 27\,\mu K$); (b) Bottle #10: $u(T_{tp}) = 29\,\mu K$, consistent results. Open square: outlier (IRMM 2008). x is given in mol mol^{-1}. See mean numerical values on Table 2.
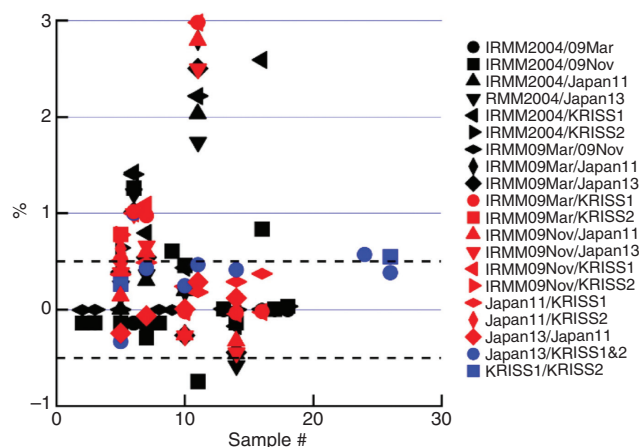

Fig. 4: Visual summary of the assays results in Table 5 in Online Appendix A3 on the same sample for ratios of pairs of laboratories. Samples # in abscissa are numbered as in Table 1. On the y-axis the deviation from identity in the ratio r of a pair of assays results, $100-(r-1)$, is shown in percent for ^{22}Ne: the broken lines indicate the 1σ level.

In the following, the analysis is limited to ^{22}Ne only, since $x(^{21}Ne)$ variability is not thermally critical in this application, though it might be in others.

In Table 2, the summary of the results is reported: mean values and u ($k = 1$) of the assays for each of the 29 bottles for which more assays are available. As a visual aid, some cells are greyed: the darker the cell's filling, the higher the value of u. There are four samples with an overall irreproducibility that particularly affects the accuracy of thermal studies: #6, #11, #12, and #16. However, there are also six more (#5, #7, #9, #10, #14, #26) whose temperature-equivalent uncertainties seriously affect the total budget of the thermal studies: in total, 10 out of 22 bottles. The reasons for this range from a laboratory's analytical precision not being sufficient for the needs of the thermal studies to an inter-laboratory non-reproducibility that was impossible to understand and resolve.

In an effort to understand the quality of the assays, the above three methods were used for comparing the data.

In cases of both non-calibrated and calibrated spectrometers, when a laboratory provides isotopic composition data on several samples and replicates the assays at two different times, one may assume that each time all the results stay within the uncertainty reported by each laboratory. Forming the ratios of the assay results pairs can check this. The values of the ratio depend on the calibration factors (known or not), but by the same extent. Thus, one should expect a reproducibility of these values within the variability of the assays reported by each laboratory.
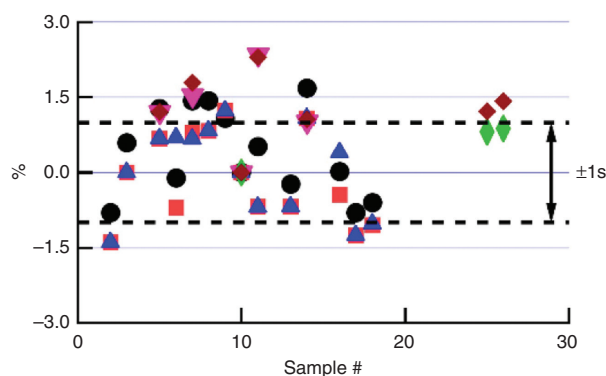
Fig. 5: Visual summary, as in Table 6 of Online Appendix A3, of all *pair-ratios* of the assay result on a single sample to the assay result of a reference laboratory on the same sample, for ^{22}Ne. Here only results for reference #11 are shown; for #5 and #10 see Online Appendix, Fig. 11. The null deviation constitutes the ideal situation: broken lines *indicate the standard deviation ±s of the set*: ±1 %. Sample # in abscissa are numbered according to Table 1. On the *y*-axis is the relative deviation in % from identity in the ratio *r* of a pair of assays results, 100−(*r*−1).
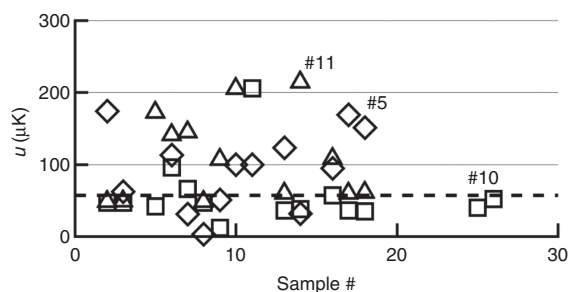

