

Identification of equilibrium state of hydroxyl protons in vodkas by ^1H NMR spectroscopy

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Abstract

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Introduction. The aim of this work is to identification of equilibrium state of hydroxyl proton of ethanol and water in vodkas, using ^1H NMR spectroscopy.

Materials and methods. Aqueous-alcoholic mixtures (AAM, vodkas) was prepared by volumetric method. NMR spectra was obtained according to the manuals of FT-NMR Bruker Avance II (400 MHz) spectrometer and Bruker TopSpin. As an external standard for deuterium stabilisation and chemical shifts determination was used a deuterioacetone in special form glass capillare inserted in NMR tube.

Results and discussion. Experimentally determined elements thermodynamic equilibrium of hydroxyl proton of ethanol and water in vodkas, using ^1H NMR spectroscopy. In this work, we identified three groups of samples with equilibrium of hydroxyl protons of water and ethanol: steady; transitional; unsteady equilibrium.

Steady equilibrium is characterized by a presence in hydroxyl group combined unitary signal of $\text{EtOH}+\text{H}_2\text{O}$. The component of protons of $\text{EtOH}+\text{H}_2\text{O}$ in each sample presented as singlet (s), located in a «weak field» with a chemical shift, which is in a range $\delta_{\text{EtOH}+\text{H}_2\text{O}}=4,75-4,80$ ppm. Waveform of $\text{EtOH}+\text{H}_2\text{O}$ protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the center line.

It was found that the transitional equilibrium characterized by a presence of hydroxyl groups two separate signals of EtOH ($\delta_{\text{EtOH}}=5,34$ ppm) and H_2O ($\delta_{\text{H}_2\text{O}}=4,75$ ppm). The difference between the chemical shifts of hydroxyl protons of ethanol (EtOH) and proton of water (H_2O) in each sample is $\Delta f_i=236$ Hz. Transitional equilibrium is characterized by the presence of hydroxyl proton, which is barely noticeable, which characterizes the transition from steady equilibrium to unsteady equilibrium. This may indicate that certain prerequisites have not yet been created to establish equilibrium structure (unsteady/steady equilibrium).

Unsteady equilibrium characterized by a presence of hydroxyl groups two separate signals of ethanol (EtOH) ($\delta_{\text{EtOH}}=5,34$ ppm), which is obvious and H_2O ($\delta_{\text{H}_2\text{O}}=4,72-4,75$ ppm). The difference between EtOH and H_2O – $\Delta f_i=248$ Hz.

Conclusion. The conducted researches set a fundamental difference of behavior of hydroxyl proton of ethanol and water in vodkas, using ^1H NMR spectroscopy. Iestablished criteriums of the systems equilibrium allow to improve the technological process of vodka on distillery enterprises, to stabilize quality of finished product.

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Introduction

Nowadays *NMR* spectroscopy has worthily gained popularity among physical methods of research in different fields of science, i.e. medicine, biology, physics, chemistry, in agriculture and industry as well. It is difficult to overestimate the role of *NMR* in food industry, in the study of complex systems from the simplest organic molecules to the most complex molecular compounds (Oliveira I.S. et al, 2007, Minoja, Napoli, 2014; Singh, Blümich, 2016; Hore, 2017) [1–4]. The most wide-spread is *NMR* spectroscopy on nuclei of hydrogen isotope ^1H (^1H -protons). They account for 90% of all the studied *NMR* spectra (Jeffrey H. Simpson, 2008; Terence N. Mitchell, Burkhard Costisella, 2007; Siegfried Stapf, Song-I Han, 2006) [5–7].

NMR spectroscopy principle of operation is based on the usage of magnetic properties of some atomic nuclei, being able to resonate at characteristic frequencies of electromagnetic spectrum in external magnetic field and, that allows to identify nuclei in different chemical environment (Oliveira I.S. et al, 2007; Jeffrey H. Simpson, 2008; Siegfried Stapf, Song-I Han, 2006) [1, 5, 7].

