INDIANA UNIVERSITY
BLOOMINGTON

NBS 22, ca. 1965

Light stable isotope reference materials: Principles and proper use

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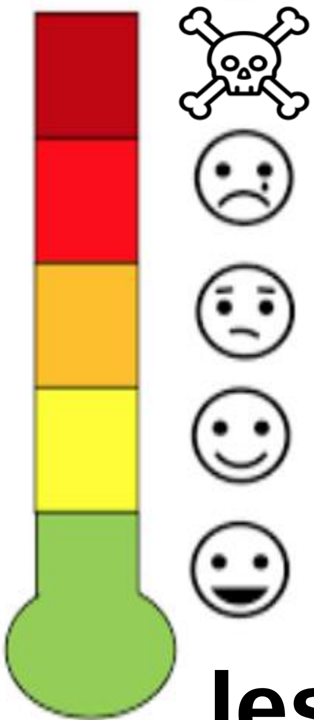
VSMOW, ca. 1980

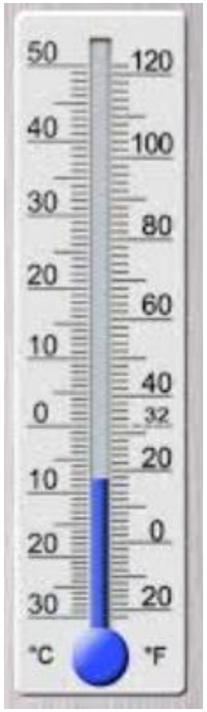
TunTwin Summer School, 18 - 21 April 2023, Ljubljana, Slovenia

Topics to be covered:

- Definition and function of stable isotope reference materials (RMs)
- Convoluted history of select RMs
- Array of competing RM outlets
- Examples of organic RM production
- Normalization of raw data with RMs
- Proper reporting of delta values



less precise



more precise

Reference Materials (RMs) are needed to position your data along common delta scales.

RMs can be:

- Gas, liquid, or solid
- Expensive *versus* cheap
- Perishable *versus* stable
- Organic *versus* inorganic
- Available *versus* hard-to-get
- Toxic *versus* harmless
- Volatile *vs*. non-volatile
- Pure compounds *versus* mixtures

Primary RMs are "international measurement standards" as defined in the *International Vocabulary of Metrology* (VIM3). They and define the scale zero or an anchor point and, if applicable, the scale span. These materials are assigned stable isotope δ-values by consensus without uncertainty, although subsampling and storage may introduce isotope fractionation. Even some primary RMs are known to have developed problems over time.

Secondary RMs are typically prepared by qualified (groups of) laboratories and have been calibrated against primary RMs. The δ-values of secondary RMs are subject to amendments and always carry analytical uncertainty. It is recommended that authors publish the used δ values of internationally distributed, secondary isotopic reference materials that were used for anchoring their measurement results to the respective stable isotope scale.

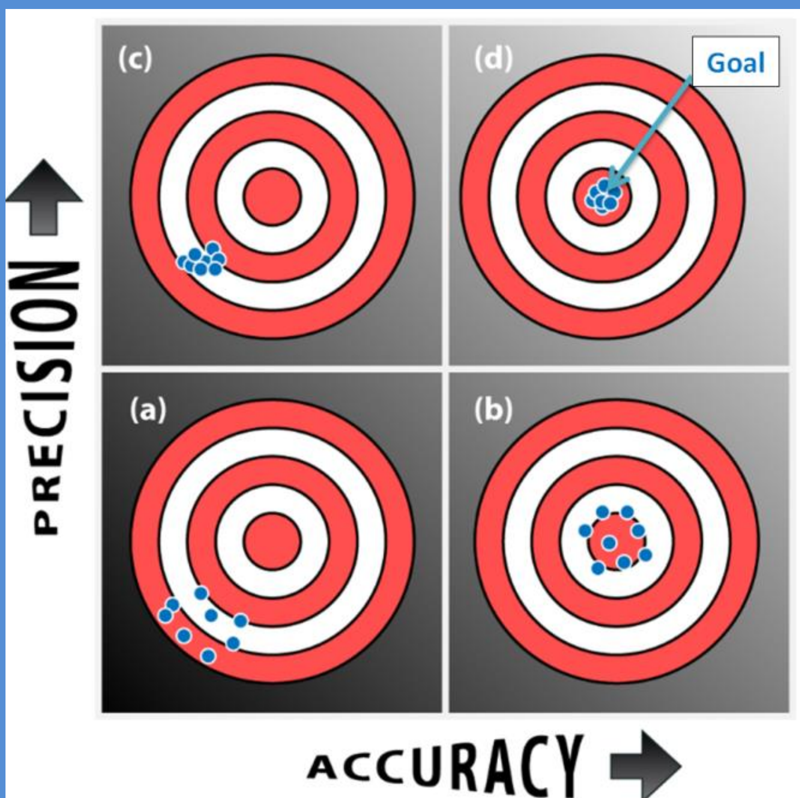
Lower-level RMs can be calibrated against higher-level RMs by laboratories to serve as working standards.

RMs are not permanent!

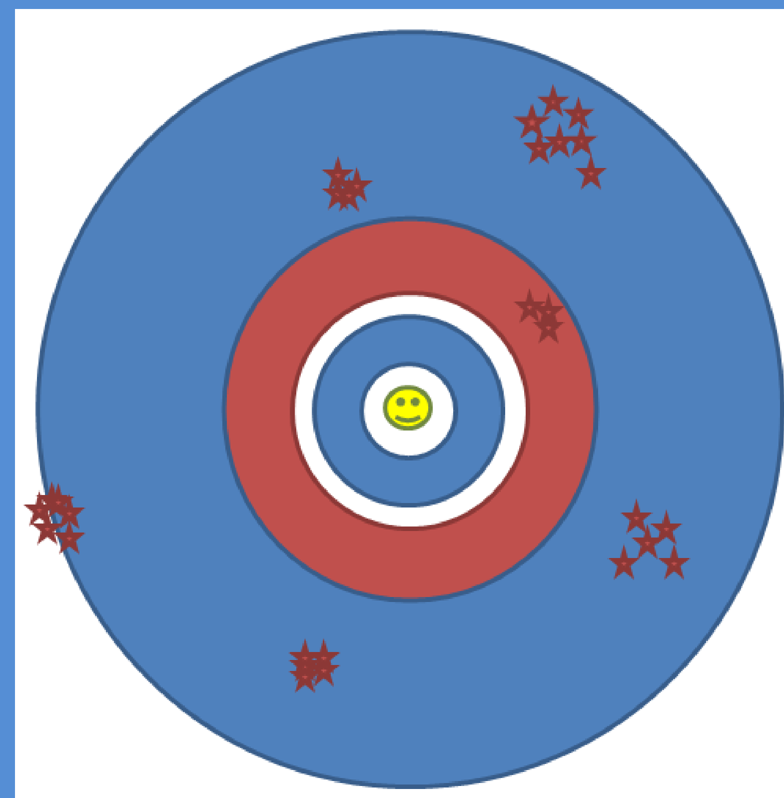
Precision *versus* Accuracy

Goal: **Improved accuracy and comparability** of reported isotopic composition (within analytical uncertainty) for the same material measured in **different laboratories**.

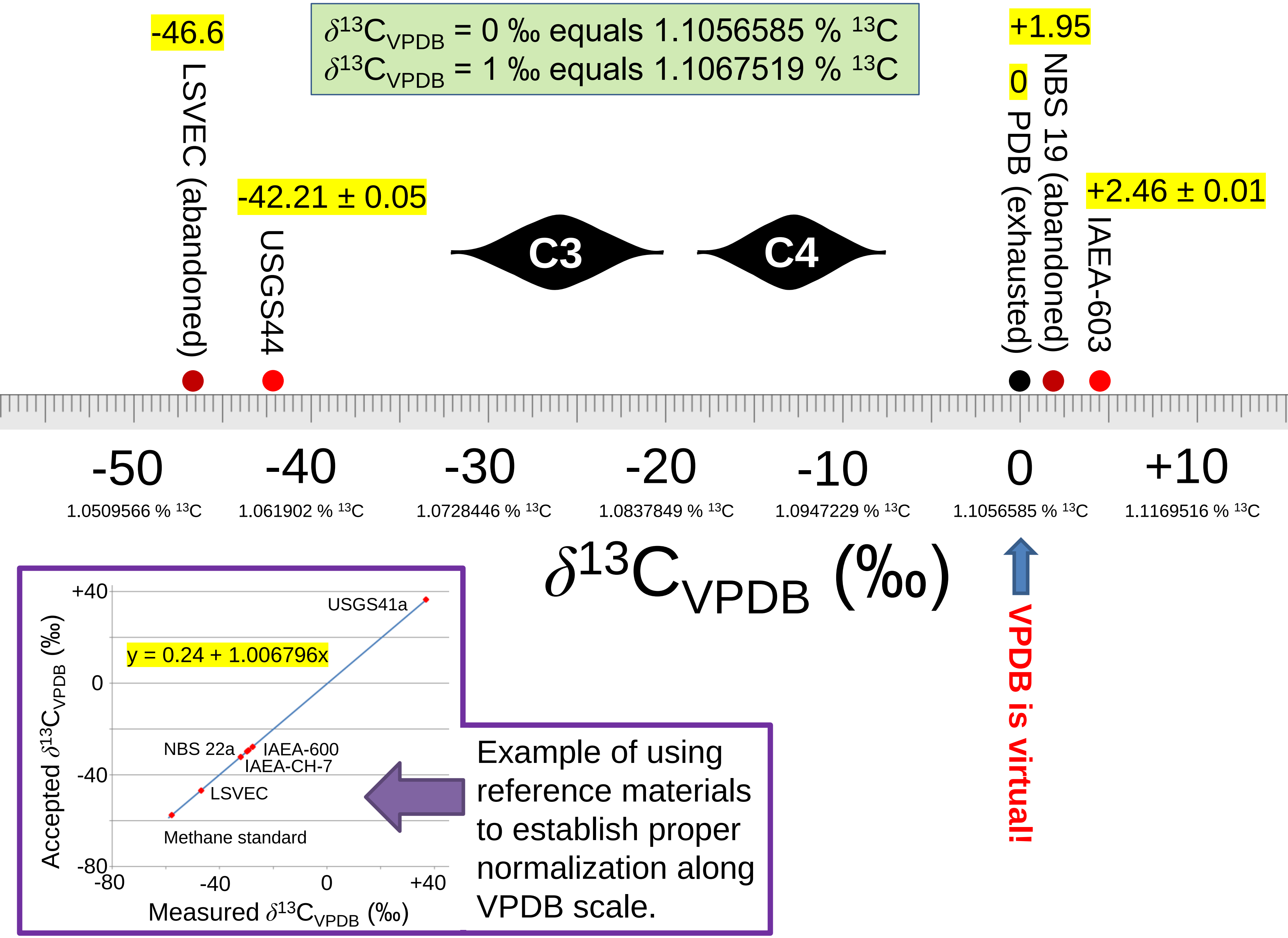
One laboratory



Several laboratories



Slide provided by Haiping Qi, USGS



$\delta^{13}C_{VPDB}$ = 0 ‰ equals 1.1056585 % ^{13}C
$\delta^{13}C_{VPDB}$ = 1 ‰ equals 1.1067519 % ^{13}C
-46.6
LSVEC (abandoned)
-42.21 ± 0.05
USGS44
C3
C4
+1.95
NBS 19 (abandoned)
0
PDB (exhausted)
+2.46 ± 0.01
IAEA-603
-50
1.0509566 % ^{13}C
-40
1.061902 % ^{13}C
-30
1.0728446 % ^{13}C
-20
1.0837849 % ^{13}C
-10
1.0947229 % ^{13}C
0
1.1056585 % ^{13}C
+10
1.1169516 % ^{13}C
$\delta^{13}C_{VPDB}$ (‰)
VPDB is virtual!
Accepted $\delta^{13}C_{VPDB}$ (‰)
+40
0
-40
-80
USGS41a
y = 0.24 + 1.006796x
NBS 22a
IAEA-600
IAEA-CH-7
LSVEC
Methane standard
-80
-40
0
+40
Measured $\delta^{13}C_{VPDB}$ (‰)
Example of using reference materials to establish proper normalization along VPDB scale.

