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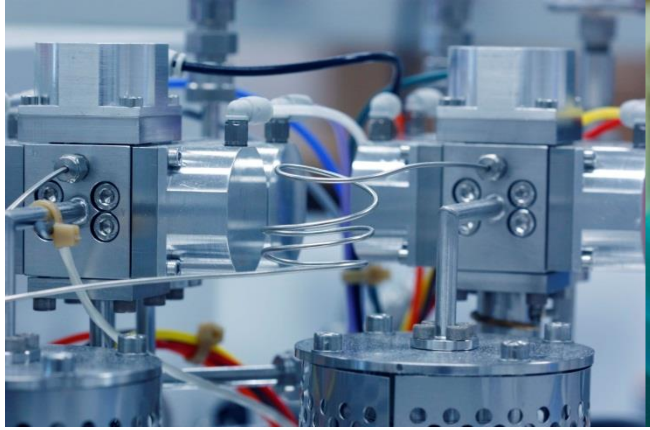
geotop Centre de Recherche sur la Dynamique du Système Terre



IRMS Standards and Calculations

Jean-François Hélie

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Why do we need reference material?

Standard or reference material?

What is a delta scale?

How do we normalize the data?

The $\delta^{13}C_{VPDB}$ is -30‰ vs. VPDB

The $\delta^{18}O_{VSMOW\text{-}SLAP}$ is -20 ‰ vs. VSMOW

The dual inlet system

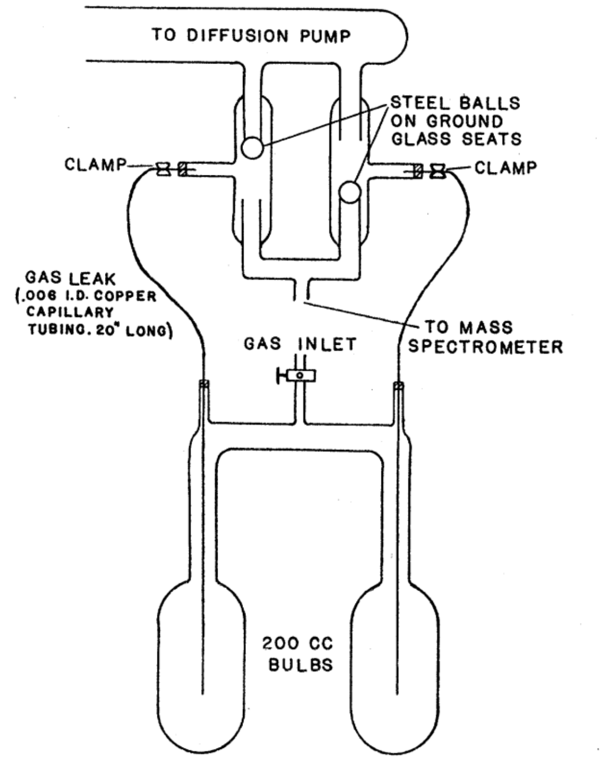
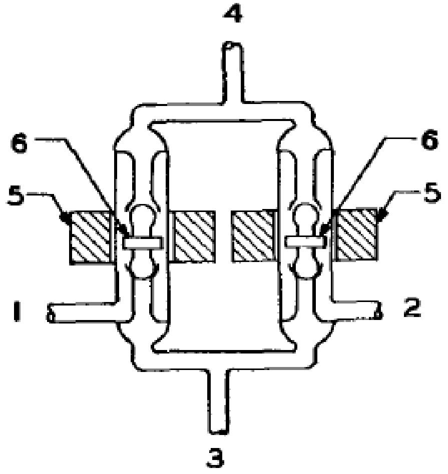


FIG. 1. Twin bulbs and gas leaks. The connecting tubing between the bulbs consisted of 25 cm of tubing of 1.13 cm^2 average cross section. The steel balls were $\frac{11}{32}$" in diameter. The pumping speed in the line marked "to diffusion pump" was about $\frac{1}{2}$ liter per second, whereas the pumping speed toward the mass spectrometer was about one percent of that value.

Murphey (1947)

FIG. 6. Valve for reversing samples. 1, inlet for sample 1; 2, inlet for sample 2; 3, outlet to waste vacuum; 4, outlet to mass spectrometer; 5, coil windings; 6, soft iron washer on glass valve.



McKinney et al. (1950)

So, we normalize to a “known” CO_2

THE REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 21, NUMBER 8 AUGUST, 1950

Improvements in Mass Spectrometers for the Measurement of Small Differences in Isotope Abundance Ratios

C. R. McKinney, J. M. McCrea, S. Epstein, H. A. Allen, and H. C. Urey
Institute for Nuclear Studies, University of Chicago, Chicago, Illinois
(Received March 30, 1950)

A Nier-type mass spectrometer and its associated electronic units have been constructed for the purpose of measuring small variations in the abundances of oxygen of mass 18 and of carbon of mass 13 in carbon dioxide, and of oxygen of mass 18 in oxygen gas, to an accuracy of ±0.01 percent of the abundance of these isotopes.

The electronic units of the necessary stability for this degree of accuracy are described. A gas feed system is described which permits fast alternate introduction of the sample of gas to be analyzed and a standard gas into the mass spectrometer. All measurements of the variation in the abundance of the oxygen and carbon isotopes are made with reference to a standard.

recorded figures are the differences in permils of the normal ratios between the sample and the standard working gas, i.e.,

$$\delta=\left(\frac{R_{\text{sample}}}{R_{\text{standard}}}-1\right)1000,$$

where R_{sample} and R_{standard} are the ratios of $CO^{16}O^{18}$ to CO_2^{16} for the unknown sample and reference gas respectively. These examples of analysis on carbon dioxide

The delta notation and the zero point

The δ (delta) value is the ratio of the quantity of a rare isotope to its abundant isotope of a sample normalized to the same ratio of a reference standard. We multiply this value by 1000 since the ratios are very small.

For exemple, for carbon isotopes :

$$\delta^{13}C = \frac{\left[\left[\frac{^{13}C}{^{12}C}\right]_{sample} - \left[\frac{^{13}C}{^{12}C}\right]_{PDB}\right]}{\left[\frac{^{13}C}{^{12}C}\right]_{PDB}} = \left[\frac{\left[\frac{^{13}C}{^{12}C}\right]_{sample}}{\left[\frac{^{13}C}{^{12}C}\right]_{PDB}}\right] - 1$$

$$\Rightarrow \quad \delta^{13}C = \left[\frac{\left[\frac{^{13}C}{^{12}C}\right]_{PDB}}{\left[\frac{^{13}C}{^{12}C}\right]_{PDB}}\right] - 1 = 0$$

Zero points for traditional stable isotopes

Hydrogen	SMOW (**S**tandard **M**ean **O**cean **W**ater)
Carbon	PDB (**P**ee **D**ee **B**elemnite)
Nitrogen	AIR (**A**mbient **I**nhalable **R**eservoir)
Oxygen	SMOW (**S**tandard **M**ean **O**cean **W**ater) or PDB
Sulfur	CDT (**C**anyon **D**iablo **T**roïlite)

VPDB and VSMOW

International Atomic Energy Agency

CONSULTANTS' GROUP MEETING ON

STABLE ISOTOPE REFERENCE SAMPLES FOR GEOCHEMICAL

AND HYDROLOGICAL INVESTIGATIONS

IAEA, Vienna 16 - 18 September 1985

Report to the Director General

by

G. Hut

Scientific Secretary of the Meeting

April 1987

Since PDB is virtually non-existent, a reference Vienna-PDB (VPDB) is introduced, defined by:

$$\delta^{13}C_{NBS19/VPDB} = +\ 1.95\ ^{o}/oo$$

$$\delta^{18}O_{NBS19/VDPB} = -\ 2.20\ ^{o}/oo$$

PDB and VPDB are virtually identical, but the use of VPDB as a reference implies that the measurements have been calibrated through NBS19.

- So… from 1995 until otherwise stated, the VPDB δ(^{13}C) is defined by assigning +1.95 ‰ to the calcium carbonate material NBS19.

- The zero point stays the same but the material used to normalize changes.

VPDB and VSMOW

- VPDB replaces PDB to avoid confusion
- VSMOW replaces SMOW to introduce SLAP as a second anchor
- A new concept is introduced here!