Fig. 6: Visual summary, reported in Table 5 in Online Appendix A3, of the standard deviation of all pair-ratios of the assay result on a single sample to the assay result of a reference laboratory (#5, diamonds; #10, squares; and #11, triangles), for ^{22}Ne as temperature-equivalent uncertainty. The broken line at 57 µK is the mean standard deviation of the whole set.

This has been done in the above three ways, as illustrated in detail in Online Appendix A3. The overall uncertainty of the comparison of samples ranges from 0.16 % to 1.3 %, a ratio of about 8 with an u_{mean} value of 0.76 % with respect to the mean value.

Its variability is indicated in the *u* column of Table 5 in Online Appendix A3. This table distinguishes the values (using italics and bold, respectively) of the ratios that differ by more than u_{mean} (taken as a quality index of the overall ratios) and u_{row} (quality of the row)—so the rows with $u_{row} \ll u_{table}$ are excluded. Figure 4 visualizes the results of Table 5 in Online Appendix A3. About 20 % of the assay/result-ratios exceed the variance of the fit of the assay results—0.5 % of the deviation value of each pair-ratio from 1.

In Table 5 in Online Appendix A3, the results may also depend on the choice of the reference sample. Thus, three different references were selected for comparing the outcomes, #5, #10, and #11, the latter being an outlier in Table 5 of Online Appendix A3. For ^{22}Ne and for each sample, in Table 6 of Online Appendix A3 pair-ratios are computed: the assay result on a sample are divided by the assay result of a reference laboratory on the same sample. The data shown in Table 6 are also visualized in Fig. 5 using the same method as Fig. 4. Once again, about 20 % of the assay-results pair-ratios exceed the dispersion of the ratios at the 1σ level—*u* =±1 %.

Table 5 in Online Appendix A3 also lists, in bold, the temperature-equivalent standard deviations exceeding 100 µK and, in *italics*, those exceeding 50 µK of each sample, as assayed in all relevant laboratories. The results are visualized here in Fig. 6. Notice that the overall standard deviation (57 µK) is slightly higher than the best overall uncertainty budget of the thermal measurements (about 50 µK).

Finally, the degree of correlation between the assay results of different laboratories was found satisfactory (for the same sample, the same value should be obtained) for the pair KRISS-University of Tokyo, while it was not for the pair KRISS-IRMM, as shown in Fig. 7.
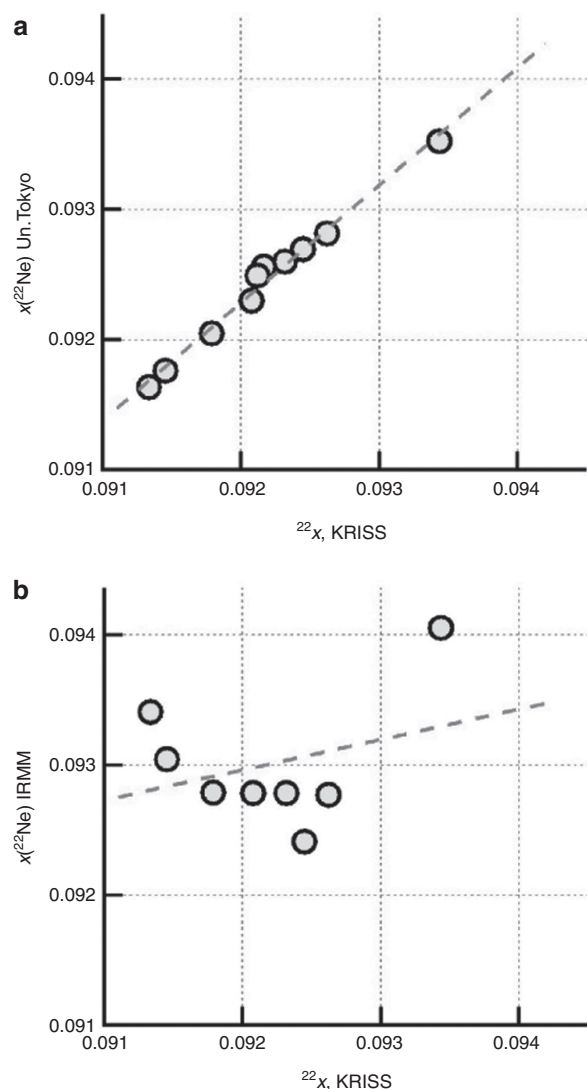
Fig. 7: Correlation of the assay results for laboratory pairs: (a) KRISS 2012-Tokyo University 2013; (b) KRISS 2012-IRMM (2009). Only KRISS assays are calibrated.

