



**DETERMINATION OF CONCENTRATIONS  $^2\text{H}$  AND  $^{17}\text{O}$  BY NMR SPECTROSCOPY METHOD IN DRINKING WATER, FRUIT AND VEGETABLES FRESH JUICES WITH INTRODUCTION OF  $\text{Eu}(\text{CF}_3\text{SO}_3)_3$  TO THE REFERENCE SAMPLE**

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**ABSTRACT**

This research presents results of approbation of method for quantitative determination of  $^2\text{H}$  by NMR spectroscopy using lanthanide shift reagent introduced to the probe as an external NMR standard regarding to which the measurement is taken. Within the process of the conducted studies it was confirmed that the most suitable chemical compound to create a reference sample was europium (III) trifluoromethanesulfonate. It was defined that the highest content of deuterium was determined in Argentine pear juice ( $144.6 \pm 2.3$  ppm), the least concentration of deuterium was found in potato juices of Russian and Egyptian origin ( $\approx 100$  ppm), as well as tomatoes from Morocco. The developed method is suitable for analysis of isotope ratios in juices.

**1. Introduction**

The main reasons that cause changes in isotopic composition of the elements, besides radioactive transformations of atoms, are various physicochemical and biological processes (Bila, *et al.* 2017; Bowen, 2011), where the main function is implemented by kinetic and thermodynamic isotope effects, which in general lead to fluctuations in isotopic composition of the same chemical compounds in different regions of our planet (Moody, *et al.* 2012; Belkoun and Houha, 2017). That's why study of isotope composition of environmental substances in natural and synthetic materials can be used for determination of geographical origin of food and drinks (Ekaykin, *et al.* 2016; Sartori, *et al.* 2015).

For determination of isotopic composition of substances various instrumental methods are

used: mass spectroscopy (Reynard, *et al.* 2016; Kuo, *et al.* 2012), IR-spectroscopy (Xiong, *et al.* 2013), nuclear magnetic resonance (NMR), including methodological approach SNIF-NMR (Jamin, *et al.* 2007; Sharifi, *et al.* 2017).

These studies are of high significance and topicality, it is explained by demand of wide range of scientific disciplines for study of isotopic composition of organogenic elements, which composition varies in biological objects of various types (Lehn, *et al.* 2015). Wherein fractionation of isotopes in nature is more expressed in those elements, which take more active part in circulation of substances in the inorganic and organic world: oxygen, hydrogen, carbon, nitrogen, sulfur (Schmidt, *et al.* 2015; Symes, *et al.* 2017).

The growing significance is conferred to study of isotope composition of water

(Ehleringer, *et al.* 2016; Chenaker, *et al.* 2017; Basov, *et al.* 2020), which influences to practically all biochemical and biophysical processes in organism (Svidlov, *et al.* 2021; Somlyai, *et al.* 2020). In particular water with artificially changed content of deuterium can significantly influence to metabolic processes in living systems (Avila, *et al.* 2012; Yaglova, *et al.* 2020, 2021; Fatemi, *et al.* 2020; Dzhimak, *et al.* 2014; Zlatska, *et al.* 2020, Zhang, *et al.* 2020).

It is known that quantitative NMR spectroscopy is one of the main precision analyze methods of deuterium concentration in liquids (Ma, *et al.* 2012), which, due to simplicity of sample preparation procedures and analytical process (Hosseini, *et al.* 2016), can be used as an express method for study of isotopic ( $^2\text{H}/^1\text{H}$ ) composition of liquids (Basov, *et al.* 2019a).

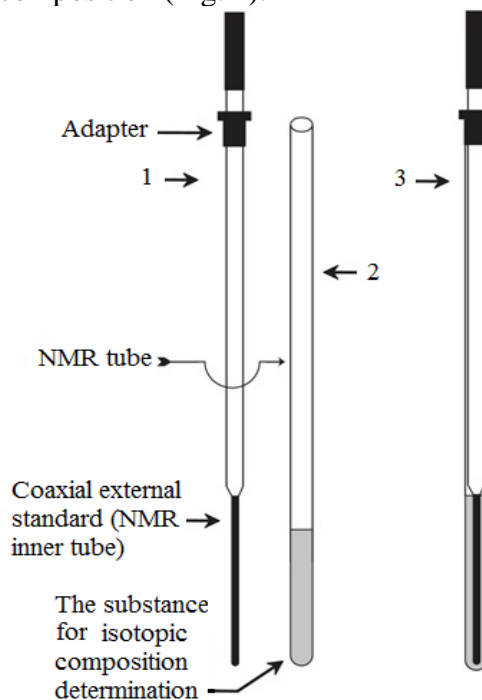
In connection with the foregoing the purpose of this research is to develop a new method for quantitative determination of oxygen isotopes  $^{17}\text{O}$  and  $^2\text{H}$  content in liquid media with help of NMR spectroscopy using a lanthanide shift reagent introduced to the probe as an external NMR standard, in relation to which the measurement is taken.

