

INTENDED USE OF THE IAEA REFERENCE MATERIALS

PART II: EXAMPLES ON REFERENCE MATERIALS CERTIFIED FOR STABLE ISOTOPE COMPOSITION

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1 INTRODUCTION

In this paper IAEA reference materials distributed by the Isotope Hydrology Unit will be discussed.¹ These reference materials are intended for the determination of the ratios of stable isotopes of light elements such as hydrogen, carbon, nitrogen, oxygen and sulfur in environmental materials. Some of the available materials are primary reference materials and define conventional scales for reporting of measurement results.

An overview on other IAEA reference materials and the general scope of the Analytical Quality Control Services (AQCS) is given in an accompanying paper² as well as in the bi-annually published AQCS catalogue.³

The Isotope Hydrology Unit is also responsible for the distribution of ¹⁴C quality assurance materials. These materials are intended for laboratories performing ¹⁴C activity measurements on natural materials and at environmental activity levels. A detailed description of these materials and their characteristics can be found elsewhere.⁴⁻⁵

1.1 Common Characteristics of the Stable Isotope Reference Materials

The reference materials distributed by the Isotope Hydrology Unit are chemically pure compounds such as carbonates, sulfates, sulfides, nitrates, graphite or polyethylene, or nearly pure natural materials like distilled water, carbonate rock, silicates, refined oil, sugar, cellulose and similar compounds.¹ These materials are distinct from the other IAEA environmental matrix materials.

Most of these materials have been prepared to serve as reference materials. Therefore much care was taken in the initial purification and homogenisation of the raw material. The majority of all 30 stable isotope reference materials was produced by scientists under IAEA technical contracts or by cooperating institutions like the National Institute for Standards and Technology (NIST) in USA or the United States Geological Survey (USGS). Some of the materials were produced directly by the IAEA Isotope Hydrology Unit. In most cases the recommended values for stable isotope ratios in these materials were determined by interlaboratory comparison exercises. For those materials issued already twenty or more years ago, the number of participating laboratories was rather limited (in some cases less than ten).

1.2 Terms used for different categories of reference materials in this paper

Several definitions for international distributed reference materials and for internal laboratory standards have to be clearly distinguished. Unfortunately there are no clear guidelines on the definitions to be used in this field. Some of the expressions are ambiguous, some other used in different context by different authors. For this paper the definitions used are explained below.

These definitions used for the various kind of materials should be clearly distinguished from each other:

- *Primary reference material*¹ (or *international standard*)⁶: a natural, synthetic or virtual material versus which, by general agreement, the relative variations of stable isotope ratios in natural compounds are expressed. It is used to define a conventional scale for reporting variations of stable isotope ratios.
- *Calibration material*¹ (or *primary standard*)⁶: a natural or synthetic compound which has been carefully calibrated versus the primary reference material, and which' calibration values have been internationally agreed and adopted. It is used in case the primary reference material is not existing or available to calibrate measurements and instruments. Each primary reference material can be referred to as a calibration material as well.
- *Reference material (RM)*: a natural or synthetic compound which has been carefully calibrated versus the primary reference material and which' property values are sufficiently homogeneous and well established and are associated with well determined uncertainties. It is used to calibrate laboratory equipment and measurement methods for analysis of materials of a composition different from that of the primary reference material. The available reference materials cover a broad spectrum of chemical compositions and a wide range of stable isotope ratios. Most existing stable isotope ratio reference materials were first investigated in interlaboratory comparison exercises and distributed as intercomparison materials. Since they were used de facto as reference materials to calibrate equipment and measurements, some years ago their status was adjusted accordingly.
- *Intercomparison material*: a natural or synthetic compound with proven homogeneity which provide the means to check the overall quality of measurements performed in comparison with that of other laboratories. Its isotopic composition is computed by averaging the results of several laboratories obtained in interlaboratory comparison exercises and in individual assays, after elimination of outliers using a 2σ interval criterion.⁷
- *Working standard (or transfer standard)*⁶: This term in stable isotope mass spectrometry is somewhat misleading since it is not describing a 'standard', but an arbitrarily chosen gas used as a reference for analysis of isotope ratios of samples in a dual-inlet mass spectrometer (see section 1.3). All measurements of prepared samples and reference materials are made versus this working standard and are later converted into an international accepted scale. A better term would be 'laboratory reference gas'
- *Internal standard (or reference standard)*⁶: This term describes materials which are carefully selected and of similar composition as the normal samples and which are used routinely as a standard to calibrate or check measurements and the measuring instruments.