The results of measurements replicated over time, internally at a laboratory or in different laboratories, show in many cases a variability that represents the dominant contribution to the uncertainty budget for modern thermal metrology.

No reliable evidence of isotopic fractionation during the transfer from the original bottles to the cells was ever obtained, although a few outlying results (not for INRIM) might suggest such an occurrence. No possible correlation was found between the reproducibility and the history of the samples, the specific chemical-physical characteristics of each sample, or their handling.

However, some attempts are illustrated in a Report that can be read in Online Appendix A1.

The criticality of the transfer of samples of gas into small containers—here a high-quality high-pressure valve (see Fig. 11 in Online Appendix A1)—was experienced for a number of samples, as shown in Table 3.

Irrespective of the fact that in neon only H_2 and N_2 can produce a significant effect on the triple point temperature (T_{tp}), [18] the data indicate that most (small) transferred samples were chemically contaminated by handling, despite a very careful conditioning procedure. In some cases (#5C, #7 and #26), incorrect purification of commercial neon may be the culprit (high H_2 residual). In others (#5C, #14 and #26, and possibly #11, #16, and #23) it may be a high contamination with air, in which case the isotopic ratio could have

Table 3: Assay results from KRISS on chemical impurities in neon after transfer of a small sample from the original gas bottles into a small sampling container (see Online Appendix A1).

Sample #	Chemical impurity content (×10^{-6})					
	$x(H_2)$	$x(CH_4)$	$x(N_2)$	$x(O_2)$	$x(Ar)$	$x(CO_2)$
5/#B[a]	**68**	0	**225**	2	3	4
5/#C[a]	**3860**	0	**656**	125	10	26
6[b]	**12**	0	**28**	0	1	101
7[b]	**2077**	0	**145**	14	3	4
10[b]	**64**	0	**1382**	3	31	22
11[b]	**40**	0	**142**	54	4	172
14[b]	**1**	0	**6864**	2196	94	44
16[b]	**58**	6	**344**	0	7	675
23[c]	—	—	**335**	82	5	2
24[c]	—	—	**260**	25	4	2
25[c]	—	—	**123**	0	726	4
26[d]	**14 752**	0	**5528**	1404	100	1

[a]Samples from NMIJ filling system. [b]Samples in INRIM/NMIJ sampling valves. [c]KRISS bottles.
[d]Sample from NMIJ bottle.
The chemical impurities with a significant effect on the neon triple-point temperature are in boldface.

possibly been altered, as well. Less clear are the cases of sample #10, showing a very high N$_2$ content, and #25, showing a very high Ar content. It was not possible to get evidence of a correlation of these facts with a possible alteration of the isotopic composition.