The long drama of the [Vienna] Pee Dee Belemnite (PDB, VPDB) isotopic scale

PDB was made in the early 1950s from powdered belemnite fossils and defined “zero permil” on the carbon delta scale. PDB existed as a small amount and was soon exhausted. It no longer exists today.

In 1982, NBS 19 from powdered limestone/marble was sieved into size fractions. It served for many years as one of two anchors of the **VPDB** scale where no material defines the zero anchor point on the carbon delta scale.

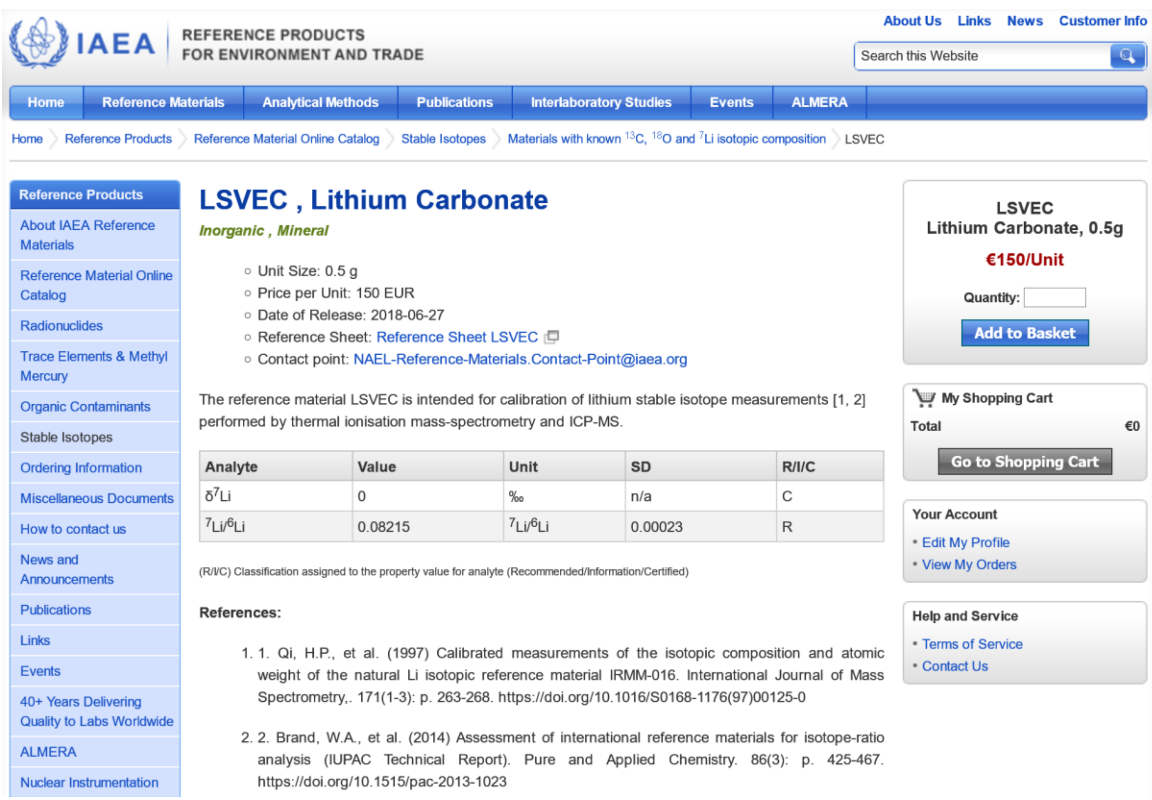
After recognizing grain size problems with supplies of NBS 19 at NIST around 2015, possible replacement carbonates were developed. NBS 19 may be replaced by IAEA-603 calcite or by a USGS carbonate reference material.

Fundamental dangers for solid reference materials:

- Homogeneity
- Grain size
- Safe storage in air
- Human error when handling powders

Disappointment of LSVEC as a carbon and oxygen stable isotope RM

Lithium carbonate was prepared by H. Svec at Iowa State University by bubbling ^{13}C-depleted carbon dioxide into alkaline lithium hydroxide solution and drying the precipitate. Together with NBS 19, it served as a second anchor **LSVEC** along the carbon VPDB scale until 2016 when it was recognized that LSVEC absorbs CO_2 from the atmosphere upon the repeated opening of vials. LSVEC has been replaced by USGS44 high purity $CaCO_3$.



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Home > Reference Products > Reference Material Online Catalog > Stable Isotopes > Materials with known ^{13}C, ^{18}O and ^{7}Li isotopic composition > LSVEC

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- ALMERA
- Nuclear Instrumentation

LSVEC , Lithium Carbonate

Inorganic , Mineral

- Unit Size: 0.5 g
- Price per Unit: 150 EUR
- Date of Release: 2018-06-27
- Reference Sheet: Reference Sheet LSVEC
- Contact point: NAEL-Reference-Materials.Contact-Point@iaea.org

The reference material LSVEC is intended for calibration of lithium stable isotope measurements [1, 2] performed by thermal ionisation mass-spectrometry and ICP-MS.

Analyte	Value	Unit	SD	R/I/C
$\delta^{7}Li$	0	‰	n/a	C
$^{7}Li/^{6}Li$	0.08215	$^{7}Li/^{6}Li$	0.00023	R

(R/I/C) Classification assigned to the property value for analyte (Recommended/Information/Certified)

References:

1. 1. Qi, H.P., et al. (1997) Calibrated measurements of the isotopic composition and atomic weight of the natural Li isotopic reference material IRMM-016. International Journal of Mass Spectrometry,. 171(1-3): p. 263-268. https://doi.org/10.1016/S0168-1176(97)00125-0
2. 2. Brand, W.A., et al. (2014) Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). Pure and Applied Chemistry. 86(3): p. 425-467. https://doi.org/10.1515/pac-2013-1023

LSVEC
Lithium Carbonate, 0.5g
€150/Unit
Quantity:
Add to Basket

My Shopping Cart
Total €0
Go to Shopping Cart

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LSVEC is still being distributed, but **only as a lithium stable isotope RM**.

Major resource with useful references by IUPAC (*International Union of Pure and Applied Chemistry*):

- History of RMs dating back to the 1950s
- Delta notation (δ)
- Primary and secondary isotopic RMs (as of 2014)
- Identical Treatment Principle

DE GRUYTER DOI 10.1515/pac-2013-1023 — Pure Appl. Chem. 2014; 86(3): 425–467

IUPAC Technical Report

Willi A. Brand*, Tyler B. Coplen, Jochen Vogl, Martin Rosner and Thomas Prohaska

Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report)[1]

Brand et al. (2014) https://doi.org/10.1515/pac-2013-1023

Table 2 The δ^2H values of hydrogen isotopic reference materials.[a]

Description	NIST RM #	Material	δ^2H_{VSMOW}	Uncertainty	References	Comment
VSMOW	8535	Water	**<u>0</u>**[b]	None	[34]	Quarantined[c]
SLAP	8537	Water	−428.5 ‰	0.1	[35]	Quarantined[c]
			−427.8 ‰	0.5	[36]	
			−428.8 ‰	1.3	[37]	
			−425.8 ‰	1.0	[38]	
			<u>−428 ‰</u>[b]	None	[34]	
SMOW		n/a	0	–	[39]	Scale discontinued [4]
VSMOW2		Water	**0**	0.3 ‰	[40]	
SLAP2		Water	**−427.5 ‰**	0.3 ‰	[40]	
GISP	8536	Water	**−189.7 ‰**	0.9 ‰	[41]	
GISP2		Water	−258.3 ‰	0.3 ‰	IAEA	Not yet released
NBS 1		Water	**−47.6 ‰**	n/a	[39]	Exhausted
NBS 1a		Water	**−183.3 ‰**	n/a	[39]	Exhausted
USGS45		Water	−10.3 ‰	0.4 ‰	[42]	
USGS46		Water	−235.8 ‰	0.7 ‰	[43]	
USGS47		Water	−150.2 ‰	0.5 ‰	[44]	
USGS48		Water	−2.0 ‰	0.4 ‰	[45]	
NBS 22	8539	Oil	−119.2 ‰	0.7 ‰	[46]	
			−116.9 ‰	0.8 ‰	[47]	
NBS 30	8538	Biotite	−65.7 ‰	0.3 ‰	[41]	
NGS1	8559	Natural gas (coal origin)	−138 ‰ (CH_4)	~5 ‰	[48]	Exhausted
NGS2	8560	Natural gas (petroleum origin)	−173 ‰ (CH_4)	~2.5 ‰	[48]	Exhausted
NGS2	8560	Natural gas (petroleum origin)	−121 ‰ (C_2H_6)	~7 ‰	[48]	Exhausted
NGS3	8561	Natural gas (biogenic)	−176 ‰ (CH_4)	~1 ‰	[48]	Exhausted
IAEA-CH-7	8540	Polyethylene foil	**−100.3 ‰**	2.0 ‰	[41]	
USGS42		Human hair (Tibetan)	**−78.5 ‰**	2.3 ‰	[49, 50]	
USGS43		Human hair (Indian)	**−50.3 ‰**	2.8 ‰	[49, 50]	

[a]Values for hydrogen isotope deltas are supplied with one place after the decimal point. They are listed in chronological order of the cited literature. In the case of multiple entries, values recommended by the Commission of Isotopic Abundances and Atomic Weights (CIAAW) are listed in bold font; those defining a scale are underlined in bold font. The latter have no associated uncertainty (by definition).
[b]Exact values defining the $\delta^2H_{VSMOW\text{-}SLAP}$ scale. Please note that both scale-defining materials, VSMOW for the scale origin and SLAP for the scale span, are given without uncertainty. These are fixed consensus values. They cannot be changed without changing the scale as well.
[c]Still available from the Reston Stable Isotope Laboratory of the U.S. Geological Survey.

Primary RMs

Secondary RMs

Brand *et al.* (2014) https://doi.org/10.1515/pac-2013-1023

Shop around to get the best deal…

No single supplier has all RMs available. Some suppliers may be cheaper than others. First obtain an overview on all available RMs and then select those that are useful and affordable for your needs.