Bloch F. obtained ^1H *NMR* spectra with “low-resolution” of H_2O for the first time in 1946 (Bloch et al. 1946) [8], and in 1951 Arnold J.T. for the first time obtained ^1H *NMR* spectra with “high-resolution” of ethanol $\text{C}_2\text{H}_5\text{OH}$ (Arnold et al. 1951) [9]. Up to now, many scientists (Oliveira I.S. et al, 2007; Jeffrey H. Simpson, 2008; Bing Yan, 2004; Edwin D. Becker, 2002; Edwin D. Becker et al, 2002; Gerard J. Martin, Maryvonne L. Martin, 2002; S.A. Richards, J.C. Hollerton, 2011; Jacob Bart, 2009; Cherif Ibrahima Khalil Diop et al, 2012; Bao Qiong Li et al, 2017; N.R. Sucupira et al, 2017) [1, 5, 10, 11–18] bring ethanol *NMR* spectrums as the simplest and best understood from the analytical point of view of the substance.

At the same time *NMR* spectroscopy exhibits variations in characteristics of ethanol such as chemical shift, spin-spin interactions and the effect of chemical exchange (Oliveira I.S. et al, 2007; Edwin D. Becker, 2002; Gerard J. Martin, Maryvonne L. Martin, 2002; S.A. Richards, J.C. Hollerton, 2011) [1, 11, 13, 14] in solutions.

Vodka is a simple physico-chemical system: mixture of ethanol and water. But every brand has some observable differences on the molecular level and as to the taste perception. Studies conducted by Hu N. and others in the work (Hu et al, 2010) [19] prove that these differences are significant either on the stage of AAM making or in the final product – commercial vodka. The main differences are connected with hydrogen bonds (with their strength) that is proved by different research methods, for example by ^1H *NMR* spectroscopy, *FTIR* spectroscopy, Raman spectroscopy. The results of the ^1H *NMR* and *FTIR* spectroscopy researches show that in water there are hydrates with the structure of $\text{EtOH}^*(5,3\pm 0,1)\text{H}_2\text{O}$, that are observed either in AAM or in vodka. Authors (Hu et al, 2010) [19] connect hydrate proportion $\text{EtOH}^*(5,3\pm 0,1)\text{H}_2\text{O}$ and its influence on the following organoleptic indicators of vodka.

In the work by Nose A. and others (Nose et al, 2005) [20] the influence of admixtures such as salts, acids and phenols on the strengthening of hydrogen bonds in AAM and in finished products as well, in this case sake, is studied. In the work (Hu et al, 2010) [19] it is set that admixture bonds influence on molecular dynamics in the process of ethanol hydration.

In the work (Hu et al, 2010) [19] the notion “structurability” had introduced, that is “ability to structuring”, a parameter that determines the ability of vodka (or in a wide sence the alcoholic products) to order molecules of water in its structure.

In the work (Hu et al, 2010) [19] great attention is given to ^1H *NMR* spectra of the *OH* proton of water and alcohol. Protons of water in all the samples was found as a narrow signal with the chemical shift on about 5 ppm. Spectra also showed that in some samples there appears the second widened peak of the *OH* signal that is on the 5,5 ppm. That low-field peak is the signal of *OH*-ethanol that separated from the conditionally high-field signals of *OH*-water.

Presence of the separate *OH*-ethanol signal in the samples (according to the opinion of the authors (Hu et al, 2010) [19]) points out weak hydrogen bonds of ethanol.