5 Inter-comparison of thermal analyses

During the Isotopic-Neon Project EURAMET 770 [12], 39 samples, including the majority of the above 28 gas samples, were analysed. Most of the samples were sealed in cryogenic metal cells (up to 40 years old since sealing [16]). They were subjected to thermal measurements in 9 thermometry laboratories from metrological institutions around the world (see list in Online Appendix A6). The triple point was realized and the liquidus temperature measured with the calorimetric technique, with uncertainties ($k = 1$) ranging from 0.20 mK down to 20 to 30 µK, depending on the laboratory.
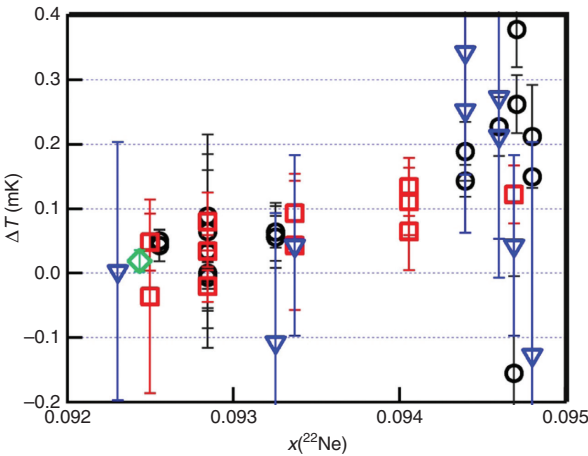

Fig. 8: Thermal measurements on neon of known isotopic composition: differences in the values of T_{tp}. Different symbols are for different measurement series: the bars indicate the standard measurement uncertainties ($k = 1$).

The sensitivity of the measured temperatures to the isotopic composition was found to be 0.147 35 μK per 10^{-6} of $x(^{22}Ne)$ and 0.077 85 μK per 10^{-6} of $x(^{21}Ne)$.

All differences ΔT are relative to cell Ec2Ne ($x(^{22}Ne)$ = 0.093 360) and the ternary line is normalized to cross zero at the same value of $x(^{22}Ne)$. $x(^{22}Ne)_{IUPAC}$ = 0.0925. A few outlying data are omitted.

In Fig. 8 the measurements are collected in the period ranging from 1998 (MRA KC CCT-K2) [19] to 2003–2014 by a total of 9 laboratories around the world. The hyphens indicate the uncertainties associated with the measurements ($k = 1$).

Figure 9 shows the final results of the thermal measurements [8]; the standard deviation of the fit is 0.062 mK. To compute the final results of the thermal studies (the triple point temperatures), the result of a specific assay was chosen for each sample from among those available and reported in the first part of this paper.

In a single case it was possible to perform more careful studies concerning the possible change over the years of the isotopic composition in an original bottle: bottle #11.
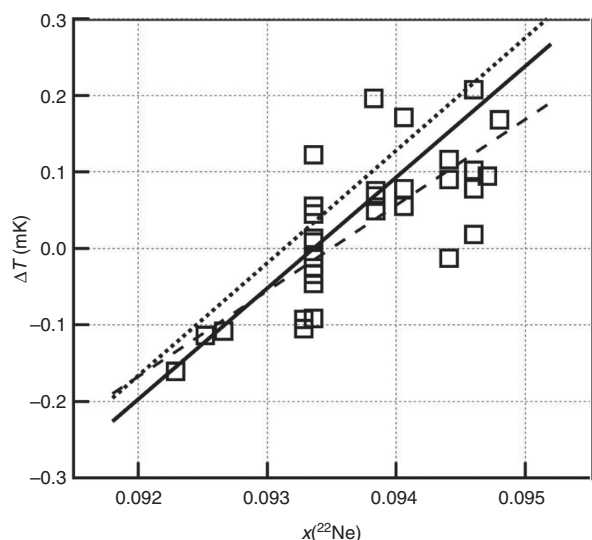

