

Instrumental base and abilities of the Analytical Center for Isotope Investigations of IMCES SB RAS

D A Kalashnikova¹, M V Kabanov¹, V N Melkov¹, and G V Simonova^{1,2}

¹Institute of Monitoring of Climatic and Ecological Systems, Siberian Branch of the Russian Academy of Sciences (IMCES SB RAS), 10/3, Academicheskyy ave., Tomsk, Russia

²National Research Tomsk State University, 36, Lenin ave., Tomsk, Russia

E-mail: galina_simonova@inbox.ru

Abstract. The available up-to-date equipment allows us to perform various research tasks using modern scientific tools. The article shows examples of how data on the composition of stable isotopes can be used in biology, environmental studies, archeology, and paleoclimatology. In addition to stable isotopes, radioactive isotopes ¹⁴C and ³H are studied. An 1220 Quantulus spectrometer-radiometer is used to determine their specific activity. Investigations on the tritium specific activity in aqueous samples and tritium water isolated from tree ring cellulose on background and anthropogenically loaded sites are carried out. An analysis of carbon specific activity allows performing radiocarbon dating of bottom sediments, peat deposits, and archaeological samples. A qualitative elemental analysis is carried out using a Hitachi TM-1000 microscope equipped with an X-ray spectral analyzer.

1. Introduction

The main working area of the Analytical Center of IMCES SB RAS is collecting physical, chemical, and radiation data on environmental indicators. This data is the base for solving paleoclimatic and ecological issues. The availability of up-to-date equipment (a Hitachi TM-1000 microscope with an X-ray spectral analyzer; a 1220 Quantulus spectrometer-radiometer; a mass spectrometer complex: a DELTA V Advantage isotope mass spectrometer for determining isotope ratios, a Flash 2000 elemental analyzer, a TRACE GC ULTRA gas chromatograph, GasBench II – a system study of carbonates and water samples, and an ISQ single quadrupole mass spectrometer) allows one to perform various research tasks of modern science using the latest scientific tools (Figure 1).

2. Mass-spectrometry of stable isotopes

The fundamental principle of mass spectrometry is the conversion of neutral particles into charged particles followed by their separation by the mass-to-charge ratio value (m/z). This method allows not only identifying chemical compounds, but also determining the isotope composition of the elements forming the molecule.

In nature most elements have two or more stable isotopes, and the easiest of them are the most common ones. The isotope composition of light elements can change as a result of isotope fractionation during natural chemical and climatic processes [1]. The isotope composition is defined as



$$\delta^n X = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] \times 1000, [\text{‰}]$$

where nX is the ^2H , ^{13}C , ^{15}N , ^{18}O or ^{34}S isotope, R_{sample} and R_{standard} are the values of the ratio of the heavy isotope to the light isotope in the sample and reference material, respectively.

