Some traceability problems in analytical assays of interest in thermal metrology

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**Until 2005: CNR, Istituto di Metrologia “G.Colonnetti” (IMGC), Torino, Italy*

Why worry about isotopic composition in thermal metrology?

- **Sample-to-sample variations in isotopic composition may contribute to** measurable differences **between standards maintained by the National Metrology Institutes**
  → ***Compositional variations may result from intrinsic differences in the compositions of natural sources or from fractionation as a result of processing operations***
- **The presence of more than one isotope may degrade the quality of standards.**
- **The isotopic composition must be known with a sufficiently low uncertainty and the analytical assay must give the absolute composition, being not the relative one sufficient, since the standards are referring to the thermodynamic state of the substances. Consequently, the traceability of the chemical assays is a requirement.**

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The temperature standard: ITS-90 Fixed Points

- **Physical state**: specified as two or three phase equilibrium
  - → Triple Points (TP): H_2, Ne, O_2, Ar, Hg and H_2O
  - → Melting Point (MP): Ga
  - → Liquid-Vapor Points (VP): ^3He, ^4He and H_2
  - → Freezing Points (FP): In, Sn, Zn, Al, Ag, Au, Cu
- **Chemically pure**: unspecified, but generally taken as highest available (the definition is for ideally pure substances –no chemical impurities)
- **Isotopic composition**: loosely specified
  - → Uniquely specified in one case only (^3He),
  - → H_2O TP: "substantially" that of ocean water (*formerly*)
  - → all others are specified only as "natural isotopic composition", except, from 2005, H_2 (*SLAP*) and H_2O (*VSMOW*) .

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What is meant by “Natural” Isotopic Composition?

- Isotopes found in nature generally vary in composition
- Natural processes can fractionate elemental isotopes
  - → Not all natural systems are in isotopic equilibrium

- Terrestrial Abundance may not be uniform or constant
  - →terrestrial ^{1} cosmic abundance
- *Handbook values should be treated as terrestrial averages (at best)*
- Composition depends on the source:
  - →Primordial (Stellar)
  - →Terrestrial Atmospheric (e.g. Meteoric, etc.)
- …And, or the genesis:
  - →Radiogenic (e.g. the stable daughters of radionuclides)
  - →Lithogenic (*Nucleogenic*, neutron activation in crustal rocks of U or Th)
  - →Cosmogenic
  - →Anthropogenic

- Isotopic fractionation can also occur during industrial processes

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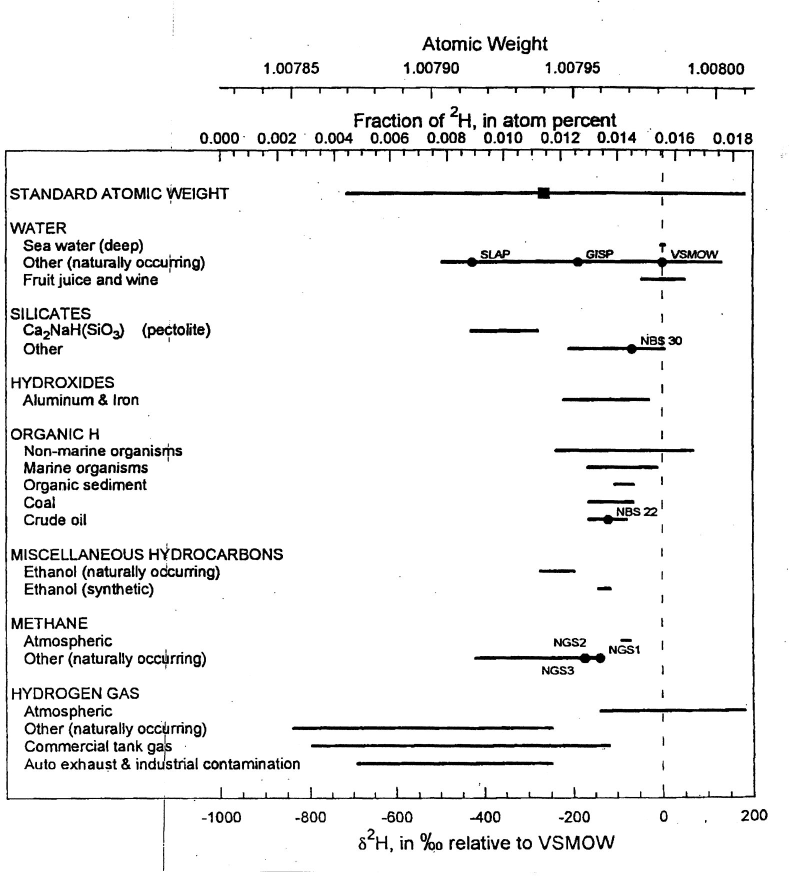
Hydrogen