Discontinuance of SMOW and PDB

SIR — Confusion exists in the reporting of stable hydrogen, carbon and oxygen isotope results, because the supply of the PDB (Peedee belemnite) standard has been exhausted and because SMOW (standard mean ocean water) does not have a unique definition. Because laboratories do not use the same reference material to establish their isotope-ratio scales, different laboratories report widely varying values for the same material.

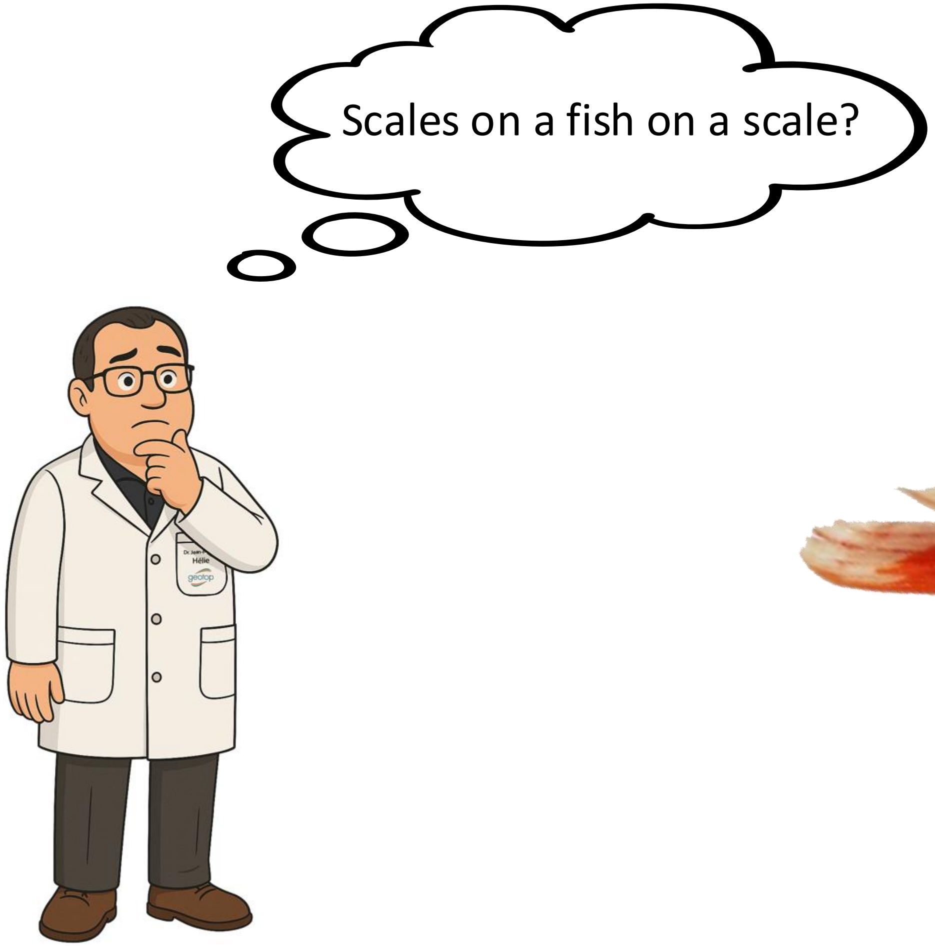
To eliminate confusion in the reporting of light stable isotope ratios, the Commission on Atomic Weights and Isotopic Abundances of the International Union of Pure and Applied Chemistry has recommended[1,2] that the use of SMOW and PDB be discontinued and that isotope abundances of hydrogen-, carbon- and oxygen-bearing materials be reported relative to the reference water VSMOW (Vienna standard mean ocean water) and to VPDB (Vienna Peedee belemnite), defined by adopting a $\delta^{13}C$ value of +1.95‰ and a $\delta^{18}O$ value of –2.20‰ for NBS 19 carbonate relative to VPDB. The isotope abundance scales should be normalized so that SLAP (standard light Antarctic precipitation) has a $\delta^{2}H$ and $\delta^{18}O$ of −428 and −55.5‰, respectively, relative to VSMOW. If the isotope abundance measurement of a sample depends on an isotopic fractionation factor, this should be reported.

Tyler B. Coplen
Commission on Atomic Weights and Isotopic Abundances,
International Union of Pure and Applied Chemistry,
US Geological Survey,
Reston, Virginia 22092, USA

1. IUPAC *Pure appl. Chem.* **66,** 2423–2444 (1994).
2. Coplen, T.B. *Pure appl. Chem.* **66,** 273–276 (1994).

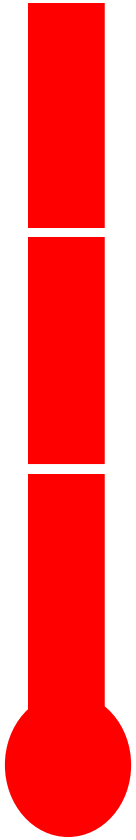
NATURE · VOL 375 · 25 MAY 1995

Now we need to talk about scales…



Temperature scales

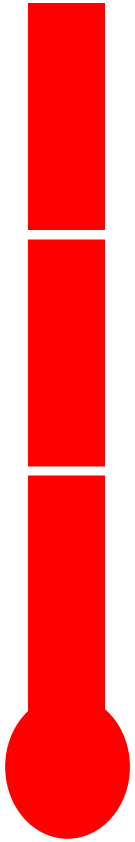
Fahrenheit:



96°F — Human body

0°F — NH_4Cl – water – ice mix

Celsius:



100°C — Water boiling

0°C — Water freezing

ITS-90:

Table 1. The fixed points of the International Temperature Scale of 1990 (ITS-90)

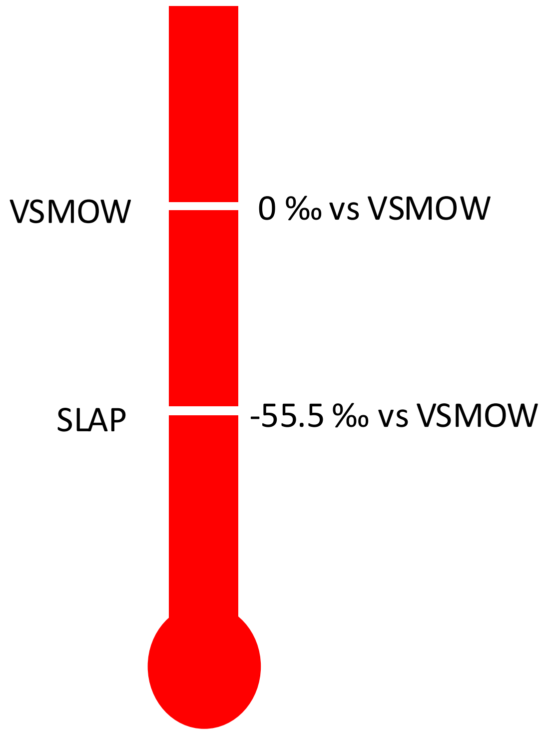
	T (K)	*t* (°C)
Triple point of hydrogen	13.8033	–259.3467
Triple point of neon	24.5561	–248.5939
Triple point of oxygen	54.3584	–218.7916
Triple point of argon	83.8058	–189.3442
Triple point of mercury	234.3156	–38.8344
Triple point of water	273.16	0.01
Melting point of gallium	302.9146	29.7646
Freezing point of indium	429.7485	156.5985
Freezing point of tin	505.078	231.928
Freezing point of zinc	692.677	419.527
Freezing point of aluminium	933.473	660.323
Freezing point of silver	1234.93	961.78
Freezing point of gold	1337.33	1064.18
Freezing point of copper	1357.77	1084.62

The freezing and melting points are at one standard atmosphere pressure. 'Triple points' refer to the unique temperature at which the three phases (solid, liquid and vapour) coexist at equilibrium.

