Acknowledgements

This manuscript has benefited from helpful reviews by Dr. Christine France (Smithsonian Museum Conservation Institute, Suitland, Maryland, USA) and two anonymous reviewers. We thank Drs. L. I. Wassenaar (International Atomic Energy Agency), K. Hobson (Environment Canada, Saskatoon, Saskatchewan, Canada), and G. Koehler (Environment Canada, Saskatoon, Saskatchewan, Canada) for helpful discussions about isotopic analysis of keratins. The support of the U.S. Geological Survey National Research Program made this report possible. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

A revision in hydrogen isotopic composition of USGS42 and USGS43 human-hair stable isotopic reference materials for forensic science^{*}

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Abstract

The hydrogen isotopic composition ($\delta^2\text{H}_{\text{VSMOW-SLAP}}$) of USGS42 and USGS43 human hair stable isotopic reference materials, normalized to the VSMOW (Vienna-Standard Mean Ocean Water)–SLAP (Standard Light Antarctic Precipitation) scale, was originally determined with a high temperature conversion technique using an elemental analyzer (TC/EA) with a glassy carbon tube and glassy carbon filling and analysis by isotope-ratio mass spectrometer (IRMS). However, the TC/EA IRMS method can produce inaccurate $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ results when analyzing nitrogen-bearing organic substances owing to the formation of hydrogen cyanide (HCN), leading to non-quantitative conversion of a sample into molecular hydrogen (H_2) for IRMS analysis. A single-oven, chromium-filled, elemental analyzer (Cr-EA) coupled to an IRMS substantially improves the measurement quality and reliability of hydrogen isotopic analysis of hydrogen- and nitrogen-bearing organic material because hot chromium scavenges all reactive elements except hydrogen. USGS42 and USGS43 human hair isotopic reference materials have been analyzed with the Cr-EA IRMS method, and the $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ values of their non-exchangeable hydrogen fractions have been revised:

USGS42 (Tibetan Hair) $\delta^2\text{H}_{\text{VSMOW-SLAP}} = -72.9 \pm 2.2 \text{ ‰}$ ($n = 6$)

USGS43 (Indian Hair) $\delta^2\text{H}_{\text{VSMOW-SLAP}} = -44.4 \pm 2.0 \text{ ‰}$ ($n = 6$)

On average, these revised $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ values are 5.7 ‰ more positive than those previously measured. It is critical that readers pay attention to the $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ of isotopic reference materials in publications as they may need to adjust the $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ measurement results of human hair in previous publications to ensure all results are on the same isotope-delta scale.

Keywords: hydrogen isotopes, keratin

1. Introduction

Human hair can provide a history of geographical movements of humans [1–5] because the isotopic composition of water ingested by humans varies geographically and the stable hydrogen ($\delta^2\text{H}_{\text{VSMOW-SLAP}}$) and oxygen isotopic compositions of human hair reflect this geographic variation in favorable cases. However, the measurement of accurate isotopic compositions of

human hair, as well as other keratin materials, is complicated by the fact that human hair has exchangeable hydrogen [6–9]. To normalize human hair stable hydrogen- and oxygen-isotope measurements to the VSMOW (Vienna-Standard Mean Ocean Water)–SLAP (Standard Light Antarctic Precipitation) scales [10], it is convenient to utilize human hair isotopic reference materials having different hydrogen and oxygen isotopic compositions. Because there were no internationally distributed stable hydrogen and oxygen isotopic reference materials of human hair, the Reston Stable Isotope Laboratory (RSIL) of the U.S. Geological Survey (USGS) prepared two such materials: USGS42 Tibetan hair and USGS43 Indian hair [11]. The $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ values of these isotopic reference materials were determined originally with dual-water equilibration at ambient temperature, followed by a high temperature conversion technique using an elemental analyzer (TC/EA) with a glassy carbon tube and glassy carbon filling, with analysis by an isotope-ratio mass spectrometer (IRMS) [12]. In 2015, Gehre et al. [13] pointed out that the TC/EA IRMS method can produce inaccurate $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ results when analyzing nitrogen-bearing organic substances owing to the formation of hydrogen cyanide (HCN), which leads to non-quantitative conversion of a hydrogen- and nitrogen-bearing sample into molecular hydrogen (H_2). Gehre et al. [13] determined that a single-oven, chromium-filled elemental analyzer (Cr-EA) coupled to an IRMS substantially improves the measurement quality and reliability of hydrogen isotopic analysis of hydrogen- and nitrogen-bearing organic material because hot chromium scavenges all reactive elements except hydrogen. The observation of Gehre et al. [13] was further confirmed by Nair et al. [14] by determining $\delta^2\text{H}$ values of selected hydrogen- and nitrogen-bearing compounds with the chromium-enhanced reactor. For the majority of compounds studied, a significant relationship was observed between the amount of missing H_2 and the number of nitrogen atoms in molecules, suggesting pyrolytic formation of HCN as a byproduct. Because hair keratin contains about 15.3 % nitrogen by mass [11], the probability of formation of hydrogen cyanide (HCN), leading to non-quantitative conversion of a sample into molecular hydrogen, has been investigated with the Cr-EA method. Revised $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ values of USGS42 and USGS43 human hair isotopic reference materials performed with the Cr-EA preparative method are presented herein.

