

Absolute isotopic scale for deuterium analysis of natural waters. Absolute D/H ratio for SMOW¹

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ABSTRACT

The absolute isotopic ratios of the hydrogen content of two reference water standards called "SMOW"² and "SLAP"³ were measured to define an absolute isotopic scale. This isotopic scale can be used to normalize measurements of the natural isotopic variations in waters. The principle of the method used to define the zero of the scale is given. The absolute D/H ratios of SMOW and SLAP were measured by mass spectrometric comparison with calibration mixtures prepared in the laboratory. The following values are obtained:

$$\left(\frac{D}{H}\right)_{\text{SMOW}} = 155.76 \pm 0.05 \times 10^{-6}$$

$$\left(\frac{D}{H}\right)_{\text{SLAP}} = 89.02 \pm 0.05 \times 10^{-6}$$

$$\delta^0/_{\infty} \text{SLAP/SMOV} = 428.50 \pm 0.10$$

Samples of about 20 cc of the reference standards SMOW and SLAP are available from the International Atomic Energy Agency, on request.

Introduction

Variations of the isotopic abundance of hydrogen in natural waters are most often expressed in δ units based on a standard, generally SMOW. Graig (1961) has defined SMOW with respect to NBS 1 as $(D/H)_{\text{SMOW}} = 1.050 (D/H)_{\text{NBS 1}}$. From the definition of δ units it is clear that different values of the D/H ratio assigned to SMOW will correspond to different scales for δ 's. Extreme values for the absolute D/H ratio for NBS 1 have been found to be 149×10^{-6} (Horibe, 1960), and 154×10^{-6} (Roth, 1963), that is for SMOW absolute D/H ratios of 156.45×10^{-6} and 161.7×10^{-6} . These discrepancies explain at least partially why results obtained from different laboratories for the same samples are not in good agreement as shown by

Halevy (1967). Moreover, when samples with very low deuterium content are to be measured (i.e. measurements on lunar samples), one may question the significance of δ values approaching 1 000 ‰ if the zero of the isotopic scale is not precisely known.

In order to obtain *coherent* measurements it has been shown previously (Hagemann et al., 1968) that the assignment of deuterium content of natural waters requires the use of two reference standards. The measurements will be also accurate if the isotopic scale is defined with absolute values according to the relation

$$\delta_{\text{sample/st}_1} = \frac{l_{\text{sample}} - l_{\text{st}_1}}{l_{\text{st}_2} - l_{\text{st}_1}} \delta_{\text{st}_2/\text{st}_1}$$

where l are the readings on the mass spectrometer.

The measurements made by interpolation will be coherent but will be exact only if the δ between the two standards is correctly known.

¹ Work performed under contract with the International Atomic Energy Agency.

² Standard Mean Ocean Water.

³ Standard Light Antarctic Precipitation.

The purpose of this study, undertaken for the International Atomic Energy Agency, is precisely to determine the *absolute deuterium content* of two natural waters which could be considered as reference standards. It has been decided by a panel convened by I.A.E.A. that:

(1) these two standards should be such that practically the entire range of deuterium concentrations of natural waters lies between their D/H ratios, and (2) that one of them should have a D/H ratio as close as possible to SMOW, so that it can validly represent an actual SMOW sample. This latter standard was prepared in the laboratory of Professor H. Graig by distillation of Pacific Ocean water. It was compared in our laboratory with a sample of NBS 1 and its D/H ratio was found equal to $1.0499 (D/H)_{NBS1}$, a value in excellent agreement with the previous definition (Craig, 1961). Reasonably, therefore, this standard can be called SMOW. The depleted standard, previously called SNOW by the I.A.E.A., was obtained from snow collected on the Antarctic continent. In order to avoid its possible confusion in the future with SMOW, we propose the name SLAP (Standard Light Antarctic Precipitation).

Experimental

In order to obtain accurate absolute isotopic ratios of both standards SMOW and SLAP, the method used is based on the mass spectrometric comparison of these two standards with calibration mixtures. These calibration mixtures were prepared by mixing weighed amounts of heavy water with almost pure H_2O , both having very well known isotopic ratios. These last two waters are the two primary standards of the laboratory. The molar concentration of the heavy water, measured by infra-red spectroscopy (Ceccaldi, 1964), is equal to 0.99847 ± 0.00002 . The absolute isotopic ratio of the almost pure H_2O is equal to $1.71 \pm 0.03 \times 10^{-6}$. The principle of the method used to measure this ratio will be given. A detailed description can be found in a previous work (Hagemann et al., 1968).

I. Measurement of the absolute D/H ratio of a water sample with very low deuterium content

The deuterium content of water after reduction to hydrogen over a uranium furnace is

measured with a mass spectrometer. The principal difficulty encountered due to an ion molecule reaction, is the presence of H_2^+ ions which are generally not separated from HD^+ ions. Obviously, the main point is to determine the reading on the mass spectrometer for a water sample without deuterium. The method developed in this laboratory involves the production of water vapour with an isotopic ratio very close to zero using a small distillation column directly in the line of the mass spectrometer. This column is shown in Fig. 1.