## 2. Materials and methods

In this work there was used a device - NMR Fourier spectrometer 400 MHz (FT NMR SYSTEM model JNM-ECA 400) with a sensor 40TH5AT / FG2 of the following technical characteristics: induction of constant magnetic field - 9.389766 T; frequency range - from 10 to 400 MHz with increment of 0.01 Hz; the resonance frequency of  $^2\text{H}$  nuclei is 61.37 MHz, the resonance frequency of  $^{17}\text{O}$  nuclei is 54.22 MHz (tuned by the device); 1H sensitivity:  $\geq 220$  (for 0.1% solution of ethylbenzene in deuteriochloroform); drift of constant magnetic field: less than 4 Hz/h; the width of  $^1\text{H}$  NMR signal at half-height: not more than 0.45 Hz (for 0.1% solution of ethylbenzene in deuteriochloroform).

For the studied sample the calibrated main NMR-ampoule with a diameter of  $4.97 \pm 0.013$

mm and a length of 178 mm was used. The substance studied for its isotopic composition was placed into the ampoule. Also there was a calibrated internal NMR-ampoule (coaxial external standard) with length of end capillary 32 mm. and capacity of 40 ml, which was inserted into the main NMR-ampoule and contained a reference substance with the same molecular structure as the substance being determined but with known isotopic composition (Fig. 1).



**Figure 1.** Schematic image of the NMR-ampoule (2) with the substance studied for isotopic composition; coaxial external standard (1) with solution  $(\text{CF}_3\text{SO}_3)_3\text{Eu}$  in water with known concentration of  $^2\text{H}$  and  $^{17}\text{O}$ ; the system of the standard inserted into the ampoule (3)

There was used a number of calibration samples of pure water with impurity content of no more than 0.01% by mass and with known content of isotope deuterium and oxygen  $^{17}\text{O}$  in accordance with the international standard introduced by the IAEA (VSMOW and SLAP). For the method of determination of ratio  $^2\text{H}/^1\text{H}$  and  $^{17}\text{O}/^{16}\text{O}$  the sample of water containing  $(\text{CF}_3\text{SO}_3)_3\text{Eu}$  was placed into the internal NMR-ampoule, wherein the content of deuterium or  $^{17}\text{O}$  water in this solution must correspond to the

studied range of deuterium concentrations in the object being measured.

All experiments with the series of samples, including calibration samples, were carried out under identical conditions of NMR measurements and under the same settings of device. For measurements on  $^2\text{H}$  nuclei we have chosen the optimum values: amplification 60; displacement 5 ppm; sweep 10 ppm; time of observation of free induction decay 6 s.; scans range 256; relaxation delay  $10 \cdot T_1 (^2\text{H}_2\text{O}) \geq 7$  s.; temperature inside the resonator is  $25^\circ\text{C}$ . For measurements on  $^{17}\text{O}$  nuclei we selected the optimal parameters: amplification 90; displacement (-10) ppm; sweep 80 ppm; time of observation of free induction decay 60 ms.; scans range 10000; relaxation delay  $10 \cdot T_1 (\text{H}_2^{17}\text{O}) \geq 0.1$  s; temperature inside the resonator is  $25^\circ\text{C}$ .

The important requirement is that the spectrum must be photographed without rotation of the sample in the spectrometer, otherwise, as we have found, there may be additional errors in the determination of the isotope ratios.