- Two Stable Isotopes †
  - → ^{1}H 99.984426%
  - → ^{2}H 0.015574%
- Terrestrial Inventories
  - → Oceans
  - → Continental ground and surface water
  - → Crustal Rock and Sediments
  - → Organic Material (e.g. bio-mass, oil, natural gas)
  - → Atmosphere (only 0.5 ppm at sea level)
- Almost all commercial hydrogen gas is synthesized from organic material
- Isotopic fractionation effects in gas are very large:

$$d\ {}^2\mathrm{H} = -750 \text{ permil!}$$



Hydrogen natural variabilily
after **T.Coplen et al.,** *Pure Appl. Chem.*, Vol. 74, No. 10, pp. 1987–2017, 2002.

† **VSMOW, IUPAC, 1997**

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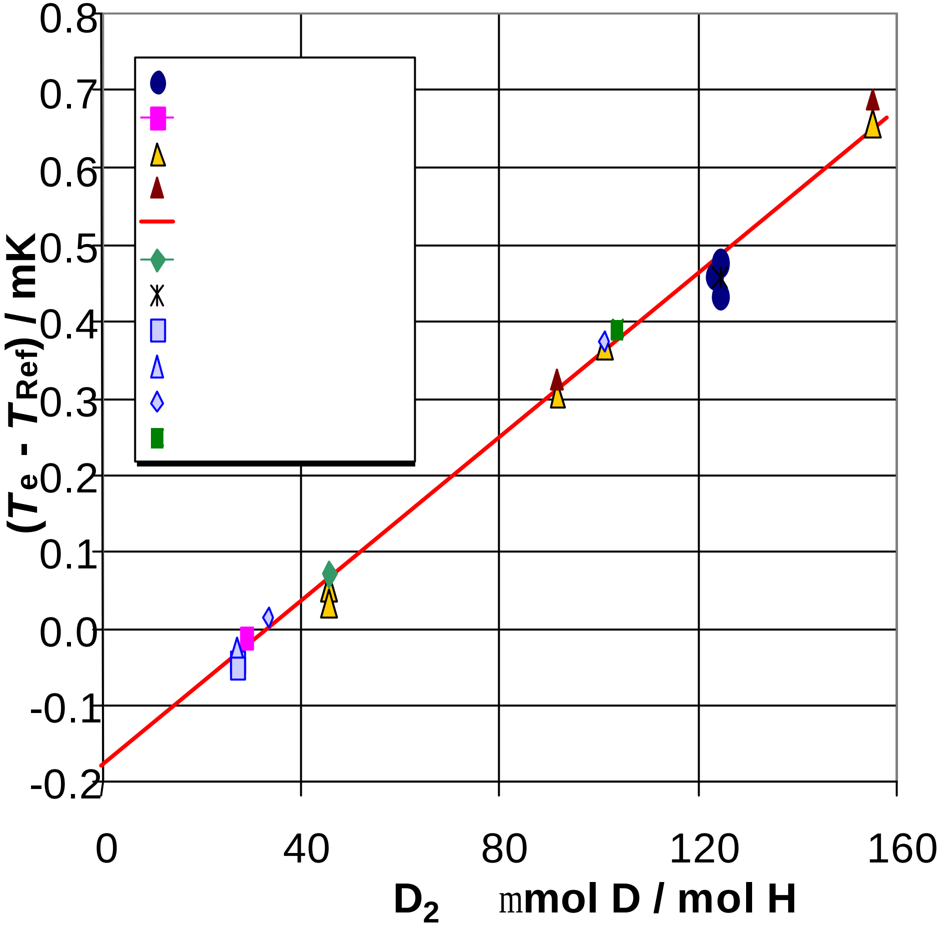
Equilibrium hydrogen fixed points