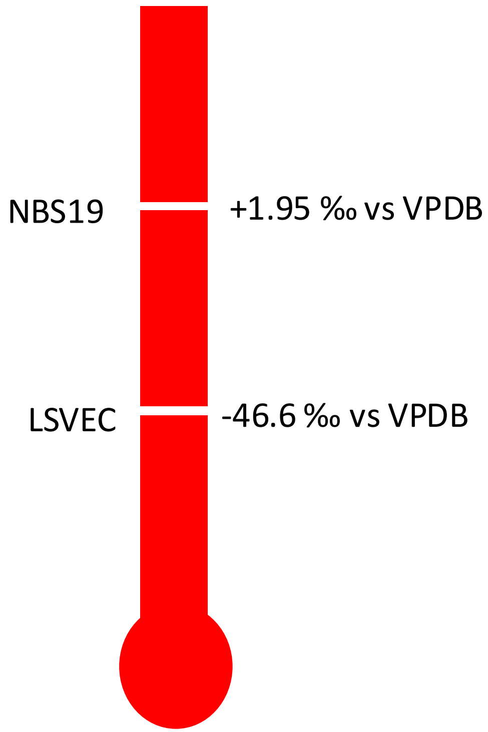
DOI: 10.1177/0020294014557405

Isotope scales

$\delta^{18}O_{VSMOW\text{-}SLAP}$:



$\delta^{13}C_{VPDB\text{-}LSVEC}$:



Scale definition vs scale realization

- An Isotope scale can be defined by one or two points.
  - Example of one point isotope delta scale: the SMOW scale defined by SMOW water (zero point)
  - Example of two point isotope delat scale: the VSMOW-SLAP scale defined by VSMOW and SLAP waters

- We can realize the definition of such a scale with existing physical reference materials.
  - Realization of the VSMOW-SLAP oxygen isotope delta scale by measuring VSMOW2 water and assigning it a delta value of 0‰ vs VSMOW and measuring SLAP2 and assigning a delta value of -55.5‰ vs VSMOW.

Scales for the traditional stable isotopes

Hydrogen	VSMOW-SLAP
Carbon	VPDB **&** VPDB-LSVEC
Nitrogen	AIR
Oxygen	VSMOW-SLAP **&** VPDB **&** VPDB-CO2
Sulfur	VCDT

Scales for the traditional stable isotopes

Hydrogen	VSMOW-SLAP
Carbon	**VPDB** & **VPDB-LSVEC**
Nitrogen	AIR
Oxygen	**VSMOW-SLAP** & **VPDB** & **VPDB-CO_2**
Sulfur	VCDT

Scale definitions for carbon and oxygen

Rapid Communications in Mass Spectrometry

WILEY

Rapid Communications in Mass Spectrometry

PERSPECTIVE OPEN ACCESS

Stable Isotope Reference Materials and Scale Definitions—Outcomes of the 2024 IAEA Experts Meeting

Federica Camin[1] | Dinka Besic[1] | Paul J. Brewer[2] | Colin E. Allison[3] | Tyler B. Coplen[4] | Philip J. H. Dunn[5] | Matthias Gehre[6] | Manfred Gröning[7] | Harro A. J. Meijer[8] | Jean-François Hélie[9] | Paola Iacumin[10] | Rebecca Kraft[11] | Bor Krajnc[12] | Steffen Kümmel[6] | Sangil Lee[13] | Juris Meija[14] | Zoltan Mester[14] | Joachim Mohn[15] | Heiko Moossen[16] | Haiping Qi[4] | Grzegorz Skrzypek[17] | Peter Sperlich[18] | Joelle Viallon[19] | Leonard I. Wassenaar[20] | Robert I. Wielgosz[19]

Rapid Communications in Mass Spectrometry, 2025;
https://doi.org/10.1002/rcm.10018

Scale definitions for carbon-13

The **VPDB** scale for the carbon-13 isotope delta value, expressed as $\delta(^{13}C)$, is defined by taking the fixed numerical value of +0.00195 for the $\delta(^{13}C)$ of the NBS 19 RM, when expressed relative to VPDB.

With 7 notes

The **VPDB-LSVEC** scale for the carbon-13 isotope delta value, expressed as $\delta(^{13}C)$, is defined by taking the fixed numerical value of +0.00195 for $\delta(^{13}C)$ of the NBS 19 RM and −0.0466 for the $\delta(^{13}C)$ of the LSVEC RM, when expressed relative to VPDB.

With 7 notes

The VPDB scale for the carbon-13 isotope delta value, expressed as $\delta(^{13}C)$, is defined by taking the fixed numerical value of +0.00195 for the $\delta(^{13}C)$ of the NBS 19 RM, when expressed relative to VPDB.

1. The quantity isotope delta is dimensionless and has the unit one. It is common practice to express numerical values of isotope delta, when multiplied by 1000, using the symbol permille (‰): For example, the consensus $\delta(^{13}C)$ value of NBS 19 is +1.95‰.

2. VPDB stands for Vienna Peedee belemnite.

3. VPDB is a virtual material; it does not and has not existed in material form. Its $\delta(^{13}C)$ value is exactly 0 on the VPDB scale.

4. The values of the $^{13}C/^{12}C$ isotope number ratio (commonly shorted to isotope ratio) [14] for the VPDB virtual material and $^{17}O/^{16}O$ and $^{18}O/^{16}O$ isotope ratios in the CO_2 gas that would be liberated from VPDB in reaction with concentrated phosphoric acid at 25°C have been measured. Values currently recommended by IUPAC for these quantities are as follows:

$R(^{13}C/^{12}C, \text{VPDB}) = 0.011113 \pm 0.000022$ (95% confidence level)
$R(^{17}O/^{16}O, \text{VPDB-}CO_2) = 0.0003907 \pm 0.0000012$
$R(^{18}O/^{16}O, \text{VPDB-}CO_2) = 0.00208839 \pm 0.00000092$
$\lambda = 0.528$ (assumed exact)

These values have been endorsed by the CIAAW in 2024 [25] and replace the recommendation of Brand, Assonov,and Coplen [26].

5. Carbonate RMs, such as NBS 19 which is quarantined [9], or IAEA-603 [27], that can be used instead of NBS 19, provide a means for analysts to realize the VPDB scale in practice. To achieve reliable measurements on the VPDB scale, IUPAC recommends the use of at least two RMs whose values have been determined relative to VPDB to minimize common sources of instrument measurement bias [28]. RM producers should demonstrate that their assigned values and the associated uncertainties on such RMs are consistent with the VPDB scale definition and with values and uncertainties of other RMs intended for the same purpose.

6. When reporting their measurement results, users should follow the minimum requirements established by IUPAC [6].

7. Carbon isotope delta values reported on the VPDB and VPDB-LSVEC scales can differ. Differences between delta values reported on the VPDB and VPDB-LSVEC scales range from +0.14‰ to +0.30‰ [22, 24] for materials with carbon isotope delta values around −45‰ and are negligible (below current analytical combined uncertainty) at carbon isotope delta values close to zero. Conversion models between the two scales can be established and used but will introduce uncertainty [22].

Scale definitions for oxygen-18

The **VSMOW-SLAP** scale for oxygen-18 isotope delta value, expressed as $\delta(^{18}O)$, is defined by taking the fixed numerical value of 0 for $\delta(^{18}O)$ value of the VSMOW RM and −0.0555 for the $\delta(^{18}O)$ value of the SLAP RM, when expressed relative to VSMOW.

With 9 notes

The **VPDB** scale for oxygen-18 isotope delta value, expressed as $\delta(^{18}O)$, is defined by taking the fixed numerical value of −0.0022 for $\delta(^{18}O)$ of the NBS 19 RM, when expressed relative to VPDB.
The **VPDB-CO_2** scale for oxygen-18 isotope delta value, expressed as $\delta(^{18}O)$, is defined by taking the fixed numerical value of −0.0022 for $\delta(^{18}O)$ of the CO_2 gas liberated from the NBS 19 RM in reactions with oversaturated phosphoric acid at 25°C, when expressed relative to VPDB-CO_2.

With 8 notes

Other scales (no official definitions)

- Hydrogen-2: The **VSMOW-SLAP** scale for hydrogen-2 isotope delta value, expressed as $\delta(^{2}H)$, is defined by taking the fixed numerical value of 0 for $\delta(^{2}H)$ value of the VSMOW RM and −0.428 for the $\delta(^{2}H)$ value of the SLAP RM, when expressed relative to VSMOW.

- Nitrogen-15: The **AIR** scale for nitrogen-15 isotope delta value, expressed as $\delta(^{15}N)$, is based on Air-N_2 with a $\delta(^{15}N)$ value of 0. For practical reasons, IAEA-N-1 ($\delta(^{15}N)_{Air\text{-}N2}$ = +0.43‰ ± 0.07‰) is commonly used as a solid RM for realizing the Air-N_2 isotope delta scale, and USGS32 ($\delta(^{15}N)_{AIR\text{-}N2}$ = +180‰) has been used as a second anchor for scale realization to normalize $\delta(^{15}N)$ data. ***This is still debated.***

- Sulfur-34: The **VCDT** scale for sulfure-34 isotope delta value, expressed as $\delta(^{34}S)$, is defined by taking the fixed numerical value of 0.003 for $\delta(^{34}S)$ value of the IAEA-S-1 RM, when expressed relative to VCDT. It is recommended that IAEA-S-2 or IAEA-S-3 RMs also be used for the VCDT scale realization.

