International Atomic Energy Agency

Metrological Traceability in Special Fields

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Example 1:

Metrological Traceability of Values Assigned to Matrix Reference Materials

Terminology related to CRMs

reference material	**certified reference material**	**standard reference material**
standard	**secondary standard**	**secondary reference material**
control sample	**laboratory control sample**	**calibration standard**
calibration solution	**calibrator**	**measurement standard (etalon)**
international (measurement) standard	**national (measurement) standard**	**primary standard**
secondary standard	**reference standard**	**working standard**
transfer standard	**travelling standard**	**multicomponent standard**
cocktail	**pure substance standard**	**matrix reference material**

Terminology related to CRMs

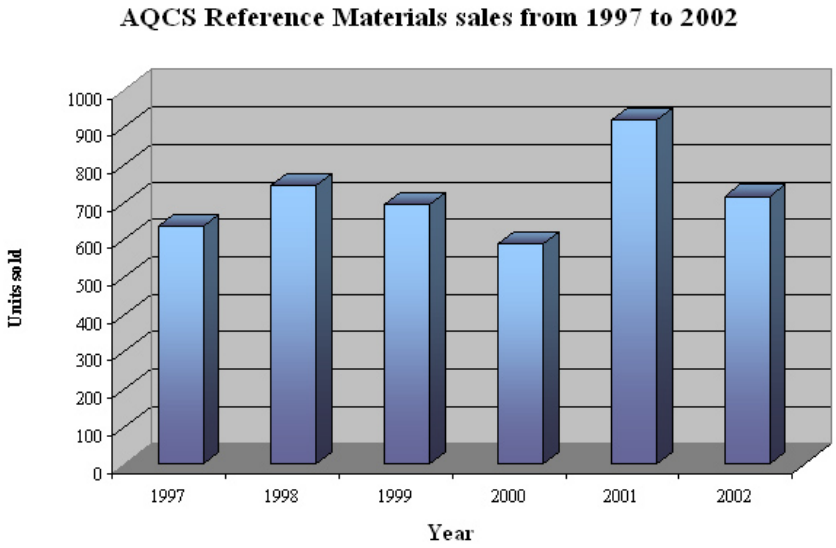
- **Matrix (compositional) reference material:** A “natural” substance more representative of laboratory samples that has been chemically characterised for one or more elements, constituents, etc. with a known uncertainty. (Note: This is not a standardised definition.)

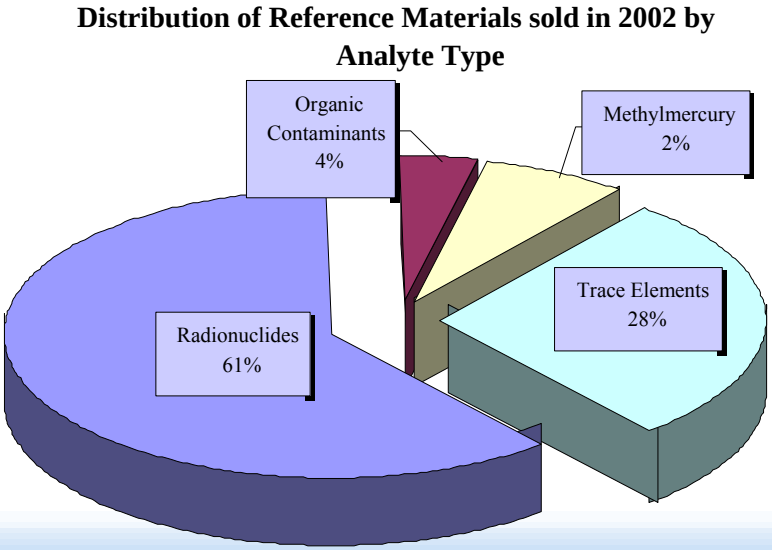
  Sub-groups: gaseous, environmental, biological, alloys, etc.