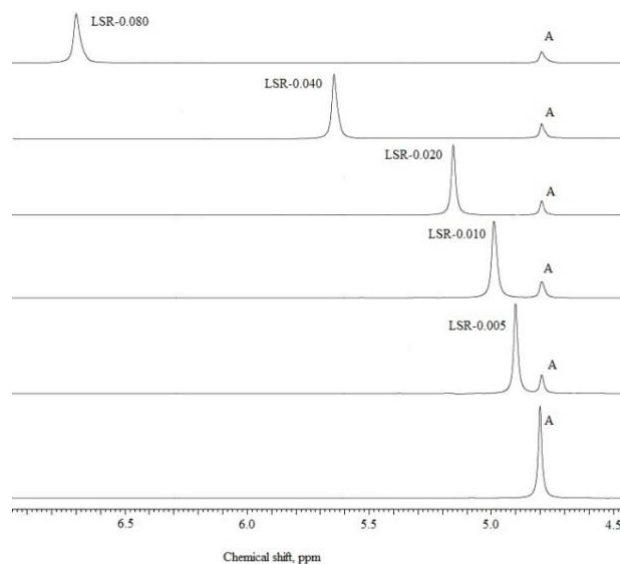
For determination of optimal concentration of lanthanide shift reagent (LSR) in the reference sample containing water, we studied the concentration dependence of europium salt from induced paramagnetic shift of the deuterium nuclei included into molecules of water composition. There was prepared a series of aqueous solutions containing 0.080 mol/l, 0.040 mol/l, 0.020 mol/l, 0.010 mol/l and 0.005 mol/l of shift reagent. Whereas for determination of concentration of oxygen isotope  $^{17}\text{O}$  there was prepared a series of aqueous solutions containing 0.200 mol/l, 0.100 mol/l, 0.050 mol/l, 0.025 mol/l of the shift reagent.

### 3. Results and discussions

#### 3.1. Justification of lanthanide shift reagent choice

The quantitative NMR experiment is based on imaging of spectrum on the nucleus of the investigated isotope under absence of magnetic saturation, wherein the measurements are taken in relation to a special probe with certain

parameters and known content of the corresponding isotopes. At this time the main task and complexity in implementation of methods for isotopes determination by quantitative NMR methods lies in development of optimal specific probes with suitable magnetic-relaxation characteristics. In this research a solution to the problem of magnetic-relaxation delay by using lanthanide shift reagents was found, which solution drastically shortens the time of experiment in comparison with the previous methods of NMR quantitative measurements. In this regard the internal NMR-ampoule contained a dissolved lanthanide shift agent (europium (III) trifluoromethanesulfonate, Sigma Aldrich, anhydrous and water-soluble) due to which reagent the NMR signal from the substance in the internal ampoule was displaced in relation to the substance being determined from the main ampoule, which allowed integration of individual spectrum signals relatively to each other (Fig. 2).



**Figure 2.** NMR spectra of solutions containing lanthanide shift reagent (LSR), LSR-0.005 - solution containing  $\text{Eu}(\text{CF}_3\text{SO}_3)_3$  in concentration of 0.005 mol/l; LSR-0.010 - a solution containing  $\text{Eu}(\text{CF}_3\text{SO}_3)_3$  in concentration of 0.010 mol/l; LSR-0.020 is a solution containing  $\text{Eu}(\text{CF}_3\text{SO}_3)_3$  in

concentration of 0.020 mol/l; LSR-0.040 - solution containing Eu (CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> in concentration of 0.040 mol/l; LSR-0.080 is a solution containing Eu (CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> in concentration of 0.080 mol/l.

The europium (III) compound was chosen from all lanthanides as the lanthanide shift reagent due to the fact that while sufficient shift effect of Eu<sup>3+</sup> the influence for the time of spin-lattice and spin-spin nuclear relaxation is small in relation to other rare-earth element compounds. This is explained by the fact that for Eu<sup>3+</sup> the main electronic state is diamagnetic (<sup>7</sup>F<sub>0</sub> term), and paramagnetism arises only due to the excited <sup>7</sup>F<sub>1</sub> state. Because of this the spin-lattice and spin-spin electron relaxation times T<sub>1e</sub> and T<sub>2e</sub> are extremely short and are about from 10<sup>-12</sup> to 10<sup>-13</sup> s. And if one takes, for example, the gadolinium ions Gd<sup>3+</sup> and Eu<sup>2+</sup>, the broadening lines of NMR have the order of electronic relaxation values 10<sup>-8</sup>-10<sup>-9</sup> sec, thus representing good NMR relaxants since its ground state is <sup>8</sup>S<sub>7/2</sub>. For this term the value of the total angular momentum is determined only by the spin, since the orbital momentum is equal to zero, and, consequently, under such conditions they do not interact with the electric field, i.e. the Stark effect does not appear, so the relaxation time of electron spin Gd<sup>3+</sup> and Eu<sup>2+</sup> will be much larger than for Eu<sup>3+</sup>.

