Status of progress towards the determination of the relationship between neon triple-point temperature T_{tp} and isotopic amount composition x

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Since the last CCT meeting, this group has published results concerning two large sets of neon gas samples (28 in total) in two publications [1, 2], attached for your convenience. The main results are summarised there in terms of isotope ratios for $n(^{22}Ne)/n(^{20}Ne)$ and $n(^{21}Ne)/n(^{20}Ne)$. Thermometric data is presented versus the normalized amount fraction $x(^{22}Ne)$.

These results are not yet sufficient for preparing a proposal similar to the one done in 2005 for hydrogen isotopic composition. The solution of neon problems are more complicated, for the following main reasons:

a) One set of thermometric data is internally consistent within a sufficiently low uncertainty (PTB) for most of the measured samples. However, the obtained value of the slope of the T_{tp} vs. $x(^{22}Ne)$ relationship significantly deviates from the value that one can obtain from a linear interpolation of the T_{tp} values for the pure ^{20}Ne and ^{22}Ne isotopes as found in the literature and for 'natural' neon. No other data set presently exists which can resolve this issue;
b) The set of all data produced so far –with the exclusion of a few data considered as outliers– does not allow a better evaluation of the slope $\Delta T_{tp}/\Delta x(^{22}Ne)$, because of the pivoting effect of some data. A bootstrap evaluation for a 95% CI for this set of data is shown in **Fig. a** below. The slope obtained from linear interpolation from pure isotopes is also shown, which is basically compatible with the bootstrap limits. Also the slope obtained from a TLS fitting and the slope obtained from fitting of PTB data *only* are reported;
c) The few available literature data for T_{tp} of pure isotopes are affected by an uncertainty of 1–1.5 mK, to be compared with the present state-of-the-art < 50 μK. In addition, it is suspected that a substantial part of the present melting range observed for 'natural' neon samples (≈0.2 mK) is due to isotopic segregation. This effect, in principle, can introduce additional unforeseen uncertainty. Only new future measurements on pure isotopes can resolve this issue;
d) Concerning the analytical assay for $x(^{22}Ne)$, the IRMM claimed relative uncertainty is 0.05%, or $u(x(^{22}Ne))=0.000\ 05$, sufficient for thermometric purposes. However, the two sets of assays (between which there is no common sample) produced two clusters of ^{22}Ne-^{20}Ne compositions significantly separated from each other (see Fig.1 in [2]): there is a suspicion about the actual uncertainty or about one set of assays having a bias. If such a bias does indeed exist, but is limited to the $n(^{21}Ne)/n(^{20}Ne)$ ratio alone, it will still be of no significant consequence for thermometric purposes;
e) The neon triple point temperature T_{tp} was found to be affected by nitrogen impurities by Ancsin [3], with an effect of –8 μK per μmol N_2 /mol Ne. Nitrogen was detected in some of the samples used for the measurements already performed (see **Table a** here below). It is therefore necessary to have a second independent assessment of the effect on T_{tp} of nitrogen in neon and a confirmation of its quantification.

No specific funding has been so far become available within specific collaborative Projects for continuing and completing these studies, but a sufficient number of participants (INRIM, INTiBS,

IRMM, NMIJ, NRC, VSL-NMi) having signed[1] the Agreement of the current EU iMERA Project on this theme (no funds attached to it) accepted to continue to contribute, at least for 2008, to some parts of the studies still required.

From the experience gained so far, further work is required:

1) to obtain for part of the already measured samples more data in order to be able to compute for an additional 1–3 laboratories a slope value of the T_{tp} vs. x relationship to compare with the PTB one, concerning item a). *(INRIM, INTiBS, NMIJ, VSL-NMi available);*
2) to buy, seal and measure samples of the purest available ^{22}Ne and ^{20}Ne (and ^{21}Ne if our funds allow) with an uncertainty of the order of 50 μK, in order to resolve the melting range problem and find a new value of the slope of the above relationship, to compare with the literature one (item c). *(INRIM to buy pure isotopes, prepare cells and measure samples);*
3) to make new assays linking the present groups and concerning new samples (and including the 'pure' isotopes 99.99% ^{20}Ne and 99.9% ^{22}Ne) for hopefully resolving the present discrepancy *(several participants to provide samples to IRMM)*. The issue remains that these are relative measurements. Therefore, it is also necessary to produce 1–3 artificial mixtures whose composition is obtained via the gravimetric method: this would allow having an absolute determination of the neon isotopes amount fractions (item d). (*IRMM is able and planning to produce them, having bought a sufficient quantity of pure isotopes. NPL relevant Division is willing to help in that.*);
4) to make a new determination of the effect of N_2 in Ne, and additionally of H_2 in Ne, whose effect is known from the literature [4] but the effect in specific thermometric studies was not detected by Ancsin. It requires preparing cells filled with 'natural' neon contaminated by 100 ppm by volume of each of the two contaminants (item e). *(INRIM to prepare mixtures, provide cells, measure mixtures);*
5) to finalise the theoretical studies about neon isotope mixtures, providing guidance to the final choice of the recommendation. *(mainly NIST and NRC so far).*