Reference materials

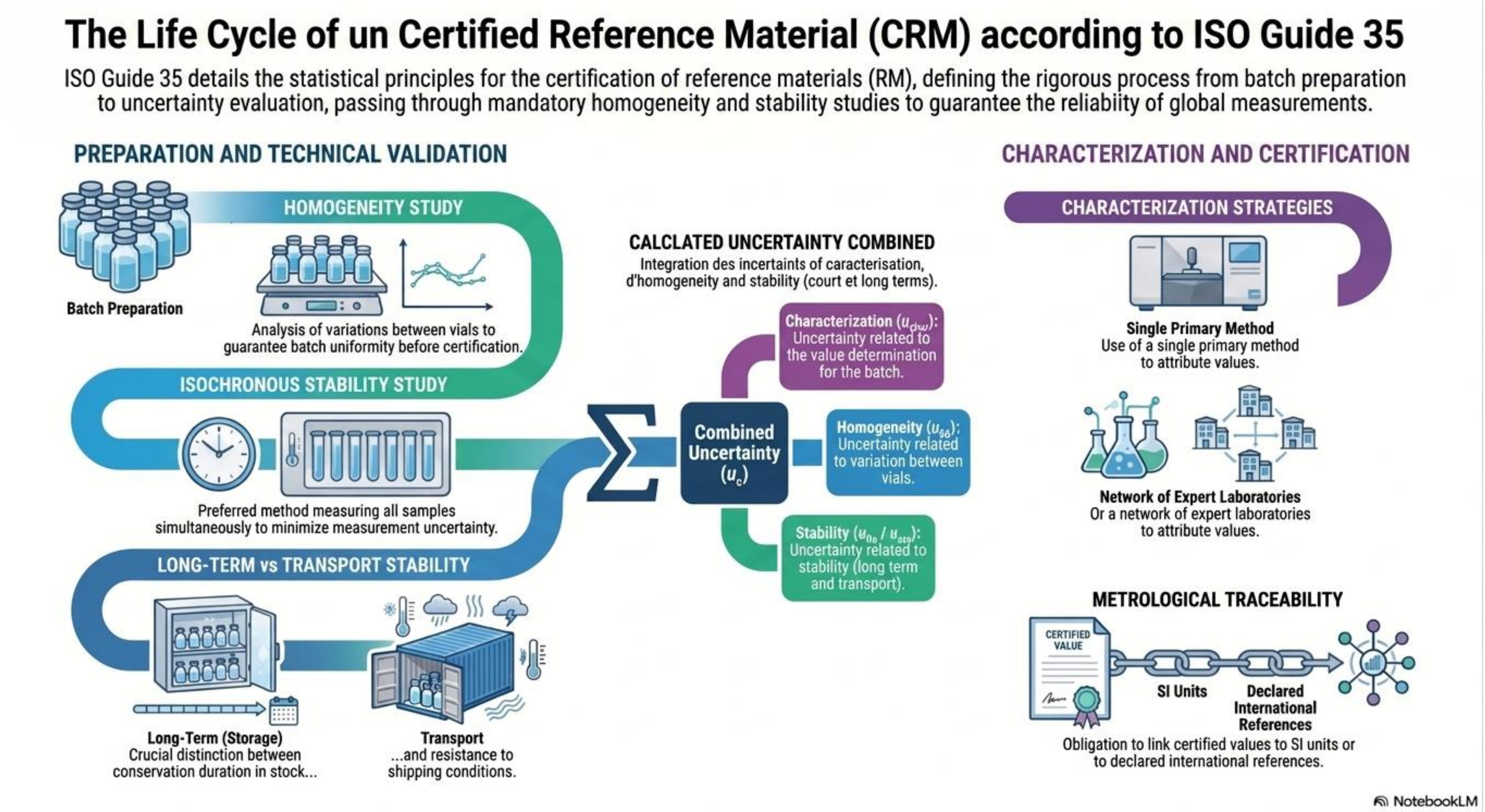
Reference number
ISO GUIDE 30:2015(E)

Reference materials — Selected terms and definitions

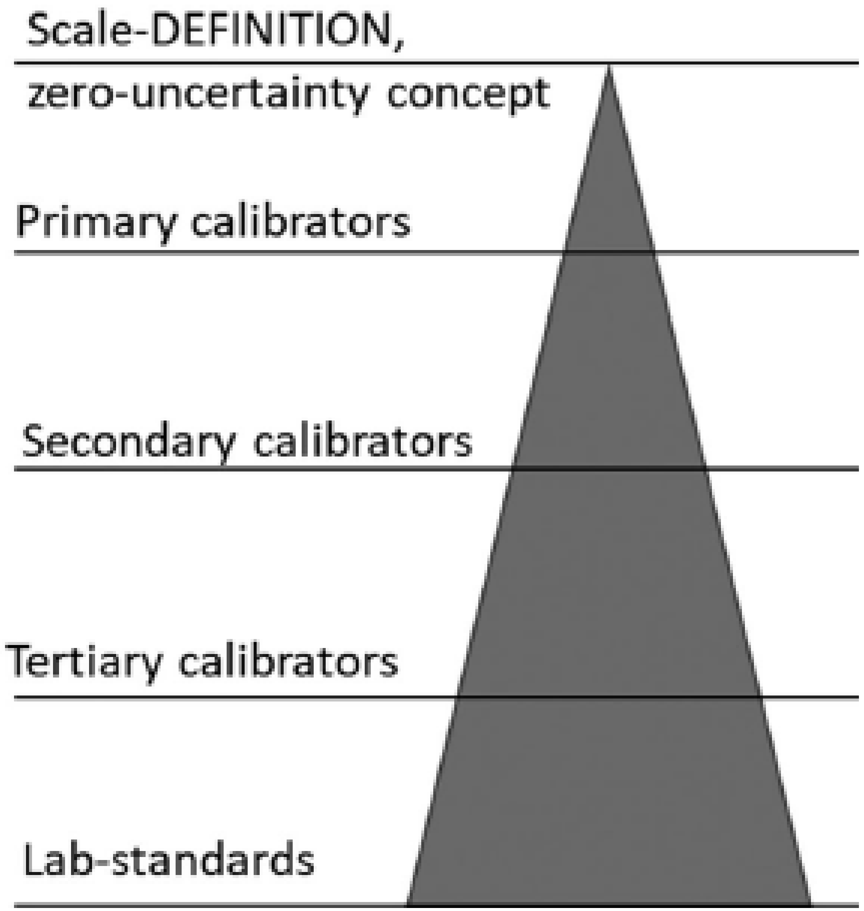
Matériaux de référence — Termes et définitions choisis

reference material
RM
material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

certified reference material
CRM
reference material (RM) characterized by a metrologically valid procedure for one or more specified properties, accompanied by an RM certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability


The Life Cycle of un Certified Reference Material (CRM) according to ISO Guide 35
ISO Guide 35 details the statistical principles for the certification of reference materials (RM), defining the rigorous process from batch preparation to uncertainty evaluation, passing through mandatory homogeneity and stability studies to guarantee the reliabiity of global measurements.
PREPARATION AND TECHNICAL VALIDATION
Batch Preparation
HOMOGENEITY STUDY
Analysis of variations between vials to guarantee batch uniformity before certification.
ISOCHRONOUS STABILITY STUDY
Preferred method measuring all samples simultaneously to minimize measurement uncertainty.
LONG-TERM vs TRANSPORT STABILITY
Long-Term (Storage)
Crucial distinction between conservation duration in stock...
Transport
...and resistance to shipping conditions.
CALCLATED UNCERTAINTY COMBINED
Integration des incertaints of caracterisation, d'homogeneity and stability (court et long terms).
Combined Uncertainty (u_c)
Characterization (u_{char}): Uncertainty related to the value determination for the batch.
Homogeneity (u_{bb}): Uncertainty related to variation between vials.
Stability (u_{lts} / u_{sts}): Uncertainty related to stability (long term and transport).
CHARACTERIZATION AND CERTIFICATION
CHARACTERIZATION STRATEGIES
Single Primary Method
Use of a single primary method to attribute values.
Network of Expert Laboratories
Or a network of expert laboratories to attribute values.
METROLOGICAL TRACEABILITY
CERTIFIED VALUE
SI Units
Declared International References
Obligation to link certified values to SI units or to declared international references.
NotebookLM

