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Isotopic Composition and Fractionation of Stable Magnesium Isotopes in Relation to Fruits Growing in Different Regions of Russia

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ABSTRACT

Background: Present study on determining the region of origin of raw materials, the authenticity of organic food products is relevant. The determination of the natural content of stable isotopes are not able to answer these questions. The solution can be obtained by studying the ratios and fractionation of stable isotopes, which provide information on the transformations of chemical elements in biological, ecological and geochemical studies.

Methods: During 2020-2021 obtained data on the content of magnesium isotopes in apple fruits of 14 varieties from three growing regions of the Russian Federation. Previously, over 10 years, a database was formed of more than 500 samples on the level of potassium, calcium, magnesium, phosphorus and nitrogen cations, depending on the variety and phase of fruit development.

Result: Research presents the results of determining the natural content of stable magnesium isotopes in apples, the isotopic composition and their fixation, depending on different regions of the growth of raw materials. The isotopic composition of apples ($^{26}Mg/^{24}Mg$) varies from 0.1669047 to 0.1782649; the deviation of the magnesium isotopic composition from the conventional standard varies within 25.52-43.52; their chemical fractionation has value: in Central Zone of Russia-185.2-212.3; South of Russia-248.0-311.5; North Caucasus-182.7-214.8.

Key words: Analysis of stable isotope ratios, Apple fruits, Growing region, Isotope fractionation, Isotopic signature, Magnesium, Stable isotopes.

INTRODUCTION

Literary sources contain a lot of information about the search for reliable identification criteria that allow to establish the region of origin of raw materials or confirm the authenticity of organic products by the content and fractionation of stable isotopes of hydrogen, carbon, oxygen, sulfur (Camin *et al*., 2011; Georgi *et al*., 2005; Finlay and Kendall, 2007; Litvinskiy *et al*., 2019). However, unlike these isotopes, information on the natural content of stable magnesium isotopes and their fractionation in food raw materials is fragmentary and very scarce (Angert *et al.,* 2019; Schmidt *et al*., 2005; Huang *et al*., 2013).

The industrial fractionation of stable isotopes of chemical elements is extremely difficult, however, in living systems this process is quite easy to implement and is an integral part of the existence of living organisms (Buchachenko, 2014). Almost all elements that have isotopes undergo fractionation.

Determining the natural abundance of stable isotopes has recently become an effective method with which to study the transformation of elements in biological and environmental studies, as well as to investigate the mechanisms of chemical reactions. The distribution of stable isotopes of light elements in various biological and abiotic systems varies significantly, so the isotope ratio is a fairly reliable criterion for recognizing biogenic and abiogenic compounds (Laursen *et al.,* 2013; Mukome *et al*., 2013).

Analysis of the isotopic composition of the objects under study allows in most cases to resolve the issue of the authenticity of organic food products or products with a protected designation of origin. One of the methods for detecting falsification of the geographical origin of food products is the determination of the ratios of stable isotopes

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$^{2}H/^{1}H$, $^{18}O/^{16}O$, $^{15}N/^{14}N$, $^{13}C/^{12}C$ and some other elements (Coplen *et al*., 2002; Rapisarda *et al*., 2010; Shin *et al*., 2017).

It should be noted that magnesium isotopes in plant objects are practically not studied. At the same time, the discovery of a nuclear magnetic isotope effect involving cations of the ^{25}Mg magnetic isotope proves that it is necessary to pay due attention to magnesium isotopes. Magnesium is an essential plant nutrient that activates more enzymes than any other cation and thus plays an important role in biological cycles. With the natural abundance of the three stable isotopes (^{24}Mg, 78.992%; ^{25}Mg, 10.003%; ^{26}Mg, 11.005%), a fractionation process can explain the characteristics of the growth of raw materials as reported by Buchachenko (2014).

Koltover *et al.* (2012) studied the effect of various magnesium isotopes on *Escherichia coli* and showed that cells grown on ^{25}Mg adapt much faster to a new environment than cells grown on non-magnetic magnesium isotopes. Mammalian studies have shown that 50% of dietary ^{26}Mg ends up in bones, 30% in muscles and 20% in other soft tissues. Plant preference for heavy magnesium isotopes suggests that there may be a difference in Mg bioavailability between agricultural and natural soils due to periodic removal of heavy Mg isotopes by crops. The pH dependence of Mg isotope fractionation can be observed in any organism with cells that follow similar Mg uptake and metabolic pathways and serve to reveal Mg cycling in ecosystems as mentioned by Buchachenko (2014).

Therefore, issues related to the study of stable isotopes of Mg and their potential as indicators in biochemical and physiological studies are of current interest. Common standard samples are known for isotopic analysis of some chemical elements (Angert *et al*., 2019; Finlay and Kendall, 2007).

The present result was undertaken to create a database on the fractionation of Mg isotopes in apples, characterizing the isotopic composition, due to the geographical growth of raw materials.

