

Caution on the Use of Liquid Nitrogen Traps in Stable Hydrogen Isotope-Ratio Mass Spectrometry

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An anomalous stable hydrogen isotopic fractionation of 4 ‰ in gaseous hydrogen has been correlated with the process of adding liquid nitrogen (LN_2) to top off the dewar of a stainless-steel water trap on a gaseous hydrogen–water platinum equilibration system. Although the cause of this isotopic fractionation is unknown, its effect can be mitigated by (1) increasing the capacity of any dewars so that they do not need to be filled during a daily analytic run, (2) interspersing isotopic reference waters among unknowns, and (3) applying a linear drift correction and linear normalization to isotopic results with a program such as Laboratory Information Management System (LIMS) for Light Stable Isotopes. With adoption of the above guidelines, measurement uncertainty can be substantially improved. For example, the long-term (months to years) $\delta^2\text{H}$ reproducibility (1σ standard deviation) of nine local isotopic reference waters analyzed daily improved substantially from about 1 ‰ to 0.58 ‰. This isotopically fractionating mechanism might affect other isotope-ratio mass spectrometers in which LN_2 is used as a moisture trap for gaseous hydrogen.

The measurement of the $\delta^2\text{H}$ of water with the H_2 – H_2O equilibration method using a platinum catalyst^{1–4} has become a routine analytical technique since the method was automated in 1991.³ The 1991 published 1σ standard deviation of $\delta^2\text{H}$ measurements of 1.3 ‰ is typical of many laboratories. During an investigation to improve this uncertainty, an anomalous hydrogen isotopic fractionation of gaseous hydrogen delivered by the equilibration system to the isotope-ratio mass spectrometer was identified. This isotopic fractionation and its mitigation is the subject of this report.

EXPERIMENTAL SECTION

At the Reston Stable Isotope Laboratory (RSIL) (<http://isotopes.usgs.gov/>) of the U.S. Geological Survey (USGS), measurement of accurate $\delta^2\text{H}$ of waters is a critical endeavor for USGS programs. The quantity $\delta^2\text{H}$ is defined by the relation

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

where $N(^2\text{H})_P$ and $N(^1\text{H})_P$ are the numbers of the two isotopes ^2H and ^1H of hydrogen in specimen P, and equivalent parameters follow for the international measurement standard Vienna Standard Mean Ocean Water (VSMOW). 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 extraneous numerical factor of 1000 should not appear in this equation and this equation should be written as a quantity equation and not as a numeric value equation.⁵

Measurements are performed at the RSIL with a 60-port Pt equilibration system connected to a VG Micromass model 602 dual inlet isotope-ratio mass spectrometer.^{3,4,6} Gaseous hydrogen is equilibrated with water at 27.01 ± 0.03 °C for a minimum of 2 h. H_2 from each sample port is expanded in turn through a stainless-steel trap immersed in liquid nitrogen (see Figure 1), with a snug-fitting lid (Figure 2), into an automated mercury piston.⁷ The purpose of the trap is to remove water from the H_2 because contaminant water in the H_2 gas is detrimental to the mass spectrometer. Isotopic results are logged to a Microsoft Access database in real time. A Microsoft Access-based program, Laboratory Information Management Program (LIMS) for Light Stable Isotopes^{8–10} is utilized to normalize¹¹ isotopic results to the VSMOW–SLAP isotope scale so that the $\delta^2\text{H}$ of Standard Light Antarctic Precipitation (SLAP) is –428 ‰ relative to Vienna Standard Mean Ocean Water (VSMOW).^{12–14}

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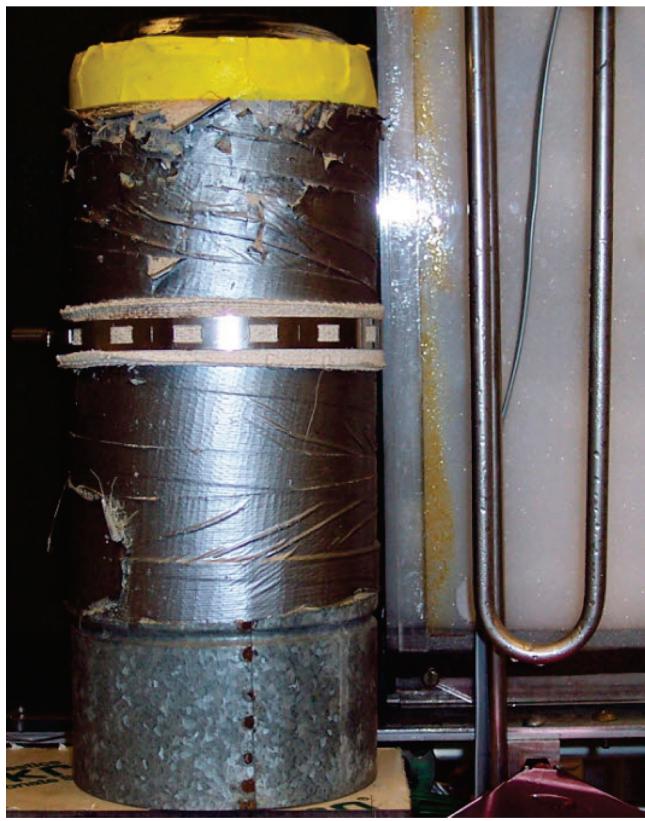


Figure 1. Liquid nitrogen dewar and $\frac{3}{8}$ in. o.d. stainless-steel tubing that freezes water in hydrogen gas samples.



