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Use of Isotope Ratio Mass Spectrometry (IRMS) Determination ($^{18}O/^{16}O$) to Assess the Local Origin of Fish and Asparagus in Western Switzerland

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Abstract: Here we present the use of isotope ratio mass spectrometry (IRMS) for the detection of mislabelling of food produced in Switzerland. The system is based on the analysis of the oxygen isotope distribution in water ($\delta^{18}O$). Depending on the location on the earth, lake or groundwater has a specific isotopic distribution, which can serve as a fingerprint in order to verify whether a product has grown by means of the corresponding water. This report presents specifically the IRMS technique and the results obtained in the origin detection of fish grown in selected Swiss lakes as well as asparagus grown in Valais ground. Strengths and limitations of the method are presented for both cited products; on one hand, the technique is relatively universal for any product which contains significant water but on the other hand, it necessitates a rather heavy workload to build up a database of water $\delta^{18}O$ values of products of different origins. This analytical tool is part of the concept of combating fraud currently in use in Switzerland.

Keywords: Asparagus · Authentication · Fish · Fraud · IRMS

1. Introduction

Water is universally present in living organisms on the planet. Its chemical composition differs when water has been in contact with different soils leading to different mineralisations. Similarly, the distribution of stable isotopes such as oxygen-18 (^{18}O) and deuterium (^{2}H or D) in water is dependent on the geographical localisation on Earth. This distribution is due to different factors such as multiple distillation/dilution due to evaporation and rainfall; this effect was first reported in 1935 by Dole,[1] who provided the early analytical evidence of heavy isotopes in Lake Michigan water. Since this discovery, analytical methods have been proposed to perform the measurement of $^{18}O/^{16}O$ ratio of water at different positions on Earth. One of the methods is to use the capacity of CO_2 to dissolve in water. It is known that CO_2 can exchange its oxygen atoms with water in a few hours.[2] Epstein proposes a method in which a water sample is placed into contact with CO_2 for three days, permitting an exchange of ^{18}O from the water to CO_2 followed by a mass spectrometry analysis of the equilibrated CO_2.[3] It is then possible to measure and interpret the distribution of heavy isotopes in rain depending on different factors such as the distance from the ocean or the elevation over sea level.[4] It became clear that across a continent, the rainwater closer to the ocean presents a higher concentration of the heavy isotope, since this would precipitate before the lighter isotope. During the evolution of these specific methods, it became obvious that there was a need for a conventional reference shared by the scientific community in order to exchange results on the subject: this reference was decided to be the Vienna Standard Mean Ocean Water (V-SMOW) and the unit of expression of results is $\delta^{18}O$ as defined in Eqn. (1):

$$\delta^{18}O = \left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{sample}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}} - 1 \right) * 1000\ ‰ \quad (1)$$

Besides climate and rainfall studies, this method has also been applied to characterise isotopic water composition in living organisms. For example the isotopic water composition of plants grown under different growth conditions has been studied; Dunbar and Wilson[5] showed that $^{18}O/^{16}O$ isotopic distribution analysis in water extracted from plants revealed a higher concentration of heavy isotopes (^{18}O) than the groundwater: *"$^{18}O/^{16}O$ measurements performed on water extracted from various sections of grown plants, showed that the enrichment was found to occur in the following order: leaves > fruit > stem ≥ ground water."* The authors indicate *"that the physical process causing this enrichment was probably evaporation, i.e. evapotranspiration."*

This pioneer work showed that it is possible to obtain a geographical distribution of rain water in different locations and that botanical and metabolite features impact on the ^{18}O content in the plant water. Based on this evidence, several studies have been conducted to measure the $\delta^{18}O$ value of water content of fruit,[6] juices,[7] purees[8] or alcoholic beverages[9,10] in order to detect origin fraud or illegal dilution.[9–11] Official controls have already been reported in 2006 in Germany for asparagus origin detection with $\delta^{18}O$ isotopic ratio of asparagus water.[12]