RM hierarchy



Received: 5 August 2020 | Revised: 23 October 2020 | Accepted: 6 December 2020
DOI: 10.1002/rcm.9018

RESEARCH ARTICLE

Rapid Communications in Mass Spectrometry WILEY

On the metrological traceability and hierarchy of stable isotope reference materials aimed at realisation of the VPDB scale: Revision of the VPDB $\delta^{13}C$ scale based on multipoint scale-anchoring RMs

Sergey Assonov[1]* | Ales Fajgelj[1]* | Colin Allison[2] | Manfred Gröning[1]

[1]International Atomic Energy Agency, Wagramer Strasse 5, Vienna, A-1400, Austria
[2]CSIRO, Climate Science Centre, Aspendale, Victoria, 3195, Australia

RM hierarchy

- **Scale defining RM**: A reference material that defines the isotope delta scale. It defines the zero-point of a delta scale.
- **Scale realizing RM**: RMs of the highest metrological quality. They have the smallest uncertainty with respect to the scale defining RMs.
- **All other RMs**: RM that has an assigned isotope delta value and associated uncertainty that is consistent with the scale definition.

Pure and Applied Chemistry

Comprehensive assessment of international reference materials for isotope ratio analysis using delta scales (IUPAC Technical Report)

Manfred Gröning, Philip J.H. Dunn, John K. Böhlke, Willi A. Brand, Federica Camin, Tyler B. Coplen, Monika Horsky, Johanna Irrgeher, Wenshuai Li, Jacqueline L. Mann, Juris Meija, Harro A.J. Meijer, Thomas Prohaska, Grzegorz Skrzypek, Yoshio Takahashi, Jochen Vogl, Thomas Walczyk, Jun Wang, Michael Wieser, Tetsuya Yokoyama, Igor Zivkovic.

Reference sheets

IAEA
International Atomic Energy Agency
Atoms for Peace

International Atomic Energy Agency
Department of Nuclear Sciences and Applications
IAEA Environment Laboratories

Vienna International Centre, P.O. Box 100, 1400 Vienna, Austria

REFERENCE SHEET

CERTIFIED REFERENCE MATERIAL

IAEA-603 (calcite)

Stable Isotope Reference Material for $\delta^{13}C$ and $\delta^{18}O$

Assigned $\delta^{13}C$ and $\delta^{18}O$ values for the stable isotopic composition of IAEA-603 expressed in per mille (‰) on the respective VPDB scales [1]

	Assigned value[(1)]	Combined standard uncertainty[(2)] at 1σ-level
$\delta^{13}C$, ‰ on the VPDB $\delta^{13}C$ scale	+2.46	±0.01
$\delta^{18}O$, ‰ on the VPDB $\delta^{18}O$ scale	-2.37	±0.04

[(1)] The values and combined uncertainties were calculated from the raw data obtained by stable isotope mass-spectrometry directly vs remaining NBS19 material, including the necessary ^{17}O isotopic correction [1, 2], and the weighing uncertainties following [1, 3, 4]. Value and uncertainty for $\delta^{13}C$ provided here are rounded to two digits, values with the full three digit resolution are given in Table 2.
[(2)] The uncertainty is expressed as a combined standard uncertainty (1σ-level) using a coverage factor k = 1, and estimated in accordance with the JCGM 100:2008 'Evaluation of measurement data – Guide to the expression of uncertainty in measurement' [3] and ISO Guide 35 'Reference materials – General and statistical principles for certification [4].

USGS
science for a changing world

United States Geological Survey

Reston Stable Isotope Laboratory

Report of Stable Isotopic Composition

Reference Material USGS53-0.25 µL

Lake Shala Distilled Water

(Hydrogen and Oxygen Isotopes in Water Sealed in a Silver Tube)

This reference material (RM) is intended for calibration of stable hydrogen (δ^2H) and oxygen ($\delta^{18}O$) measurements of unknown water or hydrogen- or oxygen-bearing substances with a TC/EA (thermal conversion/elemental analyzer) and an isotope-ratio mass spectrometer by quantifying drift with time and isotope-ratio-scale contraction. This RM consists of 0.25 µL of USGS53 Lake Shala Distilled Water [1] sealed in a silver tube [2]. This RM is issued in quantities of 50 sealed silver tubes per bottle. There is no limit on distribution. Glass ampoules containing 5 mL of USGS53 water are available from the Reston Stable Isotope Laboratory.

Recommended Values: Stable hydrogen and oxygen isotopic compositions are expressed herein as delta values [3] relative to VSMOW (Standard Mean Ocean Water) on scales normalized such that the δ^2H and $\delta^{18}O$ values of SLAP (Standard Light Antarctic Precipitation) are –428 ‰ and –55.5 ‰, respectively [4,5]. The isotopic compositions of USGS53-0.25 µL are identical to that of USGS53 [1], except that each combined standard uncertainty value (μ_C) has been increased to account for hydrogen and oxygen blanks, both of which were below detection.

Stable hydrogen isotopic composition:	$\delta^2H_{VSMOW-SLAP}$ = +40.2 ± 0.5 ‰
Stable oxygen isotopic composition:	$\delta^{18}O_{VSMOW-SLAP}$ = +5.47 ± 0.04 ‰
Nominal volume of water:	0.25 µL (Although the RSIL attempts to ensure that each silver tube has the same volume of water, slight differences are observed owing to variations of the inside diameter of the silver tubing provided by the manufacturer. The typical relative variation in volume among 50 tubes is ±3 %, but this cannot be guaranteed.)

Technical coordination for this RM was provided by Haiping Qi of the RSIL.

Reston, Virginia 20192
December 2, 2019

Tyler B. Coplen, Director
Reston Stable Isotope Laboratory

Elemental Microanalysis Ltd

Certificate of Analysis

Isotopic Reference Material EMA-P1

Cat. No. B2203 - Certificate No: 132358

General

The isotopic values listed below were generated from results submitted by a group of 28 participating isotope laboratories in an International interlaboratory comparison study. A range of CF-IRMS instrumentation was utilized during this study.
This standard has been isotopically characterised to allow use in both combustion and pyrolysis techniques.

Results are traceable to primary isotope standards issued by the I.A.E.A. This isotopic reference material (IRM) should not be considered a substitute for those primary reference materials.
The results presented in the table below are following a statistical evaluation and treatment of submitted data.
The number of laboratories submitting data for each isotope is shown.

Total element is also certified with results traceable to N.I.S.T Standard reference materials (SRM) acetanilide 141d and cystine 143d.
The uncertainty in the certified value is expressed as expanded uncertainty, U, at 95% confidence and is calculated in accordance with ISO/IEC17025 according to GUM (Guidelines to Uncertainty in Measurement). Confidence limits include those due to sampling variation, weighing, calibration and measurement errors. The certified values are based upon the results of 8 determinations.

Isotope Results

	^{13}C V-PDB	^{18}O V-SMOW	^2H V-SMOW	^{34}S V-CDT
MEAN VALUE ‰	-27.85	+20.99	-25.30	-3.01
σ (1s.d.) ‰	0.12	0.72	5.10	0.54
No. of laboratories	19	11	8	9

