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ISOTOPE MASS SPECTROMETRY APPLICATION FOR THE ABIOGENIC ALCOHOLS DETECTION IN GRAPE WINES

Abstract. Practice shows, that a single indicator д^{13}C ‰, characterizing the ratio of stable isotopes of ^{13}C/^{12}C carbon, in some cases is not enough to detect alcohol in alcohol wines of an innocent origin, especially when abiogenic alcohols are introduced into the product. The instrumental base for obtaining characteristics of isotopes elements of ethanol molecules was Delta V Advantage of the Thermo Fisher Scientific (USA) mass spectrometer complex , which provides a precise analysis of prevalence ratios of ^{13}C/^{12}C, ^{18}O/^{16}O, D/H isotopes. It has been established that the isotope characteristics of abiogenic alcohol oxygen, obtained by hydration of ethylene significantly differ from this index for all alcohols of plant origin. The isotope characteristics of most vegetable alcohols oxygen fit within the range д^{18}O‰ from 5.38‰ to 16.29‰, and only for beetroot alcohol the numerical values are somewhat lower, namely: 1.66–2.05 ‰. At the same time, the value of д^{18}O‰ in abiogenic ethanol has a negative sign and amounts to minus 14.21 ‰ – minus 15.20 ‰. These significant differences allow us to use this indicator to establish the nature of the used alcohols – vegetable or abiogenic origin. Analyzing the indicator дD ‰, it can be noted that the hydrogen of the abiogenic alcohol is noticeably "heavier" than the hydrogen, contained in the alcohols of vegetable origin and is minus 140‰ – minus 153‰ against minus 213‰ – minus 266‰. Using the values obtained, 24 samples of table wines were examined. Two samples had a value of д^{13}C minus 28.22‰ and minus 28.41‰, respectively, д^{18}O minus 1.0‰ and minus 0.76‰, which indicates the presence of abiogenic alcohol in the product. "Heavy" hydrogen дD (minus 172.66‰) and дD (minus 169.43‰), not characteristic for alcohols from plant raw materials, only confirm the conclusion. Similar studies have been conducted for liquor wines. Thus, by measuring the isotopic characteristics of the three elements of alcohol molecules – carbon, oxygen and hydrogen, the presence of alcohols of abiogenic origin can be detected with high degree of certainty in wines.

Keywords: wine, beverage identification, isotope mass spectrometry, wine ethanol, abiogenic alcohols, isotope ratio of ethanol molecules elements.

Introduction. Currently, the world produces a wide range of alcoholic drinks on grape and fruit raw materials. The main types of wine products from grapes are wine, liqueur (special) wines, sparkling wines, flavored wines, wine drinks, as well as alcoholic drinks above 37.5% - grape vodka, brandy, cognac, armagnac, etc.

To control the quality and authenticity of wine production, various methods of analysis are used. Normed indicators are defined in each batch of products, and these quantities are set in national and interstate standards of the type "general technical conditions". However, the fulfillment of the requirements of standards of this type ensures only confirmed conformity of the product to a certain species, characterizes its commercial properties and can't guarantee its authenticity.

In case of doubt the expert, he has the right to apply national and interstate standards of the form "identification". The most informative among them are the standards developed in recent years, based on the use of instrumental methods of analysis. These include, first of all, methods, based on the principle of isotope mass spectrometry.

This method showed high efficiency in determining the authenticity of grape wines. It is known that the most common way of falsification of this product type to introduce alcohols of an innocent origin after diluting the wine with water to provide the necessary conditions for alcohol.

Also, the introduction of cane and beet sugars, and, in addition, corn glucose-fructose syrup in diluted wort, followed by fermentation to obtain the necessary alcohol fermentation. In any case, exogenous alcohols appear in the wine after these operations, which is prohibited by law. Their presence can be detected using the method of isotope mass spectrometry [1-6].

Thus, the determination of carbon characteristics of native ethanol, contained in natural wines and cognacs (д^{13}C), which is usually in the range from minus 26‰ to minus 29‰, allowed to reveal the introduction of alcohols of an innocent origin, as they have values different from grape ethanol, namely: from minus 11‰ to minus 25‰. However, over time, falsifiers found a loophole in the method, adding to the alcohols from botanical origin an "abiogenic alcohol" that has isotope characteristics of carbon д^{13}C from minus 32‰ to minus 35‰.