1.3 Conventional Scales for Reporting Stable Isotope Ratios

The analysis for stable isotope ratios is almost exclusively performed by mass spectrometry. The samples are firstly converted into a suitable gas containing isotopes of the element under investigation and are then analysed in dual-inlet mass spectrometer, where the isotopic composition of the sample gas is directly compared with that of a gas working standard. The analytical procedure includes also the measurement of internal laboratory standards of similar chemical composition as the sample. The internal laboratory standards have to be carefully calibrated versus the available reference materials and ensure the traceability of results.

The natural variations of the stable isotope ratios of light elements are rather small. For example, the total range of the variation of $^{18}\text{O}/^{16}\text{O}$ in water and ice on earth is in the order of only seven percent and increases to about ten percent for all natural oxygen bearing materials.⁸ For hydrogen isotopes with their large relative mass differences the variations of $^2\text{H}/^1\text{H}$ reach higher values of about 80 % for natural hydrogen bearing compounds.

In virtually all applications of stable isotopes in earth sciences the relative deviation of the isotopic ratio from a standard is of interest rather than the “absolute” isotopic ratio of the given sample. Therefore, a material is selected as a primary standard and its stable isotope ratio defines the zero point of a relative conventional scale. The easiest example is nitrogen, where the isotopic composition of nitrogen in atmospheric air is taken as the primary standard. For convenience the measurements are not reported as isotope ratios, but given as relative deviation from the isotope ratio of the standard according to the following formula:

$$d = \frac{R_{SA} - R_{ST}}{R_{ST}} \quad (1)$$

with δ (e.g. $\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$) being the normalised difference of the isotope concentration ratios R ($^2\text{H}/^1\text{H}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$, $^{34}\text{S}/^{32}\text{S}$) of the sample and the standard (e.g. $\delta^{15}\text{N}$ with air N_2 as standard). As the differences between sample and standard are normally very small, the δ -values are usually expressed as per mille difference (parts per thousand).⁹

The accuracy of measurements in experienced laboratories is in the order of ± 0.1 ‰ for $\delta^{18}\text{O}$ and ± 1 ‰ for $\delta^2\text{H}$ or even better. This is possible due to the special analysis arrangement with direct comparison of sample isotope ratios to those of the working standard during the measurement and due to the daily calibration of the mass spectrometer and the sample preparation lines with suitable internal standards (internal laboratory sub-standards calibrated against international reference materials).

The so called δ -scales for stable isotope ratios of the elements hydrogen, carbon, nitrogen, oxygen and sulfur are good examples for conventional scales. The knowledge on the absolute isotope ratio of a given material is not necessary for their use, since these scales are defined completely arbitrarily versus a chosen primary reference material. For oxygen and hydrogen ocean water was chosen as the largest accessible reservoir on earth and in view of the slight variations in isotopic composition throughout the oceans a hypothetically well mixed mean ocean water was selected as the reference (called SMOW - Standard Mean Ocean Water). This is a good example for a scale based on a virtual material not realised in nature. In case of carbon, marine carbonate of organic origin in a certain geological formation in the USA was selected (PeeDee Belemnite, PDB); for nitrogen, atmospheric nitrogen was the obvious choice; and for sulfur, material from a meteorite was selected and expected to be representative for the mean cosmic abundance of sulfur isotopes (Cañon Diablo Troilite, CDT).

However, the main persisting problem was the proper calibration between different laboratories since the primary standard for oxygen and hydrogen did not exist at all, and both original materials

defining the δ -scales for carbon and sulfur (PDB and CDT) were exhausted since some time. The IAEA therefore initiated the production of new reference materials which were calibrated with the best available techniques relative to the original δ -scales of the respective elements. Beside many other materials, these activities resulted in the production of the three materials VSMOW (water), NBS19 (carbonate), and IAEA-S-1 (silver sulfide), which were adopted by international agreement as calibration materials after extensive tests by experienced laboratories. These calibration materials were used to define the zero-point of new δ -scales named VSMOW, VPDB and VCDT which should be as close as possible to the original SMOW, PDB and CDT δ -scales (the V standing for Vienna in all three cases).

As an example the development of the scales in the case of hydrogen and oxygen isotope ratio standards will be presented.

