Applied Geochemistry 98 (2018) 17–21

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

New determination of the ^{3}He mixing ratio in the Earth's lower atmosphere from an international tritium intercomparison exercise

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ARTICLE INFO

Editorial handling by Prof. M. Kersten

Keywords:
Helium-3
Tritium
Mass spectrometry

ABSTRACT

The light isotope of helium, ^{3}He, is essentially a primordial substance entrapped within the Earth's interior during the formation of the planet. It is released into the atmosphere by volcanic/magmatic activity, and eventually escapes to outer space. ^{3}He is also produced by the radioactive beta-decay of tritium. Hence, measurements of ^{3}He can be used to derive the concentration of tritium. The so-called "^{3}He ingrowth" method uses a mass spectrometer to detect the amount of ^{3}He that accumulates in a sample during a given period of storage. The ^{3}He measurements are classically calibrated against an air standard. The method thus relies on the accurate knowledge of the atmospheric mixing ratio of ^{3}He. This value is based on mass spectrometric measurements with gravimetrically or volumetrically prepared ^{3}He standard mixtures. Here, we apply the ^{3}He ingrowth method in reverse, using a solution of tritiated water prepared for an international comparison of tritium activity measurements to precisely determine the ^{3}He mixing ratio of our air standard. The measured atmospheric mixing ratio of ^{3}He, based on a series of ten measurements, is [^{3}He] = 7.12 ± 0.06 ppt. This value is between 1% and 2% lower than previous determinations reported in the literature. However, all results remain statistically consistent.

1. Introduction

In the ^{3}He ingrowth method, the activity of tritium is determined via the mass spectrometric measurement of the helium-3 (^{3}He) produced by the radioactive decay of tritium (Clarke et al., 1976). Because the atmospheric residence time of helium (~10^6 years) is much longer than the mixing time of the atmosphere (~10 years only), the ^{3}He content of the atmosphere is the same over the whole globe (Glückauf and Paneth, 1946; Jean-Baptiste and Fourré, 2012). Air is thus a convenient ^{3}He standard, that is classically used by the tritium laboratories applying the ^{3}He ingrowth technique. The value of the ^{3}He mixing ratio in atmospheric air is therefore an important parameter because any uncertainty in this value directly affects the measured tritium concentrations. This value appears to be reasonably well known: One direct determination was by Davidson and Emerson (1990). They used mass spectrometry with gravimetrically prepared ^{3}He standards and found a value of 7.27 ± 0.20 ppt; other relevant publications (Table 1), which concern the ^{4}He content of air (Glückauf, 1944, 1946; Oliver et al., 1984; Holland and Emerson, 1987) and the ^{3}He/^{4}He ratio of air (Mamyrin et al., 1970; Clarke et al., 1976; Sano et al., 1988; Hoffman and Nier, 1993) lead to a mean value of 7.21 with a standard uncertainty of the mean equal to ± 0.07 ppt (calculated by a bootstrap technique). However, all these determinations rely on gravimetrically or volumetrically prepared ^{3}He mixtures. Therefore, we thought that determining the atmospheric mixing ratio of ^{3}He using a totally independent method would be of some interest. Because we routinely use the ^{3}He ingrowth method for tritium measurements (Jean-Baptiste et al., 1992, 2010), we were able to apply the ^{3}He ingrowth method in reverse, using a solution of tritiated water prepared for an international comparison of tritium activity measurements to determine the ^{3}He mixing ratio of our air standard.

2. The CCIR(II) 2009 International Tritium Intercomparison

An international comparison of activity measurements of a solution of tritiated water was organised by the Consultative Committee for Ionizing Radiation (CCIR) in 2009. The tritiated water was prepared and dispatched to the participants by the Laboratoire National Henri Becquerel (LNHB), the French National Metrology Institute for radioactivity standards. Fifteen laboratories took part in the exercise (Table 2) and reported a total of 22 independent results. Most laboratories applied the triple-to-double coincidence ratio (TDCR) method in

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https://doi.org/10.1016/j.apgeochem.2018.09.003
Received 31 July 2018; Received in revised form 4 September 2018; Accepted 4 September 2018

Table 1

Atmospheric ^{4}He mixing ratios and ^{3}He/^{4}He values from the literature.