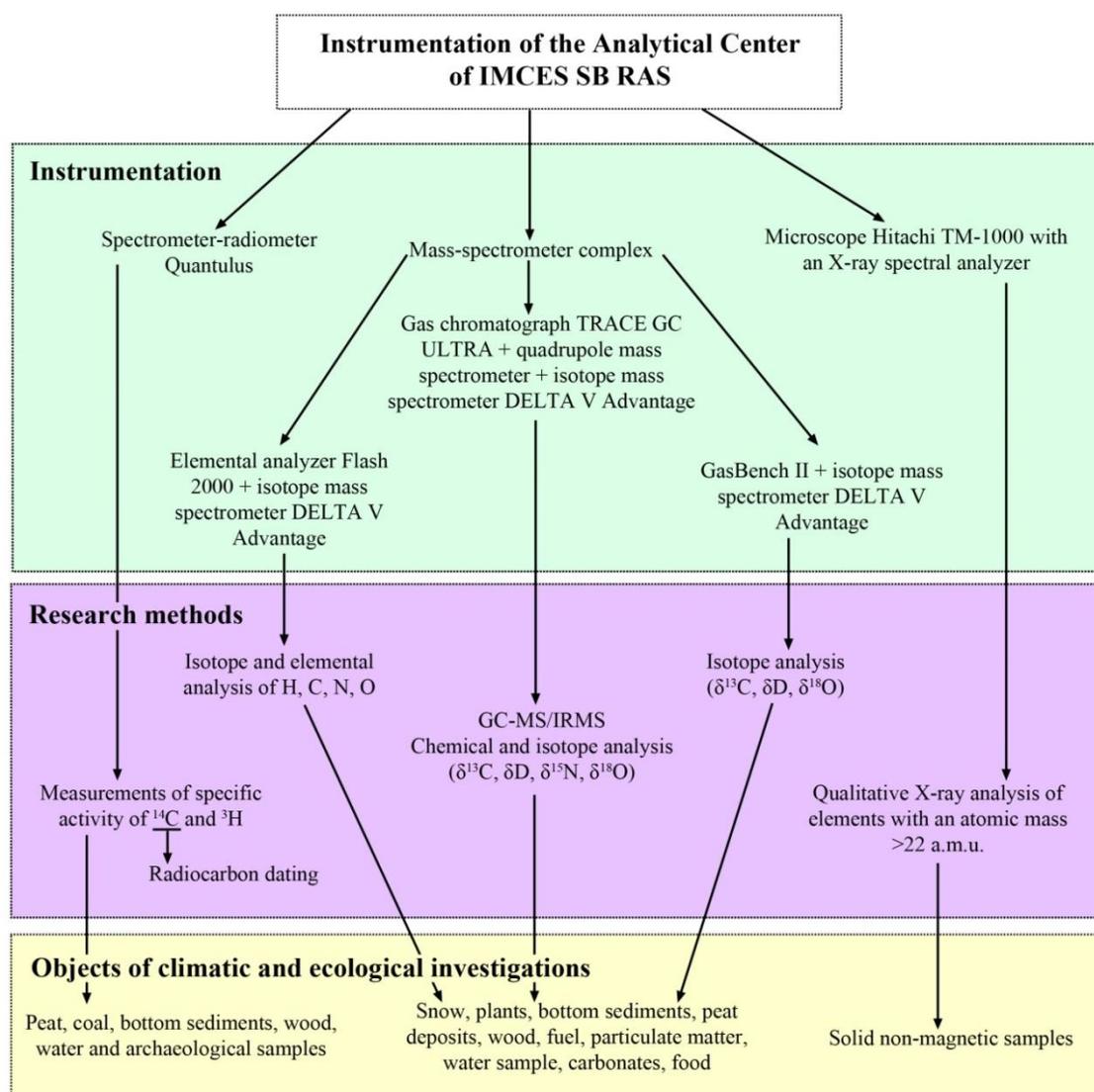


Figure 1. Instrumentation, methods, and objects of investigations of Analytical Center of IMCES SB RAS.

The mass spectrometer complex available at IMCES SB RAS makes it possible to measure the elemental and isotopic composition of light elements (C, H, N, O) and chemical compounds of a sample. Data on the stable isotopes composition of these elements are successfully used in solving issues in geology, biology, ecology, archeology, and paleoclimatology [2–6].

2.1. Climate investigation

Fractionation of isotopes is a natural or artificial shift of the isotopic composition of any element. In nature, fractionation occurs as a result of various physicochemical processes whose rate depends

primarily on temperature. Hydrogen and oxygen are markers of climatic changes, since they depend on the environmental conditions and allow one to restore information about the climate characteristics for a certain time for the territory under study. Isotopes can also be used to derive information about the geographical location: the isotope composition of samples near seas and oceans is more enriched in heavy isotopes. That is, the farther from the sea into the inland of the continent, the lighter the isotope composition of the studied samples.

The isotope composition of atmospheric precipitation is represented by oxygen and hydrogen stable isotopes. The complexity in determining the oxygen isotope composition is in the impossibility of direct mass-spectrometric analysis of water. However, this issue is solved by the method of isotope equilibration of water with standard CO₂ and subsequent isotope analysis of equilibrated CO₂.

Since precipitation is formed due to cooling of the atmospheric water vapor, there is a relationship between the content of stable isotopes in the precipitation and temperature. Atmospheric precipitation samples were collected in February - May 2015 at the meteorological site of IMCES SB RAS. The dependence of the average daily temperature and the oxygen isotope composition of precipitation is shown in Figure 2.