1.4 Definition of the Scales for Reporting Hydrogen and Oxygen Isotope Ratios

First the historical development is presented to establish the scales for reporting hydrogen and oxygen isotope ratios, primarily intended for measurements on water samples and extended to other hydrogen and oxygen bearing materials.

Already in 1953 “average ocean water” was suggested and used as reference point for measurements.¹⁰ Since no ‘average ocean water’ exists, this concept was refined in 1961 by defining the hypothetical Standard Mean Ocean Water (SMOW).¹¹ Its isotopic composition was defined as a weighted average of the available measurements of the isotopic composition in the main oceanic water masses. But since SMOW was just a concept and never existed as real water sample, it couldn’t be used for calibration of laboratory measurements.

However, the isotopic ratios of SMOW were defined with respect to the existing water standard NBS-1¹² of the US National Bureau of Standards, used earlier for an interlaboratory comparison. So for the first time a physically existing material was used to calibrate different laboratories to the SMOW scale. NBS-1 was readily available for world-wide distribution together with another water standard called NBS-1A obtained from melted snow with an lower abundance of the heavier isotopes. During an IAEA interlaboratory comparison in 1965 serious doubts were confirmed concerning the preservation of the NBS-1 water standard and possible changes of its isotopic composition.

At an IAEA Panel Meeting in 1966 it was therefore recommended to establish a pair of two new standards, the first one being as close as possible to the defined SMOW and the other one with an abundance of the heavier isotopes close to the lowest limits observed in natural water.

The new standard with an isotopic composition as close as possible to SMOW was prepared by H. Craig. It was obtained by mixing distilled ocean water with small amounts of other waters in order to adjust its isotopic composition as close as possible to that of the defined SMOW. This task was complicated due to the required adjustment of both the isotopic composition of hydrogen and of oxygen. This standard was ready in 1968 and was called Vienna Standard Mean Ocean Water (VSMOW). According to the control analyses performed by Craig VSMOW has the same $^{18}\text{O}/^{16}\text{O}$ ratio as the defined SMOW, but a slightly lower $^2\text{H}/^1\text{H}$ ratio or respectively a slightly negative $\delta^2\text{H}$ value (-0.2‰). However, this slight difference is about a factor of four to five lower than the analytical uncertainty of most laboratories. Absolute isotope ratios on VSMOW were determined for $^{18}\text{O}/^{16}\text{O}$,¹³ for $^{17}\text{O}/^{16}\text{O}$ ¹⁴ as well as for $^2\text{H}/^1\text{H}$.^{15,16,17}

The second standard was obtained by E. Picciotto from melting a firm sample at Plateau Station, Antarctica. This material was named Standard Light Antarctic Precipitation (SLAP). The absolute isotope ratios of SLAP were determined only for $^2\text{H}/^1\text{H}$,^{15,16,17} absolute $^{18}\text{O}/^{16}\text{O}$ ratios for SLAP were computed from those of VSMOW by using its assigned value of $\delta^{18}\text{O}=-55.5$ ‰ versus VSMOW (see below).

All four materials VSMOW, SLAP, NBS-1, NBS-1A (the latter both transferred to IAEA from the National Bureau of Standards) were then distributed by the IAEA Isotope Hydrology Laboratory.

In 1976 an IAEA Consultants' Meeting was convened in order to discuss the isotope results on these standards obtained so far from laboratories and to advise on future action on standardization of stable isotope measurements.¹⁸

The recommendation of the experts concerning water standards was to express all future results as δ -values relative to VSMOW in order to resolve confusion on results expressed in non-corresponding scales. It was stated that the coherence between δ -values reported by different laboratories could be improved by adopting fixed δ -values for a second water reference standard. The experts recommended to adopt SLAP for this purpose and to normalize the ^{18}O and ^2H δ -scales relative to this standard. In Table 1 the δ -values are listed with those of VSMOW being by definition at zero and those of SLAP established by the weighted mean of results from different laboratories. The established $\delta^2\text{H}$ -value for SLAP is in remarkable good agreement with the available absolute hydrogen isotope ratio determination of the two materials using isotope dilution methods (deviation expressed as $\delta^2\text{H}$ smaller than 0.5‰).

