Reference values for the stable isotopic composition of the certified reference material GRESP

Table 1: $\delta^2H$ and $\delta^{18}O$ reference values for the certified reference material GRESP and the associated combined uncertainties (1σ level; using a coverage factor of $k=1$), all expressed on the respective VSMOW-SLAP scale.

<table>
<thead>
<tr>
<th>IAEA material name</th>
<th>Reference value</th>
<th>Combined uncertainty</th>
<th>Reference value</th>
<th>Combined uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRESP (Water)</td>
<td>-257.8</td>
<td>0.4</td>
<td>-33.39</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Detailed information on the origin, production and characterization of the reference material GRESP can be found in its detailed certification report [1].
Purpose of the material

GRESP (Greenland Summit Precipitation) has been prepared at the IAEA to provide a water quality control material to check the calibration by the VSMOW2 and SLAP2 international measurement standards.

GRESP is certified for its hydrogen and oxygen stable isotopic composition, on a δ-scale as defined by the isotopic compositions of the two water international measurement standards VSMOW2 and SLAP2 [2] and denoted with $\delta^2{H}_{\text{VSMOW-SLAP}}$ and $\delta^{18}{O}_{\text{VSMOW-SLAP}}$, respectively [2]. Details on the δ-scales and normalization are given in [3]; see also the certification report [1].

Origin and preparation

The new reference material GRESP replaces the previous material GISP available until 2012 [4]. Please note that the isotopic composition of GRESP is entirely different from that of its predecessor material GISP, despite that it also originates from snow sampled at the Greenland inland ice sheet. During the time of preparation, the working name for GRESP initially was “GISP2” but has been changed to “GRESP” to avoid any confusion due to the different isotopic compositions and other uses of that name.

GRESP originates from melted snow used as a drinking water supply in the scientific research station “Summit Station” on the Greenland ice shelf (www.summitcamp.org). In 2008, 400 litres of water were shipped to the IAEA from the scientific Greenland Summit Station, derived from this melted snow. The water was thoroughly mixed and transferred into two specially designed stainless-steel tanks, with a 300 litres tank constituting the GRESP reference material.

Subsequently, from this tank individual samples were prepared in flame sealed glass ampoules. So far in two sequences about 4600 samples of 20mL size and 4000 samples of 4mL size were filled and carefully flame sealed from the master steel container to avoid any evaporation. All ampoules were then oven-sterilized for 8 hours at 105 °C, which constituted at the same time an individual leak test for each ampoule, as ampoules were placed upside down in the oven. A first set of analyses from bulk samples and large size ampoules was performed at the Isotope Hydrology Laboratory in 2009 and 2010, and further analyses were carried out in 2013 and 2016-2017 at the Terrestrial Environment Laboratory for both large and small ampoules and the bulk material. The remaining bulk amount of GRESP is kept in the original stainless-steel tank at the IAEA Terrestrial Environment Laboratory.

Homogeneity and stability of the material

An inhomogeneity assessment of GRESP has been carried out for individual flame sealed ampoules for both the produced 20 mL and the 4 mL quantities. The potential inhomogeneity of the 20 mL ampoules has been investigated by analyses of 33 randomly selected ampoules by infrared laser spectrometry. A similar assessment was performed later for fourty 4mL ampoules together with further thirteen 20mL ampoules. The isotopic data as measured from subsamples of an ampoule within one measurement day were compared with the gross daily average isotopic value. The obtained value difference for each ampoule includes components of both bias and reproducibility. In contrary the standard error as derived from all individual isotopic data of an ampoule carries only the reproducibility of the measurement system. The average value of all ampoule standard errors is therefore a proxy for the method reproducibility. Then the bias component for individual ampoules can be calculated as an estimate for the ‘between-bottle’ inhomogeneity by squaring both that observed difference from the daily mean and that of the reproducibility value, subtracting the latter one and calculating the square root of the residual [5, 6]. The inhomogeneity results varied between ‘no detectable isotopic inhomogeneity’ and maximal values of 0.019 ‰ for $\delta^{18}{O}$ and 0.22 ‰ for $\delta^2{H}$, for details see the report [1]. Altogether, the magnitude of a possible ‘between-bottle’ inhomogeneity was found to be insignificant within the assigned uncertainties for both large and small ampoules produced.
Within the achieved measurement uncertainties, no indication of instability was detected within the time period from 2009 to 2017. For details, see the certification report [1].

**Characterization study**

The $\delta^4$H and $\delta^{18}$O reference values for GRESP in Table 1 were derived from several characterization studies in direct calibration with VSMOW2 and SLAP2 each under repeatability conditions carried out in the years 2009/10, 2013, and 2016/17 using three laser spectrometry systems (Picarro water isotopic analyser types L1102-i and L2130-ii) in two IAEA laboratories (Isotope Hydrology Laboratory and Terrestrial Environment Laboratory). The total number of measurements/injections in these assessments was in the range of 940, 200 and 3200, respectively [1, 7].