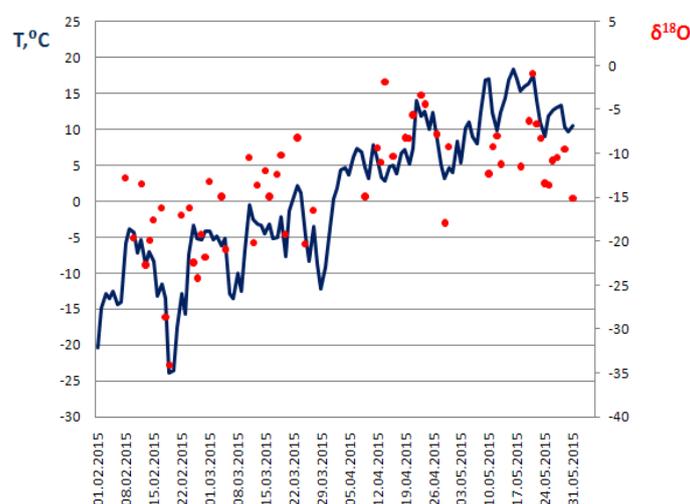


Figure 2. Isotope composition of precipitation: Tomsk, February–May 2015.

Correlation analysis showed that variations in the isotope ratios of the precipitation correlate with the air temperature. The Pearson correlation coefficient r was 0.76 ($n=56$). The isotope composition of the water in the reservoirs of Tomsk was also measured (Table 1).

Table 1. Isotope composition of $\delta^{18}\text{O}$ water of Tomsk reservoirs.

No.	Sampling site	$\delta^{18}\text{O}$, ‰
1	The Tom River	-16.7±0.1
2	The Ushayka River	-15.3±0.1
3	The Kirgizka River	-15.7±0.1
4	The Romashka River (Seversk)	-16.1±0.1
5	The Burunduk River	-15.9±0.1
6	The Burunduk Lake	-14.9±0.1
7	The Beloe Lake	-10.9±0.1
8	The Sennaya Kur'ya Lake	-15.3±0.1
9	The Zyryanskoe Lake	-10.9±0.1
10	The Krugloe Lake (Samus village)	-10.9±0.1
11	Spring water	-17.1±0.1

One can see that the isotope composition of water in the Beloe Lake, the Zyryanskoe Lake, and the Krugloe Lake is enriched in heavy oxygen isotope. This may indicate that isotopes with lighter masses evaporate more intensely and heavy ones remain. Therefore, the isotope composition of water is heavier in lakes which are not supplied with river water and warm up well. At the same time, river water has a lighter isotope composition.

Investigating the carbon, hydrogen, and oxygen isotope composition in plants and, in particular, in tree rings [7] and pollen [8] allows a conclusion on change in the climatic parameters of the environment to be drawn.

2.2. Investigation of air pollution by bioindicators

The study of the elemental and carbon and nitrogen isotope compositions in epiphytic lichens and mosses made it possible to obtain information on the environment in Tomsk and Prokopyevsk [9]. The values of the carbon isotope ratios showed different ranges: from -29‰ to -24‰ for lichens and from -34‰ to -28‰ for mosses (Figures 3, 4). The isotope composition of mosses is lighter than the isotopic composition of lichens. This reflects the difference in the biochemistry and physiology of lichens and mosses.

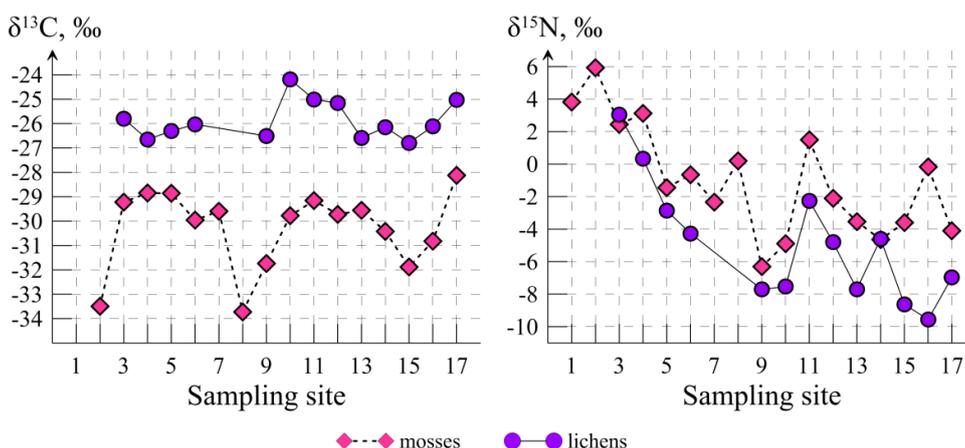


Figure 3. Average values of carbon and nitrogen isotope compositions of epiphytic mosses and lichens collected in Prokopyevsk.