Fig. 9: Results on 'natural' isotopic composition samples as measured by the various laboratories (2003–2014) [8]. Broken line on open squares: fit of the data, $\Delta T/mK = 111.990 \cdot x(^{22}Ne) - 10.471$; u_{fit} = 62 μK. Full thick line: quadratic function joining pure ^{20}Ne and IUPAC reference composition on the ternary liquidus surface; dotted line: ^{20}Ne-^{22}Ne mixture experimental liquidus line.
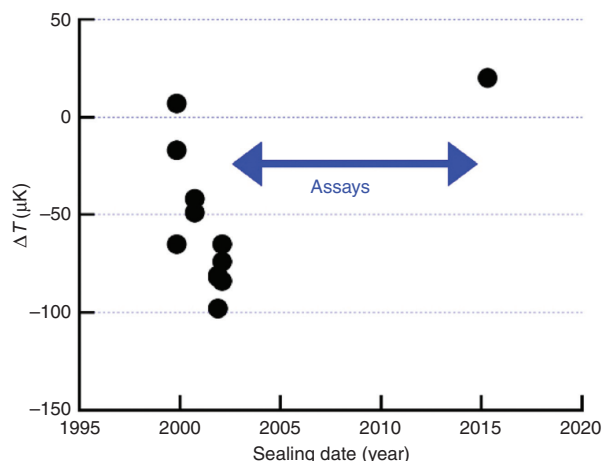

Fig. 10: Temperature differences between samples drawn at different times from the same bottle at INRIM. The zero of ΔT is chosen arbitrarily. Sealing dates (*measuring dates in parentheses*) of INRIM cells from left: Nov 1999 (*2008*), cell batch 12Ne–15Ne; Oct 2000 (*2009*) cell batch E2Ne–E4Ne; Dec 2001 (*2002*) cell Ec1Ne; Jan 2002 (*2008*) cell Ec2Ne; May 2015 (*2015*) cell Ec29Ne. Each sample realises a triple-point temperature stable in time [16].

As shown in Fig. 4, an inconsistency $\approx -1950 \times 10^{-6} \, x(^{22}\text{Ne})$ (equivalent to 285 μK) is evident between the assays made at IRMM and those made at KRISS and University of Tokyo. This change might be due to the transfer of a sample from the original bottle into a small sampling container, as already said. However, when the original bottle eventually returned from IRMM to INRIM in 2015, a new sample was sealed from it at INRIM into cell Ec29Ne, and its T_{tp} obtained as a check on that hypothesis.

In Fig. 10, the collation of ΔT_{tp} between all samples drawn directly from bottle #11 is shown. Until 2008, all the samples were within the measurement uncertainties. The 2015 sample is significantly higher, by 70 μK relative to the mean of the previous, and by 90 μK relative to the most recent 2008-mean. The latter is equivalent to a $\Delta x(^{22}\text{Ne}) = \approx -610 \times 10^{-6} \, x(^{22}\text{Ne})$. That amount accounts for only about 30 % of the observed difference in Fig. 4, thus not excluding the first hypothesis.

6 Conclusions

From a thermometric viewpoint, the issue was amply discussed at CCT, and the final results of this inter-comparison taken formally into account. This was done by including the resulting triple point temperature corrections for the deviation of the isotopic correction of the samples used from the reference (IUPAC) composition, to which the ITS-90 value T_{tp} = 25.5561 K was attributed, eliminating the ambiguity in the original Scale definition. However, to get the 50 μK uncertainty of the best realisations of the triple point, an isotopic assay is needed with an accuracy that, at best, only a few analytical laboratories in the world can currently provide. If *no correction* for isotopic composition can be reliably made, the consequence of the natural isotopic variability from sample to sample in neon is estimated by CCT to produce an uncertainty of about 0.3 mK, six times higher.

This Report illustrates the degree to which we can comply with our aimed requirement, *i.e.* that the uncertainty of the isotopic assay results on natural neon of commercial origin does not constitute the main component of the overall uncertainty budget for the neon triple point temperature (T_{tp}). In fact, as said, the state-of-the-art of the latter amounts to less than ±50 μK for the rest.

Considering the sensitivity of neon to the amount of ^{22}Ne, of approximately 0.147 μK per 10^{-6} of ^{22}Ne, and the sensitivity to chemical impurities ((-8 ± 2) μK/10^{-6} N_2, (-7 ± 3) μK/10^{-6} H_2), the precision requirements for chemical assays are quite demanding.

Until about 2009, only one laboratory in the world, IRMM, was available with the capability of performing measurements with sufficient accuracy; this specific activity was stopped in 2010. Two others then became available, first KRISS and then University of Tokyo.

The criticality of the assays prompted the thermal community to ask for replicated assays on most of the available samples. This paper is the final report on that project, performed during a time span of over 10 years.