An inter-laboratory trial has been presented by Rossmann *et al.* which reports different Europe-based laboratory measurements of $\delta^{18}O$ values in German, Italian and French wine water.[10] The results show that the wine samples originating from southern Europe and/or close to the sea, presented higher $\delta^{18}O$ values. These measurements are in good agreement with, on the one hand, the rainfall, which delivers more ^{18}O close to the sea and on the other hand, the effect of higher temperatures, which favours the evapotranspiration of the grapes and therefore increases the

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^{18}O content in the juice. In a similar way, in 2004 our laboratory investigated the authenticity of tomatoes and grape must by IRMS.[13]

Here we present the use of ^{18}O analysis of water extracted from fish and from selected Swiss lakes where the fish grew. We will show the advantage and limitation of this technique applied to detect mislabelling of fish origin. Isotopic distribution analyses in fish have already been published but these studies were mainly focused on $\delta^{13}C$ and $\delta^{15}N$. Busetto *et al.*[14] were interested in the authentication of farmed and wild turbot; Dempson *et al.*[15] did the same investigation for farmed and wild Atlantic salmon and McCarthy *et al.*[16] looked for brown trout and sea trout differentiation in eggs and alevins. In another study Jardine *et al.*[17] were focused on the ecological impact of nutrients in the isotopic ratio in fish. To the best of our knowledge no report has presented the use of $\delta^{18}O$ values of water to track mislabelling of fish origin. Since 2008, our laboratory has been building up a database of $\delta^{18}O$ values of local fish and has compared the results with fish from other producing regions.

In a second part, we present a project to track mislabelling of asparagus grown in Valais (part of Switzerland). Valais is an area surrounded by high mountains of more than 3000 m to the north and more than 4000 m to the south. This special environment results in a particular isotopic water composition which can be used to trace asparagus grown in Valais; when there is no local production, asparagus is imported to Valais mainly from France, Spain and Peru. For ten years, a database of $\delta^{18}O$ values of local grown asparagus water has been built up and compared with asparagus from other producing countries.

As an official food control laboratory, our mission is to fight fraud in origin labelling, especially for products which have been produced in our area. These collections of data for fish and asparagus allow the specificity of the method and the strategy of official control to be described which we have put in place in our region.

2. Material and Methods

2.1 *Sample Preparation*

Water extract from fish: Approximately 400 g of fillet with the skin are homogenously mixed 5–7 seconds (mixer Büchi 400, Büchi Laboratoriumstechnik, Flawil). In order to extract the water, 60 g of homogeneous sample is lightly vacuumed (VacStar S210/10BW, Verpackungsmaschinen, Sugiez) in heat-resistant bags and put in a water bath (95 °C) for 15 min (water bath W22, VWR International, Dietikon). Bags are left to cool and the aqueous phase is then collected and centrifuged for 8 min at 3'500 t/min (Eppendorf 5804R, Eppendorf, Hamburg). The supernatant is filtered through a 1 µm cellulose filter and collected in cryo-tubes (Semadeni 4193, Semadeni, Düsseldorf). The sample is ready for analysis.

Water extraction from asparagus: 400 g of asparagus samples are first wiped in order to prevent any measurement deviations due to the presence of condensation or washing water. The asparagus are then mixed (mixer Solis 843, Solis, Glattbrugg) and about 100 ml of juice is collected and centrifuged in condition: 10 min at 3'500 t/min. The supernatant is filtered through cotton wool and collected in cryo-tubes. The tube is heated for 3 min in a water bath (95 °C). Finally, the filtrate is left to cool to room temperature and is ready for analysis.

2.2 *IRMS Analysis*

For the determination of $^{18}O/^{16}O$ isotopic composition our laboratory uses the GasBench method described hereafter. This method uses the headspace principal that is based on European legislation (EC 822/97).