2. Experimental Methods

In the Reston Stable Isotope Laboratory (RSIL; <http://isotopes.usgs.gov/>) of the U.S. Geological Survey (USGS), measurement of accurate relative stable hydrogen isotope-ratio differences of water and other hydrogen-bearing substances is a critical endeavor of USGS programs. The quantity relative stable hydrogen isotope-ratio difference, $\delta^2\text{H}_{\text{VSMOW}}$, is defined by the relation [15]

$$\delta^2\text{H}_{\text{VSMOW}} = \frac{\frac{N(^2\text{H})_{\text{P}}}{N(^1\text{H})_{\text{P}}} - \frac{N(^2\text{H})_{\text{VSMOW}}}{N(^1\text{H})_{\text{VSMOW}}}}{\frac{N(^2\text{H})_{\text{VSMOW}}}{N(^1\text{H})_{\text{VSMOW}}}} \quad (1)$$

where $N(^2\text{H})_{\text{P}}$ and $N(^1\text{H})_{\text{P}}$ are the numbers of the two isotopes ^2H and ^1H of hydrogen in specimen P, and equivalent parameters follow for the international measurement standard VSMOW. Commonly an extraneous numerical factor of 1000 is added to this definition. However, to be consistent with the Système International d'Unités, the SI (known in English as the International System of Units), which is published by the Bureau International des Poids et Mesures (BIPM), the factor 1000 should not appear in this equation so that this equation is written as a coherent quantity equation and not as a numeric value equation [15,16]. The isotope scale $\delta^2\text{H}_{\text{VSMOW}}$ is normalized such that $\delta^2\text{H}_{\text{VSMOW}}$ value of the international measurement standard SLAP reference water is -428 ‰ [17], and normalized values are identified by the quantity symbol $\delta^2\text{H}_{\text{VSMOW-SLAP}}$.

The sample preparation procedure is the same as the protocol used in Qi and Coplen [12]. The hair samples were weighed and loaded into silver capsules (Costech, 41066). Two identical sets of hair reference samples were prepared. One set was equilibrated with water depleted in ^2H (w1, reference material USGS49, $\delta^2\text{H}_{\text{VSMOW}} = -393.7 \text{ ‰}$, <http://www.isotopes.usgs.gov>) and another set was equilibrated with water enriched in ^2H (w2, $\delta^2\text{H}_{\text{VSMOW}} = +400.2 \text{ ‰}$) to perform isotope-mass-balance calculations. After equilibration, samples were dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ or in glass desiccators containing Sicapent(Merck, SX0137-1, www.MerckMillipore.com). For the $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ measurements, four reference waters,