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NBS22 Oil
(Carbon and Hydrogen Isotopes in Oil)

NBS22 Oil
(Carbon and Hydrogen Isotopes in Oil)

SKU: 8539
Availability: Available for Purchase

Price: $502.00

NIST:

$502 for 1 mL

NBS 22,
ca. 1965

IAEA: €150 for 1 mL

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NBS22

Oil

Organic | 2H and 13C

- Unit Size: 1 ml
- Price per Unit: 150 EUR
- Report: n.a.
- Date of Release: 9/1/1983
- Reference Sheet: download (pdf)
- Contact point: NA-EL.Reference-Materials.Contact-Point@iaea.org

NBS 22
Oil, 1ml
€150/Unit

Quantity:

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USGS
science for a changing world

United States Geological Survey

Reston Stable Isotope Laboratory

Report of Stable Isotopic Composition

Reference Materials NBS 22a and USGS78

(Hydrogen and Carbon Isotopes in Vacuum Pump Oils)

NBS 22a	Vacuum oil, regular	1 mL	$250	δ^2H = −120.4 ‰ $\delta^{13}C$ = −29.72 ‰

$250 for 1 mL

reliable, new material!

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Nitrogen and Oxygen Isotopes in Nitrate (USGS35)

Nitrogen and Oxygen Isotopes in Nitrate (USGS35)

SKU: 8569
Availability: Available for Purchase

Price: $560.00

Please login to add to cart

$560 for 0.9 g

USGS
science for a changing world

United States Geological Survey
Reston Stable Isotope Laboratory

Report of Stable Isotopic Composition

Reference Materials USGS32, USGS34, and USGS35

(Nitrogen and Oxygen Isotopes in Nitrate)

$344 for 0.3 g

USGS35	Sodium nitrate	0.3 g	$344	$\delta^{15}N$ = +2.7 ‰ $\delta^{18}O$ = ~ +57 ‰

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IAEA-CH-7

Polyethylene

Synthetic organic polymer | 2H and 13C

- Unit Size: 3.6 g
- Price per Unit: 150 EUR
- Report: n.a.
- Date of Release: 4/1/1987
- Reference Sheet: download (pdf)
- Contact point: NA-EL.Reference-Materials.Contact-Point@iaea.org

$150 for 3.6 g

IAEA-CH-7
Polyethylene, 3.6g
€150/Unit

Quantity:

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$502 for 3.5 g

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IAEA-CH-7 (Carbon and Hydrogen Isotopes in Polyethylene Foil)

SKU: 8540
Availability: Available for Purchase

Price: $502.00

CIAAW

CIAAW COMMISSION ON ISOTOPIC ABUNDANCES AND ATOMIC WEIGHTS — INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

http://ciaaw.org/reference-materials.htm

NOT a supplier, but offers detailed information on RM isotope ratios; no complete listing, some outdated info

Distributor of RMs	Web portal or contact	Comments	RM categories
AirLiquide (international)	http://isotope.airliquide-expertisecenter.com/	Gases like CO_2 and SO_2 from cylinders can only serve as monitoring gases in on-line applications	Air, trace gases in air, CO, CO_2, SO_2, NO_x, SF_6, hydrocarbons
ANSTO (Australia)	tde@ansto.gov.au	NDF-PE77 "fishing line" is isotopically indistinguishable from USGS77 powder and can be cut to customized size and weight	Polyethylene line NDF-PE77
Elemental Microanalysis (United Kingdom)	http://www.elementalmicroanalysis.com/product_list.php?top=IRMS%20supplement&category=204&sub=Certified	Insufficient information about isotopic calibration. Website suggests single-point isotopic calibrations against other RMs (viewed 21 March 2023)	waters, carbonate, gelatin, sediment, soil, protein, flours, wood powder, urea
ERM®, European Reference Materials (Belgium)	https://crm.jrc.ec.europa.eu/c/By-application-field/Stable-isotopes/40476/	ERM® and IRMM RMs are identical and available from various vendors	Inorganic RMs, sulfur
IAEA, International Atomic Energy Agency (Austria)	https://nucleus.iaea.org/sites/ReferenceMaterials/Pages/Stable-Isotopes.aspx	Not in compliance with IUPAC (21 March 2023)	Many inorganic RMs, including waters. Few organic RMs

Distributor of RMs	Web portal or contact	Comments	RM categories
Indiana University, Department of Earth and Atmospheric Sciences (USA)	https://hcnisotopes.earth.indiana.edu/reference-materials/index.html	e.g., Schimmelmann et al., 2020, *J. Agricult. Food Chem.* **68** (39), 10852-10864. https://doi.org/10.1021/acs.jafc.0c02610	Organic RMs (gases, liquids, solids, GC-IRMS mixtures)
IRMM, Institute for Reference Materials and Measurements (Belgium)	https://crm.jrc.ec.europa.eu/c/By-application-field/Stable-isotopes/40476/	RMs from ERM® and IRMM are identical and available from various vendors	Inorganic RMs, sulfur
Airgas (formerly Isometric Instruments) (Canada)	https://www.airgas.com/stable-isotopes/form	Website offers insufficient documentation of isotopic characterisation (13 September 2018)	ALPHAGAZ™ stable isotope gases N_2, CO_2, O_2, H_2. Methane in air
NIST, National Institute of Standards and Technology (USA)	https://tsapps.nist.gov/srmext/tables/104.10.pdf	Not in compliance with IUPAC (21 March 2023)	Mostly inorganic, few organic RMs
NMI, National Measurement Institute (Australia)	chemref@measurement.gov.au; available only for WADA-accredited forensic laboratories	Tobias and Brenna, 2018, *Drug Testing and Analysis* **10** (4), 781-785 https://doi.org/10.1002/dta.2309	Steroids for carbon stable isotope ratios only
Sercon Limited, Crewe (UK)	https://sercon-instruments.com/csw/standards/standards-search/	Not in compliance with IUPAC (21 March 2023)	Pure gases N_2, CO_2, O_2, H_2, CH_4, SO_2, H_2S, SF_6. Many organic RMs.
More…			

Distributor of RMs	Web portal or contact	Comments	RM categories
SHOKO Science (Japan)	https://www.shoko-sc.co.jp/products/stable_isotope/reagent/standard/index.html	RMs partially co-developed with JAMSTEC and Indiana University; the website is in Japanese only. Contacts: info@shoko-sc.co.jp takeshi-tokai@shoko.co.jp h-satake@shoko.co.jp	Amino acids (see screenshots at bottom of this page) and some waters
USGS, United States Geological Survey, Reston, Virginia (USA)	https://www.usgs.gov/labs/reston-stable-isotope-laboratory/reference-materials-and-calibration-services	Up-to-date isotope data on website; waters available in crimp-sealed silver capillary segments Also available: LIMS for stable isotope laboratories https://isotopes.usgs.gov/research/topics/lims.html	Wide variety of organic and organic RMs
USGS, United States Geological Survey, Denver, Colorado (USA)	https://energy.usgs.gov/GeochemistryGeophysics/GeochemistryLaboratories/GasStandards.aspx	Dai et al., 2012, *Chemical Geology* **310-311**, 49-55. https://doi.org/10.1016/j.chemgeo.2012.03.008	Natural gas RMs of different geological origins (coal-related, biogas, oil-related)

Amino acids from SHOKO:

Materials	Product No.	Lot	δ13C vsVPDB(‰)	δ15N vsAir(‰)
L-Histidine	AZ1Z0	M6M9675	-11.4	-7.60
L-Histidine	AZ1Z0	M5P8062	-10.7	-7.60
L-Alanine	AZ1Z0	M5R9452	-19.9	-1.20
L-Alanine	AZ1Z0	M8A0384	-18.5	-1.02
Glycine	AZ300	M9R2283	-32.3	1.12
L-Alanine	AZ100	M6H8119	-19.6	1.54
L-Alanine	AZ100	M9R2064	-19.9	1.79
L-Alanine	AZ100	SS05	-19.6	3.70
L-Alanine	AZ100	M6R397405	-19.6	5.00
L-Alanine	AZ100	SS09	-19.6	8.70
L-Alanine	AZ101	M6R397410	-19.6	10.1
L-Alanine	AZ101	SS13	-19.6	13.7
L-Alanine	AZ101	SS16	-19.6	16.1
L-Alanine	AZ102	M0H912820	-19.9	20.6
L-Alanine	AZ102	SS25	-19.6	26.1

Selling Unit: 1g

Materials	Product No.	Lot	δ13C vsVPDB(‰)	δ15N vsAir(‰)
L-Aspartic Acid	AZ203	M1B6432N35	-23.9	35.4
L-Glutamic Acid	AZ104	M1E7683N45	-13.8	45.6
L-Alanine	AZ104-01	M0R3337N40	-17.9	43.3
Phenylalanine	AZ100-01	M0N1811NA	-11.2	1.70
Glycine	AZ3Z2CN	CN-01	-32.4	-25.9
L-Methionine	AZ2Z0	D00129520	-29.3	-3.87
L-Leucine	AZ200	LAH0629	-28.3	5.57
L-(+)-Norleucine	AZ201	LAM3141mix	-28.7	18.2
L-Hydroxyproline	AZ1Z0	LAM3262	-12.5	-9.08
Amino Acid Set 9**	ACZ1Z2NZ204SET	(3nmol N)		

**; Asp,Glu,Ala,Phe,Gly,Met,Leu,Ile,Hyp Set

Selling Unit:100mg

Reference Materials and Calibration Services

By Reston Stable Isotope Laboratory (RSIL)

Prices for Isotopic Reference Materials and Calibration Services

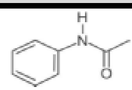
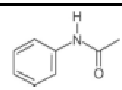
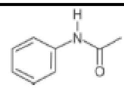
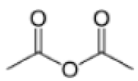
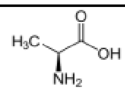
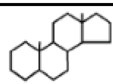
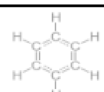
Click on ID Number to access the Report of Isotopic Composition.
Last updated: May 3, 2022.