References	^{3}He/^{4}He ($\times 10^6$)
Mamyrin et al. (1970)	1.399 ± 0.013
Clarke et al. (1976)	1.384 ± 0.006
Sano et al. (1988)	1.343 ± 0.013
Davidson and Emerson, 1990	1.393 ± 0.014
Hoffman and Nier (1993)	1.371 ± 0.019
References	**^{4}He (ppm)**
Glückauf (1944)	5.24 ± 0.03
Glückauf (1946)	5.239 ± 0.004
Oliver et al. (1984)	5.222 ± 0.0017
Holland and Emerson (1987)	5.220 ± 0.0041

liquid scintillation counting (LSC). The TDCR method is a primary standardization method of measuring radioactivity, mainly used by metrology laboratories. It requires a special liquid scintillation (LS) counter equipped with three photomultipliers (A, B and C) in coincidence. Such instrumentation is generally designed and constructed by national metrology laboratories around the world. The TDCR system allows the observation of double AB, BC, and CA and triple ABC coincidences, making it possible to measure the absolute activity of the radioactive solution, independently of the detection efficiency (Broda et al., 1988; Broda and Pochwalski, 1992; Cassette and Vatin, 1992; Stanga et al., 2006).

The reference time and date used were 00:00 UTC, 31 May 2009 -. The Power-Moderated weighted Mean formalism – PMM (Pommé, 2012) was used to evaluate the Key Comparison Reference Value (KCRV). The value given by the MKEH (Budapest, Hungary) was identified as an outlier by the PMM procedure. In addition, the results of BARC, IRMM obtained by methods using ^{3}H external standards were not used to calculate the KCRV The KCRV calculated using the PMM method is thus 37.10 ± 0.19 Bq/mg, corresponding to a relative uncertainty of 0.51% (Ratel and Michotte, in prep.). A summary of the results is given in Fig. 1 and Table 2.

3. Method

3.1. Dilution procedure

Half a liter of a tritium solution was prepared from the tritiated water distributed for the CCIR(II) 2009 International Tritium Intercomparison by two-step gravimetric dilution with "tritium-free" groundwater (0.09 ± 0.01 Bq/kg). First, in a glove box flushed with argon, a few drops (113.05 ± 0.01 mg) of the initial tritiated water were added with a syringe to 11.02 ± 0.02 g of "tritium-free" water. Then, in the same way, 135.52 ± 0.01 mg of this water was in turn added to 473.20 ± 0.02 g of "tritium-free" water, leading to a reduction factor of the initial tritium concentration of $(3.435 \pm 0.007) \times 10^5$ and a final solution of ~100 Bq/kg. The weighing process consisted in weighing the empty and the filled containers and, in case of the tritium standard, the transfer container (syringe) before and after the transfer. All dilutions were performed using calibrated balances and calibrated weights traceable to the French national mass standards, checking the zero reading and making test weights before and after each weighing process. Buoyancy corrections were applied. The combined uncertainty of the weighing procedure was calculated according to the Guide to the expression of uncertainty in measurement (JCGM, 2008).

3.2. Sample preparation and ^{3}He mass spectrometry

Ten 100 ml low-helium diffusivity Corning 1724 glass bulbs were filled with approximately 40 g of the prepared standard solution. To minimize ^{3}He blank, the bulbs were pre-baked in a flow of argon at 600 °C for 24 h to remove the helium dissolved in the glass. The samples were degassed using a routine procedure (Jean-Baptiste et al., 1992). However, to avoid any bias due to isotope fractionation that might have occurred during pumping, a special water trap at 77 K was inserted between the sample and the pumping unit to trap water vapor and to transfer it back into the sample at the end of the degassing.