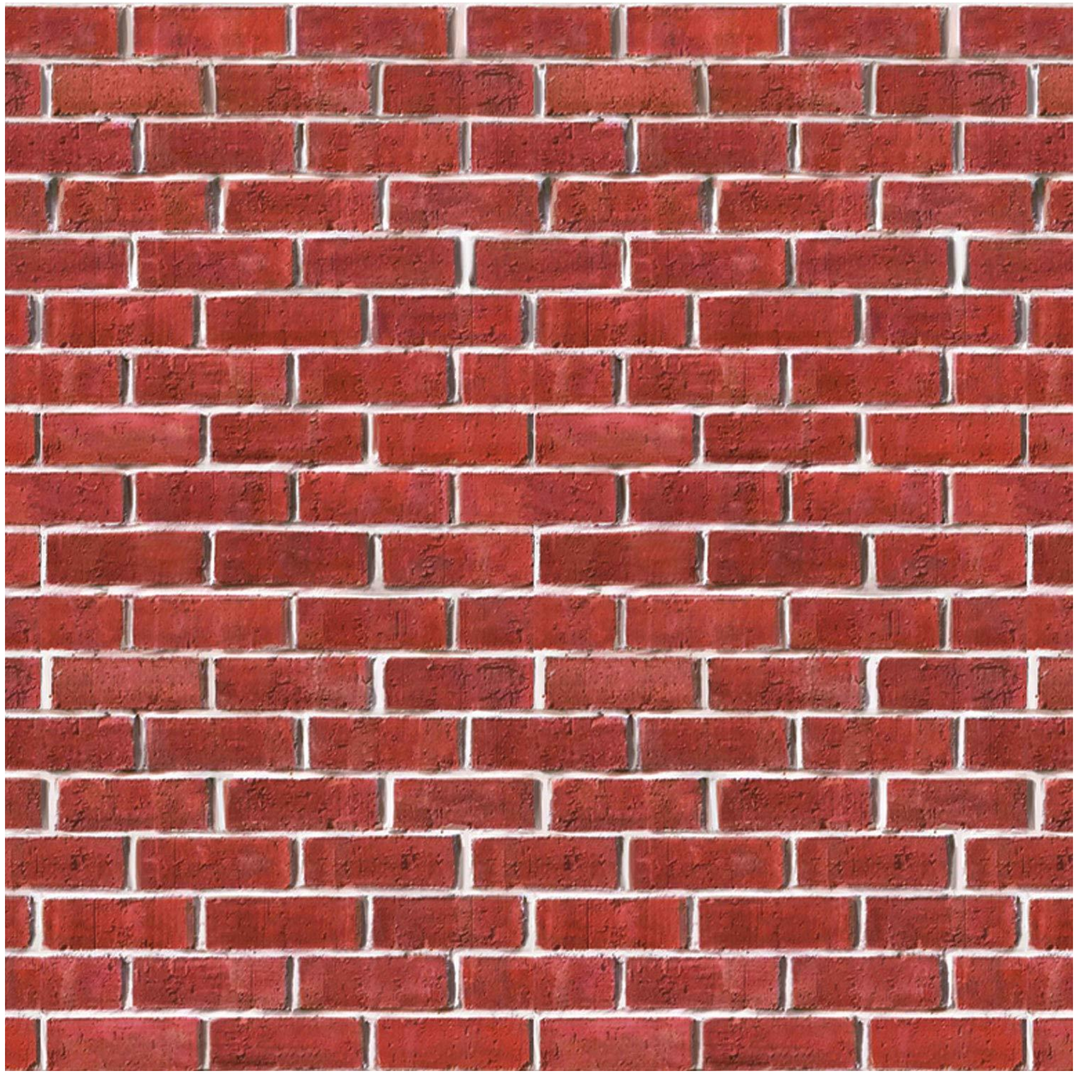
Element Results

	C	O	H	S
ELEMENT %	61.51	20.87	3.46	13.85
U %	0.16	0.29	0.05	0.16

Reference materials

VPDB scale

		$\delta^{13}C$(VPDB)
IAEA-603	CaCO3	+2.46±0.01
IAEA-610	CaCO3	-9.109 ± 0.012
IAEA-611	CaCO3	-30.795 ± 0.013
IAEA-612	CaCO3	-36.722 ± 0.015



VPDB-LSVEC scale

		$\delta^{13}C$(VPDB-LSVEC)
USGS44	CaCO3	-42.21 ± 0.05
IAEA-601	Benzoic Acid	-28.81 ± 0.04
IAEA-602	Benzoic Acid	-28,85 ± 0.04
IAEA-CH-6	Sucrose	-10.45 ± 0.03
IAEA-CH-7	polyethylene	-32.15 ± 0.05
NBS22	Oil	-30.03 ± 0.03
USGS24	Graphite	-16.05 ± 0.04
USGS61	Caffeine	-35.05 ± 0.04
USGS62	Caffeine	-14.79 ± 0.04
USGS63	Caffeine	-1.17 ± 0.04
USGS64	Glycine	-40.81 ± 0.04
USGS65	Glycine	-20.29 ± 0.04
USGS66	Glycine	-0.67 ± 0.04
USGS67	n-hexadecane	-34.50± 0.05
USGS68	n-hexadecane	-10.55 ± 0.04
USGS69	n-hexadecane	-0.57 ± 0.04
USGS70	C20 Fame	-30.53 ± 0.04
USGS71	C20 Fame	-10.50 ± 0.04
USGS72	C20 Fame	-1.54 ± 0.04
USGS73	L-valine	-24.03 ± 0.04
USGS74	L-valine	-9.3 ± 0.04
USGS75	L-valine	+0.49 ± 0.07
USGS76	C17 FAME	-31.36 ± 0.04
USGS77	Polyethylene	-30.71 ± 0.04
USGS78	Oil	-29.72 ± 0.05

Jumping from one scale to another

δ^{13}C: VPDB-LSVEC to VPDB

$$\delta^{13}C_{VPDB} = -0.003 \pm 0.020 + [(1-0.0043 \pm 0.0009) \times \delta^{13}C_{VPDB\text{-}LSVEC}$$

Hélie et al., 2022. Discontinuity in the Realization of the Vienna Peedee Belemnite Carbon Isotope Ratio Scale. https://doi.org/10.1021/acs.analchem.1c02458

δ^{18}O: VPDB to VSMOW

$$\delta^{18}O_{VPDB} = 0.97001 \times \delta^{18}O_{VSMOW\text{-}SLAP} - 29.99$$

Coplen et al., 2002. U.S. Geological Survey Water-Resources Investigations Report 01-4222 https://pubs.usgs.gov/wri/wri014222/

Reference materials

Water standards available:

- VSMOW2 & SLAP2: 1 ampoule (20 ml) 180 € each
- USGS45-50: 144 ampoules (5 ml) 1444 $USD
- Elemental Microanalysis (set of 5 vials) ???

Normalizing internal standards

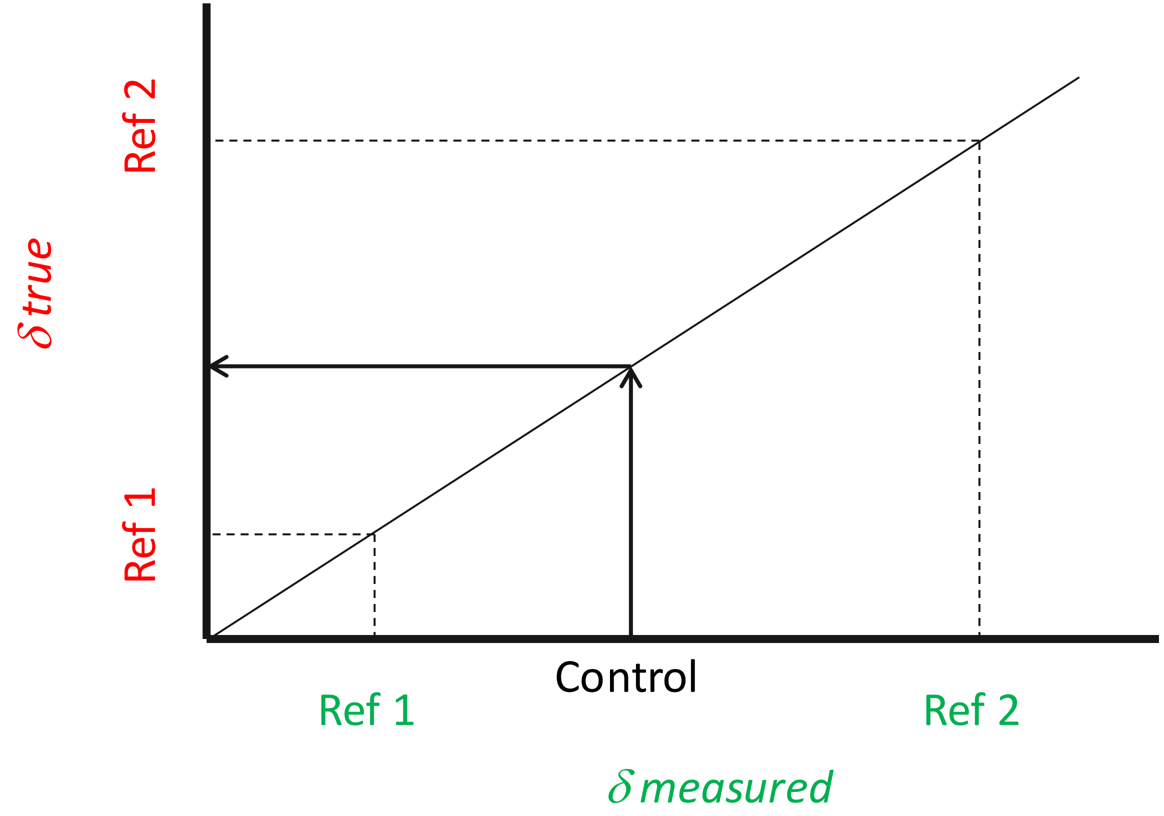
Leucine $\delta^{13}C_{(VPDB\text{-}LSVEC)}$ = -28.74 ± 0.04 ‰