Reference Number and Report of Isotopic Composition	Description of Material	Amount	Price	Isotope Values
USGS24	Graphite	0.8 g	\$158	$\delta^{13}C$ = —16.05 ‰
USGS25	Ammonium sulfate	> 0.6 g	\$297	$\delta^{15}N$ = —30.41 ‰
USGS26	Ammonium sulfate	> 0.8 g	\$297	$\delta^{15}N$ = +53.75 ‰
USGS32	Potassium nitrate	0.3 g	\$344	$\delta^{15}N$ = +180 ‰ $\delta^{18}O$ = ~ +25.5 ‰
USGS34	Potassium nitrate	0.3 g	\$344	$\delta^{15}N$ = —1.8 ‰ $\delta^{18}O$ = ~ —28 ‰
USGS35	Sodium nitrate	0.3 g	\$344	$\delta^{15}N$ = +2.7 ‰ $\delta^{18}O$ = ~ +57 ‰

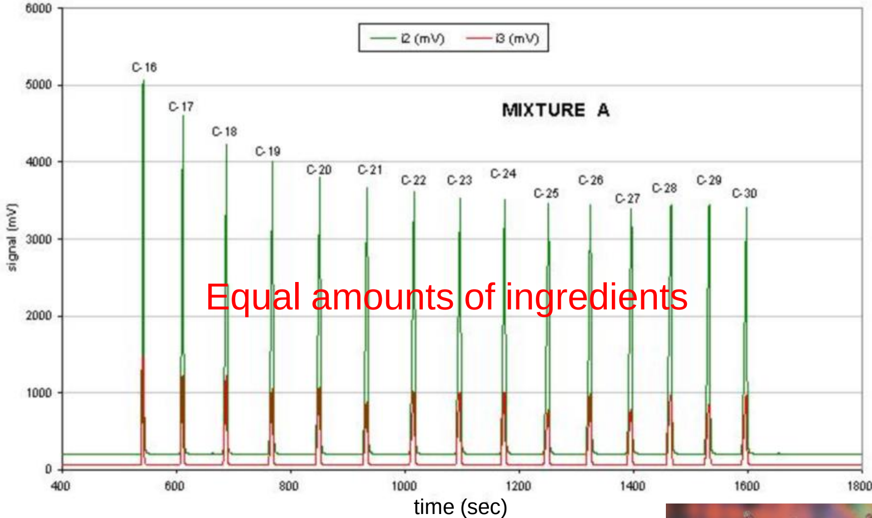
Indiana University offers a large variety of organic RMs

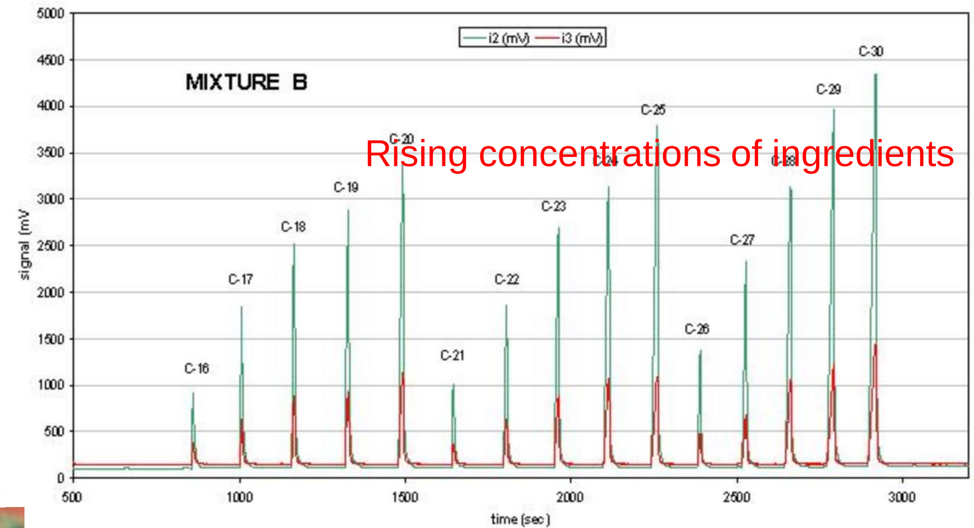
https://hcnisotopes.earth.indiana.edu/doc/alphabetical-list-of-all-reference-materials.pdf

https://hcnisotopes.earth.indiana.edu/reference-materials/index.html

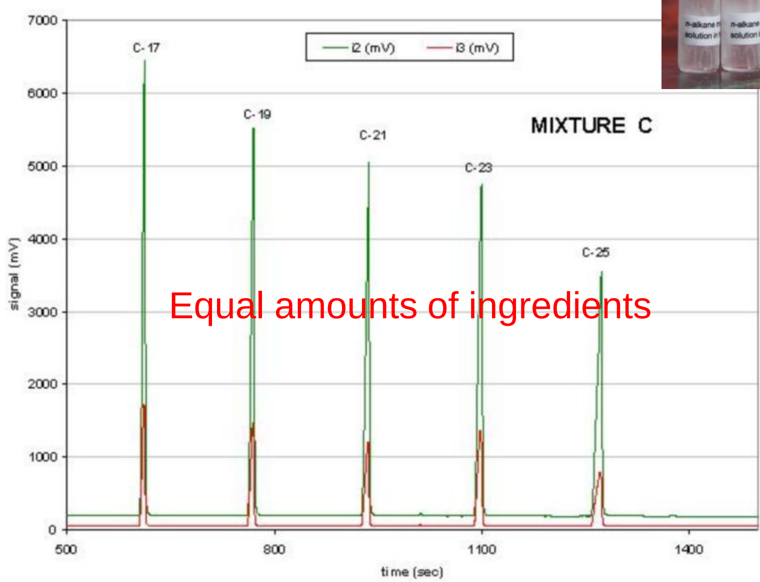
Version 27 May 2021 **Alphabetic listing of compounds** formula, CAS #, purity, amount, type of packaging, price in US $	**Structure or comment**	δ^2H (mean value in ‰ vs. VSMOW, ± 1σ) (range) (# of measurements)	δ^{13}C (mean value in ‰ vs. VPDB, ± 1σ) (range) (# of measurements)	δ^{15}N (mean value in ‰ vs. AIR, ± 1σ) (range) (# of measurements)	δ^{18}O and δ^{34}S (mean values in ‰ vs. VSMOW or VCDT, ± 1σ) (range) (# of measurements)
Acetanilide #1, C_8H_9NO, CAS # 103-84-4, in glass vial, 5 g US $250, 2 g US $150		not determined (contains exchangeable hydrogen)	**-29.53** ± 0.01 ‰ from -29.51 to -29.54 ‰ n = 6	**+1.18** ± 0.02 ‰ from +1.16 to +1.21 ‰ n = 4	not determined
Acetanilide #2, C_8H_9NO, CAS # 103-84-4, in glass vial, 2 g US $250		not determined (contains exchangeable hydrogen)	**-29.50** ± 0.02 ‰ from -29.48 to -29.53 ‰ n = 4	**+19.56** ± 0.03 ‰ from +19.53 to +19.60 ‰ n = 7	not determined
Acetanilide #3, C_8H_9NO, CAS # 103-84-4, in glass vial, 2 g US $250		not determined (contains exchangeable hydrogen)	**-29.50** ± 0.02 ‰ from -29.49 to -29.52 ‰ n = 4	**+40.57** ± 0.06 ‰ from +40.52 to +40.66 ‰ n = 6	not determined
Acetic anhydride, $C_4H_6O_3$, CAS # 108-24-7, 99.5 %, ca. 1 mL sealed under argon in glass ampoule, US $250.		**-133.2** ± 2.1 ‰ from -131.5 to -136.0 ‰ n = 4	**-20.98** ± 0.03 ‰ from -20.94 to -21.01 ‰ n = 4	not applicable	not determined
L-Alanine, $C_3H_7NO_2$, CAS # 56-41-7, produced by SI Science in Japan, 100 mg in crimp-sealed glass vial, US $250		not determined (contains exchangeable hydrogen)	**-17.93** ± 0.02 ‰ from -17.90 to -17.96 ‰ n = 5	**+43.25** ± 0.07 ‰ from +43.16 to +43.34 ‰ n = 4	not determined
5α-Androstane #3, $C_{19}H_{32}$, CAS # 438-22-2, at least 5 mg in crimp-sealed glass vial, US $250		**-293.2** ± 1.0 ‰ from -292.0 to -294.6 ‰ n = 6	**-31.35** ± 0.01 ‰ from -31.34 to -31.37 ‰ n = 5	not applicable	not applicable
Benzene #1, C_6H_6, CAS # 71-43-2, 99.8 %, 0.5 mL sealed under argon in glass ampoule, US $250		-62.4 ± 1.1 ‰ from -60.9 to -63.7 ‰ n = 5	-27.68 ± 0.01 ‰ from -27.67 to -27.69 ‰ n = 4	not applicable	not applicable

Compound-specific hydrogen and carbon stable isotope RM mixtures in hexane available from Indiana University

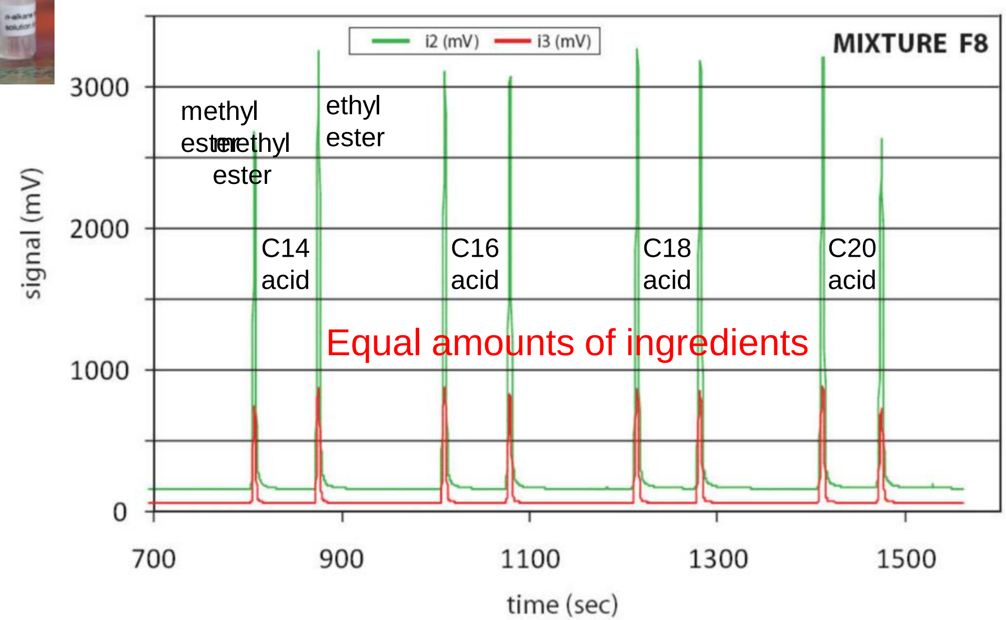




Pure *n*-alkanes
dissolved in hexane



Pure *n*-alkanoic acid esters dissolved in hexane



How are RMs made and why are they expensive?

International RMs are typically produced by experienced laboratories by, or in collaboration with international or governmental agencies. Ring-testing by groups of qualified laboratories enhances trustworthiness. The overall cost of developing a single RM often exceeds € 20,000.
Purchasing an RM is not like buying a chemical. You invest in quality assurance.