VSMOW, GISP ($\delta^2\text{H}_{\text{VSMOW}} = -189.7 \text{ ‰}$), UC03 ($\delta^2\text{H}_{\text{VSMOW}} = +68.5 \text{ ‰}$, reference material UC03, <http://www.isotopes.usgs.gov>) and UC04 ($\delta^2\text{H}_{\text{VSMOW}} = +113.6 \text{ ‰}$, reference material UC04, <http://www.isotopes.usgs.gov>) sealed in silver tubes using a semi-automated sealing technique [18] were interspersed among human hair reference samples. The isotopic analyses were performed using a TC/EA (Thermo Finnigan, Bremen, Germany) reduction unit equipped with a Costech (Valencia, California) Zero-Blank 100-position autosampler, a ConFlo IV gas introduction system (Thermo Fisher, Bremen, Germany), and a Delta^{plus} XP IRMS (Thermo Fisher, Bremen, Germany). The glassy carbon tube inside of the ceramic tube, normally used for the TC/EA, was removed. The ceramic tube was filled from the bottom to the top with 5 cm of silver wool, 10 cm of glassy carbon chips, 0.8 cm of quartz wool, and 3 cm of chromium powder (200 micron, 99.0 % purity, PN CR006020/2, Goodfellow, Huntingdon PE29 6WR England). The filling height was the same as that of the glassy carbon-filled tube in the TC/EA. The silver and sample residues were removed every 200 to 250 samples. The helium carrier gas (106 mL min^{-1}) was fed from the top, as originally supplied. The original 0.6-m, 6.35-mm, 5-Å-zeolite GC column of the TC/EA was replaced by a 1.0-m GC column of the same diameter and zeolite GC column. The reactor temperature was set at 1200 °C and the GC temperature was maintained at 90 °C . LIMS (Laboratory Information Management Program) for Light Stable Isotopes [19] was utilized to normalize isotopic results to the VSMOW-SLAP hydrogen-isotope scale [10,17].

3. Results, Discussion, and Conclusions

Human hair consists of three pools of hydrogen:[11] Pool A is absorbed water that can be removed with sufficient pumping under vacuum or in glass desiccator containing Sicapent; Pool B is a reservoir containing exchangeable hydrogen, but no exchangeable oxygen, and the hydrogen cannot be removed, even by evacuation; Pool C is hair that contains non-exchangeable hydrogen and oxygen. The stable hydrogen isotopic composition of the non-exchangeable fractions of USGS42 and USGS43, Pool C, were determined using the methods in Coplen and Qi [11], Qi and Coplen [12], and the chromium method described in this study. Six sets of samples of USGS42 and USGS43 were processed through dual-water equilibration, drying, and isotopic

analysis. Seven to eleven aliquots of each material were analyzed in each run. Two sets of samples were dried in an evacuated desiccator containing Sicapent and four sets of samples were dried by vacuum oven at 40 °C. The results of USGS42 and USGS43 measurements are presented in Table 1. The amount fraction of exchangeable hydrogen, $x(H)_{ex}$, was calculated based on equation (2):

$$x(H)_{ex} = \frac{\delta^2H_{tot1} - \delta^2H_{tot2}}{\delta^2H_{w1} - \delta^2H_{w2}} \quad (2)$$

where δ^2H_{tot1} and δ^2H_{tot2} are the δ^2H values of total hydrogen of the same keratin material that equilibrated with waters w1 and w2, respectively. The non-exchangeable hydrogen δ^2H_{nex} in pool C was calculated using equation (3):

$$\delta^2H_{nex} = \frac{\delta^2H_{tot} - x(H)_{ex} \delta^2H_{ex}}{(1 - x(H)_{nex})} \quad (3)$$

The isotopic composition of the exchangeable hydrogen is fixed by the waters w1 and w2 that are used for equilibration. Therefore $\delta^2H_{ex} = \delta^2H_{w1}$ or δ^2H_{w2} . The non-exchangeable hydrogen δ^2H_{nex} values in Table 1 remained consistent in spite of variations in the amount fraction of exchangeable hydrogen, $x(H)_{ex}$, between 0.075 and 0.155. This observation agreed with Meier-Augenstein et al.'s conclusion in 2011 [20]. The first and the last sets of amount fractions were not considered when calculating the overall average amount fraction of exchangeable hydrogen from all the equilibration procedures because their values (11.2 % and 15.5 % from USGS42 and 10.3 % and 15.2 % from USGS43) are higher than those values found in most of the literature [2,6,11, 12] and from the theoretically expected value of 0.099 in human hair [20]. The amount fraction of exchangeable hydrogen, x_{H-ex} , of USGS42 was identical (8.6 %) in this work to that of the original study [11]. However, the amount fraction of USGS43 was 8.2 % in this study, compared to 9.0 %, determined in the original work [11]. The reasons for the difference could be the variation in experimental conditions, such as initial hair sample condition (weighed out under different humidity), tightness of wrapped silver capsules [21], slight difference of pressure in the glass desiccators when samples were equilibrated, slight differences in drying time and