Figure 2. Two-piece plastic lid for dewar that minimizes heat gain and loss of liquid nitrogen in dewar. Two pieces snap together around $\frac{3}{8}$ in. stainless-steel tubing shown in Figure 1.

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

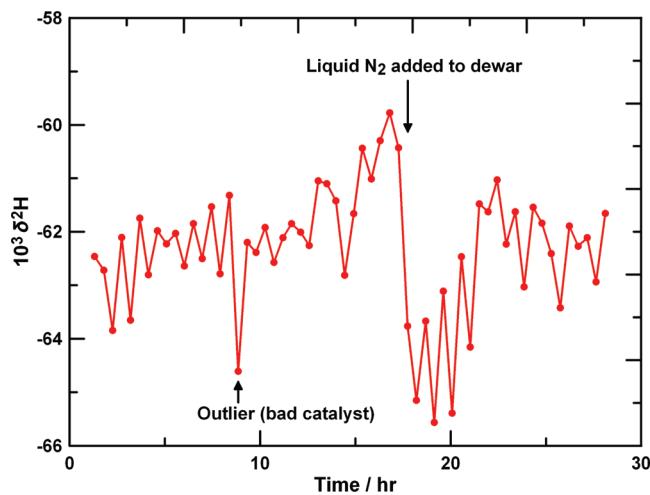


Figure 3. Hydrogen isotopic composition of the same local laboratory reference water loaded in all ports of the RSIL Pt-equilibration, isotope-ratio mass spectrometer.

RESULTS, DISCUSSION, AND CONCLUSIONS

Figure 3 shows the $\delta^2\text{H}$ of identical reference waters loaded into all ports of the RSIL Pt-equilibration, isotope-ratio mass spectrometer. One outlier is identified in Figure 3. After about 17.5 h, LN_2 was added to the dewar that maintains the stainless-steel cold trap at approximately -190°C because the trap was nearly empty. The next sample loaded and analyzed was depleted in ^2H by approximately 4 % relative to previous samples. The cause of this isotopic fractionation of H_2 transferred to the mass spectrometer is unknown, but we speculate below.

The RSIL solution was to increase the capacity of the dewar used to cool the stainless steel transfer line and freeze water (Figure 1). The capacity was doubled, and the opening of the dewar was fitted with a snug-fitting lid (Figure 2) to minimize entrance of warm laboratory air. In addition, the standard operating procedure of the RSIL was modified so that LN_2 is not added to the dewar once the mass spectrometer has begun analyzing samples of an analytic run. The $\delta^2\text{H}$ measurements with these changes during one analytic run with identical local reference waters in each port are shown in Figure 4. One might hypothesize that the increase in the $\delta^2\text{H}$ value over a sequence is due to change of the $\delta^2\text{H}$ of the working standard gas as it is consumed. However, the working standard is very large and lasts for more than a month, and the weekly drift is very small.¹⁵

The change in isotopic composition is linear over time, suggesting that it might be related to the magnitude of the coldest stainless steel surface area in the dewar. We speculate that there is bonding of gaseous hydrogen on the cold surface of the stainless steel as a hydrogen sample is loaded into the piston. We speculate that deuterium is preferentially absorbed on the cold stainless steel. When the LN_2 level is higher, there is more of the coldest surface, so the δ value is lower because of this preferential absorption.

The standard operating procedure in the RSIL is to intersperse two Antarctic reference waters and nine local tap isotopic reference

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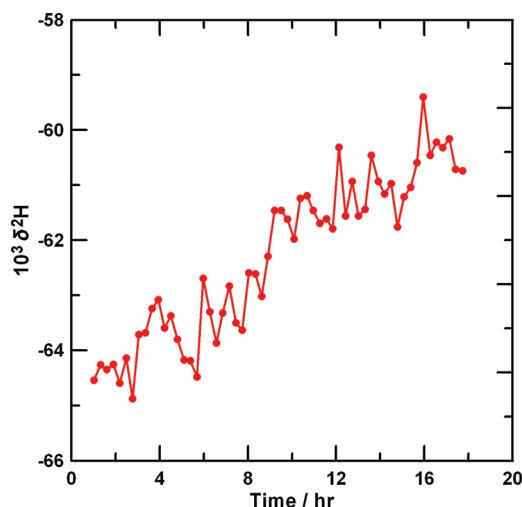


Figure 4. Hydrogen isotopic composition of the same local laboratory reference water loaded in all ports of the RSIL Pt-equilibration, isotope-ratio mass spectrometer after the capacity of the dewar that traps water vapor was increased. At the end of the run, the dewar was not in need of a LN₂ recharge as it had 10 h of cooling capacity remaining.

waters among unknown water samples. Prior to an increase in the capacity of the LN₂ dewar, the 1σ standard deviation of these 9 tap reference waters after normalization with LIMS for Light Stable Isotopes averaged about 1 %. Subsequently, the 1σ

standard deviation substantially improved to 0.58 ‰ over a 6 month period. Instrumental in achieving these high-quality $\delta^2\text{H}$ measurements is the procedure of interspersing local isotopic reference materials among unknowns¹⁶ and normalizing $\delta^2\text{H}$ values¹¹ to the VSMOW–SLAP scale using LIMS for Light Stable Isotopes.^{8–10}

It should be anticipated that any hydrogen isotope-ratio mass spectrometer utilizing LN₂ for trapping water may be affected by the hydrogen isotopic fraction, and workers should optimize analysis protocols to minimize the impact of such isotopic fractionations. Keeping liquid nitrogen levels constant might be an effective solution in addition to the solutions provided above.

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