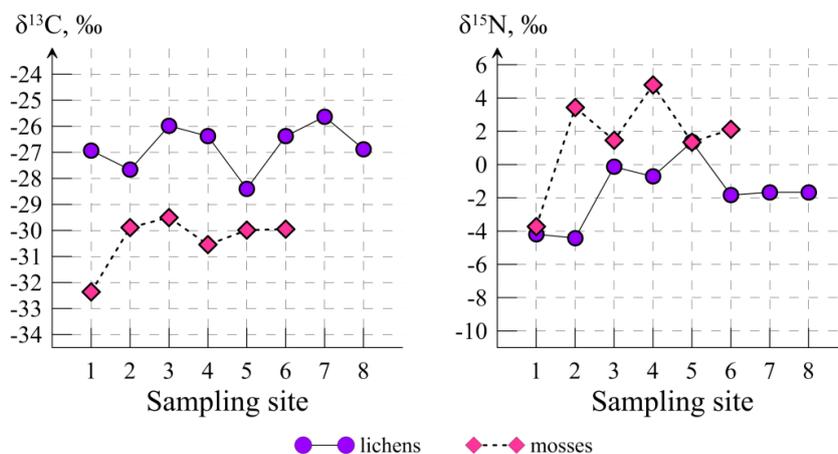


Figure 4. Average values of carbon and nitrogen isotope compositions of epiphytic mosses and lichens collected in Tomsk.

$\delta^{13}\text{C}$ values of mosses are more consistent with the photosynthesis of C3 plants. For different sampling sites, the same variations in the deviation of the isotope composition are observed (the isotope composition maximum and minimum of mosses and lichens correlate).

A comparative analysis of the isotope composition of lichens growing in Prokopyevsk and Tomsk showed that the carbon isotope composition in lichens for Prokopyevsk is heavier by 2 ppm. This can be explained by the geographical location. Tomsk is located to the north of Prokopyevsk, and the average air temperature during the vegetation period is lower and, as is known, the carbon isotope composition is lighter for territories with colder climate [10]. The carbon isotope composition in mosses for Prokopyevsk has a lighter value unlike lichens. The lightest isotope composition (-33.5 and -33.8‰) was recorded for Prokopyevsk in the territories where mines are located. This is explained by the presence of methane, which enriches the air isotope composition by light isotopes.

The average isotope composition value of nitrogen in mosses and lichens for Tomsk is heavier than the average for Prokopyevsk. The isotope compositions of mosses and lichens enriched in ^{15}N indicate a greater contribution of sources emitting oxidized forms of N (road transport, industrial facilities, power plants, and individual heating systems).

2.3. Investigation of food product authenticity

The study of chemical and isotope composition of food products is one of the most important areas of research. Chromatographic methods are usually used in Russia to identify falsification of food products and raw materials. Determination of stable isotope composition is considered to be an effective method of establishing the geographic origin, as well as facts of falsification of food products. Fractionation of carbon isotopes in photosynthesis, as well as fractionation of carbon and nitrogen isotopes in the biochemical (microbial) transformation of organic matter is most important when investigating food [11].

We tested the possibility of using the isotope mass spectrometry method to establish the fact of falsification by the example of honey. Honey is produced from both nectar of plants and honey dew by honey bees. Some components of honey (traces of organic acids, carbohydrates, water, enzymes, amino acids, pollen, and wax) are due to maturation of honey, some of them are added by bees and some of them are derived from plants. Honey adulteration is based on two different methods: 1) "dilution" of honey by water addition, and extension with sugar and syrups (e.g. corn syrup, high fructose corn syrup (HFCS)), 2) bee-feeding with sugars and syrup or artificial honey and mislabelling concerning the floral or geographical origin [12].