Table 1 Oxygen and hydrogen d -values versus VSMOW assigned to the existing water reference materials (NBS-1 and NBS-1A d -values are reported versus SMOW)

Name	$\delta^{18}\text{O}$ [‰]	$\delta^2\text{H}$ [‰]
VSMOW	0	0
SLAP	-55.5	-428
GISP	-24.8±0.05	-189.5±1.0
NBS-1	-7.94	-47.6
NBS-1A	-24.33	-183.3

The definition of VSMOW as zero of the oxygen and hydrogen δ -scales and the adoption of fixed δ -values for SLAP is therefore a slight modification of the original definition of a δ -scale in formula (1):

$$d = \left(\frac{R_{SA} - R_{ST}}{R_{ST}} \cdot d_{SLAP} / \frac{R_{SLAP} - R_{VSMOW}}{R_{VSMOW}} \right), \quad (2)$$

with the additional term in the bracket being the normalization of the respective scale in terms of pre-defined hydrogen and oxygen isotope ratios of the two standards (table 1).

The two scales defined in equation (1) for SMOW and in (2) for VSMOW coincide only if $R_{SMOW} \equiv R_{VSMOW}$ and if the adopted δ -values for SLAP in table 1 correspond to the true ones as defined by equation (1) for both hydrogen and oxygen. From the reported measurements of NBS1 and VSMOW a slight offset of the zero-point of the two scales could be concluded (offsets of 0.05‰ and 0.5‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively), but which was well within the limits of measurement uncertainty of most laboratories.¹⁹ Both offsets were a bit larger than evaluated before by Craig. However, due to the scatter of the individual results the stated mean offset should not be applied for conversion from one scale to the other.

A third water standard was proposed during the same meeting in 1976¹⁹ with an isotopic composition intermediate between VSMOW and SLAP. This material was obtained from Greenland firn in 1978 and was called GISP (Greenland Ice Sheet Precipitation). GISP is intended to prove the successful calibration as performed with VSMOW and SLAP and the linearity of the measuring system. Results of two interlaboratory comparisons investigating GISP are published in IAEA

reports.^{20,7} It was noted that the accordance of results from different laboratories improved by a factor of more than two when the data were normalized using SLAP as second standard in addition to VSMOW.

2 INTENDED USE OF REFERENCE MATERIALS

2.1 Recent situation for IAEA RMs

The reference materials dedicated for the determination of stable isotope ratios at environmental level are distributed by the IAEA and on its behalf by NIST. A considerable number of units of these reference materials are distributed per year by the IAEA (figure 1) in spite of the established rigid rule on the distribution of these reference materials allowing only the order of one unit of each material per laboratory in a given three years period (see paragraph 2.1.5 below).

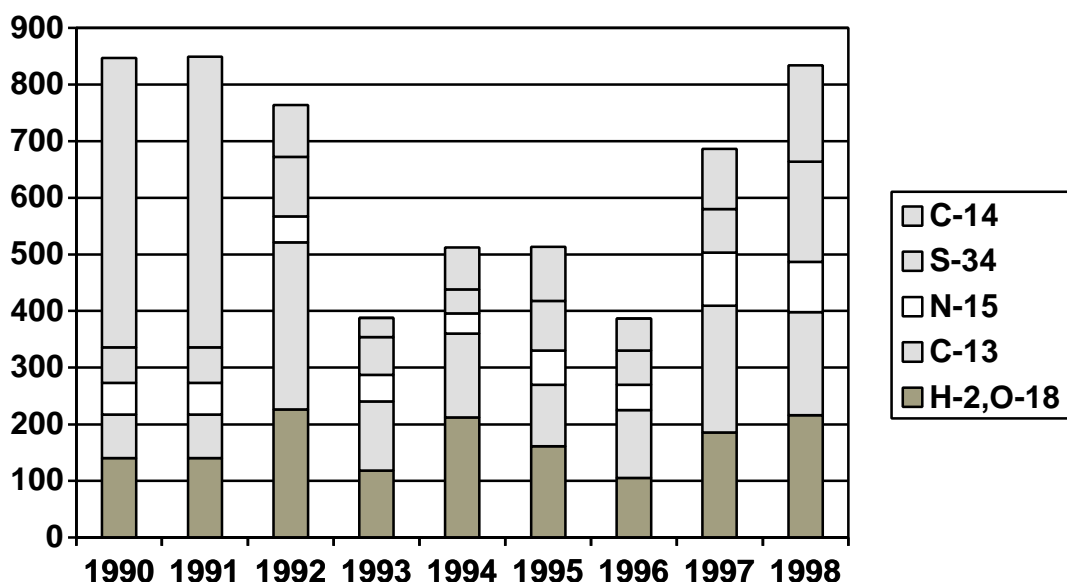


Figure 1 Number of reference materials distributed by the IAEA Isotope Hydrology Unit per year. These figures include all types of RMs and also those RMs which are distributed free of charge (e.g. ¹⁴C), for calibration studies of RMs and for interlaboratory comparisons.