- ***e*-H_2 VP_2, (101 kPa) 20.27 K**
  - →**Heavier gases will have lower VP, or higher *T* at constant *P***
  - →**Use ideal solution of H_2 and HD to predict *DT* at constant *P***
  - →**Archival data on *P-T* of HD from NBS, Hoge and Arnold, 1951**
  - →**Condensation and Evaporation Lines (vapor/liquid ratio dependence)**
- ***e*-H_2 VP_1, (33 kPa) 17.03 K**
  - →**Same as above**
- ***e*-H_2 TP, 13.8033 K**
  - →**Heavier gases will have higher melting temperatures**
  - →**Archival Data on melting *p*-H_2+HD: Bereznyak, *et. al.* , *Soviet JETP*, 1970.**
  - →**2.8 mK/(mmol HD/mol H_2) ® ~ 1.0 mK ambiguity for natural compositions**
  - →**~ 600 mK uncertainty ambiguity from commercial tank gas**
  - →**Total range observed in recent studies: ~ 700 mK (aimed 20 mK)**

Sufficient chemical assay uncertainty available from geochemists



Slope: (5,4$_2$ ± 0,3$_1$) mK per mmol D/mol H

(*Fellmuth et al., Metrologia 2005*)

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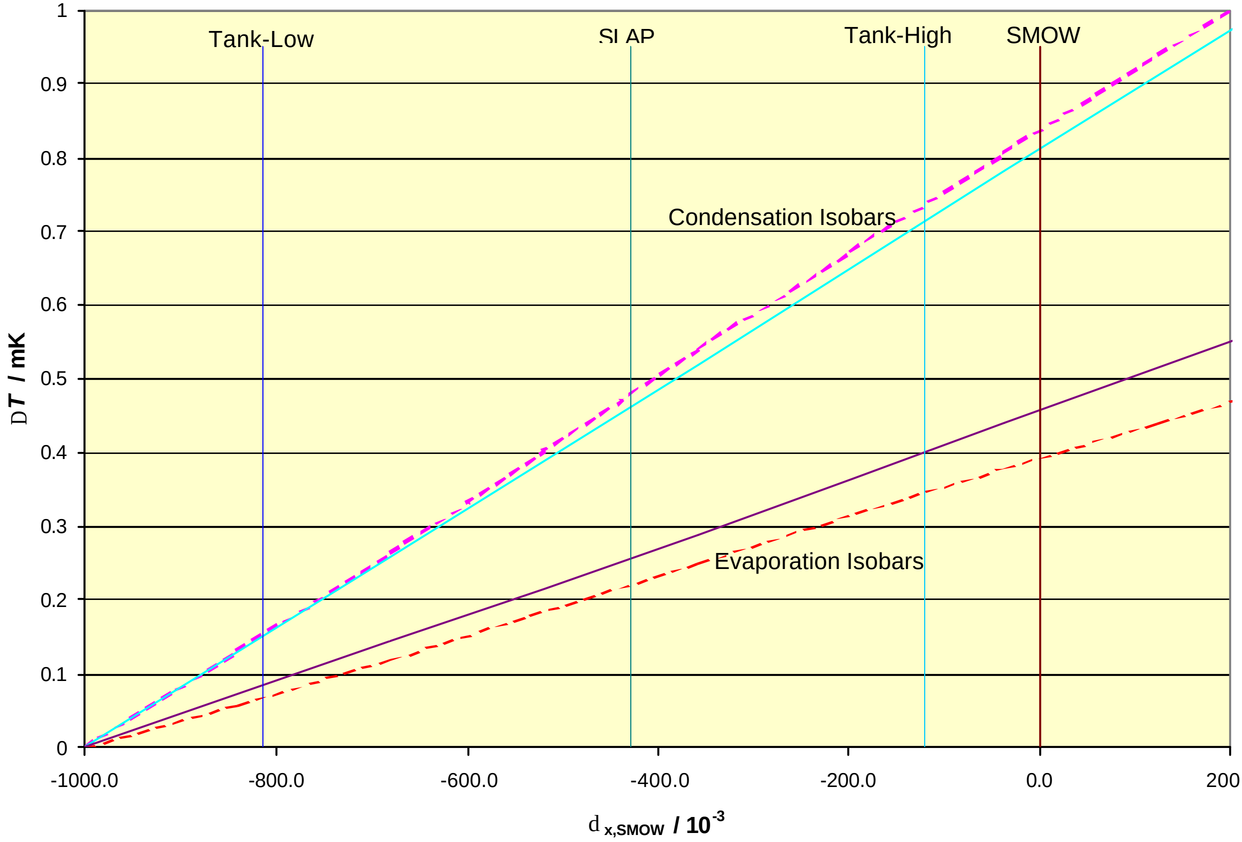
Liquid-vapour equilibria in hydrogen isotope mixtures