It consists of a Pyrex tube 50 cm long and of 4 mm internal diameter. At the bottom a 50 cc flask is used as a boiler. The capillary of the inlet line of the mass spectrometer fits at the top of the condenser. Between this capillary and the ion source a uranium furnace reduces quantitatively water vapour to hydrogen. A 15 cc water sample carefully outgassed is introduced into the flask by complete distillation.

This system provides a depletion greater than 5 000 of the vapour at the top with respect to the water at the bottom of the column. Starting with low deuterium content water ($D/H = 10^{-6}$) this leads to vapour with a D/H ratio less than 10^{-9} , i.e. negligible within the precision of the measurements (about 10^{-8}). Moreover, such a system has the advantage of a "dynamic equilibrium". It is not imperative that the walls release absolutely no ordinary water, whose D/H ratio is about 150×10^{-6} , in order to avoid harmful contamination. As a distillation column provides continuous transport of deuterium towards the bottom and, if this transport is large compared with the rate of release from the walls, the latter does not affect the results. It was demonstrated in preliminary experiments that this condition was fulfilled here (Hagemann et al., 1968).

The mass spectrometer used for these measurements has essentially the same ion optics as described by Nief (1959). It is equipped with an automatic device for numerical measurements of ion currents, delivering results at regular periods with a sensitivity better than 0.01×10^{-6} .

The measurements are usually made with an ion current at mass 2 of 4×10^{-9} A. Under these conditions the H_2^+ peak is less than 9×10^{-14} A.

The absolute isotopic ratio of the low deuterium content water, which serves as the primary standard in the laboratory was found by this method to be $1.71 \pm 0.03 \times 10^{-6}$.

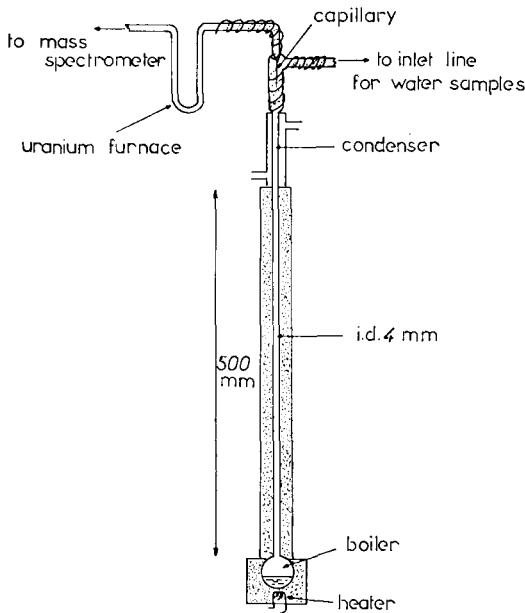


Fig. 1. Distillation column used to prepare water vapour with almost zero deuterium content ($D/H < 10^{-9}$) in the line of the mass spectrometer.

This absolute isotopic ratio was checked by preparing about 20 cc of water without deuterium, with a distillation column similar to the one described above, but equipped with a reservoir at the top. This reservoir permitted the recovery, after a 60-day run under known conditions, of 20 cc of water with a calculated D/H ratio less than 0.01×10^{-6} .

The accurate mass spectrometric comparison between this water and the primary standard mentioned above led to the assignment to the latter of an absolute isotopic ratio equal to $1.72 \pm 0.01 \times 10^{-6}$.

Thus, both methods agree to within 0.01×10^{-6} .

After defining the zero of the isotopic scale, the absolute (D/H) ratios of SMOW and SLAP were measured.

II. Absolute isotopic ratios of SMOW and SLAP

The absolute D/H ratios of SMOW and SLAP were determined using calibration mixtures of known D/H ratios prepared by mixing weighed amounts of the two primary laboratory standards. To prepare the calibration mixtures, a syringe is used to inject the waters which

constitute the mixture into a 100 cc flask. The preparation is performed in a glove box under dry nitrogen flow. The weights are known to a precision of ± 0.1 mg. The ^{18}O isotopic composition of the primary laboratory standards is taken into account in calculating the D/H ratios. Then, with the mass spectrometer, these calibration mixtures were accurately compared to SMOW and SLAP.

Four calibration mixtures, E_1 to E_4 , were prepared, two with ratios close to that of SMOW and two with ratios close to that of SLAP (Table 1).

To improve the accuracy of the results, two other methods based on the same principle were used. In one of these, heavy water was not used. The calibration mixtures, E_5 to E_8 , with D/H ratios close to that of SLAP are prepared by mixing known amounts of SMOW and light water. This method allows the accurate determination of the $\delta \%$ of SLAP relative to SMOW. In the other method the light primary laboratory standard is not used. The calibration mixtures, E_9 to E_{12} , with D/H ratios close to that of SMOW are prepared by mixing known amounts of SLAP and heavy water. This method is used to determine independently the difference between the absolute D/H ratios of SMOW and SLAP.