### 3.2. Determination of optimal concentration of Eu<sup>3+</sup> for estimation of content of <sup>2</sup>H and <sup>17</sup>O in liquid media

We conducted a series of NMR experiments to determine the spin-lattice and spin-spin nuclear relaxation times for <sup>2</sup>H and <sup>17</sup>O nuclei in presence of Eu<sup>3+</sup> in a wide range of concentrations (from 0.001 to 0.200 mol/l of Eu<sup>3+</sup>) by method “inversion-recovery” (for T<sub>1</sub>) and CPMG (for T<sub>2</sub>). The obtained results confirmed the theoretical justification of choice of europium (III) as a LSR for purposes of this research, as the changes of time of nuclear relaxation depended insignificantly from increase of Eu<sup>3+</sup> concentration. For <sup>2</sup>H nuclei without introduction of Eu<sup>3+</sup> the T<sub>1</sub> time was 0.43 ± 0.02 s., while introduction of 0.080 mol/l

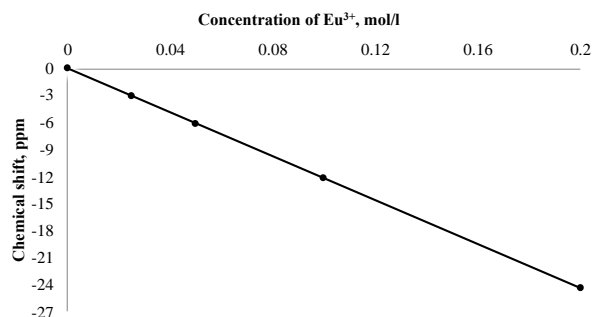
of Eu<sup>3+</sup> changed this time to 0.36 ± 0.02 s. Accordingly T<sub>2</sub> without Eu<sup>3+</sup> was 0.35 ± 0.05 s., and with addition of 0.080 mol/l of Eu<sup>3+</sup> this time changed to 0.23 ± 0.05 s. Similarly, for <sup>17</sup>O nuclei without addition of Eu<sup>3+</sup> the T<sub>1</sub> time was 0.007 ± 0.001 s., and with addition of 0.200 mol/l of Eu<sup>3+</sup> this time changed to 0.005 ± 0.001 s. Moreover, the <sup>17</sup>O nucleus, having a high electric quadrupole moment, relaxes under quadrupole mechanism, consequently T<sub>1</sub> = T<sub>2</sub>, which was observed by us in the experiment. Accordingly, T<sub>2</sub> without Eu<sup>3+</sup> was equal to 0.007 ± 0.001 s., and with addition of 0.200 mol / l of Eu<sup>3+</sup> it changed to 0.005 ± 0.001 s.

The results of the obtained spectra of deuterium in the prepared solutions show an appreciable displacement of the NMR signal in dependence of concentration of Eu<sup>3+</sup> ions in the semi-heavy water (Fig. 2). This is caused by presence of strong pseudo-contact (dipole-dipole) interaction of Eu<sup>3+</sup> ions with deuterium atoms. In NMR spectra on deuterium nuclei we observe two spectra spaced along the scale of chemical displacements of NMR signals – from deuterium of water with europium (III) trifluoromethanesulfonate dissolved there, located in the inner insert into the ampoule, and from the deuterium of studied water in the ampule itself.

By changing the percentage of deuterium water content, from the natural content of about 0.015% to 98% of deuterium contained in heavy water, we showed that the paramagnetic shift is the same for the whole range of deuterium concentrations and depends only on concentration of Eu<sup>3+</sup> ions. On the basis of quantitative experiments to determine the isotope ratio of <sup>2</sup>H / <sup>1</sup>H in water (Fig. 2), water solutions and in biological fluids, it was found that the most optimal value of Eu<sup>3+</sup> concentration in a reference water sample was 0.045 ± 0.005 mol/l.