Most of the data reported here concern assays on $x(^{22}\text{Ne})$, being critical for T_{tp}, but the outcomes concern also $x(^{21}\text{Ne})$, which may be critical in other applications. The analysis is less complete for the latter, and restricted to illustration in Online Appendices A3, A4. Data are also available on repeated assays on high-purity ^{22}Ne and ^{21}Ne. In Online Appendix A6, the relevant publications on this aspect and about the preparation of the three artificial mixtures at KRISS are listed, where the neon isotopic mixture is also treated as a ternary system, as it really is,.

The final aim of these studies was the establishment of a sufficiently accurate relationship T_{tp} *vs.* $x(^{22}\text{Ne})$ (and $x(^{21}\text{Ne})$), [10, 17]: the reader can easily understand from Fig. 8 that the results obtained in the attempt to get this information *via* thermal measurements of T_{tp} were not successful. This was the reason to resort, after a few years, to high-purity isotopes. However, part of the reason is to be attributed to the even less available expertise in measuring the chemical impurities accurately. The importance and difficulty of this can be understood from Table 3. When the results from chemical impurity assays were available and reliable, it was possible, by performing the due corrections, to obtain thermal data consistent to within (30 to 50) μK for largely different contents of the relevant impurities (H_2 and N_2).

One can thus conclude that only one laboratory (KRISS) consistently supplied reliable assays for ^{22}Ne with an uncertainty level sufficient for the present state-of-the-art uncertainty of some types of thermal measurements. Triple points as thermometric fixed points need accurate assays, as do other domains using gases, like acoustic gas thermometry with helium and argon. However, a selection between the assays made on the same sample was in general needed to ensure the best consistency of the thermal measurements. The use of a mean value of a set of assay results too often inflates the associated uncertainty—and not so infrequently the resulting uncertainty was higher than reported by the laboratory.

Outlying results in the assays were more frequent than desirable. This is not only potentially caused by the mass-spectrometric technique, but also by the *different stages of manipulation* of the gas itself, though without firm evidence. Experience has shown that, whenever possible, the samples *must be drawn* from the original bottles. Manipulation systems can be built which minimize or avoid contamination in handling. However, these systems *should always be equipped* with a residual gas analyser (RGA), in order to get direct evidence of the cleanliness of the system, and especially of the sampling metal container. All-metal "high-vacuum" systems (valves included) should be preferred for the highest confidence.

For the reasons laid out in this report, it would be highly desirable for the thermal community to have other laboratories available in the future able to perform absolute measurements by calibrating their apparatus with calibrated artificial mixtures with the same excellent competences in analytical assays presently shown only at KRISS, possibly corroborated by inter-laboratory comparisons. Also, the Laboratory at the University of Tokyo is still available for non-calibrated assays. No further relevant information is available today to the authors.

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Graphical abstract

Peter P. M. Steur, Iinseok Yang, Jin Srog Kim, Tohru Nakano, Keisuke Nagao and Franco Pavese

An inter-comparison of isotopic composition of neon *via* chemical assays and thermal analyses (IUPAC Technical Report)

IUPAC Technical Report: Results are reported of a 2003–2014 study on the effect of isotopic composition on the triple point temperature of neon in the frame of a Project involving 11 countries, using natural neon from commercial sources of different isotopic composition, high-purity ^{20}Ne and ^{22}Ne isotopes, and certified artificial isotopic mixtures. It comprised: analytical assays from 3 laboratories (131 assays in total of samples taken from 31 different bottles with chemical purity 4N to 5N5+, with up to 12 assays per sample. These tests are critically needed for top-accuracy thermometric thermal analyses, made on 39 samples with an accuracy up to better than 50 μK, for the determination of $T_{tp,Ne}$. The results of the inter-comparison showed discrepancies especially for $x(^{22}$Ne) in 'natural' neon, for the same gas bottle equivalent to 165 μK ($k = 1$), and for a single testing laboratory to ≈100 μK ($k = 1$).

Keywords: chemical purity assay; international intercomparison; isotopes; isotopic composition assay; neon; thermal analysis; triple point temperature