0.5mL of water extract (sample prepared previously) is collected in a 10 mL-vial (Labco Limited: Extainer 9RK8W). The air in the vials is replaced with an equilibration gas composed of a mixture of 0.4% CO_2 in He 5.0 (SL Gaz, 1.5 bar) and left to equilibrate for 18 h at 26.8 °C.

A maximum of 96 samples can be placed in the heat block of the autosampler. At the end of the equilibration H_2O and CO_2 totally exchanged their oxygen by the following isotopic reaction (Eqn. (2)):

$$C^{16}O^{16}O + H_2{}^{18}O \leftrightarrows C^{16}O^{18}O + H_2{}^{16}O \quad (2)$$

For the measurement, a new needle is introduced in the vial to inject the mix He/CO_2 (sample) (Fig. 1) into the Gasbench II Delta Mat 252 (Thermo Fisher Scientific, Bremen, Germany) by means of a carrier gas (He 5.0, SL Gaz, 1.3 bar).

In Fig. 2, a scheme of the GasBench II is shown. After the sample preparation and the injection of He, the gas passes through the first water removal unit that removes steam in order to prevent the condensation of steam that can block the small channels in the system and distort the analysis.

Fig. 3 shows the water removal unit. It is constituted of a Nafion™ tube that acts as a semipermeable membrane and removes the water molecules present in the gas. The outside of the tube is rinsed with a flow of He. A high water concentration gradient is created between the inside and outside and water molecules pass through the Nafion™ wall. The remaining gas therefore contains hardly any water.

After the first water removal unit, the gas enters a Valco multi-Port. In 'load' mode, the sample joins the sampling loop (volume 100 µL) and He is directly injected into the gas chromatography (GC) column. In 'inject' mode, He joins the sampling loop and pushes the sample in the GC column.

The GC column is a CP Poraplot Q fused silica 27.5 m (inc. 2.5 m particle trap) × 0.32 mm (CP7551). The chromatograph is maintained at 50 °C to get a good separation of CO_2, N_2 and O_2. At the exit of the column there is a second water removal that catches the residual H_2O.

The gas (sample) reaches the Mass Spectrometer Delta^{Plus} Advantage (Thermo

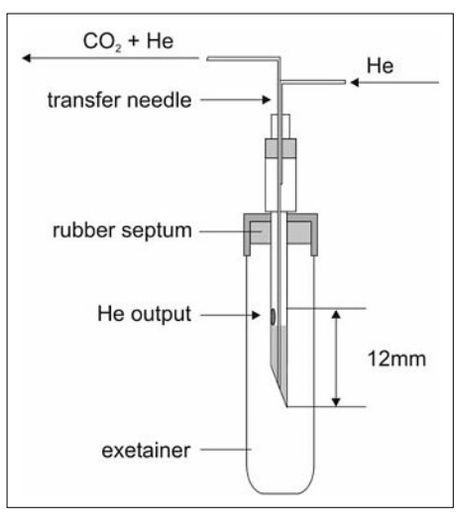

Fig. 1. Schema of the measurement needle (Thermo Fisher Electronic, 2014).[18]

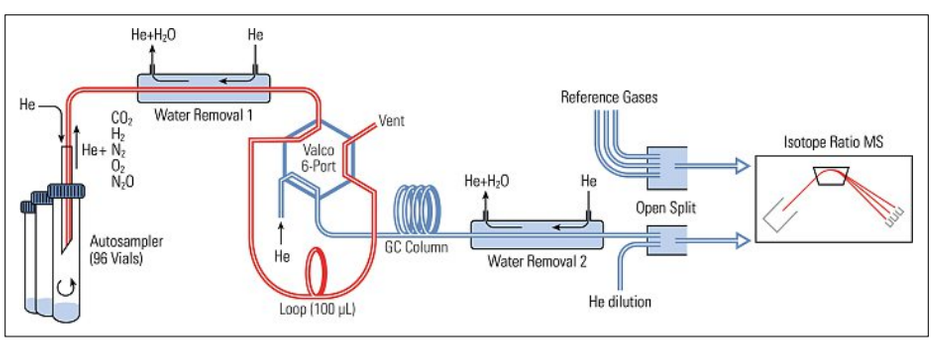

Fig. 2. Schematic construction of the GasBench (Thermo Fisher Electronic, 2014).[18]