A comparative analysis of the isotope composition of carbon in honey and its protein fraction reveals the presence of sugar syrup in honey [13]. The hydrocarbon and protein components of natural undiluted honey are formed simultaneously and from a single source. Therefore, the abundance of the carbon isotope in honey and in the protein isolated from it should be the same. The difference in the isotope composition by more than -1‰ indicates falsification of honey by sugar. The results of carbon isotope analysis in samples of purchased honey at retail trade fairs and directly at apiaries are shown in Figure 5. It was found that 7 of 17 honey samples were diluted with sugar. In two samples of honey the difference between the $\delta^{13}\text{C}$ of the protein fraction and the original honey was more than 1‰ , which indicates dilution of these honeys with cane sugar by more than 7%. The isotope composition of honey is informative not only for detecting honey falsification, but it can serve as a kind of marker for the geographical origin of honey.

3. Radioisotope analysis

In environmental investigations radioactive isotopes of light elements (radiocarbon and tritium) are used in addition to stable isotopes. The specific activity of these elements is determined by the liquid-scintillation method at the 1220 Quantulus spectrometer-radiometer (Tomsk Collective Use Center of SB RAS). This method is based on counting the number of particles that are formed during the nuclear decay per unit time.

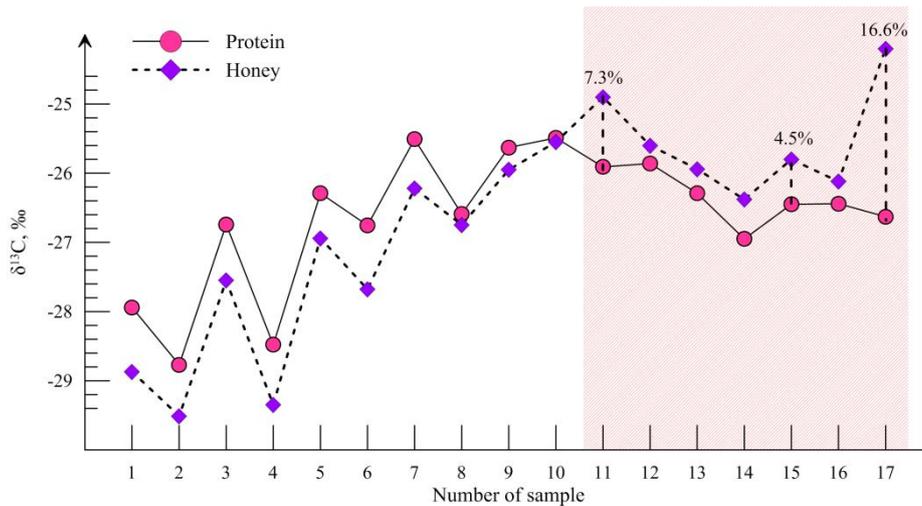


Figure 5. δ¹³C of honey samples. Falsified honey is shown in the color zone.

3.1. Measurements of tritium specific activity

Studies of the tritium specific activity in aqueous samples (atmospheric precipitation, birch sap, samples of man-made and natural water) were conducted at the Analytical Center of IMCES SB RAS [14]. Also, the tritium water isolated from wood cellulose was studied for background and anthropogenically loaded areas (Figure 6) [15]. For this purpose, a special device for isolation of tritium water from organic samples was developed [16].