It is believed that these activities can be completed at last by mid-2009 so that within 2009 a recommendation can be prepared for initial discussion with CCT WG1, before being submitted to CCT.

References

[1] F Pavese, B Fellmuth, D Head, Y Hermier, K D Hill, S Valkiers, "Evidence of a Systematic Deviation of Isotopic Composition of Neon of Available Sources from the 'Natural Composition", *Analytical Chemistry* **77** (2005) 5076-5080

[2] F Pavese, B Fellmuth, K D Hill, D Head, Y Hermier, L.Lipinski, T Nakano, A Peruzzi, H Sakurai, A Smyrka-Grzebyk, A D Steele, P P M Steur, O Tamura, W L Tew, S Valkier, L Wolber, "Progress toward the determination of the relationship triple point temperature vs. isotopic composition of neon", *Int. J. Thermophysics* **29** (2008) 57–66.

[3] J Ancsin, "Vapour pressures and triple point of neon and the influence of impurities on these properties", *Metrologia* **14** (1978) 1–7

[4] W B Streett, G H Jones, *J. Chem.Phys*. **42** (1965) 3989.

[5] http://ec.europa.eu/dgs/jrc/downloads/jrc_newsrelease_20071217_collaboration_nist.pdf

[1] NIST is restricted by charter from direct participation (i.e. as a signator) in iMERA Projects, but may participate informerly though a separate bi-lateral collaboration agreement with the IRMM [5]. NIST has continued to collaborate in the neon effort.

Table a. Typical chemical analysis of **neon** samples including N_2 as an impurity.

Producer	Lab	Bottle date	Nominal purity %	IRMM checked purity %	He ppm	H_2 ppm	N_2 ppm	Other† high-boiling ppm
Matheson A	IMGC	1977	99.995	> 99.995	<50	<25	11.3	2.7
Matheson B	IMGC	1978	99.995	> 99.995	<50	<25	6.3	2.8
Messer	IMGC	1999	> 99.999	–	< 1	< 1	< 2	< 1
Messer	PTB		> 99.999	–				
Messer	IRMM	2003	>99.995	–				
Air Water	NMIJ	2006	99.999	99.994	< 5	< 0.3	< 0.5	< 1
IceBlick	NMIJ	2003	99.999	> 99.995	< 8	< 1	< 2	< 2
Praxair	Japan	n.a.	99.999	n.a.	< 5	< 1	< 4	< 2
Iwatani	Japan	n.a.	99.999	n.a.	< 10	< 1	< 5	< 7
Carbagas	IRMM	2006	> 99.995	> 99.995				
Airgas/BOC	NIST	2006	99.999	> 99.995				
Alphagaz	INM	1999	999.999	99.992	n.a.	< 0.1	< 0.1	< 0.4
NBS-101	NIST	1954	99.99	99.991				
L'Air Liquide	INM		> 99.999	–				
Air Products	NRC		> 99.999	–				
Air Products	NPL		> 99.999	–				

†Water not included in "Other"