We also studied the concentration dependence of Eu<sup>3+</sup> ions from induced paramagnetic shift of <sup>17</sup>O oxygen nuclei included into water molecules composition. To find the optimal concentration of europium (III) trifluoromethanesulfonate in a reference sample

containing water, a series of water solutions containing 0.200 mol/l, 0.100 mol/l, 0.050 mol/l, 0.025 mol/l of europium (III) trifluoromethanesulfonate was prepared. From the obtained calibration dependence it is obvious that there is a significant displacement of NMR signal of  $^{17}\text{O}$  of water containing  $\text{Eu}^{3+}$  ions to strong field, which is characterized by a change of overall magnetic susceptibility of solution due to the presence of contact interaction of  $\text{Eu}^{3+}$  ions with  $^{17}\text{O}$ . After analyzing the obtained data we chose the optimal concentration of  $\text{Eu}^{3+}$  ions for purposes of this study at the level of 0.120 mol/l (Fig.3).



**Figure 3.** Dependence of paramagnetic chemical displacement of  $^{17}\text{O}$  water nuclei from concentration of  $\text{Eu}^{3+}$  ions in solution

**Table 1.** Deuterium content in various water samples

Water	Deuterium concentration, ppm	Water	Deuterium concentration, ppm	Water	Deuterium concentration, ppm
Tap water	150.2±0.9	Essentuki 4	151.9±1.6	Arkhyz	147.4±0.9 #
Distilled water	150.4±0.8	Dzhermuk	152.1±1.1	Vittel	157.0±2.1 #
Bidistilled water	150.1±1.3	Piligrim	155.2±1.5 #	Evian	155.6±1.6 #
Goryachiy Klyuch, borehole 934	153.0±0.8 #	Narzan	144.0±1.6 #	Aquaminerale	149.5±1.8
Serebryany istochnik	153.4±0.7 #	Mercury	145.8±2.0 #	Miniliya	159.8±1.4 #
Goryachiy Klyuch Aroma-yug	152.0±1.4	Kubay	167.3±1.9 #	Bonaqua	150.7±1.2

Note. # - Reliability of differences ( $p < 0.05$ ) in comparison with values of tap water.

### 3.3. Study of 2H concentration in fresh juices, bottled and natural waters

Among the bottled water samples a noticeably lower content of deuterium in comparison with the SMOW standard was observed in the following: the least content was found in “Narzan” water, whose deuterium values were below

the SMOW standard by 7.6% and in comparison with tap water at 4.1%, which indicates the advisability of its use in food ration to reduce content of hydrogen heavy isotopes in patient’s body (Table 1). The applicability of this issue is caused by the fact that one of the important tasks in the concept of healthy nutrition of the population is the formation of regional programs of healthy food, among other thing taking into

account the distribution of heavy isotopes in food, especially in regions with an unfavorable ecological environment (Ehleringer, *et al.* 2016), that will allow reducing impact of adverse factors to the human body. In the recent researches number of authors, while studying of deuterium depleted water (DDW) influence for isotope composition of blood and tissues plasma, it was noted that during use of this water in all organs of body there is decrease of deuterium concentration expressed in various levels (Dzhimak, *et al.* 2018; Kozin, *et al.* 2021). The most significant changes in D level were peculiar for kidneys, which after 2 weeks of experiment showed 10.8% lower deuterium content than the one of the liver and 14.2% less than the D values of the heart. An even more

significant decrease in concentration of D content was observed in blood plasma, which change was accompanied by a change in the direction of isotope D / H gradient (“plasma>>tissues” to “plasma<<tissues”) (Basov, *et al.* 2019b). The above-described changes are caused by low rate of exchange of deuterium to protium in tissues: in carbon-hydrogen bonds (R<sub>3</sub>C-D) in composition of organic substrates that have no atoms with an unshared electron pair, i.e. incapable, in contrast to hydroxyl (–O-H), sulfhydryl (–S-H), primary (–NH<sub>2</sub>) and secondary (=N-H) amino groups, to form complexes with hydrogen bonds capable to rapid exchange with D atoms while obtaining predominantly protium with water in the process of the food consumption. The observed changes of isotope composition in tissues cause nonspecific changes in metabolic and functional activity of immune defense systems, which is apparently related to the sub-stress effect of the isotope D/H gradient, including the energy exchange of the cell (Dzhimak, *et al.* 2014).