19 organic RMs USGS61 to USGS78 and NBS 22a

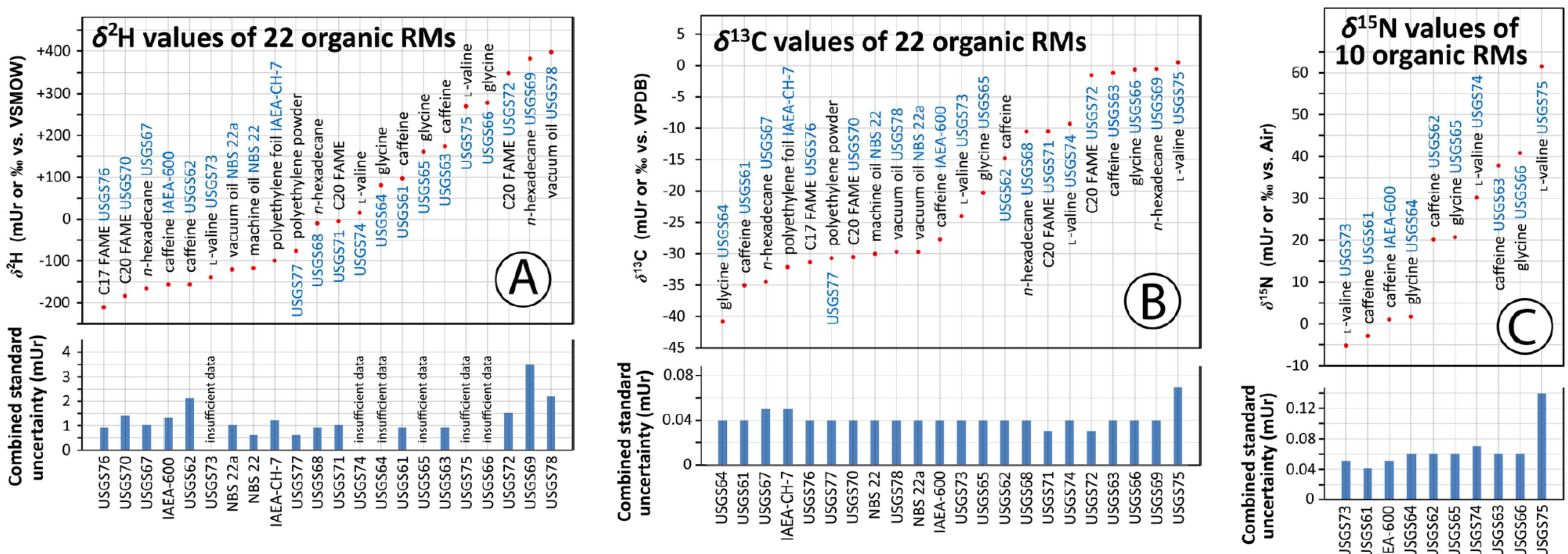
analytical chemistry

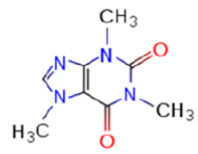
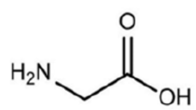
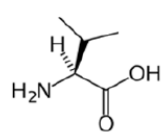
DOI: 10.1021/acs.analchem.5b04392
Anal. Chem. 2016, 88, 4294−4302

Article

pubs.acs.org/ac

Organic Reference Materials for Hydrogen, Carbon, and Nitrogen Stable Isotope-Ratio Measurements: Caffeines, *n*-Alkanes, Fatty Acid Methyl Esters, Glycines, L-Valines, Polyethylenes, and Oils

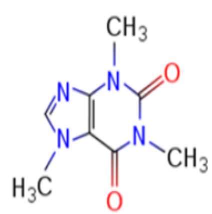


Reference ID	Chemical name	Structure or composition of material	Ring-test reference values with combined standard uncertainties (mUr or ‰) $\delta^{2}H_{VSMOW\text{-}SLAP}$	$\delta^{13}C_{VPDB\text{-}LSVEC}$	$\delta^{15}N_{Air}$
USGS61	caffeine		+96.9 ± 0.9	–35.05 ± 0.04	–2.87 ± 0.04
USGS62	caffeine		–156.1 ± 2.1	–14.79 ± 0.04	+20.17 ± 0.06
USGS63	caffeine		+174.5 ± 0.9	–1.17 ± 0.04	+37.83 ± 0.06
IAEA-600*	caffeine		–156.1 ± 1.3	–27.73 ± 0.04	+1.02 ± 0.05
USGS64	glycine		*no values indicated due to the presence of exchangeable hydrogen*	–40.81 ± 0.04	+1.76 ± 0.06
USGS65	glycine			–20.29 ± 0.04	+20.68 ± 0.06
USGS66	glycine			–0.67 ± 0.04	+40.83 ± 0.06
USGS67	*n*-hexadecane	$C_{16}H_{34}$	–166.2 ± 1.0	–34.50 ± 0.05	n.a.
USGS68	*n*-hexadecane		–10.2 ± 0.9	–10.55 ± 0.04	n.a.
USGS69	*n*-hexadecane		+381.4 ± 3.5	-0.57 ± 0.04	n.a.
USGS70	icosanoic acid methyl ester (C_{20} FAME)	$C_{20}H_{39}OOCH_3$	–183.9 ± 1.4	–30.53 ± 0.04	n.a.
USGS71	icosanoic acid methyl ester (C_{20} FAME)		–4.9 ± 1.0	–10.50 ± 0.03	n.a.
USGS72	icosanoic acid methyl ester (C_{20} FAME)		+348.3 ± 1.5	–1.54 ± 0.03	n.a.
USGS73	L-valine		*no values indicated due to the presence of exchangeable hydrogen*	–24.03 ± 0.04	–5.21 ± 0.05
USGS74	L-valine			–9.30 ± 0.04	+30.19 ± 0.07
USGS75	L-valine			+0.49 ± 0.07	+61.53 ± 0.14
USGS76	methylheptadecanoate (C_{17} FAME)	$C_{17}H_{33}OOCH_3$	–210.8 ± 0.9	–31.36 ± 0.04	n.a.
IAEA-CH-7*	polyethylene foil	$(C_2H_4)_n$	–99.2 ± 1.2	–32.14 ± 0.05	n.a.
USGS77	polyethylene powder (also extruded string)	$(C_2H_4)_n$	–75.9 ± 0.6	–30.71 ± 0.04	n.a.
NBS 22*	oil	n.a.	–117.2 ± 0.6	–30.02 ± 0.04	n.a.
NBS 22a	vacuum oil, regular	n.a.	–120.4 ± 1.0	–29.72 ± 0.04	n.a.
USGS78	vacuum oil, ^{2}H-enriched	n.a.	+397.0 ± 2.2	–29.72 ± 0.04	n.a.

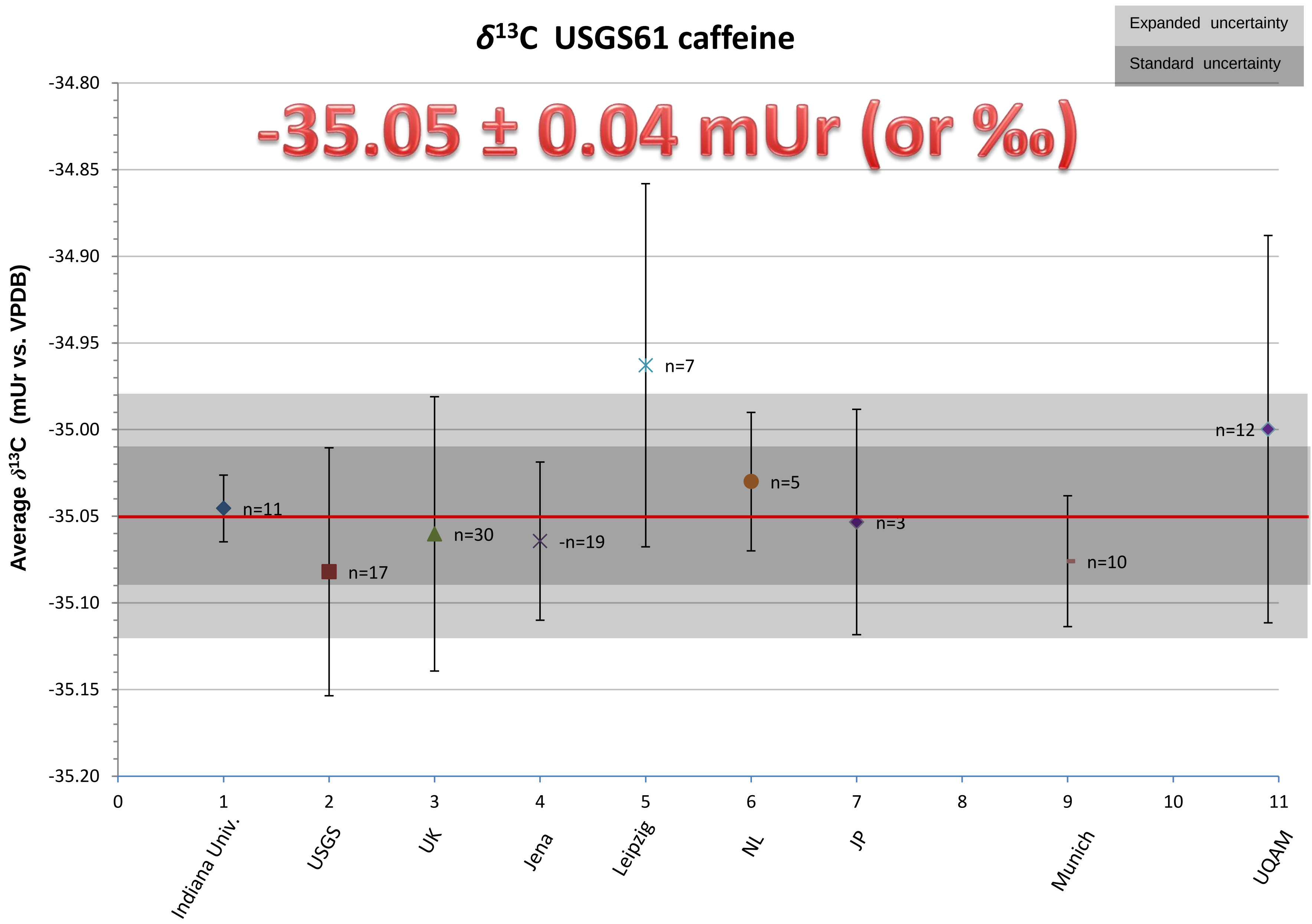
Caffeines USGS61, USGS62, USGS63

We tested and measured more than 10 batches from different suppliers. We finally chose two suppliers of the bulk raw materials plus several isotopically spiked caffeines from various suppliers, for example:

- Caffeine, 99.92 %, *Alfa-Aesar*
- Caffeine, *Coffein Compagnie Bremen*
- Caffeine 3-methyl-^{13}C, 99 atom % ^{13}C, Cambridge Isotope Laboratories, Inc.
- Caffeine 1,3-$^{15}N_2$, 99 atom % ^{15}N, Cambridge Isotope Laboratories, Inc.
- Caffeine-d3 (1-methyl-d3), 99.8 atom % ^{2}H, ICON

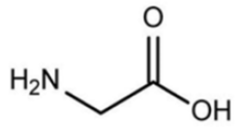
Reference ID	Chemical name	Structure or composition of material	Ring-test reference values with combined standard uncertainties (mUr or ‰)		
			$\delta^{2}H_{VSMOW-SLAP}$	$\delta^{13}C_{VPDB-LSVEC}$	$\delta^{15}N_{Air}$
USGS61	caffeine		+96.9 ± 0.9	−35.05 ± 0.04	−2.87 ± 0.04
USGS62	caffeine		−156.1 ± 2.1	−14.79 ± 0.04	+20.17 ± 0.06
USGS63	caffeine		+174.5 ± 0.9	−1.17 ± 0.04	+37.83 ± 0.06
IAEA-600*	caffeine		−156.1 ± 1.3	−27.73 ± 0.04	+1.02 ± 0.05

Distribution of USGS-caffeines:
0.5 g of powder in glass vial.