Thus, using the data isotopic characteristics unscrupulous manufacturers by adding alcohol to abiotic alcohols to vegetable spirits of non-grape origin, obtained blends with the desired characteristics д^{13}S from minus 26‰ to minus 29‰ [7-10].

Given that the use of abiogenic alcohol is strictly forbidden in the production of food products because of its high toxicity, the problem goes beyond the control of authenticity and goes into the sphere of security.

There are cases of application of abiogenic alcohol not only for falsification of wine production, but also in the production of vodka, alcoholic drinks, and other types of alcoholic drinks. Thus, the use of abiogenic alcohol has recently taken a dangerous scale, which requires adequate control measures. For this, it is necessary to make fuller use of the advantages that the method, based on the principle of isotope mass spectrometry possesses.

As already mentioned, a single indicator д^{13}C‰, characterizing the ratio of stable isotopes of ^{13}C/^{12}C carbon, in some cases is not enough to detect alcohol in alcohol wines of an innocent origin, especially when abiogenic alcohols are introduced into the product.

Abiogenic alcohol is generally obtained by hydrating ethylene with steam under pressure in the presence of a catalyst. Given that in the molecule in addition to carbon atoms of the alcohol also includes oxygen and hydrogen, it can be assumed that the relationship isotope ^{18}O/^{16}O and D/H can be significantly different from the relationship of oxygen and hydrogen isotopes alcohols of plant origin. Indeed, the oxygen of the technical water involved in the reaction for obtaining abiogenic alcohol is much easier than the oxygen of the aqueous component of plant raw materials [11-24].

Methods. The research objects were alcohols of various origins, table wines, liqueur wines. The measurements were carried out according to the "Method for Measuring the Isotope Ratios of Carbon, Oxygen, Hydrogen Ethanol to Detect the Presence of Synthetic Alcohol in Alcohol Products, as well as in Alcohol-Containing Food Flavors by Isotope Mass Spectrometry" (Certificate of Attestation No. 205-48/RA.RU.3111787- 2016/2017, FZ.1.31.2017.28360).

The instrumental base for obtaining characteristics of the isotopic composition of ethanol molecules elements was the Thermo Fisher Scientific (USA) mass spectrometer complex Delta V Advantage, which provides a precise analysis of the prevalence ratios of ^{13}C/^{12}C, ^{18}O/^{16}O, D/H isotopes.

Carbon isotope characteristics were measured relative to the international V-PDB comparison. VPDB - as an international standard, the PDB standard is adopted, which is the isotope composition of the calcium carbonate carbon of the Belemnitella Americana fossil of the late Cretaceous period from the PDB formation (South Carolina, USA). The international standard PDB is characterized by a homogeneous isotopic composition. Currently, the Vienna equivalent of the PDB-VPDB is used as an international standard.

The isotope characteristics of oxygen and hydrogen were measured relative to the international comparison model VSMOW2. VSMOW2 is the Vienna Standard Mean Ocean Wat2.

The obtained ratios of carbon isotopes (^{13}C/^{12}C), oxygen (^{18}O/^{16}O) and hydrogen (D/H) were determined in ‰, using the software of a mass spectrometer, using formula

$$X\left(\delta^{13}C_{VPDB}, \delta^{18}O_{VSMOW2}, \delta D_{VSMOW2}\right) = \frac{\left(R_{sample} - R_{ref.}\right)}{R_{ref.}} \cdot 1000, \quad (1)$$

where R_{sample} – is the ratio of carbon isotopes ($^{13}C/^{12}C$) (oxygen ($^{18}O/^{16}O$), hydrogen (D/H)) in an ethanol sample; $R_{ref.}$ – the ratio of carbon isotopes ($^{13}C/^{12}C$) (oxygen ($^{18}O/^{16}O$), hydrogen (D/H)) in the reference gas CO_2 (CO, H_2).

Results and its discussion. The isotopic characteristics of д^{13}C, д^{18}O and дD ‰ of abiogenic alcohols, as well as alcohols from various types of plant raw materials, were studied. The results are summarized in table 1.