The storage time was about 120 days. ^{3}He which accumulated during this period of time was measured with a MAP-215-50 mass spectrometer (Jean-Baptiste et al., 2010). Classically, along with the tritiugenic ^{3}He signal, a small ^{4}He signal ($n^4He_{res} < 5 \times 10^{-14}$ mol) can be detected as well. This ^{4}He corresponds to the small air residue left behind at the end of the degassing step, but also, to a minor extent, to diffusion through the glass bulb (Jean-Baptiste et al., 1989) and leaking through adapter fittings. The corresponding ^{3}He signal ($n^3He_{res} < 7 \times 10^{-20}$ mol, i.e., representing about 0.08% of the measured ^{3}He signal) can be calculated by applying the ^{3}He/^{4}He ratio of this air residue, R_{res}. The statistics of measurements on samples analysed immediately following degassing (i.e., with no tritiugenic ^{3}He contribution) show that R_{res} is identical to the ^{3}He/^{4}He ratio of air, R_a, within ± 10%. Hence R_{res} can be written as follows: $R_{res} = \alpha R_a$, with $\alpha = 1.0 \pm 0.1$. The ^{3}He blank of the inlet system, n^3He_{blank} is less than 5×10^{-20} mol. Most of it is due to the O'ring which is used to attach the glass bulb to the inlet system. The ^{3}He/^{4}He ratio of this line blank is not statistically different from R_a, hence we assume that $R_{blank} = R_{res} = \alpha R_a$.

The measurements are calibrated against an air standard drawn from a 5 L tank filled with clean air at known pressure, temperature and relative humidity conditions, through a precisely calibrated volume V = 122.2 ± 0.1 (1 σ) mm^3 (Jean-Baptiste et al., 2014). The total number of aliquots withdrawn from the 5 L tank is recorded in order to take into account the decreasing pressure in the tank. $^4He^+$ is measured on a Faraday cup. The $^3He^+$ ion beam (~250 ions/sec for an air standard with about 3.7×10^{-17} ^{3}He mole) passes through an electrostatic filter before impinging the detector (a 16-stage electron multiplier connected to a pulse counting system). The ^{3}He background is very low (< 0.05 count/sec) when employing the electrostatic filter, which constitutes the ultimate limit for the ^{3}He detection. The counting procedure consists of five series of counting of the $^3He^+$ signal interspaced by five measurements of the $^4He^+$ peak and baseline. Each series consists of ten 10-s integrations on the $^3He^+$ peak and on the baseline, corresponding to a total counting time of 500 s on the peak and 500 s on the baseline.

In routine operation, each sample measurement is followed by a standard air aliquot (Jean-Baptiste et al., 1992, 2010). A correction is routinely applied to take into account the pressure effect in the source due to the fact that the sample contains some 10^{-14} mol of gas only whereas the air aliquot contains about 10^{-10} mol of helium and neon (neon is not retained by the charcoal trap at 77 K). For this special experiment however, to avoid any additional uncertainty arising from this correction, an aliquot of the air standard was introduced in the inlet line with each sample so as to keep the pressure in the source identical for the standard and for the sample.

With this special protocol, the amount of helium-3 (n^3He_{meas}) and helium-4 (n^4He_{meas}) corresponding to the (sample + standard) measurement obeys the following equations:

$$n^3He_{meas} = n^3He_{tri} + n^3He_{std} + n^3He_{res} + n^3He_{blank} \quad (1)$$

$$n^4He_{meas} = n^4He_{std} + n^4He_{res} + n^4He_{blank} \quad (2)$$

where n^3He_{std} and n^4He_{std} are the ^{3}He and ^{4}He amount in the air standard aliquot, respectively; n^3He_{res} and n^4He_{res} are the residual amounts of ^{3}He and ^{4}He, respectively, left behind at the end of the degassing step; and n^3He_{blank}, n^4He_{blank} are the amount of ^{3}He and ^{4}He, respectively, of the blank of the inlet system. n^3He_{tri} is the amount of tritiugenic ^{3}He produced during the storage time