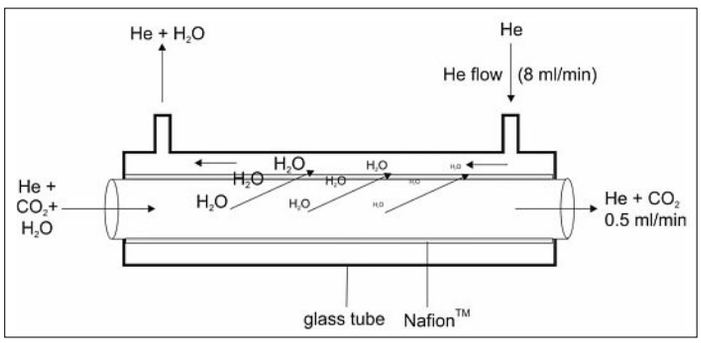

Fig. 3. Schematic construction of the water removal of the GasBench II (Thermo Fisher Electronic, 2014).[18]

Fisher Scientific, Bremen, Germany). The MS continuously measures the mass differences of the gas. For the analysis of CO_2, the atomic masses are 44 ($C^{16}O_2$), 45 ($^{13}CO_2$) and 48 ($C^{18}O_2$). $\delta^{18}O$ values are directly obtained from the simultaneous measurement of the three atomic masses; it provides the value of CO_2. The software IsoDat NT 2.0 (Thermo Fisher Scientific, Bremen, Germany) makes automatically the necessary corrections (for example interference between molecules containing ^{17}O) and gives the values for $\delta^{13}C$ and $\delta^{18}O$.

The analysis of the sample includes the measurement of three peaks of the reference gas (CO_2 5.0, SL Gaz, 2 bar) in which the values are known ($^{18}O = 0$). These peaks are used to calibrate the sample measurements relative to the reference gas and detect any change of the reference value in the sequence. After the reference peaks, the gas (sample) is measured nine times. The average value of the repetitions gives then the value of the sample. The measurements are accepted if the signals are between 2 and 8 volts (linearity) and if the standard deviation does not exceed $\delta = 0.3$. Then He (2 bar) is injected to clean the pipes (backflushing).[19] Before each pair of samples, local water from Sion is analysed ($\delta = -13.7$) to prevent drift.

This method is calibrated according to the international Standards VSMOW (Vienna Standard Mean Ocean Water, $\delta = 0$), GISP (Greenland Ice Sheet Precipitation, $\delta = -24.8$) and SLAP (Standard Light Antarctic Precipitation, $\delta = -55.5$), which are issued by the IAEA (International Atomic Energy Agency).

The reliability of the method has been intensively tested through proficiency testing between different European laboratories, which resulted in a quantitative typical incertitude of 0.4 $\delta^{18}O$.

3. Results and Discussion

3.1 *Fish*

The first tests performed with the method were to compare the isotopic composition of the water extracted from the fishes and the water from which they originate; this correlation serves as the cornerstone for the determination of the origin of food and to prevent fraud. Fig. 4 shows the correlation of $\delta^{18}O$ values of water detected in different lakes, respectively fish farms of Romandie with the $\delta^{18}O$ of the corresponding fishes.