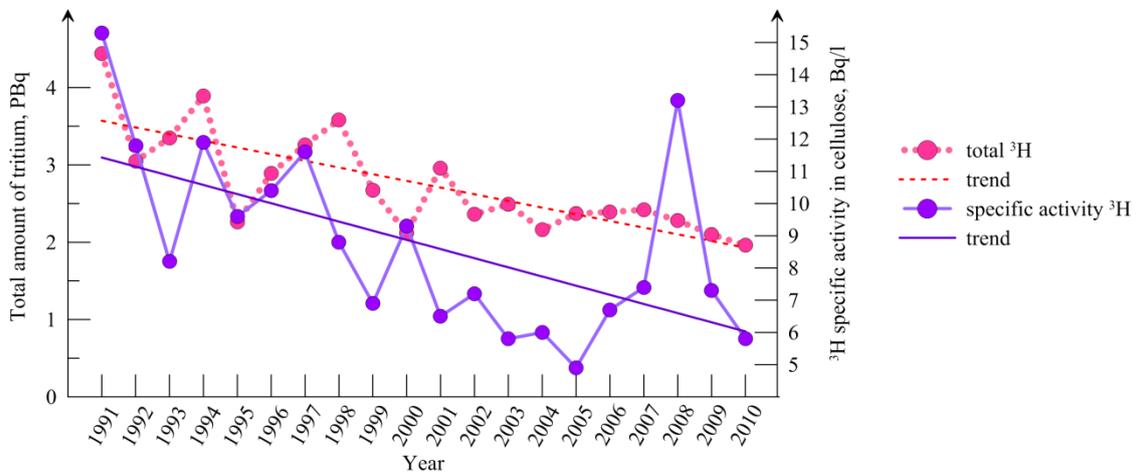


Figure 6. Activity of tritium in the cellulose of annual rings (solid line) and the total amount of tritium deposited with precipitation throughout the territory of Russia (dashed line).

A downtrend is observed according to the content of tritium in the annual ring cellulose of *Pinus sylvestris* for 1991–2010. There is a decrease in the activity from 15.3 Bq/l to 5.8 Bq/l, and this conforms with the experimental data on the activity of tritium in precipitation. The maximum of the tritium specific activity (13.2 Bq/l) was recorded in 2008. This can be explained by a planned shutdown of two reactors at the Siberian Chemical Combine.

3.2. Radiocarbon dating

Analysis of the carbon specific activity allows for radiocarbon dating of various environmental objects. Series of radiocarbon dates of wood, peat, bottom sediments from various Holocene deposits,

charcoal, and archaeological samples were obtained at the Laboratory of Bioinformation Technologies of IMCES SB RAS at the spectrometer-radiometer. For the first time, the radiocarbon age of the organic matter of frost mounds on Bely Island in the Kara Sea was determined [16]. The radiocarbon dating was determined for the peat accumulation of the khasyrey from the Sohonto Lake of the Central Yamal Peninsula located in the tundra of Western Siberia, and it allowed reconstructing the 1300 years dynamics of the khasyrey [17]. The 1220 Quantulus allows one to solve out not only geocryological, paleoclimatic, and geocological issues, but also to perform archaeological research [18].

4. Elemental analysis of environmental objects

Qualitative elemental analysis of elements with an atomic mass of more than 23 a.m.u. was carried out on a Hitachi TM-1000 electron microscope with an X-ray spectral analyzer SwiftED-TM EDS. Epiphytic mosses and lichens were analyzed on this microscope to assess the atmospheric pollution [9]. Epiphytic mosses and lichens are significantly more enriched in pollutants compared to the other representatives of the biota under aerotechnogenic influences because of their specific structure and physiology. The following elements were found in the mosses and lichens: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn, Zr, I, Ba, La, Ce, Nd, Th, Tm, and Ta.

Also, the Flash 2000 elemental analyzer as part of the mass spectrometer complex allows carrying out qualitative and quantitative elemental analysis of light elements (H, C, N, O) by high-temperature combustion of solid and liquid samples.

5. Conclusions

The instrumentation of the Analytical Center for Isotope Investigations of IMCES SB RAS allows successfully studying problems of geology, paleoclimatology and ecology, radiobiology, archeology, and authenticity of food products.

Radiocarbon dating is an important component of complex studies for the paleoclimatic and paleolandscape reconstruction of the environment, as well as long-range climate change estimates. The physicochemical methods alone do not ensure accurate results and, therefore, an integrated approach is required, for example, in combination with bioindicators. The use of the different methods provides more accurate data, because the results of each of them complement each other. For example, for reliable radiocarbon dating of ancient objects it is necessary to take into account the change in the stable carbon isotopes ratio and to make a correction when calculating the radiocarbon age. Mass spectrometry allows determining the sample's origin, which is important both for environmental and archaeological studies using elemental and stable isotope compositions.

Acknowledgments

This work was partially supported under RFBR projects no. 16-45-700941, 16-05-00521, and basic project VIII.80.2.3.