- 15 sequences
- Last 11 year
- N=58
- NBS19, NBS18, IAEACH6, IAEA601, LSVEC, IAEA603, IAEACH7, USGS24, IAEA602, NBS22

Leucine $\delta^{15}N_{(AIR)}$ = -0.06 ± 0.10 ‰

- 7 sequences
- Last 11 year
- N=53
- IAEAN1, IAEAN2, IAEAN3, USGS32, USGS25, USGS26, USGS35, USGS41

Normalization

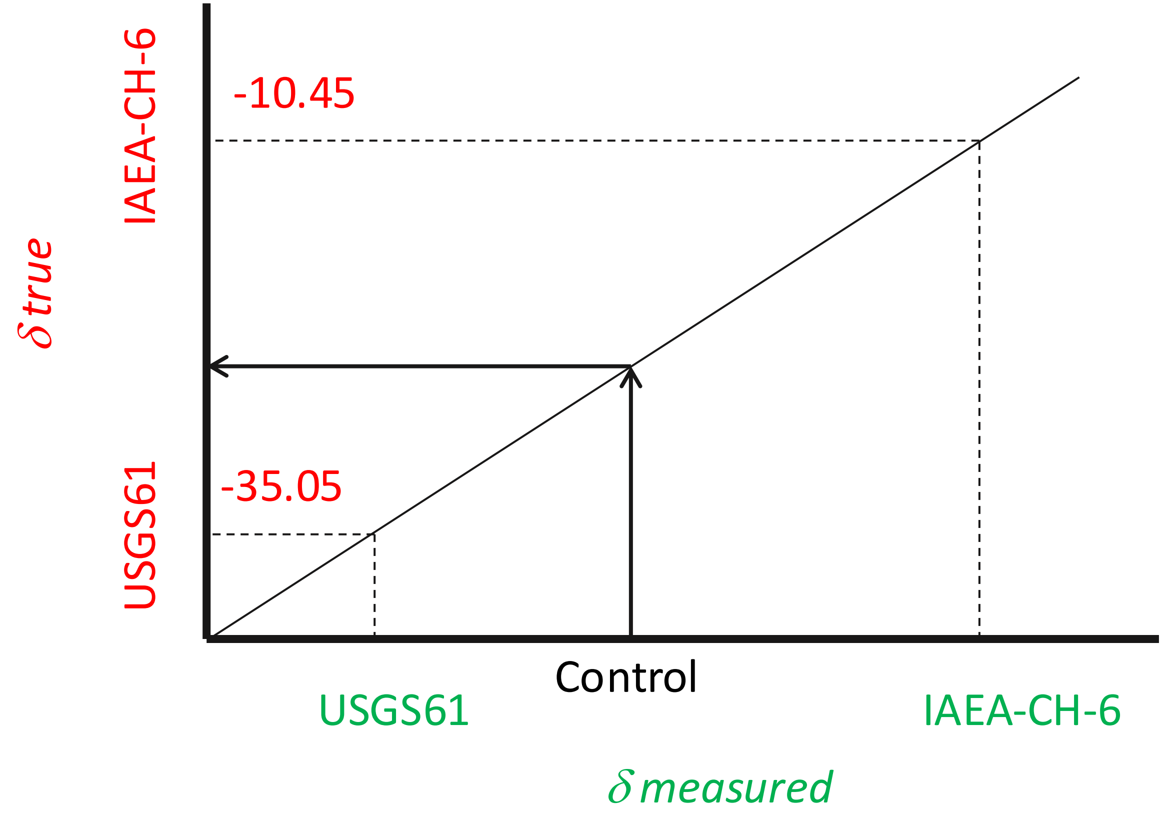


Y intercept

$$\delta_{true} = \delta_{measured} \times m + b$$

Slope

Normalization



$$\delta_{true} = \delta_{measured} \times m + b$$

Y intercept

Slope

Uncertainty propagation

Received: 2 September 2020 | Revised: 17 November 2020 | Accepted: 18 November 2020
DOI: 10.1002/rcm.9008

Check for updates

PROTOCOL

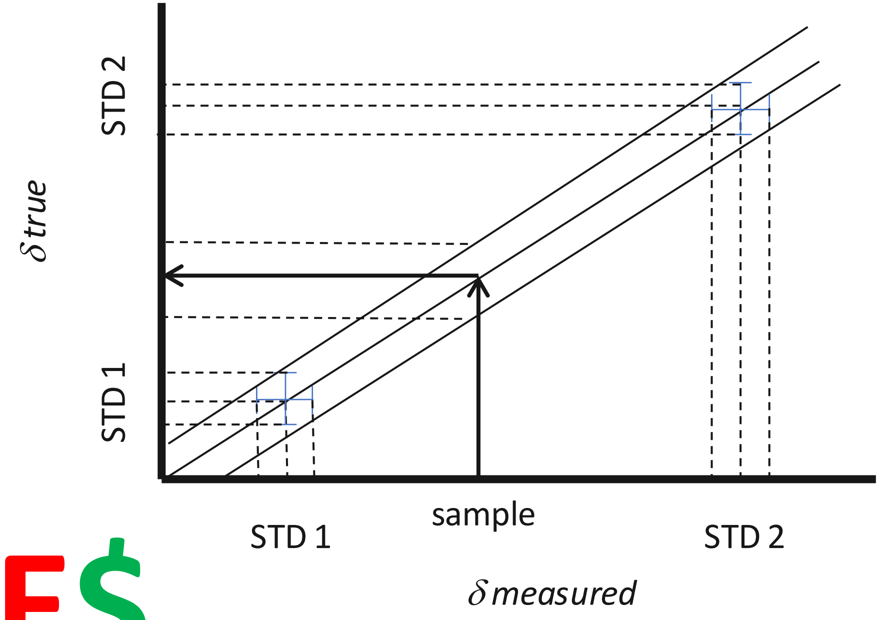
Rapid Communications in Mass Spectrometry WILEY

Designing working standards for stable H, C, and O isotope measurements in CO_2 and H_2O

Jean-François Hélie | Claude Hillaire-Marcel

$$(\delta_A \pm \sigma_A) = [(m \pm \sigma_m) \cdot (\delta_a \pm \sigma_a)] + (b \pm \sigma_b)$$

$$\sigma = \sqrt[2]{\sum \left(\frac{\partial f_i}{\partial x_i}\right)^2 \cdot \sigma_i^2}$$



$FREE TEMPLATE$

Monkey calculations…

$$(\delta_A \pm \sigma_A) = [(m \pm \sigma_m) \cdot (\delta_a \pm \sigma_a)] + (b \pm \sigma_b)$$

$$m = \left[\frac{(\delta_{R1} \pm \sigma_{R1}) - (\delta_{R2} \pm \sigma_{R2})}{(\delta_{r1} \pm \sigma_{r1}) - (\delta_{r2} \pm \sigma_{r2})}\right]$$

$$\sigma_m = \left[\frac{(\delta R1 - \delta R2)}{(\delta r1 - \delta r2)}\right] \cdot \sqrt[2]{\left[\frac{(\sigma_{R1}^2 + \sigma_{R2}^2)}{(\delta R1 - \delta R2)^2}\right] + \left[\frac{(\sigma_{r1}^2 + \sigma_{r2}^2)}{(\delta r1 - \delta r2)^2}\right]}$$

$$b = (\delta_{R1} \pm \sigma_{R1}) - [(m \pm \sigma_m) \cdot (\delta_{r1} \pm \sigma_{r1})]$$

$$\sigma_b = \sqrt[2]{\sigma_{R1}^2 + \left((m \cdot \delta r1) \cdot \sqrt[2]{\left(\frac{\sigma_m^2}{m^2}\right) + \left(\frac{\sigma_{r1}^2}{\delta r1^2}\right)}\right)^2}$$