δ13C USGS61 caffeine
Expanded uncertainty
Standard uncertainty
-35.05 ± 0.04 mUr (or ‰)
Average δ13C (mUr vs. VPDB)
-34.80
-34.85
-34.90
-34.95
-35.00
-35.05
-35.10
-35.15
-35.20
n=11
n=17
n=30
-n=19
n=7
n=5
n=3
n=10
n=12
0
1
2
3
4
5
6
7
8
9
10
11
Indiana Univ.
USGS
UK
Jena
Leipzig
NL
JP
Munich
UQAM

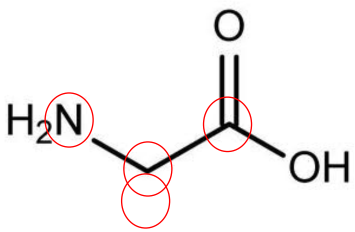
Glycines USGS64, USGS65, USGS66

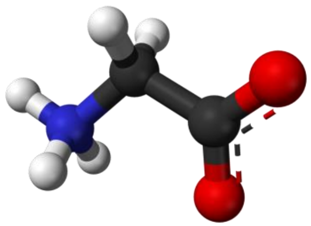
- Glycine, 99+ %,10 kg
- Isotopically spiked glycines with ^{13}C-enrichments at molecular sites 1 or 2. Our products employ ^{13}C spike ratios 1:2 in medium-enriched glycine and 2:1 in highly-enriched glycine for future use in site-specific carbon isotopic measurements. We also use 2,2-$^{2}H_2$ and ^{15}N-spiked glycines.

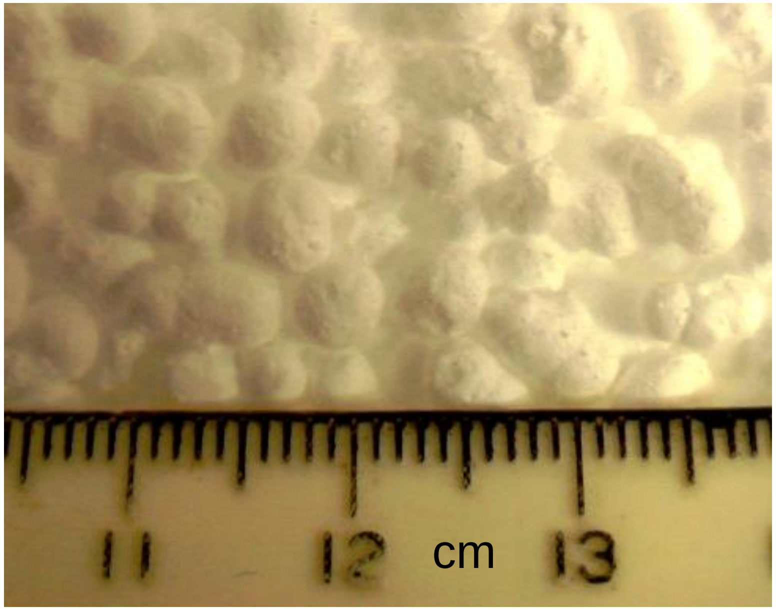
Reference ID	**Chemical name**	**Structure or composition of material**	**Ring-test reference values with combined standard uncertainties (mUr or ‰)**		
			$\delta^2H_{VSMOW-SLAP}$	$\delta^{13}C_{VPDB-LSVEC}$	$\delta^{15}N_{Air}$
USGS64	glycine		*no values indicated due to the presence of exchangeable hydrogen*	–40.81 ± 0.04	+1.76 ± 0.06
USGS65	glycine			–20.29 ± 0.04	+20.68 ± 0.06
USGS66	glycine			–0.67 ± 0.04	+40.83 ± 0.06

$C_2H_5NO_2$
odorless solid for GC, LC and EA applications.

Distribution:
0.5 g of powder in glass vial.

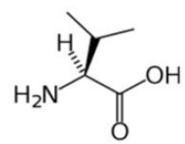






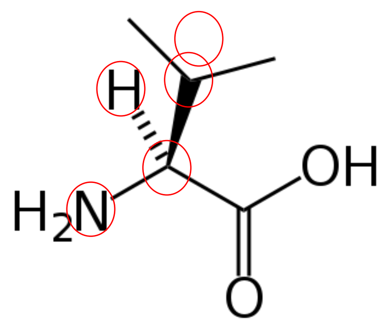
L-valines USGS73, USGS74, USGS75

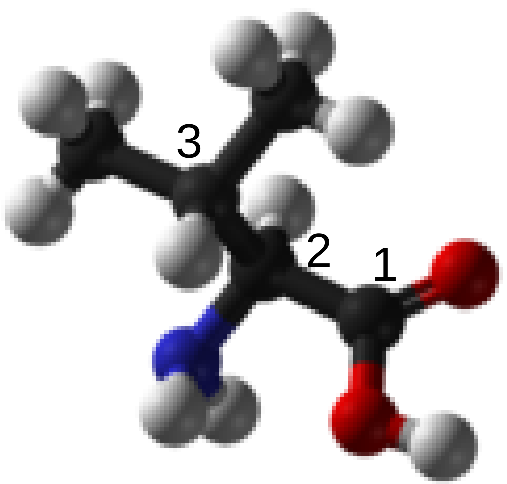
Raw materials: L-valine, 99 %, 5 kg, *Alfa Aesar;* L-valine, 4 kg, *Amino GmbH*. Site-specific ^{2}H- and ^{13}C-enrichments at different molecular sites 1, 2 and 3 are currently not measurable with high precision, but were incorporated in RMs for future use in site-specific carbon and hydrogen isotopic characterization: L-valine #2: Spike ratio 2:1 for H-molecular positions 3 and 2; spike ratio 2:1 for C-molecular positions 2 and 1. L-valine #3: Spike ratio 1:2 for H-molecular positions 3 and 2; spike ratio 1:2 for C-molecular positions 2 and 1.

Reference ID	Chemical name	Structure or composition of material	Ring-test reference values with combined standard uncertainties (mUr or ‰)		
			$\delta^{2}H_{VSMOW-SLAP}$	$\delta^{13}C_{VPDB-LSVEC}$	$\delta^{15}N_{Air}$
USGS73	L-valine		*no values indicated due to the presence of exchangeable hydrogen*	–24.03 ± 0.04	–5.21 ± 0.05
USGS74	L-valine			–9.30 ± 0.04	+30.19 ± 0.07
USGS75	L-valine			+0.49 ± 0.07	+61.53 ± 0.14

$C_2H_5NO_2$
odorless solid for GC, LC and EA applications.

Distribution:
0.5 or 0.1 g of powder in glass vial.





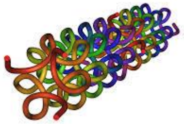
Ten food matrix reference materials USGS82 to USGS91

Honeys (carbohydrate-rich):

- honey from tropical southern Vietnam **USGS82** (fresh from wild bee hives)
- honey from prairie near Saskatoon, Canada **USGS83** (commercial product)

Vegetable oils (lipids):

- olive oil from Sicily, Italy **USGS84** (blended oil provided by Federica Camin)
- olive oil from coastal desert in Peru **USGS85** (commercial product)
- peanut oil from southern Vietnam **USGS86** (directly from rural producer)
- corn oil **USGS87** (i.e. from a C4 plant, ^{13}C-rich; commercial product from U.S.A.)

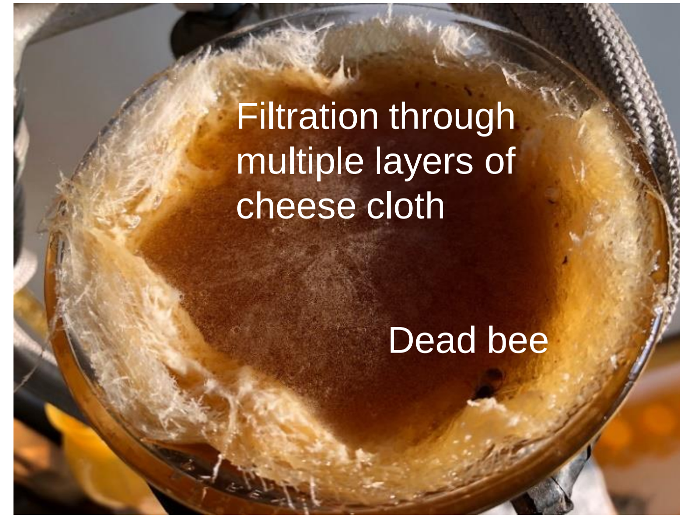


Collagens (proteinaceous):

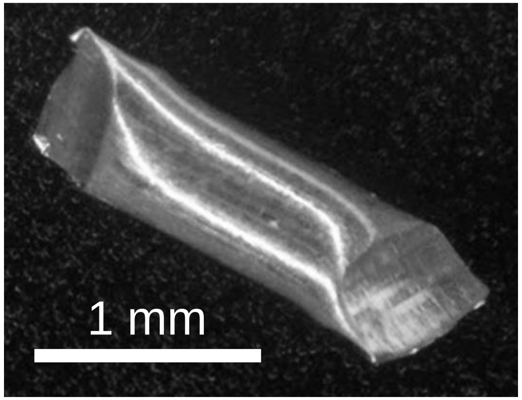
- marine collagen powder from wild-caught fish **USGS88** (commercial product)
- porcine collagen powder **USGS89** (powder, provided *via* FOA/IAEA)

Flours (carbohydrate-rich):

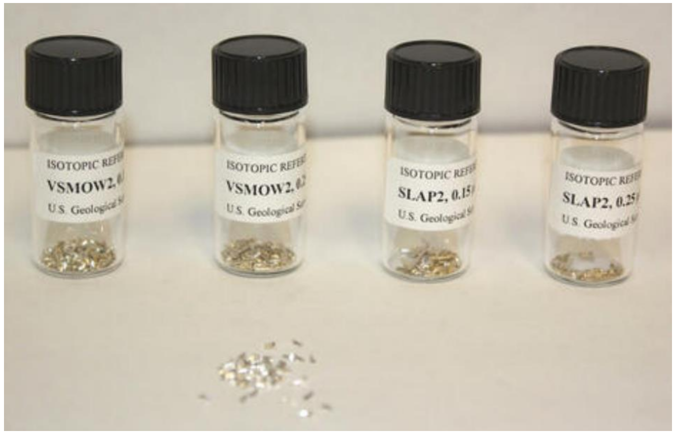
- flour from millet **USGS90** (provided by Federica Camin, from Tuscany in Italy)
- flour from rice, from southern Vietnam **USGS91** (directly from local producer)



Processing of honey



0.25-µL aliquots of waters, oils and honeys were crimp-sealed into segments of silver tubing for loading into EA carousels.

