



# Optimization of oxygen-18 ratio measurements by equilibration – Isotope ratio mass spectrometry using various water content matrices



Francois Guyon<sup>a,\*</sup>, Laetitia Gaillard<sup>a</sup>, Dana Alina Magdas<sup>b</sup>

<sup>a</sup> Service Commun des Laboratoire, 3 Avenue du Docteur Albert Schweitzer, 33600 Pessac, France

<sup>b</sup> National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat Str., 400293 Cluj-Napoca, Romania

## ARTICLE INFO

### Keywords:

Oxygen-18  
*In situ* measurement  
 Pasty matrix  
 Isotope ratio mass spectrometry

## ABSTRACT

In the acknowledge method for the determination of oxygen isotope ratio from water, the oxygen-18 ratio ( $\delta^{18}\text{O}$ ) quantification is performed on a relatively high amount of liquid solution. Recently, we proved that the oxygen-18 determinations can be made directly on a pasty matrix, using so called *in situ* measurements. In this paper, the accuracy of *in situ* measurements was demonstrated by the correspondence between  $\delta^{18}\text{O}$  values quantified *in situ* and those performed on the water, previously extracted from the pasty matrix itself. The use of matrices with various humidity (17–100% of water) allowed the construction of a model able to estimate the optimum amount of matrix requested for *in situ* equilibration according to its humidity. This study reveals that only 6  $\mu\text{L}$  of liquid (water) is enough to obtain an accurate value and that, in the experimental configuration used, the minimum water content is 20% to obtain reliable and reproducible results.

## 1. Introduction

Among organic stable isotopes, oxygen-18 ratio of water has proven to be of high interest in various research areas due to its tracing applicability: in paleoclimatology to estimate the evolution of temperature precipitation through time [1], in hydrology to study water cycle [2], in plant physiology to monitor for plant's water fractionation [3]. The water oxygen-18 content, interlinked to climate and geographical localization [4], can be used to study plant growing conditions. As a result, this  $^{18}\text{O}$  ratio can be used for beverages authentication: verification of geographical origin, detection of reconstituted beverages and addition of exogenous water [5–7]. The measurement of oxygen-18 ratio is performed through gas/liquid equilibration according to the equilibration equation:



where “l” stands for liquid. In order to link oxygen ratio to Vienna Standard Mean Ocean Water (V-SMOW), the  $\text{CO}_2$  is firstly calibrated against the international standard; oxygen-18 value correspond to the ratio of oxygen-18 content regarding oxygen-16 content, expressed as ( $\text{O}^{18}/\text{O}^{16}$ ) or  $\delta^{18}\text{O}$ . In the usual analytical procedures for  $\delta^{18}\text{O}$  measurements by equilibration/isotope ratio mass spectrometry (IRMS), a minimum volume of 200  $\mu\text{L}$  of liquid is recommended, volume that can be a limiting factor for some applications.

As a result, the idea of performing the equilibration step directly on the investigated matrix was attempted in order to reduce the preparatory stages. To our knowledge, only two examples of  $\delta^{18}\text{O}$  measurements performed *in situ*, directly on the matrix without a preliminary water extraction were previously reported [8,9]. The first work was performed on earth core to study  $\delta^{18}\text{O}$  evolution along the 2 m depth below the soil surface [8]. The second example is an analytical procedure we developed to quantify oxygen-18 ratio directly on prune paste [9] for routine analysis. *In situ* measurements of  $\delta^{18}\text{O}$  ratios allowed to establish a clear distinction between rehydrated and non-rehydrated prunes. This approach is very promising for dried and semi-dried food control. Nonetheless, the correlation between the  $\delta^{18}\text{O}$  measured *in situ* and in extracted water was missing. Thus, the robustness of the *in situ*  $\delta^{18}\text{O}$  measurement needed to be confirmed through a comparison with  $\delta^{18}\text{O}$  measured on the water extracted from the paste and using the acknowledge method.

In this study, the accuracy of *in situ* water oxygen-18 ratio measurements was confirmed by comparing the results obtained on different paste mixtures with those obtained on the water previously extracted from the pasty matrix. Then, the analysis of various paste samples with different water content were used to optimize the amount of raw material required for accurate *in situ*  $\delta^{18}\text{O}$  measurements. These information allowed the elaboration of mathematical model linking the matrix water content and the optimal amount of matrix for equilibration.