temperature, all of which are difficult to control. On average, the $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ values of USGS42 and USGS43 obtained by the chromium-filled reactor are 5.7 ‰ more positive than those previously measured (Table 2). Comparing the average hydrogen mass fraction of 6.15 %, obtained from the Cr-EA method, with that of 5.44 % determined by the C-EA method (Table 3), the estimated mass fraction of hydrogen that is not-quantitatively converted into molecular hydrogen with the Cr-EA method is about 11.5 % of the total hydrogen in hair sample. This confirms that the nitrogen contained in hair keratin does form hydrogen cyanide (HCN), leading to non-quantitative conversion of a sample into molecular hydrogen when a glassy carbon-filled reactor was used. The formation of HCN in hair resulted in a substantial shift of $\delta^2\text{H}$ values to about 7.7 ‰ more negative, similar to the observation obtained by Nair et al. [14].

The amounts of absorbed water (Pool A is absorbed water that can be removed with sufficient pumping under vacuum or in glass desiccator containing Sicapent) were also evaluated by comparing the total mass fraction of hydrogen (Table 3) in dried and non-dried USGS42 and USGS43 by both Cr-EA and C-EA methods. Several aliquots of caffeine (used in Cr-EA runs) and polyethylene powder (used in C-EA runs) with precisely weighed masses were analyzed to quantify the mass of hydrogen in hair samples. The mass fractions of absorbed water (Table 3) were derived by comparing the amounts of hydrogen in dried and non-dried hair samples. The values of absorbed water (presented in Table 3 as mass fraction of hydrogen), 2.72 % from USGS42 and 2.98 % from USGS43, were obtained from Cr-EA run in January 2016 in Reston, Virginia, USA when the average relative humidity was around 65 %. Another set of mass fractions of absorbed water, obtained from C-EA runs in February 2016, is 0.03 % and 0.06 % from USGS42 and USGS43, respectively. The large variation in hydrogen mass fraction of absorbed water indicates that the amount of absorbed water is affected by variations in relative humidity. Different amounts of absorbed water would be expected when the same material is measured in different seasons or by laboratories in different geographic locations [12]. The slight difference in mass fraction of absorbed water between USGS42 and USGS43 was likely the result of different powder sizes (USGS42 < 0.15 mm and USGS43 < 0.25 mm).

Table 1

Stable hydrogen isotopic composition of the non-exchangeable fraction of USGS42 and USGS43 human hair isotopic reference materials the using the chromium-EA sample conversion technique.

[$x_{\text{H-ex}}$ = amount fraction of exchangeable hydrogen]

Analysis date	Drying method	USGS42 $\delta^2\text{H}_{\text{VSMOW-SLAP}}$	n	$x_{\text{H-ex}}$	USGS43 $\delta^2\text{H}_{\text{VSMOW-SLAP}}$	n	$x_{\text{H-ex}}$
1/13/2015	vacuum oven	$-73.5 \pm 1.8 \text{ ‰}$	10	11.2 % ^a	$-45.1 \pm 1.3 \text{ ‰}$	10	10.3 % ^a
5/15/2015	vacuum oven	$-69.9 \pm 1.1 \text{ ‰}$	10	8.7 %	$-41.5 \pm 0.6 \text{ ‰}$	10	8.1 %
6/1/2015	vacuum oven	$-71.3 \pm 1.4 \text{ ‰}$	10	8.9 %	$-44.2 \pm 1.4 \text{ ‰}$	10	8.4 %
7/9/2015	vacuum oven	$-76.2 \pm 0.8 \text{ ‰}$	8	8.2 %	$-47.5 \pm 1.1 \text{ ‰}$	10	7.5 %
9/8/2015	Sicapent	$-72.2 \pm 0.8 \text{ ‰}$	7	8.6 %	$-45.1 \pm 1.2 \text{ ‰}$	7	8.8 %
1/15/2016	Sicapent	$-74.2 \pm 2.8 \text{ ‰}$	11	15.5 % ^a	$-43.2 \pm 1.0 \text{ ‰}$	11	15.2 % ^a
Average		$-72.9 \pm 2.2 \text{ ‰}$ (n = 6)		8.6 %	$-44.4 \pm 2.0 \text{ ‰}$ (n = 6)		8.2 %

^a $x_{\text{H-ex}}$ values are not included into average values

Table 2

Comparison of $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ values and exchangeable fractions of USGS42 and USGS43 human hair isotopic reference materials obtained by a chromium-filled reactor and a glassy carbon-filled reactor.