Each set of fish and corresponding water are measured and the mean values are represented by the black diamonds in Fig. 4; the bars represent the incertitude of 0.4 $\delta^{18}O$ as described in the Material and Method section. It can be seen that there is a rather good linear correlation (0.986) between the $\delta^{18}O$ values of fish water and of water they grew in. Small differences between water and fish may arise from either some fish metabolism that would favour one type of oxygen; however, no report could be found in the literature to support this assessment; another reason could be an inhomogeneity in water distribution in the lake where the fish were caught, for instance at the outfall of a river in a lake. In practice, it is important to distinguish the 'lake' fish from the 'production farm' fish, because some producers could sell 'production farm' fish with the label 'lake' fish, letting the customer think that he is purchasing a wild fish when in reality it comes from a fish farm. With this technique we can prevent fraud by taking water from the lake in which the fish is supposed to come from and if the $\delta^{18}O$ values are significantly different, the mislabelling will be identified. In 2013, a fish analysis campaign was undertaken with some producers, supermarkets and restaurants in western Switzerland to see if the declaration of fish was correct or not (Table 1).

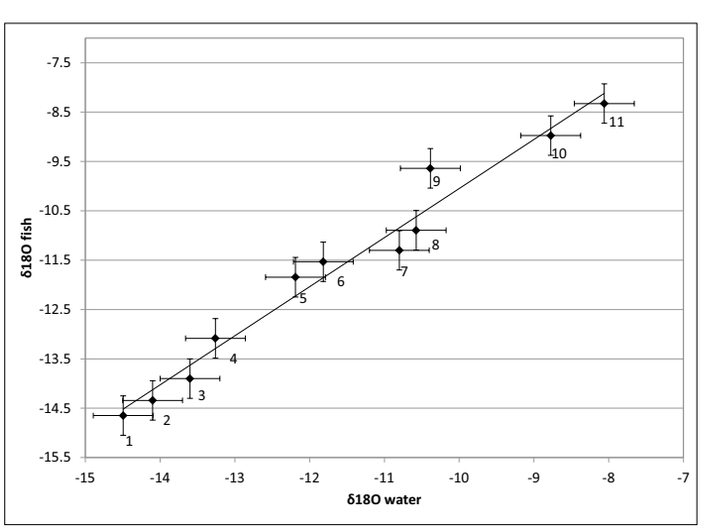

Fig. 4. Correspondence between $\delta^{18}O$ for water and $\delta^{18}O$ for fish from the Romandie (2008–13) Lakes: Lake Geneva (6), Lake of Gruyère (9) , Lake of Joux (10), Lake of Neuchâtel (11); Production farms (2), (5), (7); Stocking farms: (1), (3), (4), (8)

Most of these results conformed to the values found for Lake Geneva and Lake of Neuchâtel water shown in Fig. 4. One of the results in bold in Table 1 resulted in a remarkably low value $\delta^{18}O$ (–14.76) which cannot originate from Lake Geneva. An inspection of this case revealed a fraud since this fish did not come from Lake Geneva but from the production farm (2) in Valais.

If in some cases, it is clearly possible to distinguish between two different origins, this method has also its limitations as shown when some fish farms have values close to those from a given lake; this could be the case for instance between the fish from the pisciculture of Vionnaz (number 5) compared with the Lake Geneva (number 6). In such a case this method cannot detect differences since the method cannot distinguish two places with similar water $\delta^{18}O$ values. Another limitation is the necessity to test the value of the lake regularly since water composition may change from one year to another. Every source and river that is a tributary can change the isotopic composition of the lake depending on rainfall (quantity and composition). In our lab, we measure each year the $\delta^{18}O$ value of each lake or fish farm to feed our database. In Lake Geneva between 2008 to 2013 the $\delta^{18}O$ of water has been remarkably stable (SD = 0.13); this stability is due to its large volume of water (8.9×10^9 m^3) which buffers the variation which may arise from annual rainfall drifts. In fish farms these values may easily differ from year to year due to potential different tap water sourcing.