Table 1 – Isotope Characteristics of Ethanol Biophilic Elements of Different Origin

Sample name	Isotope Characteristics		
	д^{13}C, ‰	д^{18}O, ‰	дD, ‰
rectified ethyl alcohol: grape	-26.1 – -28.8	10.04–16.29	-200 – -240
fruit	-24.84 – -28.59	5.38–12.02	-213 – -239
grain	-24.80 – -25.87	10.27–13.57	-230 – -266
cane	-10.96 – -12.10	8.27–9.43	-215 – -230
corn	-13.84 – -15.10	10.87–11.98	-215 – -231
beet	-26.61 – -26.9	1.66–2.05	-270 – -290
abiogenic alcohols (hydration of ethylene)	-31.28 – -35.55	-14.21 – -15.20	-140 – -153

As can be seen from the data. presented in Table 1. the obtained results confirmed the assumption. that the isotope characteristics of oxygen of the abiogenic alcohol obtained by hydration of ethylene differ significantly from this index for all alcohols of plant origin. Most vegetable alcohols fit within the range of д^{18}O‰ from 5.38 to 16.29 ‰. and only for sugar beet the numerical values are somewhat lower. namely: 1.66–2.05 ‰. At the same time. the value of д^{18}O ‰ in abiogenic ethanol has a negative sign and amounts to minus 14.21 ‰ – minus 15.20 ‰. These significant differences allow us to use this indicator to establish the nature of the alcohols used - vegetable or abiogenic origin.

Analyzing the indicator дD ‰. it can be noted that the hydrogen of the abiogenic alcohol is noticeably "heavier" than the hydrogen. contained in the alcohols of vegetable origin and is minus 140 ‰ – minus 153 ‰ against minus 213 ‰ – minus 266 ‰.

Using the obtained values. 24 samples of table wines were examined. The results are summarized in table 2.

Analyzing the data of Table 2. we can conclude that all wines. except for samples 6. 12. 15. 19. are made without violation of technology. At the same time. sample 6 has values of д^{13}C and д^{18}O – minus 27.03 and 2.65 ‰. respectively. characteristic of beet alcohol or its mixture with grape ethanol. With a high probability. in the production of wine in grape must before or during fermentation process was introduced beet sugar.

The same can be said for the sample 9. which was apparently prepared by adding S4-type plants. corn glucose-fructose syrup. or cane sugar to the grape must. At least. the value of the indicator д^{13}C. equal to minus 17.45‰. speaks about this.

As for sample No. 15. having values of д^{13}C minus 28.41 ‰ and д^{18}O minus 0.76 ‰. and sample No. 18 with the values of д^{13}C minus 28.22 ‰ and д^{18}O minus 1.0 ‰. there is a fact of adding to product of abiogenic alcohol. "Heavy" hydrogen дD (minus 172.66 ‰) for sample No 15 and дD (minus 169.43 ‰) for sample No 18. not characteristic for alcohols from plant raw materials. only confirm the conclusion.

In accordance with the requirements of GOST 32715-2014 "Wine Liquors. Wine Liqueur of Protected Geographical Indications. Wine Liqueur of Protected Names of Origin Place. General Technical Conditions". liquors and distillates of grape or other vegetable origin are allowed to be added to liqueur wines. As it was said above. the legislation of the Russian Federation prohibits. the use of abiogenic ethyl alcohol for the production of food. including alcoholic products.

In the present work, when interpreting the results of measurements of the isotope characteristics of ethanol elements for liqueur wines. the numerical ranges characteristic of grape alcohols were used. as well as the isotope characteristics of ethanol extracted from plant raw materials of various origins and synthetic alcohol.