  Characterisation & certification: mainly through intercomparisons

AQCS RMs Sales Statistics

- The RM concept is applicable to many fields of science; the AQCS stock represents many matrices and analytes, principally natural matrix reference materials for radionuclides, trace elements, organic contaminants and stable isotopes.

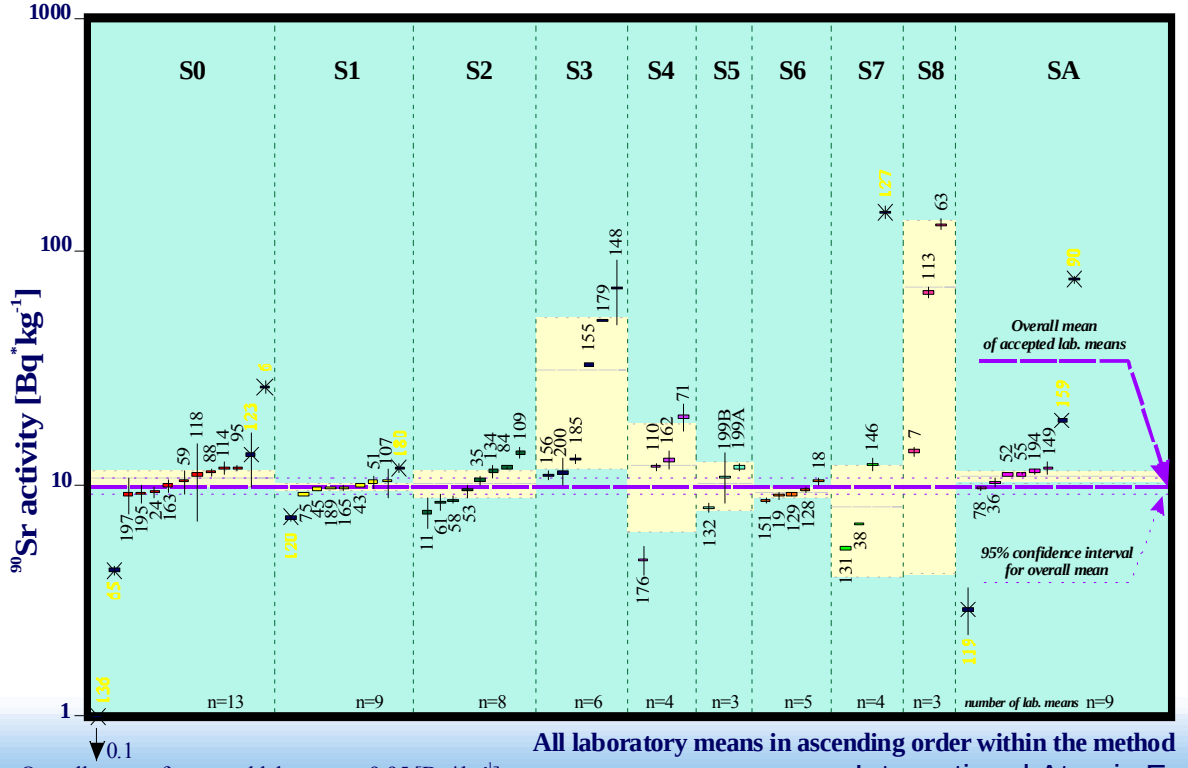




- AQCS currently serves more than 4000 customers and ships about 1300 units of reference materials, worth approximately 120 000 US $ annually.