Most of these IAEA reference materials are described by Reports of Investigation produced by the National Institute of Standards and Technology in USA. The IAEA Isotope Hydrology Laboratory is in the process of updating the available information according to the requirements as stated in ISO-Guide 31 and its recent revision.²¹ In the available NIST reports, the intended use of these materials is stated as in the following example for VSMOW, SLAP, GISP: “These Reference Materials are intended to provide samples of known isotopic composition with ²H/¹H and ¹⁸O/¹⁶O isotope ratios stated in parts per thousand difference (‰) from the VSMOW isotope-ratio standard. These RMs are not certified, but their use allows comparability of stable hydrogen and oxygen isotope-ratio data obtained by investigators in different laboratories. VSMOW and SLAP are intended for stable hydrogen and oxygen isotope-ratio calibration of water samples and of mass spectrometers for isotope-ratio analysis of all other oxygen- or hydrogen-bearing substances.”²² A similar statement is provided for the other reference materials in other issued NIST Reports of Investigation.

In the following sections, these IAEA reference materials will be discussed in respect to the ISO Guide 33²³ recommendations.

*2.1.1 Storage and Transfer of a property value.*²³ Individual units of the water and gas reference materials are stored in sealed 20 ml glass ampoules ready for distribution and any remaining bulk material is stored in sealed ten liter glass containers. When opening a sealed glass container to fill new samples for distribution, the isotopic composition of the water reference material in the filled ampoules is always compared against ampoules filled earlier from other containers. This cross-check verifies the proper storage of the materials and excludes the possibility of any significant changes of the isotopic composition during storage.

In case of the other solid reference materials they consist of materials which can be stored under ambient laboratory conditions in air-tight cap-sealed bottles and containers. In some instances the head space air is replaced by dry nitrogen or argon. Two carbonate materials are stored in desiccators under vacuum to prevent any reaction and isotopic exchange between the carbonate material, air moisture and air carbon dioxide.

*2.1.2 Establishing traceability of the measurement result.*²³ In case of the primary reference material VSMOW or the calibration materials NBS19 and IAEA-S-1 the traceability to SI units, in this case the mole, is achieved through the determination of the absolute isotope ratios of these materials using a definitive analysis method (isotope dilution method). In spite of this, until now these materials were not considered as certified RMs. One reason is the lack of information on some details of the formerly performed measurements (up to 28 years ago) required nowadays for a certification. In any case an absolute isotope ratio determination is quite useful, being an additional material-independent information which can facilitate in future the production of successor materials. However, the main purpose of these calibration materials is to give the means to the laboratory to trace their measurements back to an international accepted uniform δ -scale.

Virtually all other reference materials were established through interlaboratory comparison exercises. From a practical point of view, these RMs are in most cases the only available reference material for a specific type of substances and are therefore needed to calibrate any sample measurements versus a common scale. Some of these RMs should be considered as being traceable back only to the originating interlaboratory comparison exercise, especially those determined in the Seventies with a lack of available information on the formerly used methods, the laboratory calibration procedure and the uncertainty. This limitation should certainly not apply to these RMs which were tested only by few selected laboratories. In this case the traceability chain could be followed back directly to the primary reference material provided that these laboratories have given a detailed uncertainty budget for their measurements and sufficient information on the analysis procedures and provided all laboratory mean values and their uncertainties were taken properly into account for the final evaluation without a pure statistically driven outlier rejection. During the ongoing evaluation of the available reference materials their traceability will be re-assessed.

2.1.3 Determining the uncertainty of the measurement results.^{23,24} The reporting of uncertainty of measurement results is requested from participants in IAEA interlaboratory comparisons. However, in many cases only some of the sources of uncertainty are stated like the standard deviation of individual determinations or no uncertainty statement is provided at all. Only a few laboratories comply by stating a total uncertainty budget for their measurement process. For future assessments of the suitability of reference materials only such laboratories should be considered which provide sufficient data on their measurement uncertainty. This would certainly eliminate some of the major constraints hindering the full use of interlaboratory comparison exercises for the characterization of new reference materials in terms of traceability. As long as the principle of an uncertainty budget is not implemented in all laboratories, a provisional approximation of the combined standard uncertainty for measurements could be the assessment of internal standards and their long term behaviour. The standard deviation calculated from such a time series should be quite useful for estimation of a laboratory uncertainty as expanded standard uncertainty.