Table 2 – Table Wine Isotope Characteristics of Carbon. Oxygen and Hydrogen Ethanol

No	Sample name	Isotope Characteristics		
		д^{13}C.‰	д^{18}O.‰	дD.‰
1	White table dry wine	(-26.8)±0.2	11.56±0.25	(-239.79)±0.79
2	White table dry wine	(-27.19)±0.21	12.54±0.27	(-228.75)±0.81
3	White table dry wine	(-18.12)±0.18	8.76±0.25	(-230.01)±1.01
4	Red table dry wine	(-26.76)±0.2	10.76±0.29	(-215.42)±0.95
5	Red table dry wine	(-12.87)±0.15	8.32±0.27	(-237.31)±1.0
6	Red table dry wine	(-27.03)±0.15	2.65±0.25	(-282.01)±0.87
7	White table semidry wine	(-25.99)±0.21	9.91±0.25	(-217.09)±0.87
8	White table semidry wine	(-25.45)±0.18	10.32±0.29	(-230.34)±0.9
9	White table semidry wine	(-17.45)±0.2	9.02±0.27	(-217.09)±0.9
10	Red table semidry wine	(-26.01)±0.15	10.0±0.25	(-239.54)±0.89
11	Red table semidry wine	(-26.33)±0.2	9.89±0.29	(-213.65)±0.89
12	Red table semidry wine	(-26.60)±0.22	5.87±0.27	(-239.09)±1.02
13	White table semisweet wine	(-25.89)±0.2	10.21±0.27	(-235.21)±0.98
14	White table semisweet wine	(-10.16)±0.18	9.54±0.25	(-240.51)±1.0
15	White table semisweet wine	(-28.41)±0.2	(-0.76)±0.25	(-172.66)±1.0
16	Red table semisweet wine	(-26.75)±0.17	12.43±0.27	(-221.87)±1.01
17	Red table semisweet wine	(-10.90)±0.21	9.51±0.27	(-245.76)±0.9
18	Red table semisweet wine	(-28.22)±0.2	(-1.0)±0.25	(-169.43)±0.89
19	White table sweet wine	(-26.76)±0.2	12.98±0.29	(-211.33)±0.79
20	White table sweet wine	(-26.02)±0.18	9.87±0.27	(-225.54)±0.98
21	White table sweet wine	(-25.89)±0.19	11.43±0.29	(-209.89)±0.9
22	Red table sweet wine	(-27.02)±0.2	13.05±0.25	(-231.76)±1.0
23	Red table sweet wine	(-26.43)±0.2	10.76±0.25	(-220.19)±1.0
24	Red table sweet wine	(-15.42)±0.21	11.0±0.27	(-226.75)±1.01

The isotope characteristics of carbon, oxygen and hydrogen of ethanol isolated from liquor wines were measured. The data are presented in table 3.

As can be seen from the table. of the nine samples analyzed. only three samples (No. 1, No. 2 and No. 3) are prepared without a violation of technology. The isotope characteristics of carbon. oxygen and hydrogen of ethanol extracted from these samples are included in the numerical ranges established for alcohols of grape origin.

Table 3 – Isotope Characteristics of Carbon. Oxygen and Hydrogen Ethanol of Liqueur

Wines No	Sample name	Isotope Characteristics		
		д^{13}C.‰	д^{18}O.‰	дD.‰
1	Liqueur Wine	(-27.07)±0.18	11.09±0.3	(-227.91)±1.1
2	Liqueur Wine	(-26.65)±0.18	12.45±0.29	(-231.54)±1.09
3	Liqueur Wine	(-25.83)±0.2	10.54±0.29	(-230.54)±1.12
4	Liqueur Wine	(-23.76)±0.2	12.76±0.3	(-219.09)±1.09
5	Liqueur Wine	(-24.33)±0.21	13.04±0.28	(-247.87)±1.12
6	Liqueur Wine	(-18.09)±0.18	9.54±0.3	(-249.09)±1.1
7	Liqueur Wine	(-20.87)±0.21	8.43±0.28	(-230.21)±1.12
8	Liqueur Wine	(-11.87)±0.19	10.12±0.3	(-238.75)±1.1
9	Liqueur Wine	(-28.32)±0.2	0.31±0.3	(-180.21)±1.1

The isotope characteristics of ethanol carbon of sample No. 4 indicate the presence of alcohols of non-trivial origin. obtained from C-4 plants of the type of photosynthesis (corn. sugar cane). The values of д^{18}O and дD are included in the range established for grape alcohols.