This laser data was validated by additional measurements on GRESP using a dual inlet isotope mass spectrometry system and three further laser spectrometry systems as well as by measurements of “std13”, another fraction of the remaining GRESP bulk material stored in a separate stainless-steel tank. Further independent data (n=400) using a gravimetric mixing approach (“ILS”-samples) are explained in the report [1].

**Assignment of values - Certification procedure**

For both $\delta^4$H and $\delta^{18}$O, the calculated mean value and the calculated combined standard uncertainty are determined by combining all measurements performed in the two IAEA laboratories using three independent laser analysers (company Picarro) as well as data from other instrument types (see more details in the Certification Report [1]). All data was calibrated directly versus VSMOW2 and SLAP2 measured in the same analytical run and checked by quality control materials like GISP or internal laboratory standards. Combined standard uncertainties were calculated from measurements performed under repeatability conditions and including relevant systematic uncertainty components. Therefore, a weighted means approach for data combination could be applied [1] to derive a weighted mean value. However, the weighted means for different instruments showed discrepancies larger than their standard errors of the mean. Calculation of the combined uncertainty for the reference value did not bracket the range of results for different instruments, even when considering the uncertainty components covering upper limits for potential inhomogeneity between bottles and material stability (see the certification report [1] on details of the graphs for the probability density function of means). To account for the observed spread of data and (potential) between-instrument bias, the combined standard uncertainty was increased to the level as stated in Table 1 and denoted as standard uncertainty. This is equivalent to follow ISO Guide 35: 2017 (A.2.3.5 Grouping) [8]. The $\delta^4$H value of GRESP is $-257.8 \pm 0.4 \%o$. The $\delta^{18}$O value of GRESP is $-33.39 \pm 0.04 \%o$.

The assigned combined standard uncertainty associated to $\delta^4$H and $\delta^{18}$O reference values of VSMOW2 and SLAP2 are included in these uncertainty statements above [9]. The details concerning all reported results as well as the criteria for certification may be found in the references [1, 7].

**Statement on metrological traceability and uncertainty of assigned values**

The $\delta$-values assigned to the certified reference material GRESP are directly traceable to VSMOW2 and SLAP2 used as the highest level calibration standards on the $\delta^{18}$O-VSMOW-SLAP and $\delta^{18}$O-VSMOW-SLAP scales.

The traceability chain for $\delta^4$H and $\delta^{18}$O values by using VSMOW2 and SLAP2 as calibration standards ends with the $\delta$-values of these two materials calibrated directly against their successor materials VSMOW and SLAP. Note: use of VSMOW2 and SLAP2 guarantees the consistent use of the VSMOW-SLAP scales established in 1976 ($\delta^4$H-VSMOW-SLAP and $\delta^{18}$O-VSMOW-SLAP). Details on the VSMOW-SLAP scale and the normalization procedure during calibration are provided in [1] and [3].
**Intended use**

The certified reference material GRESP is intended as a quality control material to check the calibration using the international measurement standards VSMOW2 and SLAP2 on the VSMOW–SLAP δ-scales. Users are strongly advised to prepare their own internal standards for daily use and calibrate those standards against these international standards VSMOW2 and SLAP2 with GRESP as certified reference material for quality control.

**Instructions for handling and storage**

The original unopened ampoules should be stored at ambient temperatures in the dark. The water is intended for rapid analysis after having opened the original ampoule. The water transfer upon opening the glass ampoule to analytical vials should be done in a way preventing evaporation and contamination. Storing of remaining water, if left after analysis, or storing water in opened ampoules cannot be recommended. Therefore, the isotopic reference values do not apply for such retained portions.

**Issue and expiry date**

The GRESP reference material was released in 2018. The original reference sheet was issued on 22 May 2018. The reference values for the δ²H and δ¹⁸O composition of GRESP are valid until 31 December 2027, provided the original ampoules are handled and stored in accordance with the instructions given in this reference sheet (see “Instructions for handling and storage”). This certification is nullified if the glass ampoule container is damaged.

**Distribution and amount limits**

The material is distributed in a single 20 mL sealed glass ampoule or as a set of four 4 mL sealed glass ampoules, both denoted as one unit, from the International Atomic Energy Agency (IAEA), Vienna, Austria. Three such units of each reference material may be ordered per laboratory in a three-year period. This allows laboratories to purchase sufficient amounts of the calibration materials to perform frequent calibration of laboratory standards, and it will still ensure that the supply of these materials will last for the next decades.

GRESP is further available in a complete calibration set together with the two materials VSMOW2 and SLAP2.

**Legal disclaimer**

The IAEA makes no warranties, expressed or implied, with respect to the data contained in this reference sheet and shall not be liable for any damage that may result from the use of such data.

**Compliance with ISO Guide 31:2015**

The content of this this IAEA Reference Sheet is in compliance with the ISO Guide 31:2015: Reference materials – Contents of certificates, labels and accompanying documentation [10].

**Citation of this reference sheet**

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**Note:** Certified values as stated in this reference sheet may be updated if more information becomes available. Users of this material should ensure that the reference sheet in their possession is current. The current version can be found in the IAEA’s Reference Materials online catalogue: https://nucleus.iaea.org/sites/ReferenceMaterials/Pages/Stable-Isotopes.aspx
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REFERENCES


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