Interlaboratory Comparisons

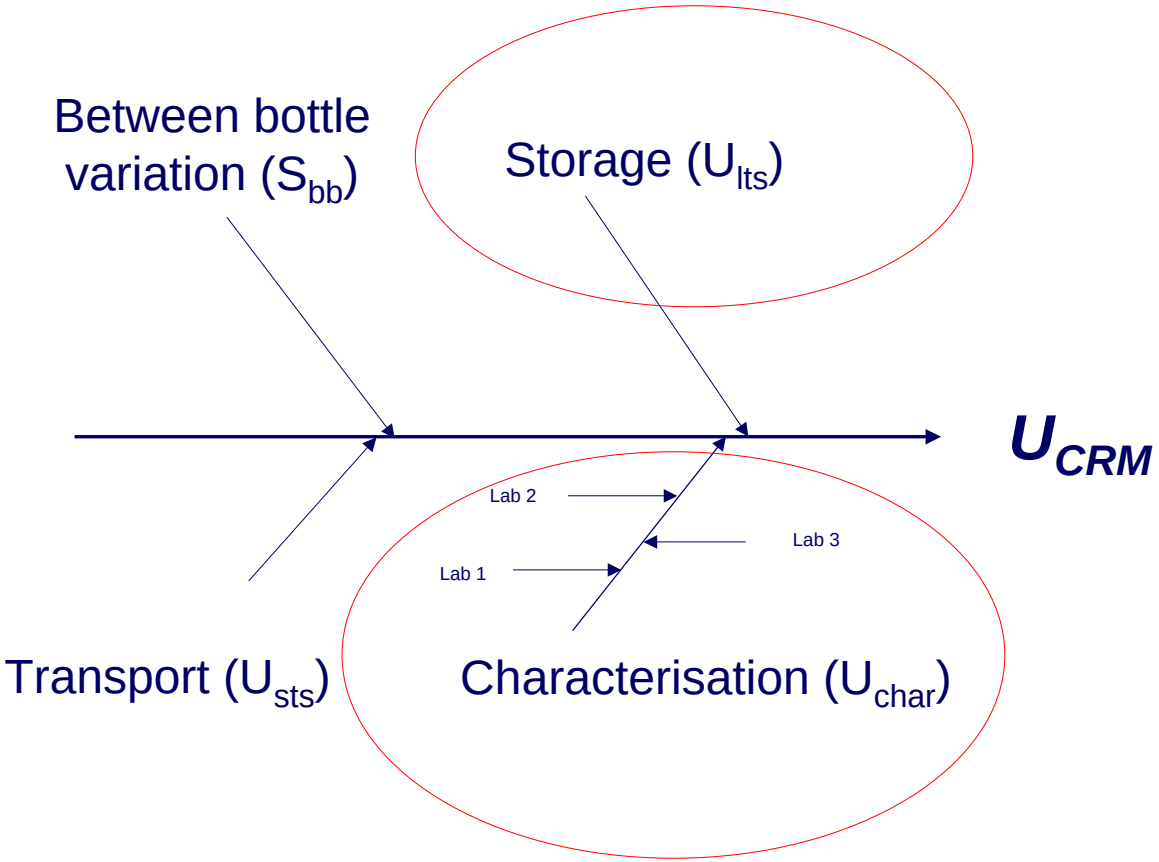
- AQCS has organized interlaboratory comparisons for the benefit of Member States laboratories on a cost free basis for over 40 years.
- These exercises represent an indispensable and cost effective tool which enable MS laboratories to compare their performance with that of other participants and also identify and rectify problems and biases with their analytical procedures.



Main metrological and quality requirements for a new generation of the IAEA RMs

- Metrological traceability of assigned property values, whenever possible to SI Units.
- Measurement uncertainty of the assigned property value expressed following the GUM principles
- Quality system according to the ISO Guide 34

Uncertainty of the assigned property values



(Ref: According to Jean Pauwels 1999)

RM's quality requirements

- As a general principle, the IAEA supports the use of ISO (ISO REMCO) Guides 30 to 35 as a basic guidance for activities related to reference materials.
- The use of ISO Guide 34 as a quality system guidance for reference materials producers is preferred.
- Small number of laboratories participating in characterisation of RM
  - reliable results assured (previous experience, QC, PT, etc.)
  - metrological traceability demonstrated
  - measurement uncertainty quantified
  - accreditation according to ISO 17025:1999 preferable