MATERIALS AND METHODS

The equipment used is an inductively coupled plasma mass spectrometer Thermo-Finnigan MAT, standard samples of stable magnesium isotopes produced by Federal State Unitary Enterprise Elektrokhimpribor Combine. The research was carried out at the Federal State Budgetary Scientific Institution “North Caucasian Federal Scientific Center for Horticulture, Viticulture, Winemaking” in the period from 2020 to 2021. Flame atomic absorption and a capillary electrophoresis system equipped with a positive polarity power supply and an ultraviolet detector were used to estimate the total Mg concentration.

The isotopic composition of the studied samples was determined using the proposed formula (Gorbunova 2018) expressed in thousandth of a deviation from the international standard. To designate the isotopic composition, it is customary to use the value of δ, which is a deviation from the generally accepted international standard, as follows: δ (‰):

$$\delta n\ X\ sample = [(R_{sample}/R_{stand}) - 1] \times 1000, \%$$

Where:

X- Element (Mg).

n- Number of 26 Mg - 26.

R_{sample}- Molar ratio of the heavy and light isotopes of an element.

R_{stand}- Isotopic prescription of the standard, equal to 0.3969.

Mathematical processing of experimental data was performed by the method of analysis of variance and descriptive statistics using the Microsoft Excel software package.

RESULTS AND DISCUSSION

In the agricultural sector of the economy, the issue of the region of origin of a particular type of raw material or fruit and berry products is quite acute. Conventional studies of the isotopic composition are unable to answer this question. A possible solution to these problems can be obtained by studying the ratios of stable isotopes common in the plant world of chemical elements. Considering the fact that the content of Mg in the soil is very high and for fundamentally different regions of cultivation, the content and ratios of the mass concentrations of isotopes can differ as found by Young *et al.* (2002) and Blattler *et al.* (2018) in this situation, it can be justified criterion for assessing the origin of raw materials in relation to fruits (apples) from a certain territory.

Qualitative indicators of vegetable raw materials are determined by many factors such as the zone of growth and agrotechnical methods of cultivation (Postnikov *et al.,* 2021; Yakovenko *et al.,* 2020; Firdous and Subhash, 2017; Kumar *et al.,* 2017; Rani and Latha, 2017). When studying the mineral composition of apple fruits, a database was formed for more than 500 samples according to the level of accumulation of magnesium cations depending on the phase of fruit development - fruit size of 8-12 mm, 40 days before ripening and removable maturity (Prichko *et al*., 2019). From the results of the research, it follows that the concentration of minerals in apples at the beginning of their development is high and as the fruits ripen and their weight increases, it constantly decreases (Prichko *et al*., 2018). So, in apples growing in the south of Russia, with a fruit size of 8-12 mm, the following Mg content was obtained - 13.7-14.5 mg/100 g; 40 days before harvesting the Mg content was 7.5-8.5 mg/100 g. In mature apples, Mg levels were - 5.0-6.0 mg 100 g (Prichko *et al.,* 2021).

To establish the isotopic composition of Mg, apples of various degrees of maturity were taken, harvested in 2020-2021, growing in the conditions of the Central Zone of Russia, in the South of Russia and the North Caucasus of the Russian Federation.

According to the authors of various literary sources, natural magnesium, consisting of three stable isotopes- ^{24}Mg, ^{25}Mg, ^{26}Mg, according to the results of their research, is represented by the following percentage of isotopes: $^{24}Mg/^{25}Mg/^{26}Mg$, respectively: ^{24}Mg 78.6% -^{25}Mg 10.1% - ^{26}Mg 11.3%, where according to these data the isotopic signature

(R) has a value of R= 0.14376 (Gorbunova 2018). According to Fernandez *et al*. (2003), the percentage of isotopes is slightly different $^{24}Mg/^{25}Mg/^{26}Mg$- (78.992%-10.00%-11.005%), while the isotope signature has a different value - R= 0.13932. The isotope signature equal to R= 0.14364 is characterized by the ratio of magnesium isotopes- 78.6% -10.11%-11.29% and at R= 0.13926 the isotope ratio is 78.99% - 10.00% -11.00%. Based on the values of generally accepted standard samples in the isotopic analysis of chemical elements, the value of the isotopic signature of a magnesium standard sample R standard is - 0.13969.

Such differences in the values of the isotopic signature of magnesium according to the results of different authors, which differ from the isotopic signature of the standard (R_{stand}= 0.13969) are associated with a study of raw materials grown in different regions of growth (Finlay *et al.,* 2007).

When determining the molar ratio of isotopes in apples, where the content of mineral substances is determined by the phase of fruit development, varietal characteristics and the region of growth, the pattern of a higher content of light magnesium ^{24}Mg was preserved when it varied from 160.0 mg/kg to 74.0 mg/kg, ^{25}Mg- from 8.0 to 17.0 mg/kg and ^{26}Mg- from 13.0 to 27.0 mg/kg, which is associated with the development phase, degree of maturity, varietal characteristics and region of growth (Table 1).

Table 1: Standard samples for isotope analysis of some chemical elements.