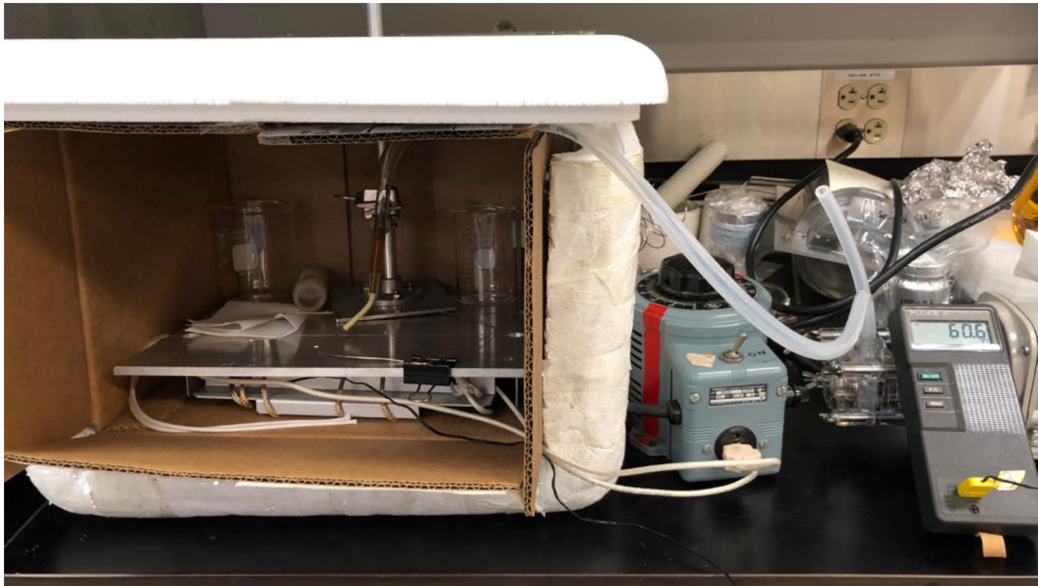


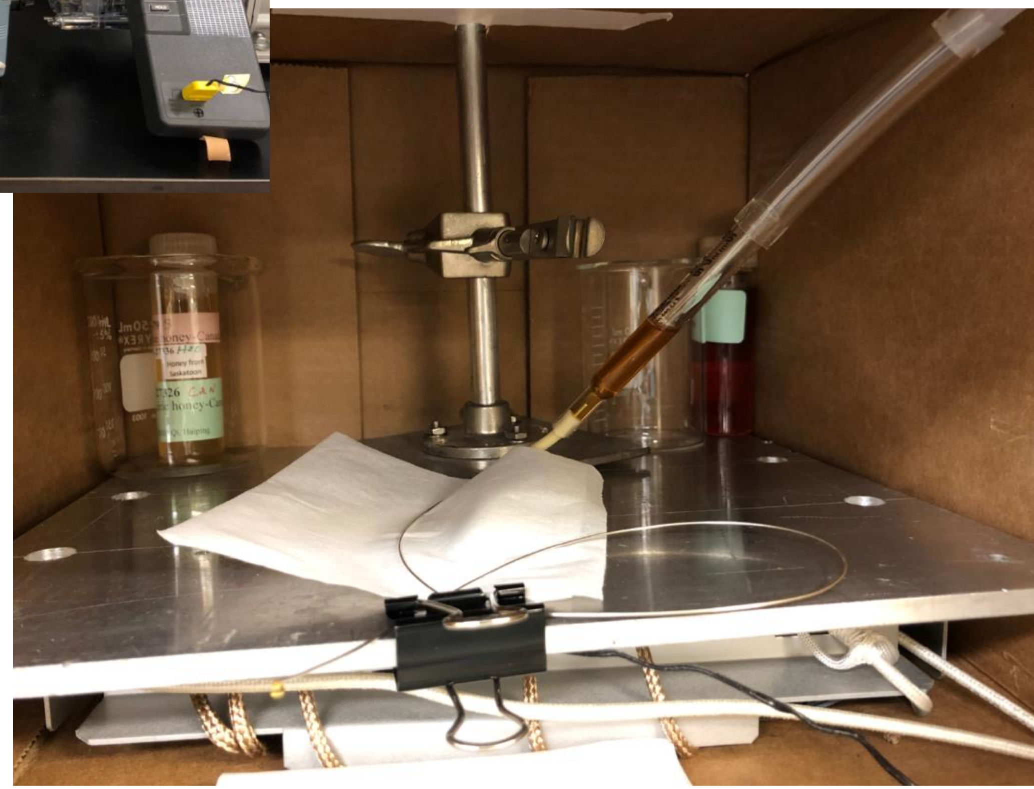
Coplen, T.B. and Qi, H. (2010) Applying the silver-tube introduction method for thermal conversion elemental analyses and a new δ^2H value for NBS 22 oil. *Rapid Communications in Mass Spectrometry* **24** (15), 2269-2276. https://10.1002/rcm.4638

Qi H, Gröning M, Coplen TB, Buck B, Mroczkowski SJ, Brand WA, Geilmann H, Gehre M (2010) Novel silver tubing method for quantitative introduction of water into high temperature conversion systems for stable hydrogen and oxygen isotopic measurements. *Rapid Communications in Mass Spectrometry* **24** (13), 1812-1827. https://doi.org/10.1002/rcm.4559

RM waters in silver tubes are available from the USGS in Reston, Virginia, USA: https://isotopes.usgs.gov/lab/referencematerials.html

Filling of silver capillary tubing with viscous honey at 60 °C





Photographs kindly provided by Dr. Haiping Qi,
U.S. Geological Survey, Reston, Virginia