In addition, the obtained results allow not only comparative assessment of the D / H isotopic load on the population while forming the food nutrition, but also will allow tracking the movement of people in different regions, which can be used in forensic studies. Thus, in a study conducted in two regions of the United States of America: East Greenbush (New York) и Fairbanks (Alaska), it was shown, that the

content of deuterium in the hair and urine correlates with its content in the food ration (O’Brien, *et al.* 2007). And when a person moves between regions, the concentration of deuterium in his/her urine changes in accordance with its concentration in the food intake. The authors suggested using similar studies to track geographical movements of a person. Similar approaches are also applicable in biology to track geographical location and migration of various fauna representatives (Reynard, *et al.* 2016; Schmidt, *et al.* 2015). Therefore, the developed method for measurement isotope ratios by the NMR method using a probe containing a lanthanide shift reagent can be used in studies of environment and for environment condition monitoring, including monitoring of isotopic composition of liquids of natural and synthetic origin, as well as for determination of blood plasma isotopic composition.

Unlike the variability of deuterium concentrations in bottled waters, the concentration of <sup>17</sup>O there did not differ significantly from its concentration in tap water, in which deuterium concentration was 371.9±1.4 ppm.

Taking into account the above-stated, we conducted investigations of the isotope D/H composition of freshly squeezed juices, the data are presented in Table 2.

**Table 2.** Concentration of deuterium in fruit and vegetables freshly squeezed juices from various geographical regions

Fresh juice, manufacturer country	Deuterium concentration, ppm	Fresh juice, manufacturer country	Deuterium concentration, ppm
from tangerine, Egypt	126.2±1.5	from tomato, Morocco	112.0±0.8
from tangerine, Pakistan	127.9±1.0	from tomato, Turkey	122.4±0.9
from tangerine, Spain	132.7±1.8	from tomato, Spain	125.2±1.3
from orange, Egypt	128.5±1.7	from tomato, Russia	120.7±0.8
from orange, Turkey (1)	121.3±1.2	from cabbage, Poland	100.6±2.2
from orange, Turkey (2)	122.1±1.1	from cabbage, Russia	113.1±2.4
from pomegranate, Israel	129.7±1.3	from cabbage, the Netherlands	114.8±1.7
from pomegranate, Turkey	122.4±0.8	from potato, Egypt	99.6±2.4
from pomegranate, Azerbaijan	120.2±0.9	from potato, Israel	102.3±1.9
from apple, USA	118.3±0.6	from potato, Russia	105.4±2.6
from apple, Spain	131.5±1.1	from pear, Argentina	144.6±2.3
from apple, Italy	123.7±1.5	from pear, South Africa	118.1±1.6

from apple, Poland	127.6±1.2	from pear, USA	122.3±0.9
from apple, Russian	128.3±0.7	from pear, Russia	126.6±1.2

To obtain water samples the freshly squeezed juices were centrifuged at speed 3000 rpm for 15 minutes. It was found that the highest content of deuterium was in juice from a pear brought from Argentina ( $144.6 \pm 2.3$  ppm), while the lowest concentration of deuterium was found in the juice from Egyptian potato ( $99.8 \pm 2.4$  ppm). In general, the reliably lower deuterium content was detected in freshly squeezed potato and cabbage juices grown in different countries, in comparison with other fruit and vegetable fresh juices. The least range of differences in the isotope D/H composition was found in freshly squeezed juices (tomato, pomegranate and oranges) from Turkish producers (deuterium concentration there ranged from 121.3 to 122.4 ppm), which evidences similar climatic conditions and technologies for growing plant products in this country.

Among the tomato fresh juices the least deuterium values were found in the juice squeezed from tomatoes grown in Morocco ( $112.0 \pm 0.8$  ppm), which was 10.5% lower than the value in tomato juice grown in Spain, 8.4% lower than in juice from tomatoes grown in Turkey, 7.2% lower than in juice of tomatoes grown in Russia. All this allows us to recommend tomato juice from Morocco in order to correct isotope violations associated with accumulation of heavy stable hydrogen isotopes in ecologically unfavorable regions.

In addition, the obtained data, especially about fruit and vegetable juices from Turkish producers, allow us to recommend isotope D/H studies as alternative confirmation of its geographical origin. The sufficiently significant variations in content of heavy non-radioactive hydrogen isotopes were noted in juices from vegetables and fruits grown in Egypt (concentration of D in juices varied from 99.6 to 128.5 ppm), Poland (concentration of D in juices varied from 100.6 to 127.6 ppm) and Russia (concentration of D in juices varied from 105.4 to 128.3 ppm). The latter factor may be caused

by the peculiarities of agrarian production, including the features of water sources used to irrigate plant crops in these regions. Therefore, to confirm this suggestion the isotopic D/H composition in water samples from various regions of southern Russia was investigated (Table 3).