Chemical element	Standard substance	R_{stand}
H	Ocean water	0.0001558
C	Fossils of belemites	0.0112372
N	Atmospheric air	0.0036765
O	Ocean water	0.0020052
S	Mineral troilite from a meteorite	0.450045
Mg	$^{26}Mg/^{24}Mg$	0.13969
Ca	$^{44}Ca/^{42}Ca$	3.21947

When calculating the percentage of isotopes in the studied samples, the percentage of isotopes associated with the mass of the isotope at the highest percentage of the light isotope ^{24}Mg is especially noticeable, the range of variation of which ranged from 77.1 to 78.7%. The percentage of ^{25}Mg isotopes in apples is from 8.2 to 9.5% of the total content and ^{26}Mg isotopes - from 13.0 to 14.0%.

Direct mass concentration and calculation of the percentage of magnesium indicate that in the studied samples the lowest content of the magnetic isotope ^{25}Mg (from 8.2 to 9.5%), both in comparison between the isotopes- ^{24}Mg and ^{26}Mg in these samples and compared to the percentage of ^{25}Mg in the isotopic signature of the standard sample.

The isotopic composition of the studied apple samples, taking into account the obtained ratios of the molar concentrations of magnesium and their percentage, causes differences in the isotopic formulation of the recipe depending on the place of growth (Table 1).

The molar concentrations of stable magnesium isotopes of different samples have a large variability due to the zone of growth, varietal characteristics, the development phase or the degree of maturity of the fruit.

Thus, the total content of magnesium isotopes in Red Delicious apples (South of Russia) was 122.0 mg/dm^3, while the molar concentration of ^{24}Mg was 93 mg/dm^3, ^{25}Mg - 11 mg/dm^3 and ^{26}Mg - 17 mg/dm^3. Analyzing the quantitative content of magnesium isotopes as a percentage of the total content, then in almost all samples the variation in isotopes is low and for ^{24}Mg is 76.5% - 78.7%, for ^{25}Mg from 8.2% to 9.5%, for ^{26}Mg from 13.0% to 14.0%. Also, the percentage ratio of isotopes (^{26}Mg, ^{25}Mg, ^{24}Mg) in all the studied samp
les has a common pattern- a higher percentage of light magnesium ^{24}Mg is observed, with a lower content of ^{26}Mg and ^{25}Mg.

Taking into account that the isotopic composition is understood as the relative abundance of the isotopes of a given element (Huang *et al.*, 2013), usually expressed as the

Table 2: Molar concentration and percentage of isotopes in apple fruits.

Sample	Molar concentration (mg/dm^3) and percentage of isotopes (%)						
	^{24}Mg mg/dm^3	^{24}Mg %	^{25}Mg mg/dm^3	^{25}Mg %	^{26}Mg mg/dm^3	^{26}Mg %	Sum of magnesium, mg/dm^3
Central zone of Russia							
Gala	124	78,5	13	8,2	21	13,3	158
Golden delicious	151	78,2	17	8,8	25	13,0	193
Red delicious	160	78,4	17	8,3	27	13,2	204
South of Russia							
Gala	74	77,4	8	9,1	13	13,5	96
Golden delicious	76	77,1	9	9,2	13	13,6	98
Red delicious	93	76,5	11	9,5	17	14,0	122
North Caucasus							
Red delicious	154	78,5	16	8,2	26	13,3	196
Golden delicious	115	78,7	12	8,2	19	13,0	146
Florina	156	78,4	17	8,5	26	13,0	199

ratio of the heavy isotope to the lightest isotope - $^{26}Mg/^{24}Mg$), the isotopic composition was calculated for each sample.

The value characterizing the isotopic composition ($^{26}Mg/^{24}Mg$) of the studied apple samples varies slightly, with the lowest values for samples from the Central Zone of Russia (average 0.1669047) and the North Caucasus (average 0.1678892). For samples of apples grown in the South of Russia, the isotopic composition has an average value of 0.1782649. If we analyze the deviation from the isotope signature of the composition of the standard R_{stand} = 0.13969 (Table 2), then we can see large differences in samples grown in different regions of cultivation. So, for apples grown in the south of Russia, the values of deviations from the isotopic signature of the standard are depending on the samples, from 34.66 to 43.52. Samples from the North Caucasus have deviations from the standard in the range - 25.52-30.00 and from the Central Zone - 25.87-29.66. Chemical fractionation, which reflects the ratio of the deviation from the isotope signature to the isotope signature of the standard, $(R_{sample}\text{-}R_{stand}) \times 1000)/R_{stand})$ was for the Central Zone of Russia- 185.2-212.3; for the South of Russia-248.0-311.5 and for the North Caucasus-182.7-214.8.

CONCLUSION

The conducted studies testify to the separation of isotopes in apple samples - this is especially pronounced in relation to ^{26}Mg, ^{25}Mg. From the present study, it was concluded that there is a tendency for a difference in the isotopic composition of the signature and chemical fractionation of Mg for apples, depending on the region of growth, due to the diversity of soils, technologies for growing fruits using organic and mineral fertilizers. There is an objective need to accumulate a database on the isotopic composition of magnesium with a larger sample of samples in order to establish the range of variation of the calculated indicator and the correspondence of apple fruits to a certain region or inconsistency of this region of production.

Conflict of interest

All authors declare that they have no conflict of interest.

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