Calculated elevation in the 33 kPa (dashed lines) and 101 kPa (solid lines) isobars for condensation and evaporation in the dilute limit of an ideal *e*-H$_2$ + HD solution.
The compositions of SLAP and VSMOW are shown along with the range of reported tank gas compositions. (Tew, 2001)

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Terrestrial origins of neon

- **Three stable isotopes of neon†**

→ ^{20}Ne	90.4838%	Primordial
→ ^{21}Ne	0.2696%	Prim.+ Nucleogenic ^{18}O(a,n)^{21}Ne
→ ^{22}Ne	9.2465%	Prim.+ Nucleogenic ^{25}Mg(n,a)^{22}Ne

- **Bulk of terrestrial inventory is atmospheric**
  - → 18.2 ppm concentration
  - → much lower than cosmic abundance
- **Most commercial neon is extracted from air, but not all**
- **Natural gas wells rich in He contain trace amounts (1 to 2 ppm) Ne**
  - → neon from NG is enriched in nucleogenic isotopes, ^{21}Ne and ^{22}Ne
  - → neon becomes concentrated in helium as byproduct of separation
  - → economics of He supply and demand could influence the source of commercial neon gas

† Air, IUPAC, 1997

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Triple Point of Neon

- $T_{90}(^{nat}\text{Ne TP}) = 24.5561$ K (defined for “natural” isotopic composition)

- Isotopic measurements, Furukawa, NBS, 1972
  - → $T(^{20}\text{Ne TP}) - T(^{nat}\text{Ne TP}) = -$ 13 mK
  - → $T(^{22}\text{Ne TP}) - T(^{nat}\text{Ne TP}) = +134$ mK
  - → In that case, “Natural” means Ne as derived from air separation
  - → Sensitivity to variations in ^{22}Ne are 1.5 mK/atom %

- For Ne gas derived from natural gas (helium separation)
  - → Keyes, OK (panhandle): ^{20}Ne 89.69%; ^{21}Ne 0.646%; ^{22}Ne 9.66%,
  - → $T(^{NG}\text{Ne}) - T(^{nat}\text{Ne TP}) = + 900$ mK (estimated) **(aimed: 20 mK)**

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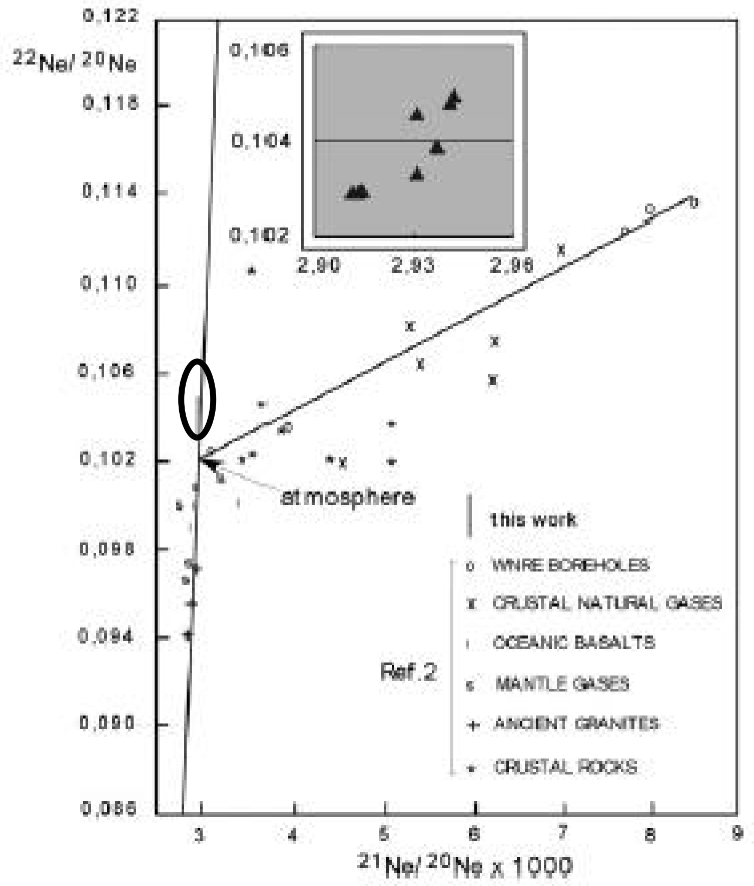
Triple Point of Neon