It is finally remarkable that this technique is not dependant on the fish species as shown in Table 1; the analysis of five fish species has demonstrated no significant impact on the $\delta^{18}O$ value; this last point illustrates the broad scope of application of the IRMS method for mislabelling detection.

Table. 1. Results of the fish analysis campaign made in 2013 for Lake Geneva and Lake Neuchâtel

Canton	Lake	Designation of fish	$\delta^{18}O$
Geneva	Geneva	Perch fillet	–11.7
Geneva	Geneva	Fera fillet	–11.9
Geneva	Geneva	Fera fillet	–11.4
Geneva	Geneva	Fera fillet	–12.1
Geneva	Geneva	Perch fillet	–11.5
Geneva	Geneva	Fera fillet	–11.7
Vaud	Geneva	Fera fillet	–11.4
Vaud	**Geneva**	**Perch fillet**	**–14.76**
Vaud	Geneva	Fera fillet	–12.14
Vaud	Geneva	Perch fillet	–11.93
Vaud	Geneva	Perch fillet	–11.53
Vaud	Geneva	Trout fillet	–10.86
Vaud	Geneva	Fera fillet	–11.86
Vaud	Geneva	Roach	–11.7
Vaud	Geneva	Trout	–12.2
Vaud	Geneva	Fera	–12.3
Vaud	Geneva	Trout	–11.7
Vaud	Geneva	Perch	–12.1
Valais	Geneva	Perch fillet	–12.3
Valais	Geneva	Fera fillet	–12.4
Valais	Geneva	Perch fillet	–11.5
Neuchâtel	Neuchâtel	Lake whitefish fillet	–9.0
Neuchâtel	Neuchâtel	Lake whitefish fillet	–8.8
Neuchâtel	Neuchâtel	Lake whitefish fillet	–8.7
Neuchâtel	Neuchâtel	Lake whitefish fillet	–8.6

3.2 *Asparagus*

To study the question of another potential fraud, we measured the $\delta^{18}O$ value in the water fraction of asparagus to determine their origin (place of production). In theory, the place where the product grows has a major role in the isotopic composition of the water (distance from the ocean, altitude and climate).

3.2.1 *Asparagus from Valais*

As said previously in the introduction, Dunbar and Wilson[5] demonstrated that there is an enrichment of the ^{18}O from the groundwater to the plant water leading to an increase of the $\delta^{18}O$ value. White asparagus can be assimilated to plant roots since it grows exclusively inside the earth and green asparagus to stem since it grows in contact with the atmosphere. To test this theory, samples of groundwater, white and green asparagus of the producing fields were taken by the laboratory inspectors directly from the field between 2006 and 2014. Fig. 5 shows the $\delta^{18}O$ value obtained for water, white and green asparagus respectively.

It can be clearly seen that these values are in good agreement with the observation of Dunbar *et al.*[5] who suggested a gradient of $\delta^{18}O$ values from groundwater < roots (white asparagus) < stem (green asparagus). The difference between groundwater and white asparagus is due to the fact that groundwater is typically at 4–5 m below the surface of the earth whereas the asparagus grows at ~40 cm from the surface where a significant evaporation of the upper layer of the soil water can favour the light isotope to evaporate and therefore lead to a concentration of heavy ones; the difference between white and green asparagus is further explained by a greater evaporation through the surface of the stem of green asparagus since they are totally in contact with the atmosphere.

In Valais, most of the production is white asparagus (240 To/year) for which special attention is given since it is locally consumed and more expensive than imported asparagus. In order to control them efficiently, we investigated the stability of asparagus values in Valais over several years to establish a general trend for our region.

As can be seen in Fig. 6, the $\delta^{18}O$ value of white asparagus water is relatively stable (approx. –10.5) in Valais over the past five years. Based on this, it is now interesting to compare whether asparagus produced in other countries has significantly different $\delta^{18}O$ values so that they can be used as a production land fingerprint.