Upgrading of selected AQCS RMs to CRMs Traceable to SI Units

Selection criteria for materials to be upgraded

- Relevance of the material for radiological measurements in environmental or nutritional investigations
- More than 100 units have been ordered over the past 5 years
- A stock of more than 500 units is still available

Upgrading of selected AQCS RMs to CRMs Traceable to SI Units

Materials selected:

- **IAEA-152** K-40, Sr-90, Cs-134, Cs-137 in milk powder
- **IAEA-312** Ra, Th, U in soil
- **IAEA-314** Ra, Th, U in stream sediment
- **SOIL-6** Sr-90, Cs-137, Ra-226 and Pu-239 in soil
- **SL-2** K-40, Sr-90, Cs-137, Pb-210, Ra-226, Ra-228, Th-228, Th-234, U-238, Pu-239/240 in lake sediment
- **IAEA-375** K-40, Sr-90, Ru-106, Sb-125, I-129, Cs-134, Cs-137, Th-232, U-238 in soil

Metrological traceability of XRF results

Traceability criteria requirements

- *Linkage to stated references*

Fe-55 standard (*equipment calibration*)

Pure metal foils, analytical grade oxides(*method calibration)*

Matrix reference materials - CRM (*method validation)*

- *Stated uncertainties*

Uncertainty budget estimation (Eg. X-ray Spectrom. 2003;32: 317- 335)

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-***Unbroken chain of comparisons*** **(through a hierarchy of standards and procedures)**

Standards	**Procedures**
SI Units	
	Method validation
CRM (matrix RM)	
	Method quantitation
Working standards	
	System optimisation
Instrument calibration stds	

The Role of Standards in Establishing the Traceability of XRF results

- **Some tools for establishing traceability in XRF analysis are the use of:**

  - ✓ **Standard reference data in method development.**
  - ✓ **Certified analytical grade chemical reagents and chemically pure substances for method calibration.**
  - ✓ **Certified/standard reference materials for method validation.**
  - ✓ **Well documented and established methods for assessment of the uncertainty of analytical results.**

The Provision of Standards for XRF Analysis

- The standard reference data are available through compilations of photon interaction cross-sections, atomic data tables and newly published literature data.
- The analytical grade reagents and chemically pure substances are obtained through tested reliable suppliers and are always accompanied by certificates
- The most frequently used certified reference materials with guaranteed traceability are obtained from NIST or similar specialized institution
- The uncertainty budged evaluation is performed in accordance with international norms and standards

Example 3:

Metrological Traceability of Stable Isotope Measurements

- The mass spectrometric measurement of natural variations of stable isotope ratios of light elements is used to delineate information on origin, age, climate and physical processes on analyzed compounds.

- It spans disciplines from hydrology to food science, from medicine to geochemistry, from biology to climate studies.

Stable Isotope Measurements

- As an example, oxygen will be discussed in more detail:

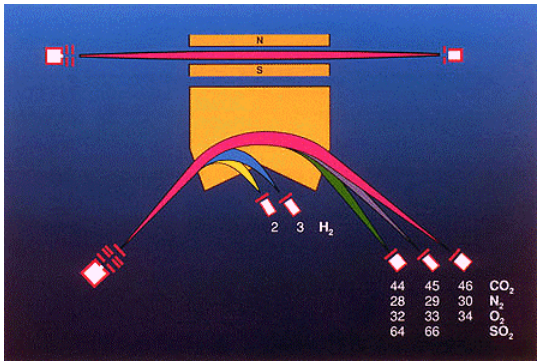
  Isotopic composition of Vienna Standard Mean Ocean Water VSMOW, used as primary reference material for stable isotope measurements on oxygen and hydrogen