Sufficient chemical assay uncertainty available only from IRMM, Geel.

Sample #	$n(^{21}\text{Ne})$ / $n(^{20}\text{Ne})$	ΔT_t/ μK	$n(^{22}\text{Ne})$ / $n(^{20}\text{Ne})$	ΔT_{tp}/ μK
7	– 0,000069	–5	0,000700	**103**
5	– 0,000043	–3	0,001610	**237**
1	– 0,000049	–3	0,001090	**160**
7	– 0,000066	–5	0,000710	**104**
3	– 0,000049	–3	0,002360	**347**
4	– 0,000043	–3	0,001670	**245**
2	– 0,000038	–3	0,002730	**401**
6	– 0,000039	–3	0,002600	**382**
7	– 0,000067	–5	0,000710	**104**

2003 data: deviations from “natural isotopic composition” (IUPAC, 1997) of the measured composition values and the corresponding effect on DT_{tp}.

(after *Pavese et al., Analytical Chemistry* 2005)

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Oxygen

- **Three stable isotopes of oxygen†**

→ ^{16}O	99.7628%
→ ^{17}O	0.0372%
→ ^{18}O	0.20004%

- **Terrestrial Inventories**
  - → **Crust - isotopically varied, usually enriched ^{18}O:**
    - – **Silicates:** d^{18}O$_{VSMOW}$ **=+5 to +28 per mil**
    - – **Nitrates:** d^{18}O$_{VSMOW}$ **=-10 to +80 per mil**
  - → **Atmosphere - isotopically very uniform, enriched ^{18}O:** d^{18}O$_{VSMOW}$ **=23.5 per mil**
  - → **Oceans - isotopically uniform in temperate zones**
- **Laboratory Oxygen**
  - → **bulk gas cryogenically separated from air**
  - → **prepared gas derived from thermal decomposition of manganates or chlorates**
- **No temperature measurements at known isotopic composition available**
- **Estimated effect on T_{tp}** *(Gonfiantini, priv.comm.)***: 20 mK for a 4% variability**

† VSMOW, IUPAC, 1997

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Argon

- **Three stable isotopes of argon †**

→^{36}Ar	**0.337 (3)%**
→^{38}Ar	**0.063 (1)%**
→^{40}Ar	**99.600 (3)%**

- **($^{40}T_{\mathrm{tp}}$ – $^{36}T_{\mathrm{tp}}$) = 59 mK, experimental**

- **Effect on T_{tp} for a variability equal to IUPAC uncertainty on ^{40}Ar : 1.5 mK**

† VSMOW, IUPAC, 1997

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Geochemistry of water

- **Natural water is a mixture of four different isotopic components:**
  - → **$^{1}H^{16}O^{1}H$**
  - → **$^{2}H^{16}O^{1}H$**
  - → **$^{1}H^{17}O^{1}H$**
  - → **$^{1}H^{18}O^{1}H$**
  - → **+ other very small concentrations of second order combinations**
- **Heavier isotopes are depleted in polar waters**
- **Relative depletion is correlated in precipitation:** $\text{d}^{2}\text{H} = 8\cdot\text{d}^{18}\text{O}+10$
- **SLAP vs. SMOW:**
  - → **$^{2}H/^{1}H$=155.74´ 10^{-6} in SMOW**
  - → **$^{2}H/^{1}H$= 89.02´ 10^{-6} in SLAP** $\text{d}^{2}\text{H}_{\text{VSMOW}}$ **= –428 per mil**
  - → **$^{18}O/^{16}O$= 2.0051 ´ 10^{-3} in SMOW**
  - → **$^{18}O/^{16}O$= 1.8938 ´ 10^{-3} in SLAP** $\text{d}^{18}\text{O}_{\text{VSMOW}}$ **= –55.5 per mil**