The value of the indicator д^{13}C for ethanol extracted from sample No. 5 equal to minus 24.33 can indicate the presence of alcohols derived from C-4 plants of the type of photosynthesis (corn. sugar cane) or about obtaining this sample from grain alcohols. The ratio of oxygen and hydrogen isotopes (д^{18}O-13.04 ‰. дD-minus 247.87). characteristic for grain alcohols. also speak of this.

Samples No. 6 and No. 7 are blended products made from biogenic alcohols of various origins. The values of д^{13}C and д^{18}O obtained for ethanol. extracted from these wines indicate the presence of alcohols. obtained from carbohydrates of C-4 plants of the type of photosynthesis. At the same time. the values of дD. equal to minus 249.09 ‰ and minus 230.21 ‰. may indicate the presence of grain alcohols.

The isotope characteristics of light elements of ethanol. extracted from sample No. 8 allow us to evaluate this sample as a counterfeit. completely prepared from sugars/alcohols made from sugar cane.

As for sample No. 9. having values of д^{13}C minus 28.32 ‰. д^{18}O. equal to 0.31 ‰ and дD minus 180.21 ‰. the fact of adding abiogenic alcohol to the product is clearly revealed here. The value of д^{18}O. close to zero. and the displacement of the isotope characteristics of hydrogen toward the increase in the share of "heavy" deuterium. unequivocally indicate the presence of alcohols of abiogenic origin.

Based on the results of the studies. the following conclusions can be drawn:

- when wine and liqueur wines are added to biogenic alcohols of an innocent origin. the isotope characteristics of the light elements of ethanol change in the direction of increasing or decreasing the proportion of "heavy" isotopes depending on the type of raw material from which the exogenous alcohol was produced;
- when abiogenic alcohols are added to wine. the oxygen and hydrogen isotopes are deeply fractionated. the value of д^{18}O goes to the negative numerical range or is close to zero. which indicates a significant increase in the fraction of the "light" isotope ^{18}O. At the same time. the proportion of deuterium increases. as evidenced by the high values of the дD. Isotope characteristics of carbon can be included in the numerical range. characteristic for alcohols of grape origin.

Thus. by measuring the isotope characteristics of the three elements of the alcohol molecule - carbon. oxygen and hydrogen. the presence of alcohols of abiogenic origin can be detected with a high degree of certainty in wines.

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ЖҮЗІМ ШАРАПТАРЫНДАҒЫ АБИОГЕНДІ СПИРТТЕРДІ АНЫҚТАУҒА ИЗОТОПТЫ МАСС-СПЕКТРОМЕТРИЯНЫ ҚОЛДАНУ

Аннотация. Тәжірибе көрсеткендей, тұрақты көмірсу изотоптарының ^{13}C/^{12}C сипаттайтын бір көрсеткіш d13C ‰, әсіресе, абиогендік спирттер өнімге қосылса, жүзім емес заттардан спирттерді анықтау үшін жеткіліксіз.

Этанол молекуласының элементтерінің изотоптарын сипаттайтын аспаптық база ^{13}C/^{12}C, ^{18}O/^{16}O, D/H изотоптарының таралу коэффициенттерін нақты талдауды қамтамасыз ететін Thermo Fisher Scientific (АҚШ) компаниясының Delta V Advantage масс-спектрометрия кешені болды. Этилен гидратациясымен алынған абиогендік спирттегі оттегінің изотоптық сипаттамалары осы көрсеткіштен өсімдік текті заттардың барлық спирттерінен айтарлықтай ерекшеленетіндігі анықталды. Көптеген өсімдіктерден алынған спирттерінің оттегінің изотоптық сипаттамалары д^{18}O‰-ден 5,38‰ ден 16,29‰-ға дейін түседі, тек қана қызылша спирті үшін сандық мәндер шамалы төмен, атап айтқанда: 1,66–2,05‰. Сонымен бірге, абиогенді этанол үшін д^{18}O‰ мәнінің мәні теріс және минус 14.21 ‰ – минус 15,20‰. болып табылады. Бұл елеулі айырмашылықтар осы көрсеткішті пайдаланып, қолданылатын спирттердің – өсімдік текті немесе абиогендік туралы айтуға мүмкіндік береді. дD‰ көрсеткішін талдай отырып, абиогендік спирттің сутегі өсімдік алкоголі бар сутегіне қарағанда айтарлықтай «ауыр» екенін және қарама қарсы минус 213‰ – минус 266 ‰ минус 140‰ – минус 153‰ екенін атап өтуге болады. Алынған мәндерді пайдалана отырып, асханалық шараптың 24 үлгісі зерттелді. Бұл жағдайда екі үлгіде д^{13}C минус 28,22 ‰ және минус 28,41‰ мәндері бар, д^{18}O минус 1,0‰