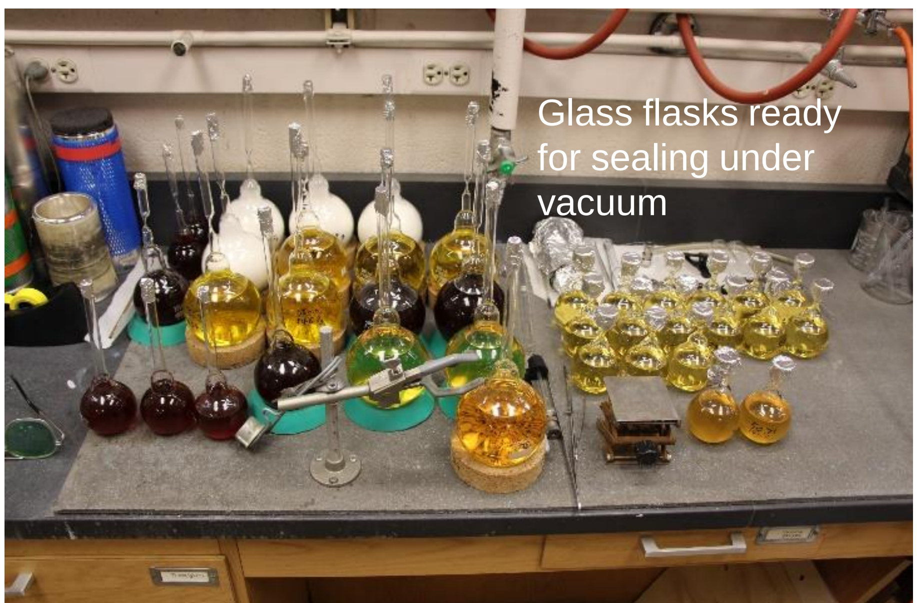

Heating neck of round-bottom borosilicate flask


Narrowing neck of round-bottom borosilicate flask

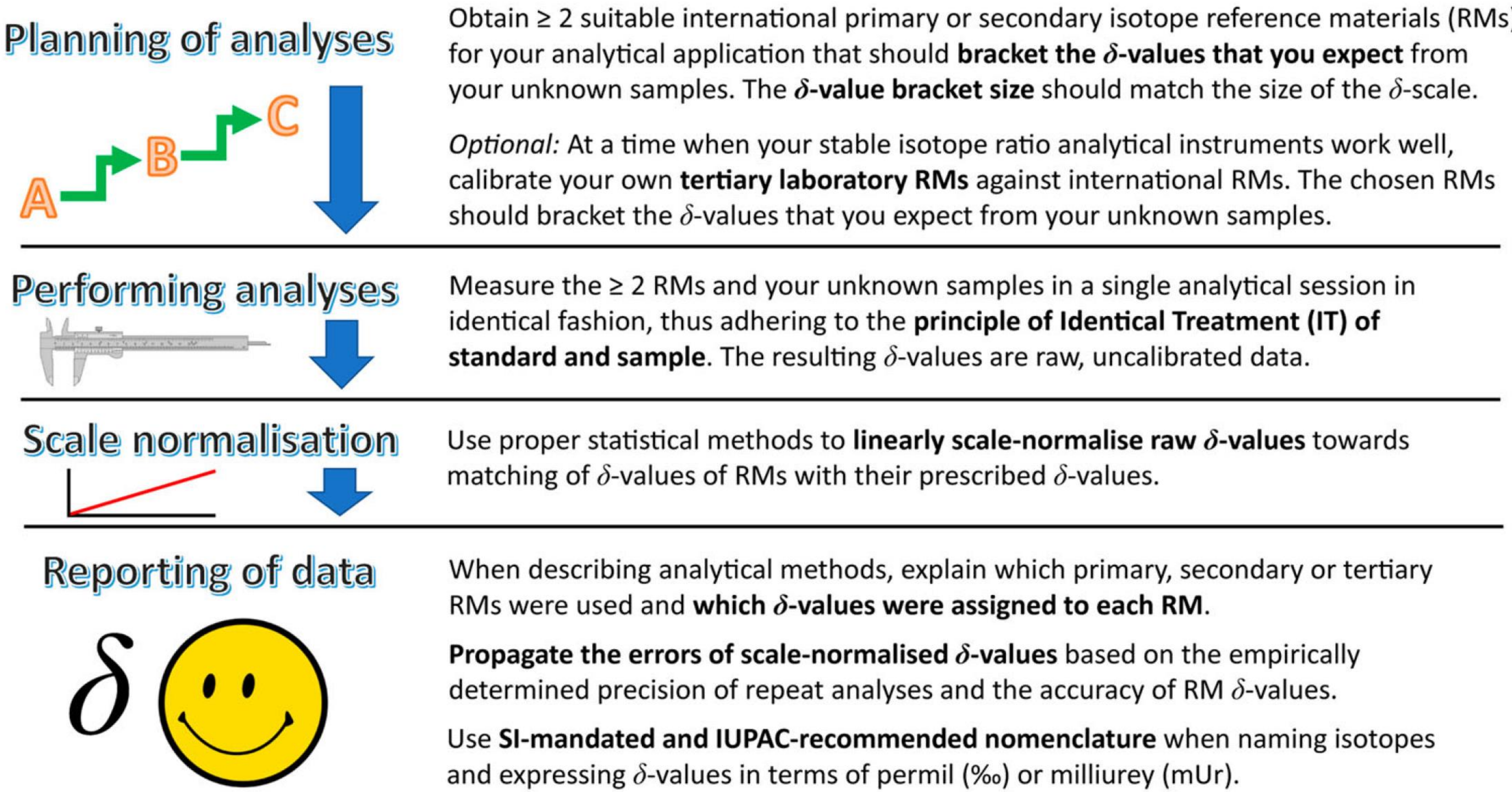

Borosilicate flask after filling with oil


Borosilicate flask with honey, sealed under vacuum


Glass ampoules with oil sealed under argon


Glass flasks ready for sealing under vacuum

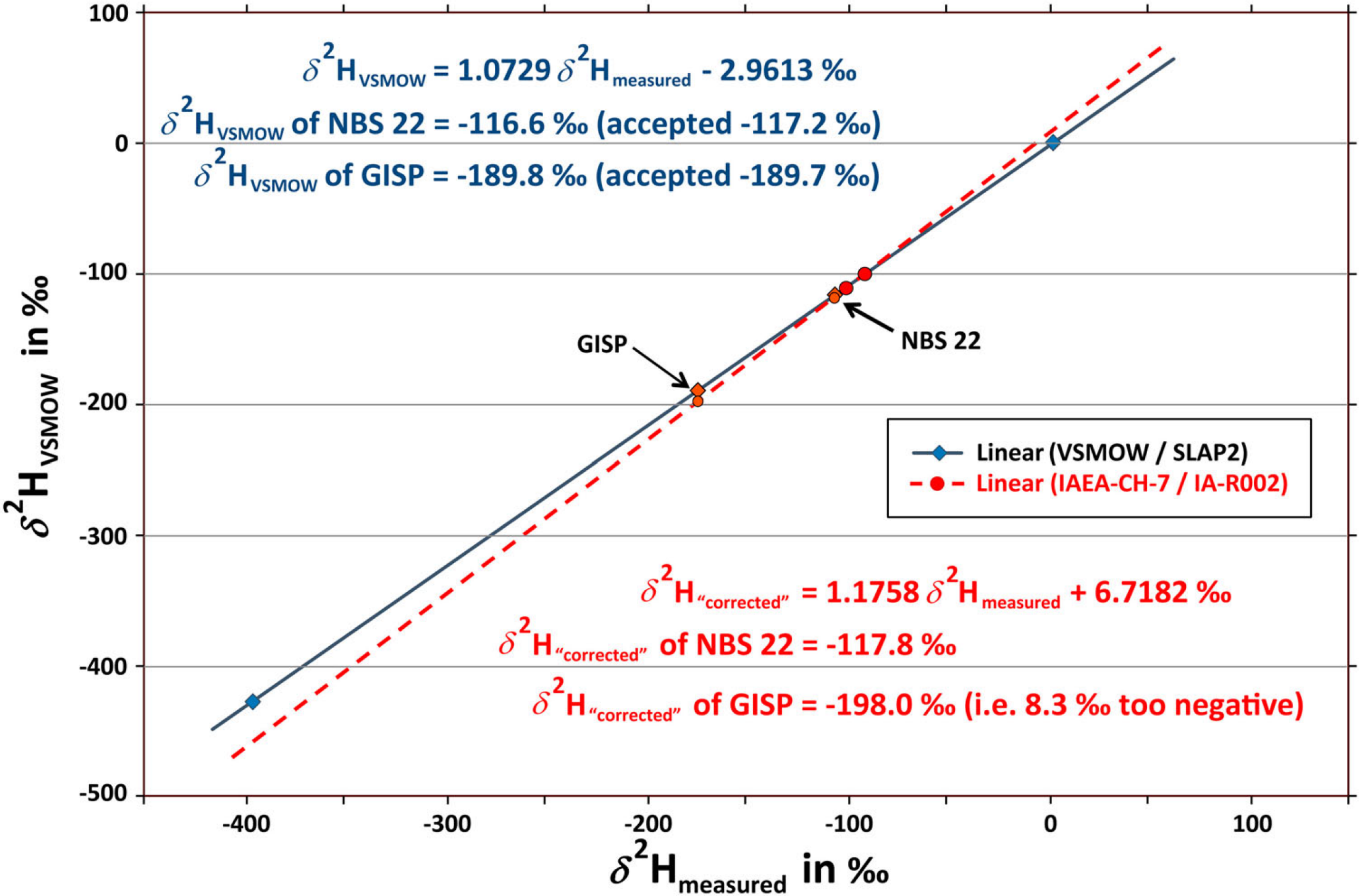

Glass flasks wrapped in foam and stored in freezer



Flowchart for isotope abundance analysis observing the identical treatment principle for both samples and RMs serving as scale anchors.

Meier-Augenstein and Schimmelmann (2019) *Isotopes in Environmental and Health Studies.* Electronic preprint: https://doi.org/10.1080/10256016.2018.1538137

Impact of RM choice as end-points for δ^2H scale normalisation on correction equation and corrected δ^2H values.



Meier-Augenstein and Schimmelmann (2019) *Isotopes in Environmental and Health Studies.* Electronic preprint: https://doi.org/10.1080/10256016.2018.1538137

Protocol

Rapid Communications in Mass Spectrometry

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(wileyonlinelibrary.com) DOI: 10.1002/rcm.5129

Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results†, ‡

Tyler B. Coplen*

U.S. Geological Survey, 431 National Center, Reston, VA 20192, USA

To minimize confusion in the expression of measurement results of stable isotope and gas-ratio measurements, recommendations based on publications of the Commission on Isotopic Abundances and Atomic Weights of the International Union of Pure and Applied Chemistry (IUPAC) are presented. Whenever feasible, entries are consistent with the Système International d'Unités, the SI (known in English as the International System of Units), and the third edition of the International Vocabulary of Basic and General Terms in Metrology (VIM, 3rd edition). The recommendations presented herein are approved by the Commission on Isotopic Abundances and Atomic Weights and are designed to clarify expression of quantities related to measurement of isotope and gas ratios to ensure that quantity equations instead of numerical value equations are used for quantity definitions. Examples of column headings consistent with quantity calculus (also called the algebra of quantities) and examples of various deprecated usages connected with the terms recommended are presented. Published in 2011 by John Wiley & Sons, Ltd.

Use spaces between numbers and all units, including % and permil:

$m = 6.4\ \mathrm{kg}$ $\delta^2\mathrm{H}_{\mathrm{VSMOW-SLAP}} = +16.4\ ‰$

$t = 14\ °\mathrm{C}$ $x(^{13}\mathrm{C}) = 1.11\ \%$

$$\delta^{18}\mathrm{O} = \left[\frac{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{P}}}{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{std}}} - 1\right] \cdot \cancel{1000}$$

The factor 1000 is an extraneous numerical factor and should be deleted from the former equation above.

All quantity symbols are printed in italic font and their superscripts and subscripts are printed in Roman upright font,[4,5] e.g. $\Delta_{\mathrm{P/Q}}$, α, x_{P}, $\varepsilon^{13}\mathrm{C}$, and $\delta^{44/42}\mathrm{Ca}_{\mathrm{standard}}$, unless superscripts or subscripts are symbols of quantities, in which case they are printed in italic font, e.g. $^{i}\mathrm{E}$.

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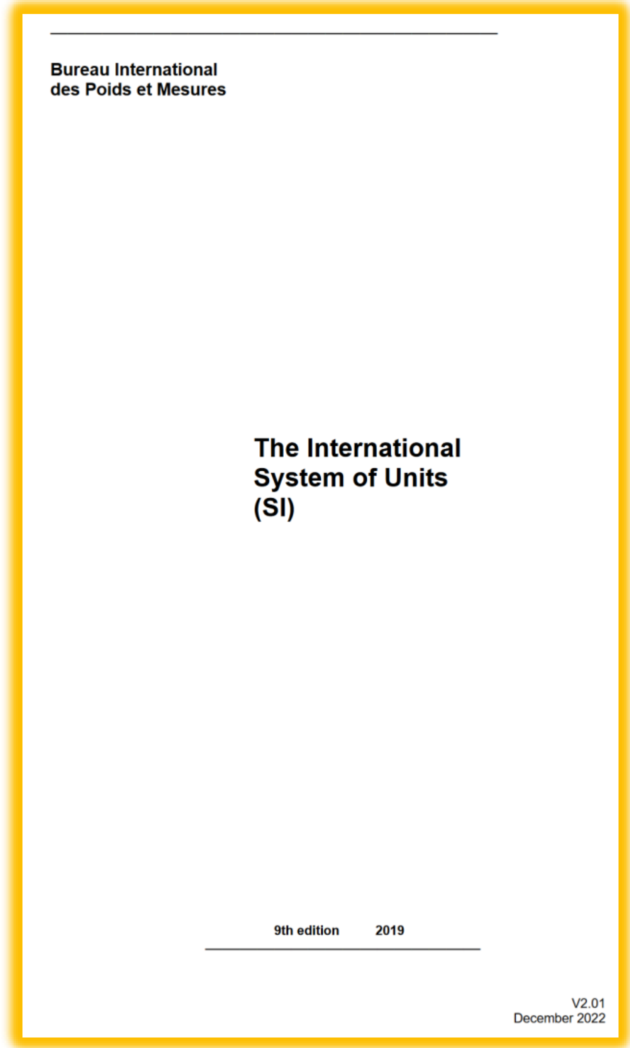
A simple SI rule states that there must be spaces between all numbers and the following SI units, including the dimensionless percent symbol (and by extension, the permil symbol). Please see the latest **SI-Brochure #9** on page 151 where the unambiguous rule is explained for %:
The internationally recognized symbol % (percent) may be used with the SI. When it is used, a space separates the number and the symbol % .

The brochure is freely available here:
https://urldefense.proofpoint.com/v2/url?u=https-3A__www.bipm.org_documents_20126_41483022_SI-2DBrochure-2D9-2DEN.pdf_2d2b50bf-2Df2b4-2D9661-2Df402-2D5f9d66e4b507&d=DwIGaQ&c=KveGjKEXiH4bMFgGs-LRbCbewnnyGW6-rJ0JK7ViA_E&r=LfV9LhyNAwLq7UZszWVAqQ0Ny4QshFsxABM0J5TqxuE&m=6HyQ6xKc5VryKI5HD4NayImvRWzw4PRmZtNnPmaOPjj1g5Rw2MfovaNIC3u5tcB-&s=fEzlsBFLm3QSTx4YxkH_EWpF75ajZA3_Hh_Ko2dyQDA&e=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IUPAC Technical Report

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Minimum requirements for publishing hydrogen, carbon, nitrogen, oxygen and sulfur stable-isotope delta results (IUPAC Technical Report)

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Abstract: Stable hydrogen, carbon, nitrogen, oxygen and sulfur (HCNOS) isotope compositions expressed as isotope-delta values are typically reported relative to international standards such as Vienna Standard Mean Ocean Water (VSMOW), Vienna Peedee belemnite (VPDB) or Vienna Cañon Diablo Troilite (VCDT). These international standards are chosen by convention and the calibration methods used to realise them in practice undergo occasional changes. To ensure longevity and reusability of published data, a comprehensive description of (1) analytical procedure, (2) traceability, (3) data processing, and (4) uncertainty evaluation is required. Following earlier International Union of Pure and Applied Chemistry documents on terminology and notations, this paper proposes minimum requirements for publishing HCNOS stable-isotope delta results. Each of the requirements are presented with illustrative examples.

1.2 Metrological traceability

Isotope-delta values for hydrogen, carbon, nitrogen, oxygen and sulfur are traceable to international standards [1, 19]. Traceability of isotope-delta values is assured by calibration of measurement results using RMs that are traceable to the international standards (a process often referred to as normalisation). Publications must list the identity of the RMs used to normalise the isotope delta results, as well as the values and uncertainties assigned to these RMs. The identity of the international standard (e.g., material with isotope-delta equal to zero) should also be stated.

1.3 Data processing

Publications should disclose how stable-isotope measurement results were normalised [7] by either providing the measurement model equation or describing the basic principles used (e.g., linear ordinary least squares regression, quadratic errors-in-variables regression or other). All other corrections applied to instrumental readings should also be stated. These include corrections for the blank, memory effects, drift, linearity/mass effects, isobaric and other interferences. Results of analyses of samples with exchangeable hydrogen or oxygen, should be accompanied by details on water equilibration with non-exchangeable RMs or comparative equilibration with matrix matched RMs [21–23].

1.4 Uncertainty evaluation

Each reported isotope-delta value needs to be accompanied by a standard uncertainty or expanded uncertainty with coverage factor and coverage probability. The procedure used to evaluate the uncertainty should be described explicitly or by citation of previous research. Simple uncertainty evaluations can be obtained from the standard deviation of a stated number of analyses of each RM, sample, or a matrix-matched QC material.

For example: The uncertainty of the reported isotope-delta values was evaluated as the standard deviation of the mean of repeated ($n = 4$) measurements of each material within a single group of analyses.

THANK YOU FOR YOUR ATTENTION

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