References

- [1] 2011 Problems of Analytical Chemistry. Isotope mass spectrometry of gas-forming elements ed Sevastyanov V S Moscow: FIZMATLIT Vernadsky Institute of Geochemistry and Analytical Chemistry of RAS **15** p 240
- [2] Kalashnikova D A, Markelova A N, Melkov V N and Simonova G V 2016 Isotopic composition of light elements of natural objects in Tomsk region as a marker of paleoclimatic changes *Russian Physics Journal* **7/2** (59) 87–93
- [3] Young G H F, McCarroll D, Loader N J and Kirchhefer A J 2010 A 500-year record of summer nearground solar radiation from tree-ring stable carbon isotopes *Holocene* **20**(3) 315–24
- [4] Pinho P, Barros C, Augusto S, Pereira M J, Maguas C and Branquinho C 2017 Using nitrogen concentration and isotopic composition in lichens to spatially assess the relative contribution of atmospheric nitrogen sources in complex landscapes *Environmental Pollution* **230** 632–38
- [5] Mašalaitė A, Garbaras A and Remeikis V 2012 Stable isotopes in environmental investigations

- Lithuanian Journal of Physics* **52**(3) 261–68
- [6] Schellenberg A, Chmielus S, Schlicht C, Camin F, Perini M, Bontempo L, Heinrich K, Kelly S D, Rossmann A, Thomas F, Jamin E and Horacek M 2010 Multielement stable isotope ratios (H, C, N, S) of honey from different European regions *Food Chemistry* **121** 770–77
- [7] Markelova A N, Volkov Y V, Simonova G V and Kalashnikova D A 2017 Isotope monitoring of forest ecosystems *Conf. Proc. 17th Int. multidisciplinary scientific geoconference SGEM 2017 (Bulgaria)* **17**(32) 885–90
- [8] Simonova G V, Blyakharchuk T A and Vetrova O V 2015 Variability of content of stable isotopes of carbon in pollen of deciduous tree species depending on weather conditions of vegetative season *Bulletin of the Tomsk Polytechnic University* **11**(326) 18–21
- [9] Simonova G V and Kalashnikova D A 2018 Mosses and lichens as indicators of atmospheric pollution *Conf. Proc. X Int. scientific and practical conf. "Actual problems of modern science" (Tomsk)* **3** 175–80
- [10] Liu X Z, Zhang Y, Li Z G, Feng T, Su Q and Song Y 2017 Carbon isotopes of C3 herbs correlate with temperature on removing the influence of precipitation across a temperature transect in the agropastoral ecotone of northern China *Ecol Evol.* **7**(24) 10582–91
- [11] Talibova A and Kolesnov A 2011 Quality and food safety assessment using the isotope mass spectrometry method *Analytica* **1**(1) 44–8
- [12] Anklam E 1998 A review of the analytical methods to determine the geographical and botanical origin of honey *Food Chemistry* **63**(4) 549–62
- [13] Vetrova O V, Kalashnikova D A, Melkov V N and Simonova G V 2017 Detection of honey adulterations with sugar syrups by stable isotope mass spectrometry *Journal of Analytical Chemistry* **72**(7) 756–60
- [14] Kabanov M V, Melkov V N, Simonova G V and Markelova A N 2012 Monitoring of tritium concentration in aqueous objects and birch sap in environs of Tomsk *Ecological Systems and Devices* **1** 42–5
- [15] Simonova G V, Kabanov M V, Markelova A N, Melkov V N and Nikolaeva S A 2013 Tritium and radiocarbon in environments in Tomsk surroundings *Journal of Radiation Safety Issues* **4** 30–44
- [16] Orekhov P T, Popov K A, Slogoda E A, Kurchatova A N, Tikhonravova Ya V, Opokina O L, Simonova G V and Melkov V N 2017 Frost mounds of Bely island in coastal marine settings of the Kara Sea *Earth's Cryosphere* **1**(XXI) 46–56
- [17] Preis Yu I, Simonova G V and Slogoda E A 2016 Detailed reconstruction of the functional state of Central Yamal khasyrey as a response to local conditions and regional climate changes in the late Holocene *IOP Conf. Series: Earth and Environmental Science* **48**(1) 012010
- [18] Tishkin A A, Melkov V N and Simonova G A 2018 Isotopic composition of carbon $\delta^{13}\text{C}$ and nitrogen $\delta^{15}\text{N}$ in the buried remains from the mounds of the Yaloman-II and III sites in Altai *Conf. Proc. Conservation and study of the cultural heritage of the Altai Territory* ed Tishkin A A, Semibratov V P (Barnaul) **XXIV** 179–86