және минус 0,76‰, бұл өнімдегі абиогендік спирт бар екендігін білдіреді. Өсімдік шикізатынан алынған спирттерге тән «ауыр» сутегі dD (минус 172.66 ‰) және dD (минус 169.43) жасалған қорытындыларды ғана растайды. Осындай зерттеулер ликер шараптары үшін өткізілді. Осылайша, спирт молекулаларының үш элементтің – көміртек, оттек және сутегінің изотоптық сипаттамаларын өлшеу арқылы, шараптың құрамында абиогендік спирттердің бар екендігі туралы жоғары сенімділікпен анықтауға болады.

Түйін сөздер: шарап, сусындарды сәйкестендіру, изотоптық масс-спектрометрия, шарап этанолы, абиогенді спирттер, этанол молекулаларының элементтерінің изотоптық қатынасы.

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ПРИМЕНЕНИЕ ИЗОТОПНОЙ МАСС-СПЕКТРОМЕТРИИ ДЛЯ ВЫЯВЛЕНИЯ АБИОГЕННЫХ СПИРТОВ В ВИНОГРАДНЫХ ВИНАХ

Аннотация. Практика показывает, что одного показателя д^{13}С‰, характеризующего отношение стабильных изотопов углерода $^{13}C/^{12}C$, в ряде случаев недостаточно для обнаружения в винах спиртов невиноградного происхождения, особенно когда в продукт внесены абиогенные спирты. Инструментальной базой, обеспечивающей получение характеристик изотопов элементов молекул этанола, служил масс-спектрометрический комплекс Delta V Advantage фирмы Thermo Fisher Scientific (США), обеспечивающий прецизионный анализ отношений распространенности $^{13}C/^{12}C$, $^{18}O/^{16}O$, D/H изотопов. Установлено, что изотопные характеристики кислорода абиогенного спирта, полученного гидратацией этилена, значительно отличаются от данного показателя для всех спиртов растительного происхождения. Изотопные характеристики кислорода большинства растительных спиртов укладываются в диапазон д^{18}О‰ от 5,38 до 16,29‰, и только для свекловичного спирта числовые значения несколько ниже, а именно: 1,66–2,05‰. В то же время значение показателя д^{18}О‰ у абиогенного этанола имеет отрицательный знак и составляет минус 14,21‰ – минус 15,20‰. Эти существенные отличия позволяют использовать данный показатель для установления природы используемых спиртов – растительного или абиогенного происхождения. Анализируя показатель дD‰, можно отметить, что водород абиогенного спирта заметно «тяжелее» водорода, содержащегося в спиртах растительного происхождения и составляет минус 140‰ – минус 153‰ против минус 213‰ – минус 266‰. Используя полученные величины, исследовали 24 образца столовых вин. При этом два образца имели значение д^{13}С минус 28,22‰ и минус 28,41‰ соответственно, д^{18}О минус 1,0‰ и минус 0,76‰, что указывает на наличие в продукте абиогенного спирта. «Тяжелый» водород дD (минус 172,66‰) и дD (минус 169,43‰), не характерный для спиртов из растительного сырья, только подтверждают сделанный вывод. Аналогичные исследования проведены для ликерных вин. Таким образом, измеряя изотопные характеристики трех элементов молекул спирта – углерода, кислорода и водорода, можно с высокой степень достоверности обнаруживать в винах присутствие спиртов абиогенного происхождения.

Ключевые слова: вино, идентификация напитков, изотопная масс-спектрометрия, винный этанол, абио-генные спирты, отношение изотопов элементов молекул этанола.

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