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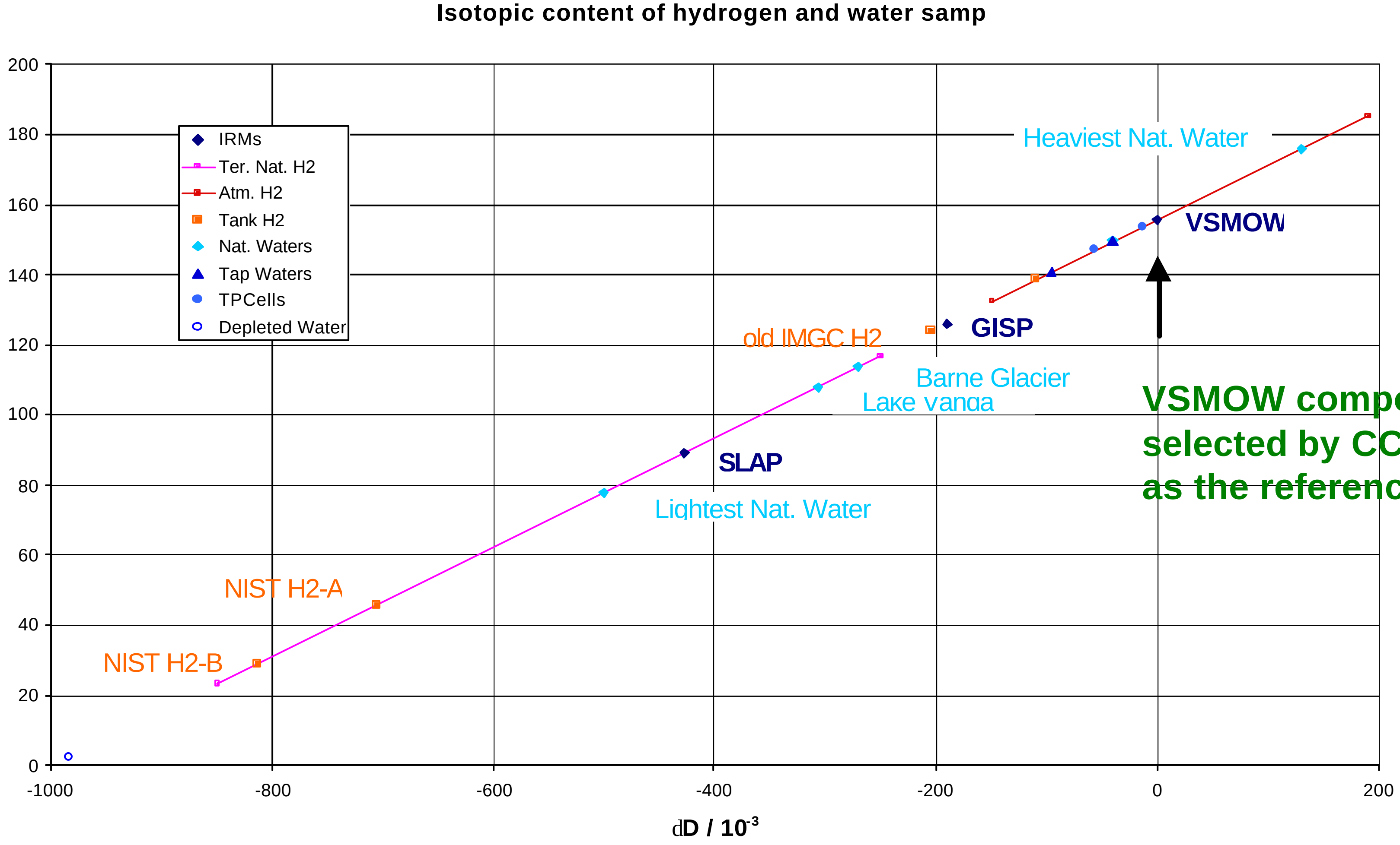
D/H content in molecular hydrogen and water