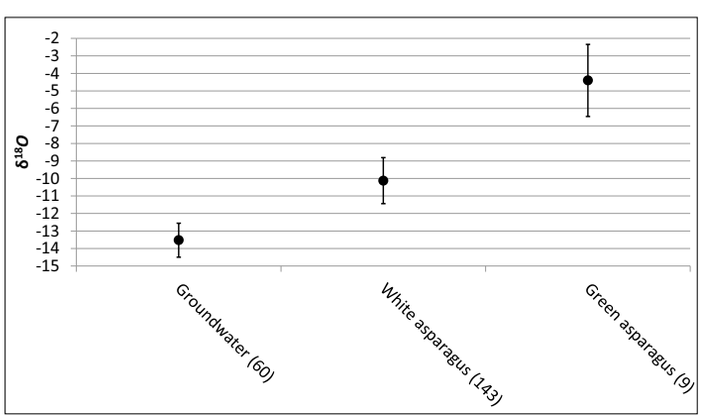

Fig. 5. Comparison of typical $\delta^{18}O$ value in Valais between groundwater (2001–2010), white and green asparagus (2006–2014) with the standard deviations (SD)/values in brackets representing numbers of samples for each type.

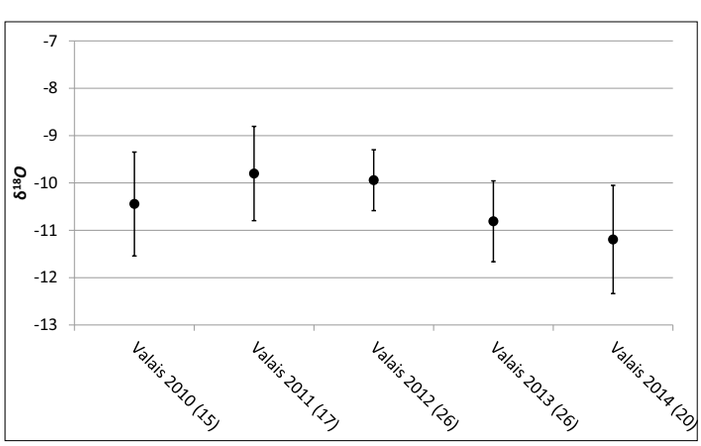

Fig. 6. Typical $\delta^{18}O$ in Valais for white asparagus for the last 5 years (2010–2014) with the standard deviations (SD)/values in brackets representing numbers of samples for each year.

3.2.2 *Differences between Producing Countries*

With the values for asparagus in Valais being stable over time, it was further studied if it is possible to differentiate them from samples that come from other countries. The foreign samples used in this project come from Spain, France, the Netherlands, Hungary, Germany, Italy, Morocco, Peru, Mexico and USA. White asparagus found on sale locally originate from all these countries. Fig. 7 reports the measured values for white asparagus from different origins.

A significant difference between Valais and other countries appears for white asparagus (> 3 $\delta^{18}O$ units); the $\delta^{18}O$ value for Valais is significantly lower than any of the other countries, which means a lower concentration of heavy isotopes. This observation is somehow correlated with precipitation water $\delta^{18}O$ values obtained from the Global Network of Isotopes in Precipitation GNIP data base of the International Atomic Energy Agency (IAEA).[20] Precipitation data are chosen according to the closest existing place relative to the region of production for each country when available: Karlsruhe/Germany (–7.79), Zaragoza/Spain (–5.66), Dax/France (–4.88), Beek/NL (–6.99), Debrecen/Hungary (–7.03), Fogliano/Italy (–4.70), Rabat/Morocco (–4.13), and Grimsel/Valais (–13.85). This impoverishment in heavy isotope can be further explained by the fact that Valais is 500 km away from the ocean and also that with higher mountains (>3000 m) all around the region, precipitations have to pass through this mountainous relief and will lose significantly their heavy isotopes due to a gravity effect before reaching the Valais area.