[$x_{\text{H-ex}}$ = amount fraction of exchangeable hydrogen]

Description	USGS42		USGS43	
	$\delta^2\text{H}_{\text{VSMOW-SLAP}}$	$x_{\text{H-ex}}$	$\delta^2\text{H}_{\text{VSMOW-SLAP}}$	$x_{\text{H-ex}}$
chromium-filled reactor (this work)	$-72.9 \pm 2.2 \text{ ‰}$	8.6 %	$-44.4 \pm 2.0 \text{ ‰}$	8.2 %
glassy carbon-filled reactor (Coplen and Qi, 2012)	$-78.5 \pm 2.3 \text{ ‰}$	8.6 %	$-50.3 \pm 2.8 \text{ ‰}$	9.0 %
Difference between two methods	5.6 ‰	0	5.9 ‰	0.8 %

Table 3.

Comparison of hydrogen mass fraction obtained from the Cr-EA method with that of determined by the C-EA method in USGS42 and USGS43, and typical mass fractions of absorbed water as hydrogen

		USGS42		USGS43		
		Cr-EA	C-EA	Cr-EA		C-EA
Description	Sample	Hydrogen mass fraction (%)	Hydrogen mass fraction (%)	Sample	Hydrogen mass fraction (%)	Hydrogen mass fraction (%)
dried	aliquot 1	6.18	5.59	aliquot 1	6.15	5.42
dried	aliquot 2	6.19	5.45	aliquot 2	6.14	5.42
dried	aliquot 3	6.20	5.47	aliquot 3	6.09	5.38
dried	aliquot 4	6.23	5.44	aliquot 4	6.06	5.40
dried	aliquot 5	6.16	5.44	aliquot 5	6.14	5.42
mean		6.19 ± 0.03	5.48 ± 0.06		6.12 ± 0.04	5.41 ± 0.02
undried	aliquot 1	6.37	5.54	aliquot 1	6.28	5.54
undried	aliquot 2	6.35	5.56	aliquot 2	6.26	5.42
undried	aliquot 3	6.37	5.52	aliquot 3	6.32	5.47
undried	aliquot 4	6.35	5.46	aliquot 4	6.29	5.45
undried	aliquot 5	6.35	5.49	aliquot 5	6.36	5.43
mean		6.36 ± 0.01	5.51 ± 0.04		6.30 ± 0.04	5.47 ± 0.05
Mass fraction of absorbed water as hydrogen ^b		2.72	0.03		2.98	0.06

^b mass fraction of total hydrogen, not the mass fraction of total material.

It is critical that readers pay attention to the $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ and $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$ values of USGS42 and USGS43 used for normalization in publications as they may need to adjust published results from previous publications to ensure that all results are on the same isotope-delta scales. It is recommended that:

- USGS42 and USGS43 be interspersed among unknowns, treated in an identical manner as unknowns, and used for normalizing to the $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ and $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$ scales,
- Authors in their articles use text such as the following when reporting results:

“The stable hydrogen and oxygen isotope-delta values of hair samples are reported relative to the VSMOW-SLAP scale; on these scales the $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ and $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$ values of USGS42 and USGS43 are -72.9 , $+8.56$, -44.4 , and $+14.11$ ‰, respectively [Coplen and Qi, 2012; Coplen and Qi, 2016].”

In this manner, readers can re-normalize measurement results to current values of USGS42 and USGS43 as they are improved with new techniques. Improved values are posted on the Web site of the RSIL (<http://isotopes.usgs.gov/lab/referencematerials.html>).

4. Source for USGS42 and USGS43

USGS42 and USGS43 human-hair isotopic reference materials are available from:

U.S. Geological Survey
Reston Stable Isotope Laboratory
431 National Center
12201 Sunrise Valley Drive
Reston, Virginia 20192
USA
<http://isotopes.usgs.gov/>
Fax: +1 703 648 5889

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