VSMOW composition selected by CCT as the reference (2005)

Triple point of water – 1

- **Triple Point of Water (TPW) definition of the SI Kelvin**
    - **→Adopted by the CCT in 1954**
    - **→definition does not refer to ocean water or any isotopic composition**
- **TPW cells**
    - **→are almost always derived from continental (fresh) surface water**
    - **→temperate latitudes**
- **ITS-90**
    - **→specifies an isotopic composition “substantially” that of ocean water**
- **Natural water variations affect on TPW (aimed 10–20 mK)**
    - **→200 mK typical between polar fresh and polar sea ice**
    - **→30 mK to 50 mK between temperate continental and ocean water**
    - **→250 mK (estimated) between SLAP and SMOW**

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Triple point of water – 2

Laboratory	**Date**	**96/2-96/1 /mK**	**96/3-96/1 /mK**	**96/4-96/1 /mK**	**98/1-96/1 /mK**	**std. dev. /mK**
MSL	Sept. 96	-0.156	-0.178	0.038		0.013
NIST	May 97	-0.150	-0.172	0.020		0.012
MSL	Apr. 98				-0.989	0.040
NPL	Aug. 98	-0.116	-0.154	0.034		0.034
NIST	Nov. 98				-0.960	0.014
NPL	June 00	-0.139	-0.155		-0.988	0.040
MSL	Apr. 02	-0.135	-0.151	0.051	-0.963	0.014
mean	D***T***	**-0.145**	**-0.165**	**0.034**	**-0.964**	
sm		**0.007**	**0.005**	**0.006**	**0.008**	

(After *D R White, T D Dransfield, G F Strouse, W L Tew, R L Rusby, J Gray, TMCSI 8, ISA, New York, 2003.*)

If Kiyosawa’s correction values are adopted, the uncertainty in the isotope corrections for typical cells is almost certainly within 10 µK, may be within 1 µK.

Metal fixed points

Fixed Point	T_{90} / °C	Isotopes	Fixed Point	T_{90} / °C	Isotopes
Hg	**-38.8344**	**7**	(Al	660.323	1)
Ga	29.7646	2	Ag	961.78	2
In	156.5985	2	(Au	1064.18	1)
Sn	**231.928**	**10**	Cu	1084.62	2
Zn	**419.527**	**5**			

No T – x data presently available sufficent for thermal metrology

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Why worry about **chemical impurities** in thermal metrology?