**Table 3.** Deuterium content in water samples, taken from surface and underground water sources in the southern region of the Russian Federation

Subject of investigation	Water from borehole 1	Water from borehole 2	Glacial water	Water from artesian well
Deuterium concentration, ppm	151.8±2.3	153.2±1.6	132.7±2.0	149.1±1.4

It was found that depending on the water source the ratio of light and heavy non-radioactive hydrogen isotopes can significantly differ in various geographic regions, especially significant differences between glacial water and water pumped from boreholes ( $\Delta D$  accounted from 16.4 to 20.5 ppm). That's why the change of deuterium content in plant products will also depend on the water supply source (surface or underground), used for irrigation of the plant cultures. Certain influence on fluctuation in deuterium concentration in plants can be caused by climatic factors, primarily atmospheric precipitations, which ensure formation of specific hydrological mode in each territory. It is necessary to note that much lower content of deuterium is found in freshly squeezed juices from potatoes and cabbage in comparison with other fruit and vegetable fresh juices.

At the same time the concentration of  $^{17}\text{O}$  did not significantly change in waters obtained from surface and underground sources in the southern regions of the Russian Federation and varied within the range from 371.6 to 373.8 ppm, which indicates lower variability of

concentrations of heavy oxygen isotopes in comparison with deuterium concentrations, and first of all allows us to recommend determination of the D/H ratio in analysis of isotopic composition of products from different geographical origin.

Taking into account the data on capability of reduced deuterium concentrations in blood and tissues of internal organs to change the functional activity of the nonspecific immune defense system, the consumption of products and water with lower content of heavy non-radioactive hydrogen isotopes may increase the nonspecific resistance of the organism. In connection with this the determination of isotope D/H composition of phytonutrients by this developed method using the lanthanide shift reagent  $\text{Eu}(\text{CF}_3\text{SO}_3)_3$  is the additional criterion for defining of quality of the manufactured food products of plant origin.

#### 4. Conclusions

As a result of the implemented research, there was developed a method for measuring the content of  $^2\text{H}$  and  $^{17}\text{O}$  isotopes in liquid medium using quantitative nuclear magnetic resonance. Among the considered paramagnetic metal ions the three-charged cation of europium ( $\text{Eu}^{3+}$ ) proved to be the most suitable for relaxation and shifting characteristics for the purposes of this research. The most suitable chemical compound containing  $\text{Eu}^{3+}$  for its use in capacity of shift reagent for water solutions for study of isotopic composition was europium (III) trifluoromethanesulfonate. According to the results of research of the dependence of chemical shifts of  $^2\text{H}$  and  $^{17}\text{O}$  nuclei from concentration of europium (III) trifluoromethanesulfonate, the specific values of paramagnetic chemical shift were determined, which allowed to establish the necessary concentration of  $\text{Eu}^{3+}$  ions for external standards (reference samples) to determine the isotopic composition of substances. The concentration of  $\text{Eu}^{3+}$  ions in determination of  $^{17}\text{O}/^{16}\text{O}$  ratio was 0.120 mol/l, and the ratio  $^2\text{H}/^1\text{H}$  was 0.045 mol/l. It is shown that use of shift reagents makes it possible to increase the informational content of

the NMR spectra. The developed methods for measurement of isotope ratios by NMR method using probes containing shift reagent can be used to solve environmental problems and to monitor the environment state, including for control of the isotopic composition of liquids of natural and synthetic origin.

With the help of developed method the concentration of deuterium was measured in fresh fruit and vegetables juices obtained from range of vegetables and fruits of various geographical origin. It was found that the highest content of deuterium was in juice of the Argentine pear (144.6 ppm), the least concentration of deuterium was found in the potato juices of Russian and Egyptian origin ( $\approx 100$  ppm). Among the tomato fresh juice the least deuterium values were found in the juice obtained from tomatoes grown in Morocco (112.0 ppm). In general, the significantly lower deuterium content was detected in freshly squeezed juices of potato and cabbage grown in different countries, in comparison with other fruit and vegetable fresh juices. The concentration of  $^{17}\text{O}$  did not change significantly in waters obtained from surface and underground sources in the southern regions of the Russian Federation and varied within the range from 371.6 to 373.8 ppm, which indicates lower variability of heavy oxygen isotopes concentrations in comparison with deuterium concentrations in the same natural water sources.

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