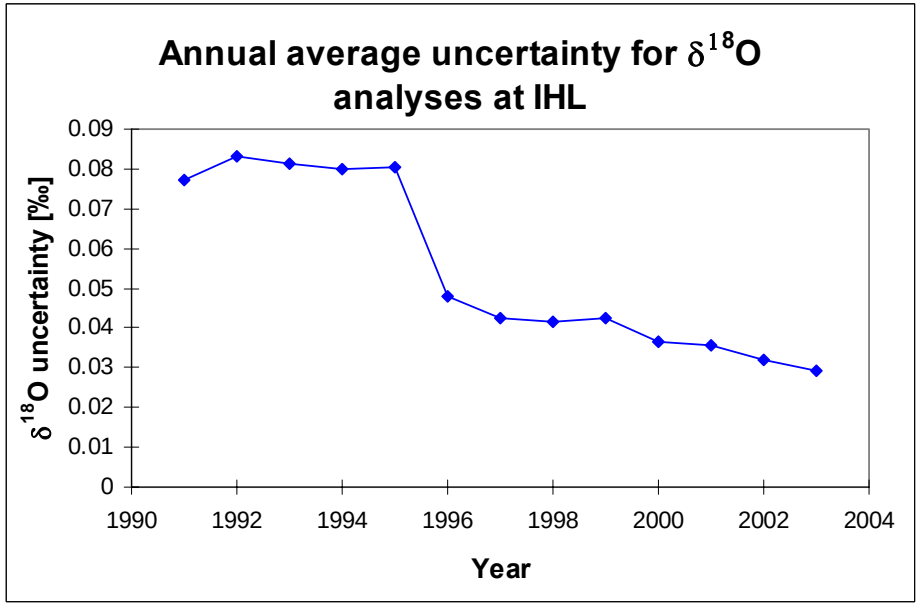
	^{16}O	^{17}O	^{18}O
Isotopic abundance	0.9976206(5)	0.0003790(9)	0.0020004(5)

Total variability of oxygen stable isotope ratios in natural materials on earth:

$$R^{18}O/^{16}O = 0.0020052 \pm 10\ \%$$

- **In most real studies the variation of the isotopic ratio R is much lower (only about ± 1-2 ‰)**
- **Required high precision of ratio measurements of about ± 0.1 ‰ can be achieved only by relative measurements comparing directly sample and standard**





δ-Scales

For convenience a new scale is introduced (conventional δ-scale) to report only deviations between ratios R with VSMOW artificially defined as the zero point for all measurements and serving as primary reference material:

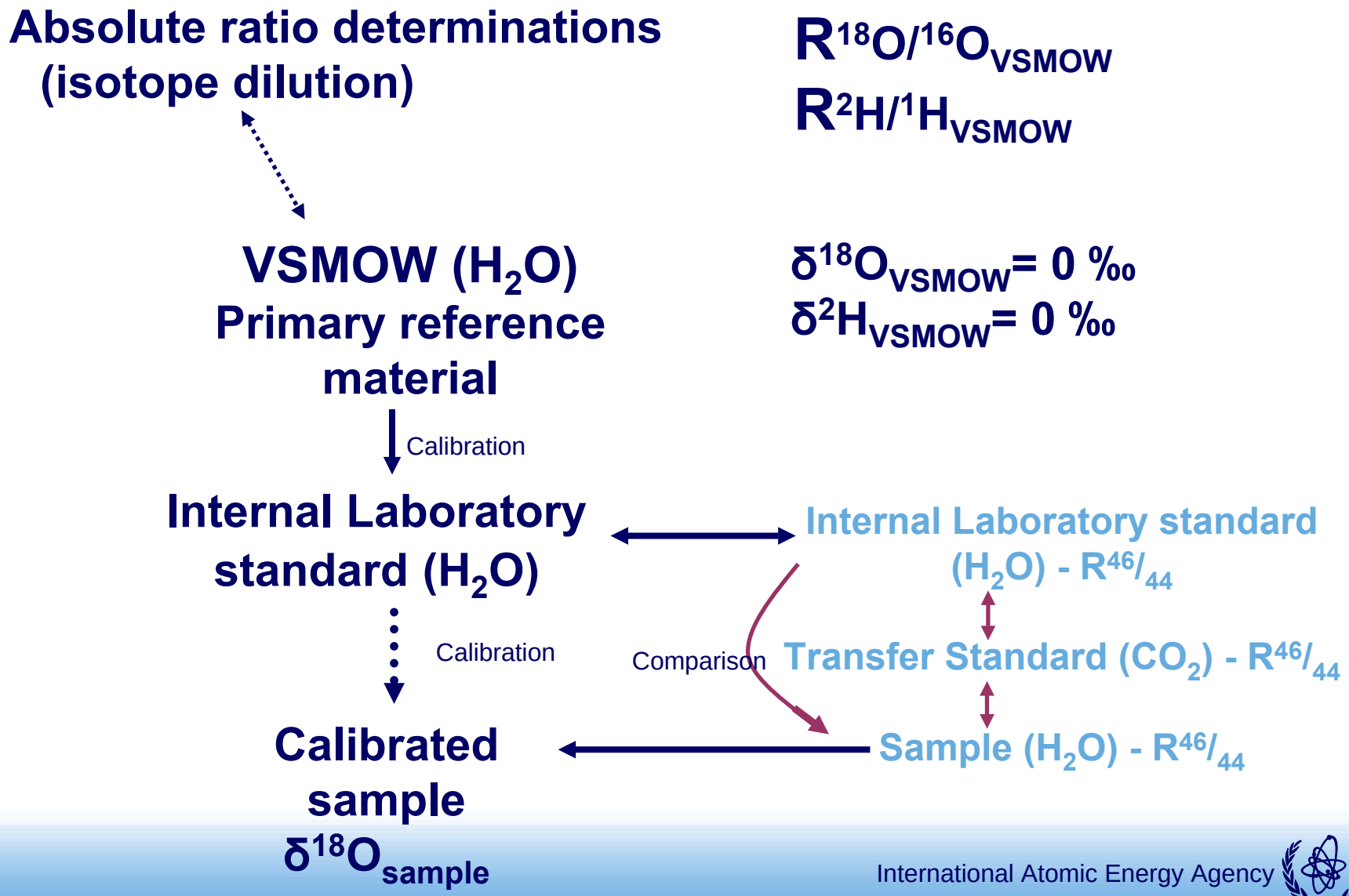
$$\delta^{18}O\ [‰] = \frac{(R^{18}O/^{16}O_{sample} - R^{18}O/^{16}O_{VSMOW})}{R^{18}O/^{16}O_{VSMOW}} \cdot 1000$$

with the definition: $\delta^{18}O_{VSMOW} \stackrel{!}{=} 0\ ‰!$

$$R^{18}O/^{16}O_{VSMOW} = 0.0020052 \Leftrightarrow \delta^{18}O_{VSMOW} \neq 0\ ‰$$

$$R^{18}O/^{16}O_{sample} = 0.0020072 \Leftrightarrow \delta^{18}O_{sample} = 1\ ‰$$