The results are summarized in Table 1.

Table 1. Experimental results for R_{SLAP} , R_{SMOW} and $\delta \%$ SLAP/SMOW

Calibration mixtures	Constituents	Absolute values SMOW and SLAP
E_1		SLAP = 89.04×10^{-6}
E_2	Heavy water	SLAP = 89.00×10^{-6}
E_3	+	SMOW = 155.75×10^{-6}
E_4	Very light water	SMOW = 155.78×10^{-6}
E_5		$\delta \%$ SLAP/SMOW = -428.58
E_6	SMOW	$\delta \%$ SLAP/SMOW = -428.51
E_7	+	$\delta \%$ SLAP/SMOW = -428.47
E_8	Very light water	$\delta \%$ SLAP/SMOW = -428.45
E_9	SLAP	$R_{SMOW} - R_{SLAP} = 66.63 \times 10^{-6}$
E_{10}	+	$R_{SMOW} - R_{SLAP} = 66.68 \times 10^{-6}$
E_{11}	heavy water	$R_{SMOW} - R_{SLAP} = 66.78 \times 10^{-6}$
E_{12}	water	$R_{SMOW} - R_{SLAP} = 66.74 \times 10^{-6}$

Discussion

From the calibration mixtures E_1 to E_4 , the absolute D/H ratios are:

$$R_{\text{SMOW}} = 155.76 \pm 0.05 \times 10^{-6}$$

$$R_{\text{SLAP}} = 89.02 \pm 0.05 \times 10^{-6}$$

The quoted uncertainty includes the uncertainty of the measurements on the mass spectrometer, (0.02×10^{-6}) and that of the absolute ratio of the light primary standard (0.03×10^{-6}).

From the above values, the following are deduced directly

$$R_{\text{SMOW}} - R_{\text{SLAP}} = 66.74 \pm 0.04 \times 10^{-6}$$

$$\delta \text{‰ SLAP/SMOW} = -428.48 \pm 0.25$$

The absolute value of $\delta \text{‰ SLAP/SMOW}$ is found with the best accuracy from the E_5 to E_8 calibration mixtures: $\delta \text{‰ SLAP/SMOW} = -428.50 \pm 0.10$.

This value is in excellent agreement with that obtained from E_1 to E_4 .

The mean value for the difference $R_{\text{SMOW}} - R_{\text{SLAP}}$ is found to be $66.71 \pm 0.08 \times 10^{-6}$ from E_9 to E_{12} , this value is also in good agreement with the one deduced from E_1 to E_4 .

We retain the following absolute values:

$$R_{\text{SMOW}} = 155.76 \pm 0.05 \times 10^{-6}$$

$$R_{\text{SLAP}} = 89.02 \pm 0.05 \times 10^{-6}$$

$$\delta \text{‰ SLAP/SMOW} = -428.50 \pm 0.10$$

Conclusions

The calibration mixtures prepared in three different ways lead to coherent results which confirm the validity of their method of preparation. The precision of this preparation method combined with the sensitivity of the device used for the numerical measurement of ion currents on the mass spectrometer have permitted the definition of the absolute D/H ratios of the standards SMOW and SLAP to a high accuracy. The value obtained for the ratio of SMOW is appreciably lower, from 2 to 4% than the one adopted in most laboratories.

The D/H ratios measured for SMOW and SLAP and more precisely the $\delta \text{‰ SLAP/SMOW}$ define an absolute isotopic scale which may be used to normalize measurements of the natural isotopic variations in waters.

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АБСОЛЮТНЫЕ ИЗОТОПНЫЕ ШКАЛЫ ДЛЯ АНАЛИЗА СОДЕРЖАНИЯ ДЕЙТЕРИЯ В ПРИРОДНЫХ ВОДАХ. АБСОЛЮТНОЕ ОТНОШЕНИЕ D/H ДЛЯ SMOW.

С целью определения абсолютной изотопной шкалы были измерены абсолютные отношения содержаний изотопов водорода для двух отсчетных стандартов воды, называемых «SMOW» и «SLAP». Эта изотопная шкала может быть использована для стандартизации и нормализации измерений естественных вариаций изотопического состава в различных образцах воды. Дается принцип метода, использованного для определения нуля шкалы. Абсолютные отношения D/H для «SMOW» и «SLAP» были измерены путем масс-спектро-

метрических сравнений с калиброванными смесями, приготовленными в лаборатории. Получены следующие значения:

$$(D/H)_{\text{SMOW}} = 155,76 \pm 0,05 \times 10^{-6},$$

$$(D/H)_{\text{SLAP}} = 89,02 \pm 0,05 \times 10^{-6},$$

$$\delta \text{‰}_{\text{SLAP/SMOW}} = -428,50 \pm 0,10.$$

Образцы SMOW и SLAP объемом около 20 см³ можно получить по запросу из Международного агентства по атомной энергии.