2.1.4 Calibration of an apparatus and assessment of a measurement method. As pointed out, one of the main applications of the existing reference materials for stable isotope ratio assay is the calibration of equipment and measurement procedures. Due to the large spectrum of investigated substances in isotope hydrology and isotope geochemistry a variety of reference materials was produced to enable a calibration with a material as similar as possible.

2.1.5 Use of reference materials for quality control purposes. The available reference materials are intended to calibrate internal standards prepared by the individual laboratories. The RMs are NOT intended to be used themselves for quality control purposes. For the distribution of all stable isotope ratio reference materials a rather strict rule applies: Each laboratory is entitled to order one unit of any reference material only once in a three years period. This limitation was set to preserve the availability of the valuable reference materials for the maximal possible time and therefore to ensure the comparability of results from laboratories over long times.

2.2 Future Plans

Holding a key role in producing and distributing reference materials for the determination of ratios of stable isotopes in light elements, the International Atomic Energy Agency follows as much as possible the latest requirements for the production of reference materials and developments in the metrological part of isotope geochemistry. In regular intervals of two to three years Advisory Group and Consultants Meeting are convened to discuss the latest approaches and new developments in stable isotope reference materials and to focus the IAEA activities on the main priorities.

Recently developed analytical techniques enable laboratories to analyze sample amounts ten to hundred times smaller than some years ago on their isotopic composition (for example by gas chromatography isotope ratio mass spectrometry GC-IRMS, or the use of Elementar Analyzers for on-line combustion of samples). At the same time these methods challenge the established system of reference materials in view of the required homogeneity of the existing RMs for such small amounts, which was not taken in consideration at the time of their production. The Isotope Hydrology Unit therefore has started the re-evaluation of the existing materials in order to derive the best possible information on the former production steps and on the homogeneity and uncertainty of the established recommended values. This implies significant efforts for this Unit in order to carefully assess the established materials. This task should not be delegated to other laboratories in view of the problems of the lack of traceability and rigorous uncertainty assessment in many laboratories and in recognition of the limitations for experienced laboratories to dedicate themselves to time consuming and expensive tasks at an on principle cost-free basis. As part of the development of an quality assurance system for the IAEA laboratories the Isotope Hydrology Unit aims to update the existing protocols to comply to the requirements of the quality assurance system as well as to the necessary preconditions for the characterization and certification of reference materials.

2.2.1 Existing RMs for the assessment of stable isotope ratios in water samples. The existing know-how in the Isotope Hydrology Unit for high precision analysis of stable isotope ratios in water samples has already resulted in a project to produce a successor material for VSMOW. VSMOW is expected to be exhausted within the next seven to ten years. Since all measurements of hydrogen and oxygen isotope ratios base in principle on this material, the production of a suitable replacement has high priority. It was decided in accordance with the recommendation of an IAEA consultants meeting to initiate the production of a water indistinguishable in its hydrogen and oxygen isotopic composition from the existing VSMOW. In order to be able to also reproduce the ratios of ^{17}O and ^{18}O , isotopically enriched water could not be used to adjust its isotopic composition. Therefore three natural raw water were identified with their isotopic composition as close as possible to VSMOW but with slight differences therein to allow a triangular mixing approach to produce the final water (figure 2).