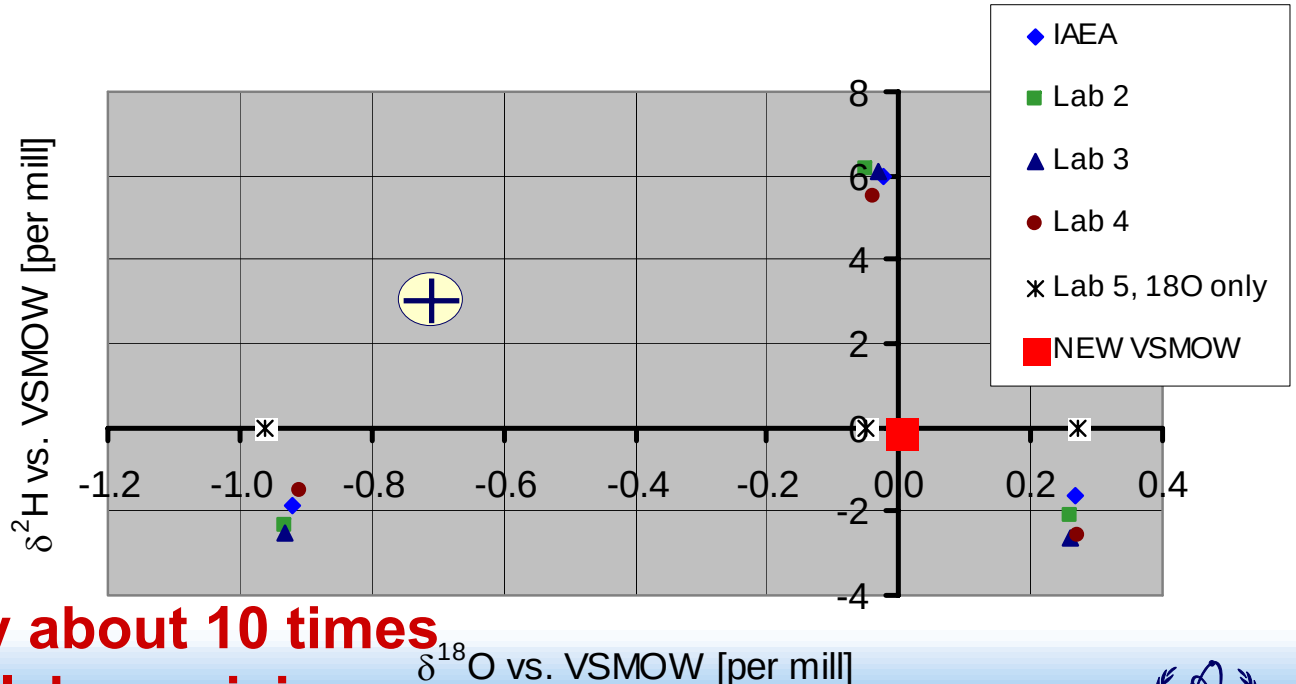
Traceability Scheme



Keeping δ-scales consistent

- **VSMOW: 70 litres produced in 1967; distributed in 20ml amounts in sealed glass ampoules (1 unit per 3yrs)**
- **Only 7 litres left at IAEA, 5 litres at NIST !**
- **Replacement prepared by IAEA and calibrated by 5 laboratories: NewVSMOW – 300 litres**

	$\delta^{18}O$ [‰]	$\delta^{2}H$ [‰]
Deviation NewVSMOW vs. VSMOW	**0.002**	**-0.12**
Uncertainty NewVSMOW (no. of analyses)	**±0.007 (125)**	**±0.09 (118)**
Uncertainty VSMOW (no. of analyses)	**±0.006 (109)**	**±0.08 (115)**



⇒ Calibr. uncertainty about 10 times smaller than routine lab precision

NewSLAP-Project

- second water standard used to normalize the VSMOW δ-scale :
- Standard Light Antarctic Precipitation SLAP
$\delta^{18}O_{SLAP}$= -55.5 ‰

Successor material also already in preparation with isotopic composition close to SLAP from mixing two raw waters from Southpole and from Vostok

⇒ Replacements for both primary reference materials prepared in quantities sufficient for estimated 30-50 years

Necessary Change of Standards

- SMOW ⇒ VSMOW: Vienna–SMOW (H, O)
- PDB ⇒ VPDB: Vienna–PDB (C)
- CDT ⇒ VCDT: Vienna–CDT (S)

- PDB and CDT standards depletion (already decades ago) forced establishment of new artefacts to keep scales consistent (NBS19 and IAEA-S-1)
- SMOW never existed physically

Carbon Stable Isotopes

- NBS19 carbonate as calibrator, defines VPDB-scale. Several other carbonates available, as well as CO2 RMs.
- Several organic carbon materials exist (oil, sucrose, polyethylene, cellulose), but reveal relatively large uncertainties
- Problem of consistent calibration of organic versus inorganic carbon reference materials
- Demand to create various new RMs with different compounds