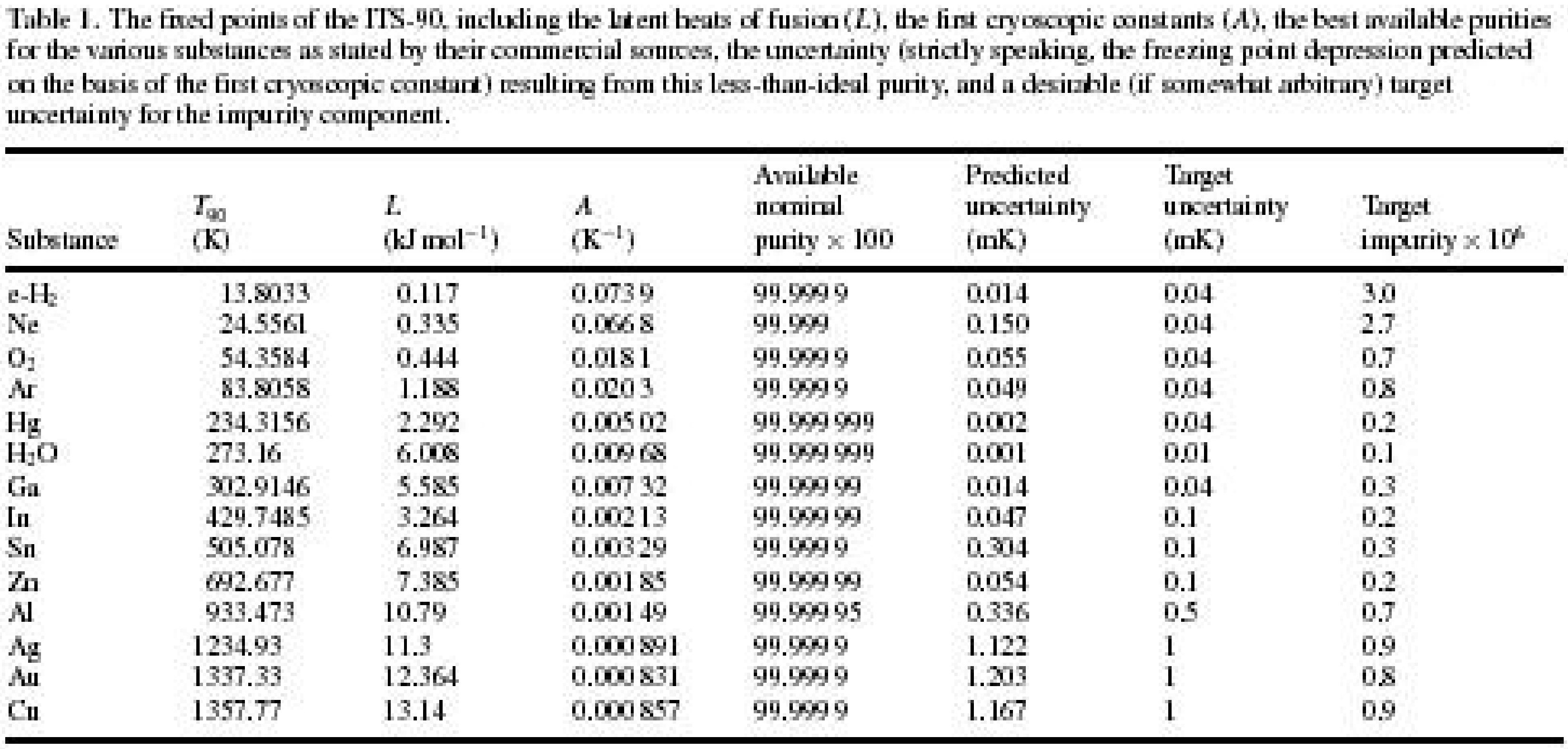

Table 1. The fixed points of the ITS-90, including the latent heats of fusion (L), the first cryoscopic constants (A), the best available purities for the various substances as stated by their commercial sources, the uncertainty (strictly speaking, the freezing point depression predicted on the basis of the first cryoscopic constant) resulting from this less-than-ideal purity, and a desirable (if somewhat arbitrary) target uncertainty for the impurity component.

Substance	T_{90} (K)	L (kJ mol^{-1})	A (K^{-1})	Available nominal purity × 100	Predicted uncertainty (mK)	Target uncertainty (mK)	Target impurity × 10^6
e-H_2	13.8033	0.117	0.0739	99.9999	0.014	0.04	3.0
Ne	24.5561	0.335	0.0668	99.999	0.150	0.04	2.7
O_2	54.3584	0.444	0.0181	99.9999	0.055	0.04	0.7
Ar	83.8058	1.188	0.0203	99.9999	0.049	0.04	0.8
Hg	234.3156	2.292	0.00502	99.999999	0.002	0.04	0.2
H_2O	273.16	6.008	0.00968	99.999999	0.001	0.01	0.1
Ga	302.9146	5.585	0.00732	99.99999	0.014	0.04	0.3
In	429.7485	3.264	0.00213	99.99999	0.047	0.1	0.2
Sn	505.078	6.987	0.00329	99.9999	0.304	0.1	0.3
Zn	692.677	7.385	0.00185	99.99999	0.054	0.1	0.2
Al	933.473	10.79	0.00149	99.99995	0.336	0.5	0.7
Ag	1234.93	11.3	0.000891	99.9999	1.122	1	0.9
Au	1337.33	12.364	0.000831	99.9999	1.203	1	0.8
Cu	1357.77	13.14	0.000857	99.9999	1.167	1	0.9

(After *K D Hill and S Rudtsch, Metrologia 42 (2005) L1-L4*)

Individual chemical impurities critically affect some of the temperature standards.
Reliable and traceable assays are needed for low-concentrations.

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