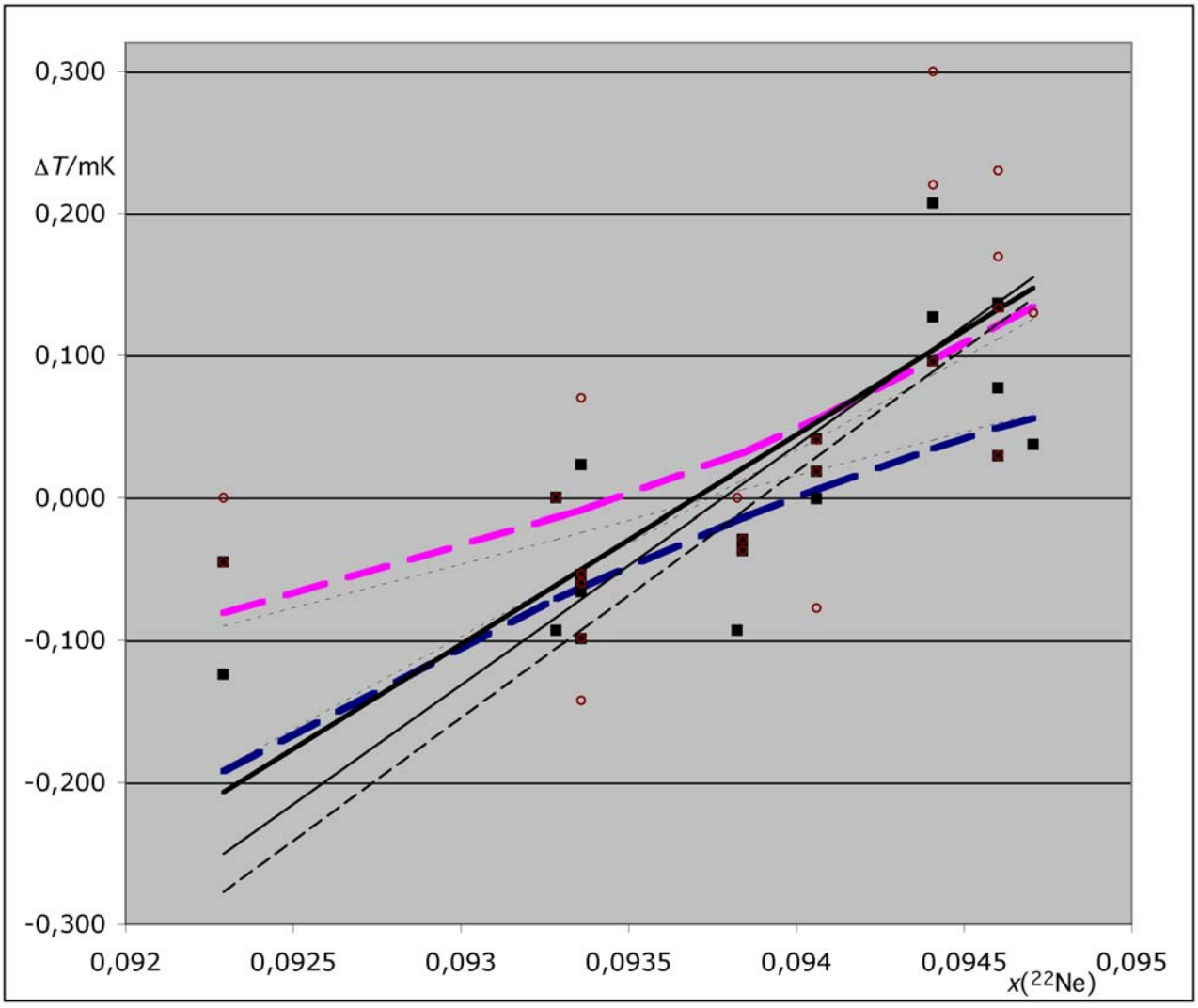

Fig. a. Present results about the T_{tp} vs. x relationship for ^{22}Ne in ^{20}Ne.
Open dots– Original data from 4 series of data (floating with each other)
Black squares– Data with optimised relative positions of the series by translation (series #1 (PTB taken as reference, i.e. un-translated) using the LSM with fixed effect (LSMFE) with error on ΔT only.
Fitted curves– Thick broken lines: bootstrap 95% CI fitting variability estimate from the LSMFE-optimised data with errors on both variables; very thin dotted lines: min (slope 61.6 mK per ^{22}Ne amount concentration in Ne) and max (131 mK per ^{22}Ne amount concentration in Ne); black thick line: slope evaluation from literature data on pure isotopes (147 mK per ^{22}Ne amount concentration in Ne*; arbitrary vertical position*); full black line: slope computed by using TLS on LSMFE-optimised data with error on both variables (168 mK per ^{22}Ne amount concentration in Ne); broken black line: slope from fit of PTB data alone (omitting outlying INM cell and IMGC very old cells Ne1 and Ne3) (173 mK per ^{22}Ne amount concentration in Ne).