\* Corresponding author.

E-mail addresses: [guyonfra@gmail.com](mailto:guyonfra@gmail.com), [Labo33@scl.finances.gouv.fr](mailto:Labo33@scl.finances.gouv.fr) (F. Guyon).

<https://doi.org/10.1016/j.talanta.2018.07.022>

Received 29 April 2018; Received in revised form 6 July 2018; Accepted 10 July 2018

Available online 11 July 2018

0039-9140/ © 2018 Elsevier B.V. All rights reserved.

## 2. Material and method

### 2.1. Reagents

Carrier gas (Helium, 5.6 grade), reference gas (CO<sub>2</sub>, 4.5 grade), equilibrium gas (CO<sub>2</sub>/helium 5% ± 2%) were provided by Linde (Bassens, Bordeaux, France). Oxygen 18 standards were provided by the IRMM (Geel, Belgium; standard reference: BCR 658) and IAEA (Vienna, Austria; standard reference: V-SMOW-2).

### 2.2. Samples

Water comes from a 10 L tank of laboratory tap water with δ<sup>18</sup>O ratio internally calibrated. Vegetables and dry fruits samples come from the grocery store. At reception the samples were stoned, then crushed in an analytical mill to get a homogeneous paste that is stored at –10 °C until analysis. Homemade mixtures were elaborated using two kinds of prunes “regular” and “mi-cuit” that corresponds, respectively, to plums dried to 20–22% humidity and then rehydrated to 35% humidity and to plums only dried to 35% humidity before commercialization.

### 2.3. Water content measurements

Sample water content was quantified by conductivity according to the method described in the AOAC official method compendium [10]. This method was applied to dried fruits with a 10–40% water content. For vegetables with a higher water content, the average value found in the literature has been used for model construction. [11]

### 2.4. Water extraction system

A cryogenic distillation system under static vacuum was used to extract the water from the pasty matrix. Four grams of the paste were spread onto the vial walls in order to enhance the evaporation surface. At room temperature, the vials with the samples were connected to a vacuum line (10<sup>–3</sup> Torr) via a water collecting tube plunge into liquid nitrogen [12]. This water extraction step took around 6 h. The quantitative recovery was checked by mass difference between recuperated water weight and expected water weight computed from water content determined by official method AOAC 934.06 [13]. Under these conditions, a volume of 1.3 ± 0.05 mL was collected and an aliquot (0.2 mL) was directly transferred in 1.5 mL vial for δ<sup>18</sup>O measurements. The water, in excess or for postpone measurements, was kept in a capped vial at 4 °C without any water preservation of the headspace by inert gas filling.

### 2.5. Oxygen 18 measurements

δ<sup>18</sup>O was quantified by two techniques whether it was performed on the extracted water or *in situ* on the paste. **Extracted water:** δ<sup>18</sup>O ratio was quantified on a Liquid-Water Isotope Analyzer (DLT-100, Los Gatos Research). Extracted water samples were kept at 24 °C overnight before being measured. Internal working temperature of Liquid-Water Isotope Analyzer was in the range of 28.5–28.9 °C. For each sample, two replicates were measured six times each. Oxygen 18 isotopic values were calibrated against internally validated laboratory standards (*Std*): *Std. 1* (–11.54‰); *Std. 2* (–7.14‰); *Std. 3* (–2.96‰). The δ<sup>18</sup>O standardization values against international standards. ***In situ* water:** The full protocol was previously described in ref. 9. Briefly, the paste is manually spread onto the maximum surface of the vial walls. On [Supplementary Fig. S-1](#), two pictures illustrate the deposition of the prunes paste on the cell wall of a vial (Labco Limited, UK, ref 728 W, H: 49 mm, internal diameter: 8 mm). The amount of paste is controlled by weight. Then, the vial are sealed, placed in automatic equilibrium system, AES (Multiflow, Elementar, Villeurbanne, France). This thermostatically-controlled (40 °C) system allows the automatic injection of

the equilibrium gas, CO<sub>2</sub>/He 5% after an headspace flush with this gas and the recovery of the headspace gas for oxygen-18 quantification by isotope ratio monitoring by mass spectrometry (irm-AES/MS, Isoprime/elementar) after a 6 h equilibrium step.

