United States Geological Survey

Reston Stable Isotope Laboratory

Report of Stable Isotopic Composition

Reference Material USGS42

(Hydrogen and Oxygen Isotopes in Tibetan Human Hair)

This reference material (RM) is mainly intended for calibration of stable hydrogen (δ^2H) and oxygen (δ^{18}O) measurements of unknown human and mammalian hair with a TC/EA (thermal conversion/elemental analyzer) connected to an isotope-ratio mass spectrometer [1,2]. This RM consists of 0.5 g of Tibetan human hair [1,2]. There is no limit on distribution. USGS42 was prepared by the Reston Stable Isotope Laboratory (RSIL) of the U.S. Geological Survey, Reston, Virginia [1].

Recommended Values: Stable hydrogen and oxygen isotopic compositions are expressed herein as delta values [3] relative to VSMOW (Vienna Standard Mean Ocean Water) on scales normalized such that the δ^2H and δ^{18}O values of SLAP (Standard Light Antarctic Precipitation) are –428 ‰ and –55.5 ‰, respectively [4,5]. The δ^2H and δ^{18}O values, mass fractions of hydrogen and oxygen, and mole fractions of hydrogen and oxygen in USGS42 are [1,2]:

Stable hydrogen isotopic composition (non-exchangeable fraction):	$\delta^2H_{VSMOW\text{-}SLAP}$ = –72.9 ± 2.2 ‰ (n = 6)
Mass fraction of total hydrogen:	w_H = 6.2 %
Mole fraction of exchangeable hydrogen:	$x_{H\text{-}ex}$ = 8.6 ± 0.3 %
Stable oxygen isotopic composition:	$\delta^{18}O_{VSMOW\text{-}SLAP}$ = +8.56 ± 0.10 ‰ (n = 18)
Mass fraction of oxygen:	w_O = 22 %
Mole fraction of absorbed water (as O):	$x_{abs\text{-}O}$ = ~8 %

Technical coordination for this RM was provided by Haiping Qi of the U.S. Geological Survey Reston Stable Isotope Laboratory.

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Tyler B. Coplen, Director
Reston Stable Isotope Laboratory

While USGS42 is intended for δ^2H and δ^{18}O measurements, it also is suitable for measurements of the stable isotopes of carbon (δ^{13}C), nitrogen (δ^{15}N), and sulfur (δ^{34}S) in human and mammalian hair. Stable carbon isotopic compositions are expressed relative to VPDB (Vienna Peedee belemnite) on a scale normalized such that the δ^{13}C values of NBS 19 calcium carbonate and LSVEC lithium carbonate are +1.95 ‰ and –46.6 ‰, respectively [6]. Stable nitrogen isotopic compositions are expressed relative to atmospheric nitrogen, which is isotopically homogenous [7]. Stable sulfur isotopic compositions are expressed relative to VCDT (Vienna Cañon Diablo troilite) on a scale normalized such that the δ^{34}S value of IAEA-S-1 silver sulfide is –0.3 ‰ [8]. Stable carbon, nitrogen, and sulfur isotopic compositions and mole fractions of carbon, nitrogen, and sulfur of USGS42 are [1]:

Stable carbon isotopic composition:	$\delta^{13}C_{VPDB\text{-}LSVEC} = -21.09 \pm 0.10$ ‰ (n = 50)
Mass fraction of carbon:	$w_C = 45.7$ %
Stable nitrogen isotopic composition:	$\delta^{15}N_{AIR} = +8.05 \pm 0.10$ ‰ (n = 50)
Mass fraction of nitrogen:	$w_N = 15.3$ %
Stable sulfur isotopic composition:	$\delta^{34}S_{VCDT} = +7.84 \pm 0.25$ ‰ (n = 32)
Mass fraction of sulfur:	$w_S = 4.4$ %

Expiration of Reference Value: The reference values for the isotopic composition of USGS42 are valid until December 31, 2036, provided the RM is handled in accordance with the instructions given in this Report of Stable Isotopic Composition (see "Instructions for Use"). A reference value is nullified if the RM is damaged, contaminated, or otherwise modified.

Maintenance of RM Report of Stable Isotopic Composition: The U.S. Geological Survey RSIL will monitor this RM and will notify the purchaser if substantive technical changes occur that affects its isotopic composition.

Distribution and Stability: USGS42 is stable at normal room temperatures. The RSIL has monitored this RM for a period of two years, and no change in isotopic composition has been observed. To minimize the potential for contamination, it is recommended that this RM be stored in the container in which it is supplied.

Instructions for Use: Unknown hair samples and hair reference materials analyzed for both δ^2H and δ^{18}O values typically need to be equilibrated with laboratory air at ambient temperature simultaneously for at least 5 days. Unknowns and references need to be thoroughly dried before isotopic analyses [9]. To quantify drift with time and for isotope-ratio-scale contraction, it is suggested that a pair of hair reference materials with different δ^2H and δ^{18}O values should be used. Another such material is USGS43 Indian human hair. It is suggested that the mass of USGS42, other references (such as USGS43 human hair), and unknowns should be identical to minimize or cancel biases. It is also recommended that one should make the unknown sample powder size as close as possible to the size of USGS42, recognizing that in some studies the sample cannot be pulverized. Experimental studies

indicate that improved measurement results are achieved by analyzing samples for $\delta^{18}O$ measurements with a TC/EA [1,10]. The $\delta^{2}H$ values of hydrogen-bearing keratins should be measured by a chromium-filled, elemental analyzer coupled to an isotope-ratio mass spectrometer [11]. In this manner, the production of hydrogen cyanide, which can lead to non-quantitative conversion of hydrogen in samples to gaseous H_2, will be minimized and analytical results will be improved. More detailed instructions for use are given in Coplen and Qi [1,2].

Reporting of Stable-isotope-delta Values: The following recommendations are provided for reporting of stable hydrogen and oxygen isotope-delta values. It is recommended that:

- The $\delta^{2}H$ values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP on a scale where the $\delta^{2}H$ of SLAP = –428 ‰ exactly [4,5].
- The $\delta^{18}O$ values of all oxygen-bearing substances be expressed relative to VSMOW-SLAP or relative to Vienna Peedee belemnite (VPDB; for carbonates) on a scale such that $\delta^{18}O_{SLAP2}$ = –55.5 ‰ or $\delta^{18}O_{NBS19}$ = –2.2 ‰, respectively [5].
- Authors report delta values of international distributed (secondary) isotopic reference materials as though they had been interspersed among and used for normalization of unknowns, as appropriate for the measurement method. In this manner, measurement results can be adjusted in the future as analytical methods improve and consensus values of internationally distributed isotopic reference materials change. Example text is:

  > **"The $\delta^{2}H$ and $\delta^{18}O$ values of human-hair samples are reported relative to the VSMOW-SLAP scales, and on these scales the $\delta^{2}H$ and $\delta^{18}O$ values of USGS42 and USGS43 are –72.9, +8.56, –44.4, and +14.11 ‰, respectively [1, 2]."**

- Reporting of delta values relative to SMOW and PDB (Peedee belemnite) be discontinued [12].

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