Better tools

Anal Bioanal Chem
https://doi.org/10.1007/s00216-017-0659-1

CrossMark

RESEARCH PAPER

Uncertainty evaluation in normalization of isotope delta measurement results against international reference materials

Juris Meija[1] · Michelle M. G. Chartrand[1]

Research Article

Rapid Communications in Mass Spectrometry

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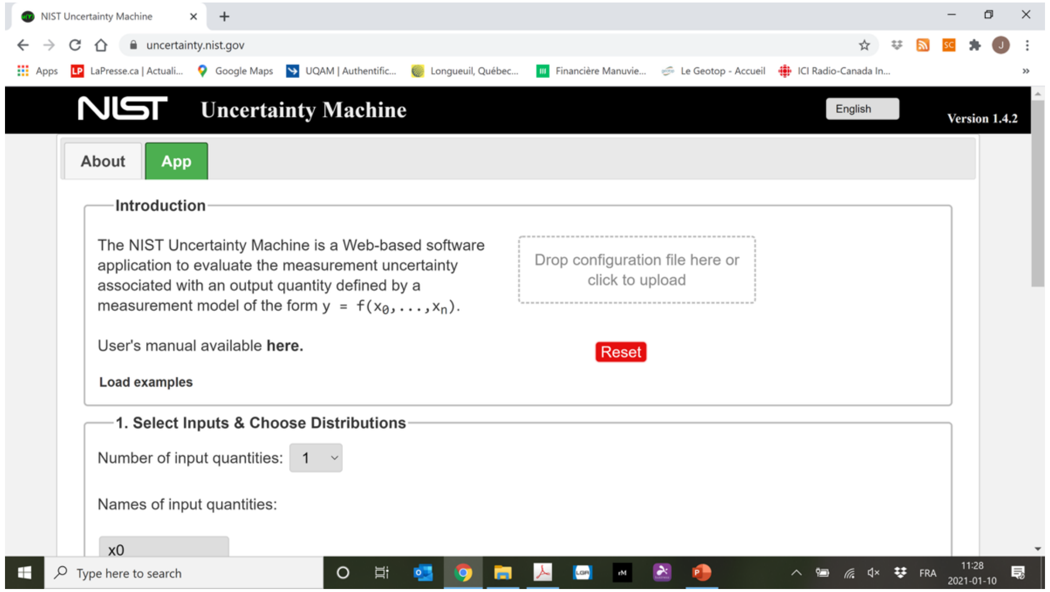
Rapid Commun. Mass Spectrom. **2011**, *25*, 2711–2720
(wileyonlinelibrary.com) DOI: 10.1002/rcm.5074

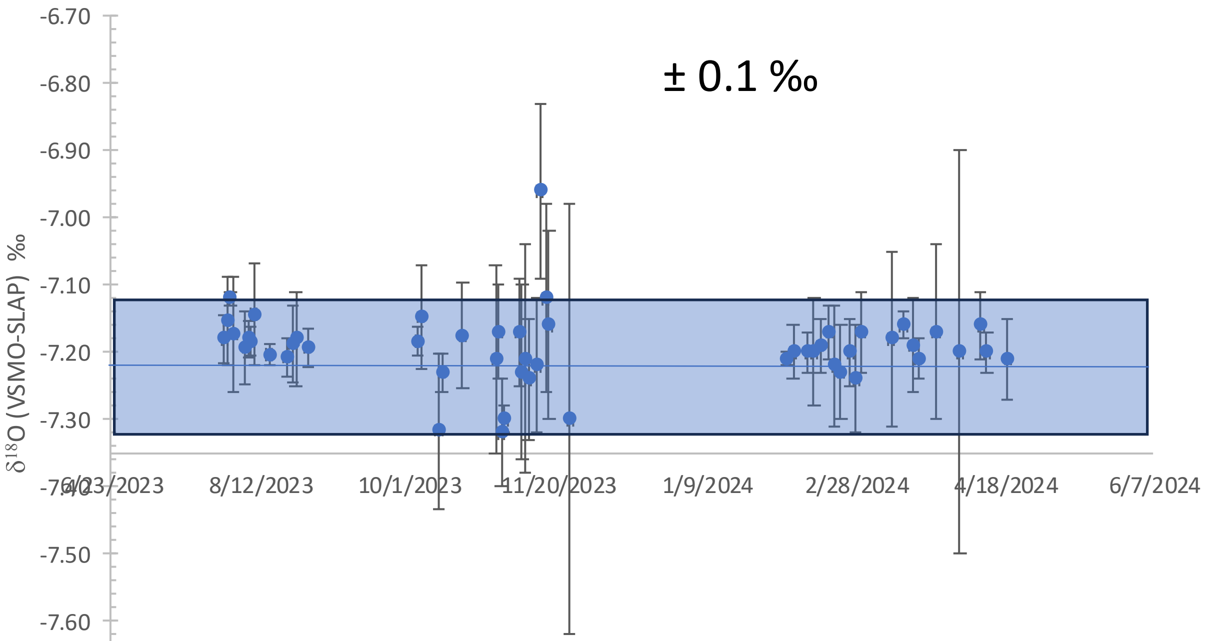
Improved water δ^2H and $\delta^{18}O$ calibration and calculation of measurement uncertainty using a simple software tool†

Manfred Gröning*
Terrestrial Environment Laboratory, Environmental Laboratories, Department of Nuclear Applications, International Atomic Energy Agency, A1400 Vienna, Austria

https://metrology.shinyapps.io/isotope-delta-calibration/



QA/QC



± 0.1 ‰
-6.70
-6.80
-6.90
-7.00
-7.10
-7.20
-7.30
-7.40
-7.50
-7.60
-7.70
δ18O (VSMO-SLAP) ‰
6/23/2023
8/12/2023
10/1/2023
11/20/2023
1/9/2024
2/28/2024
4/18/2024
6/7/2024

Titre

- How many **different** standards?
- How many **replicates** of each standard should be done?

RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2010; **24**: 2697–2705
Published online in Wiley Online Library (wileyonlinelibrary.com) DOI: 10.1002/rcm.4684

RCM

Error propagation in normalization of stable isotope data: a Monte Carlo analysis

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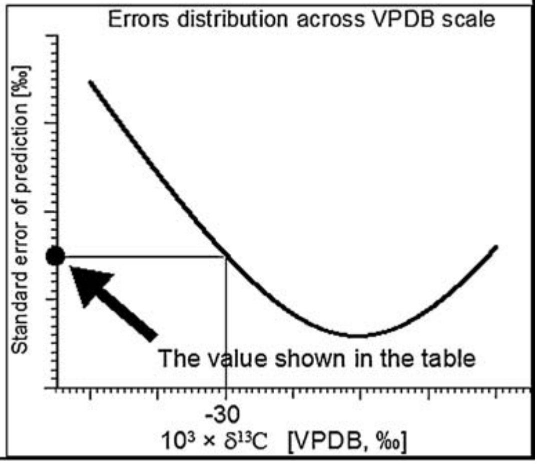
Errors for a hypothetical sample having true $10^3 \times \delta^{13}C$ value of -30‰ for the best selection of standards.

Number of repetitions of each std \ Number of used stds	2	3	4	5	6	7	8	9
1	0.035	0.026	0.025	0.022	0.021	0.019	0.019	0.018
2	0.025	0.019	0.018	0.015	0.014	0.014	0.013	0.013
3	0.020	0.015	0.015	0.013	0.012	0.011	0.011	0.010
4	0.018	0.013	0.013	0.011	0.010	0.010	0.009	0.009
5	0.016	0.012	0.011	0.010	0.009	0.009	0.008	0.008
6	0.014	0.011	0.010	0.009	0.008	0.008	0.008	
7	0.013	0.010	0.010	0.008	0.008			
8	0.012	0.009	0.009	0.008	0.007			
9	0.012	0.009	0.008	0.007				
10	0.011	0.008	0.008					
11	0.011	0.008	0.008					
12	0.010	0.008	0.007					
13	0.010	0.007						
14	0.009	0.007						
15	0.009	0.007						
16	0.009	0.007						
17	0.009							
18	0.008							
19	0.008							
20	0.008							
21	0.008							
22	0.008							
23	0.007							
24	0.007							



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