### 2.6. Isotope ratio computation

Masses measured by irm/MS correspond to <sup>12</sup>C<sup>16</sup>O<sub>2</sub> (*m/z* = 44) and <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O (*m/z* = 46). All the provided oxygen 18 isotope ratio (δ<sup>18</sup>O) are expressed against the international standard, Vienna- standard Mean Ocean Water (V-SMOW-2) according to

$$\delta^{18}\text{O}(\text{‰}) = \left( \left[ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \right] - 1 \right) \times 1000. \quad (2)$$

## 3. Results and discussion

### 3.1. Relation between extracted water and *in situ* oxygen 18 isotope ratios

Oxygen 18 isotope ratio (δ<sup>18</sup>O) is determined after the equilibrium step between oxygen atoms of the CO<sub>2</sub> gas added in the vial (gas mixture CO<sub>2</sub>/He, 5%) and water oxygen ratio of the investigated samples. Usually, in the acknowledge methods, δ<sup>18</sup>O measurements are performed on 200 μL of liquid after an equilibrium step of 6 h at 40 °C. In most applications (*i.e.* Food science, hydrology...), this analysis is always performed on liquid water. Due to the need of the market to extend these applications to other food commodities with a low water content, but which could be adulterated by water addition, we recently developed an alternative to the classical approach. Thus, the feasibility of δ<sup>18</sup>O measurement directly performed on the *in situ* water contained in a pasty matrix was demonstrated [9]. Nonetheless, the pending question was the demonstration that δ<sup>18</sup>O ratio measured *in situ* on the pasty matrix was similar to the δ<sup>18</sup>O ratio obtained on the water recovered after extraction from the paste. For this purpose, a distillation system under static vacuum was used to extract the paste water. An optimal amount of paste was found to be in the range 3–5 g. Under these conditions, the measurements on water extracted from 3 portions of the same sample led to a variation of δ<sup>18</sup>O values lower than 0.24‰. It demonstrated that no isotope fractionation occurs during the water distillation and recovery step. Therefore, for the purpose of this study, the amount of prune paste was fixed at 4 g being spread at the maximum of the cell wall surface to facilitate a complete water extraction.

Two samples of mi-cuit prunes (MCP, δ<sup>18</sup>O = 10.78 and 7.56‰) and two others of regular prunes (RP, δ<sup>18</sup>O = 1.98 and 0.26‰) were, respectively, used to prepare 2 different batches: each one was composed by the two initial prune paste, MCP and RP, and the 4 mixtures with various amount of MCP incorporated to RP (in a percentage of 20%, 50%, 80% and 90%). The mixtures were prepared using an analytical mill in order to obtain a homogeneous amount of prune paste (60 g). The first batch was prepared using MCP having δ<sup>18</sup>O = 10.78‰ and RP with δ<sup>18</sup>O = 1.98‰ while the second batch by using the two other prune pastes. In the [insert of Fig. 1](#), δ<sup>18</sup>O value, measured *in situ*, as a function of the MCP percentage in the mixture was illustrated. As expected, the oxygen-18 value raises with increase of the MCP amount in the mixture. The correlation factor (R<sup>2</sup>) was founded to be 0.98, indicating that the mixtures are homogenous and that the method is highly sensitive to detect the ratio MCP/RP from mixtures as far as δ<sup>18</sup>O values of the starting materials are known.

In the second experiment, total water contained in the pastes (MCP, RP and mixtures) was recovered using a specific distillation system which heats the 4 g of paste under vacuum. The extracted water vapors were condensed in a water trap dived in a liquid nitrogen bath. δ<sup>18</sup>O value of the extracted water was then measured using an Liquid-Water Isotope Analyzer. δ<sup>18</sup>O values measured by the two analytical methods (*in situ* and on extracted water) were correlated in [Fig. 1](#). A correlation factor of 0.97 and a 0.68% standard deviation were found between the

Download English Version:

<https://daneshyari.com/en/article/7676100>

Download Persian Version:

<https://daneshyari.com/article/7676100>

[Daneshyari.com](https://daneshyari.com)