A similar study has also been conducted for green asparagus; Fig. 8 presents the typical values measured in green asparagus originating from different countries.

A significant shift of about 4 $\delta^{18}O$ can distinguish green asparagus grown in Valais from that grown in other countries. It can be concluded that a significant shift can be observed for Valais regarding other producing countries, similar to the observation made above for white asparagus.

These results are significant for fighting fraud that can exist in Valais. In practice when a value of asparagus seems suspicious, an inspection on the field may be useful to confirm/refute the suspicion.

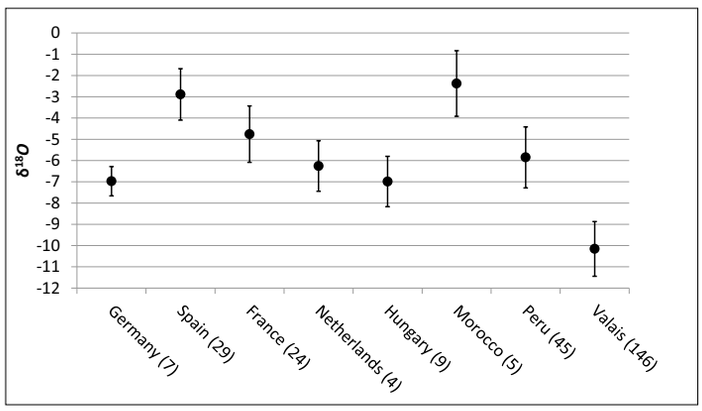

Fig. 7. Typical $\delta^{18}O$ for white asparagus in various countries (2006–2014) with the standard deviations (SD)/values in brackets representing numbers of samples for each country.

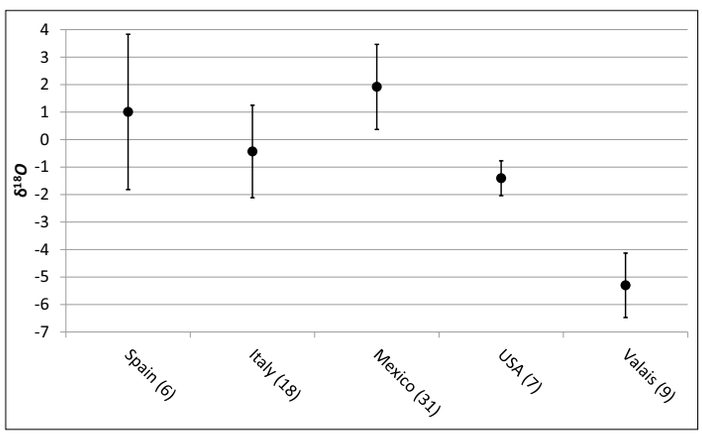

Fig. 8. Typical $\delta^{18}O$ for green asparagus in various countries (2006–2014) with the standard deviations (SD)/values in brackets representing numbers of samples for each country.

4. Conclusion

Fraud in food product labelling has become a growing problem in every country due to free trade globalization, when the food market is crowded by products at lower prices. It is a challenge for each official laboratory to be able to differentiate local production from other ones in order to protect the consumer. The geographical situation of the Valais, which provides a specific $\delta^{18}O$ in water, has an undeniable role in the authentication of locally grown food products. The results presented above for fish and asparagus allow us to determine whether they were grown in our area or not.

Whether for asparagus and fish, it is essential to interpret the results obtained with restraint. If a sample seems suspicious, it is necessary to launch a detailed investigation to know the reason why the sample is out of limits. After that, the potential fraud may be confirmed or refuted.

IRMS is a good and relatively universal method for the determination of isotopes in foods, but it requires significant work to build up the databases. Moreover the material is expensive. More recently IR spectroscopic methods have been developed to measure the occurrence of stable isotopes which may potentially reduce the cost and the complexity of analysis[21] and therefore democratize this kind of testing.

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