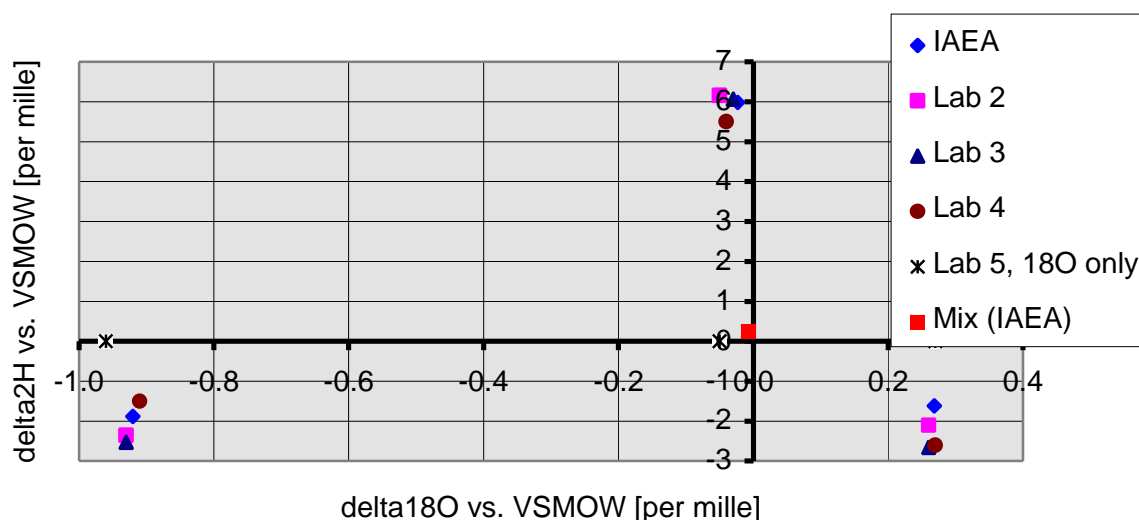


Figure 2 Calibration of three raw water for mixing a replacement for VSMOW by five laboratories (VSMOW being at the origin of the coordinate cross) and the preliminary result of a first trial mixing of the three components (big square close to the coordinate origin of the plot).

The three raw water were sampled, transferred to the Isotope Hydrology Unit and calibrated. This calibration was verified with the results of four other high precision stable isotope laboratories which were in accordance by better than $\pm 0.02\text{‰}$ for $\delta^{18}\text{O}$ and by better than $\pm 0.3\text{‰}$ for $\delta^2\text{H}$ (see figure 2). In the next step the three raw water will be mixed gravimetrically to produce the new standard which will then be tested carefully for any isotopic deviation from VSMOW.

Meanwhile the first attempts are initiated to obtain ice from the inner parts of Antarctica to produce a replacement for SLAP within the next years.

2.2.2 Existing RMs for carbon, sulfur and nitrogen isotopes. An intercalibration for the available sulfur stable isotope reference materials was started in 1998 in order to produce a consistent set of recommended values of all these RMs based on the VCDT scale. The evaluation of the results is ongoing.

A similar re-assessment is planned for some inorganic carbon RMs for 1999 in cooperation with NIST and invited laboratories. The Isotope Hydrology Unit has already upgraded its equipment to be able to test all existing inorganic carbon RMs and to produce new ones.

No similar activity is planned so far for nitrogen isotope RMs. The situation there seems to be satisfactory.

In view of the increasing importance of the determination of stable isotope ratios in organic materials (food authentication, medicine, biology, hydrogeology and isotope geochemistry), steps are foreseen to implement an appropriate analytical capability in the Isotope Hydrology Unit within the next two years for a high-precision determination of carbon isotopes in organic matter, mainly to be used for the certification of new reference materials.

2.2.3 New reference materials to be produced in future. The analytical capabilities of the Isotope Hydrology Unit should be upgraded to enable it to determine the isotopic composition of all existing reference materials. So far, nitrogen and sulfur isotopes cannot be measured at all and the capability for carbon analysis in organic matter is just being developed. Due to the increasing constraints for other laboratories to perform measurements on IAEA reference materials for homogeneity tests on a cost-free basis and in order to keep control over the data evaluation, this effort seems to be necessary. The establishment of recommended values for future reference materials will not rely anymore on interlaboratory comparison exercises, but will be based on extensive measurements in the IAEA

Isotope Hydrology Unit and the comparison of those results with a few selected laboratories of proven competence.

2.2.4 *Interlaboratory comparison exercises and proficiency tests.* The main focus of such exercises in the future will be to support quality assurance in stable isotope laboratories. Proficiency tests will be performed with selected laboratories where appropriate and desired by using well calibrated internal standards stored and used in the Isotope Hydrology Laboratory.

2.2.5 *Distribution of reference materials.* In general it would be desirable to change the distribution policy for future reference materials and allow laboratories to order these RMs more frequently. This implies that much larger batches of future RMs have to be prepared and handled. In the case of the successor material for VSMOW, about 200 litre will be produced, which is about three times more than previously for VSMOW.

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