The preliminary conducted 1H NMR studies, which are described in a work (Kuzmin O. et al, 2013–2014) [21–24], relate to the study of hydroxyl protons of AAM modifications in the process of making vodkas. The obtained results give grounds to assert a fundamental difference in the behavior AAM prepared from the alcohol and water passing through various processes. During the study we have determined the systems of unsteady and steady balance depending on the transformation of hydroxyl proton's of ethanol and water. Systems with unsteady balance typical for AAM used with ethanol and drinking water, with a tasting score – 9,43 points. This also includes the AAM made from ethanol and demineralized by the reverse osmosis water, with a tasting score – 9,30 points. Systems with a steady balance that are typical for AAM made of ethanol and water softened by *Na*-cationization, with tasting score – 9,49 points were defined.

Thus, in the work (Kuzmin O. et al, 2013–2014) [21–24] was established experimental evidence of stationary nature / (non- stationary) of thermodynamic balance, taking into account the organoleptic characteristics of AAM in dependence on water treatment method and time of system's functioning. However, the questions related to internal mechanism's specification and the rate of establishment of thermodynamic balance depending on type of water used in the process of creating the AAM are remain unsolved.

The aim of this work is to identification of equilibrium state of hydroxyl proton of ethanol and water in vodkas, using 1H NMR spectroscopy.

Materials and methods

1H NMR analysis of AAM was conducted with the usage of:

– *FT-NMR* Bruker Avance II spectrometer (400 MHz) equipped with 5–mm broadband inverse *Z*-gradient probe; thermostatic system (+25°C ... +100°C). The measurement error of the chemical shifts for 1H is $\pm 0,005$ ppm;

– Specially shaped capillary with acetone- d_6 ($(CD_3)_2CO$) (atomic fraction of deuterium – 99,88 %; moisture content – 0,018%; *bp*=+56,3 °C, *mp*=–94 °C; chemical shift of the residual proton 1H $\delta=2,75$ ppm);

– High accuracy ampoules №507–HP for high resolution *NMR*'s spectroscopy (400 MHz);

– Volumetric pipette;

– Dispenser;

– Sample of vodkas, flavored vodkas and moonshine, produced in Ukraine were used as experimental material for 1H NMR spectroscopy.

Experimental studies of 1H NMR were carried out in the following order:

– Preparation of samples to research;

– Recording of 1H NMR spectrum;

– Conclusion and interpretation of work results.

Work methodology (Kuzmin et al, 2013–2014) [21–24]:

– 0,3 ml of vodka prepared with a volumetric pipette with a predetermined strength ($40,0 \pm 0,2$)% vol. External standard separated from the testing substance which is required for deuterium stabilization system of spectrometer (deuterium solvent acetone- d_6) is added into an ampoule in a special form capillary. The obvious advantage of using the external standard is the fact that standard substance's molecules and test's solution do not interact with each other;

– 1H NMR spectra records and data processing were performed according to the instruction of *FT-NMR* Bruker Avance II spectrometer (400 MHz).

Results and discussions

The 31 sample of vodkas, produced in Ukraine were used as experimental material for 1H NMR spectroscopy. These samples were divided into 3 groups with steady equilibrium, transitional and unsteady equilibrium of protons hydroxyl group. Figure 1–31 shows proton spectra of vodkas for the following groups of protons: CH_3 ; CH_2 ; H_2O ; $EtOH$. Where Δf_1 – is deviation between proton's hydroxyl group of ethanol ($EtOH$) and water (H_2O), Hz; Δf_2 – is deviation between proton's hydroxyl group of water (H_2O) and a methylene group of protons of ethanol (CH_2), Hz; Δf_3 – is deviation between ethanol's methylene group of protons (CH_2) and ethanol's methyl group of protons (CH_3), Hz.

The group of vodkas with steady equilibrium. This group has included 12 samples of vodkas (Figures 1–12). The selected samples of vodkas with a steady equilibrium characterized by a unitary signal of hydroxyl group ($EtOH+H_2O$). The component of protons of $EtOH+H_2O$ in each sample presented as singlet (*s*), located in a weak field with a chemical shift in a range $\delta_{EtOH+H_2O}=4,75-4,80$ ppm. Waveform of $EtOH+H_2O$ protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the center line.

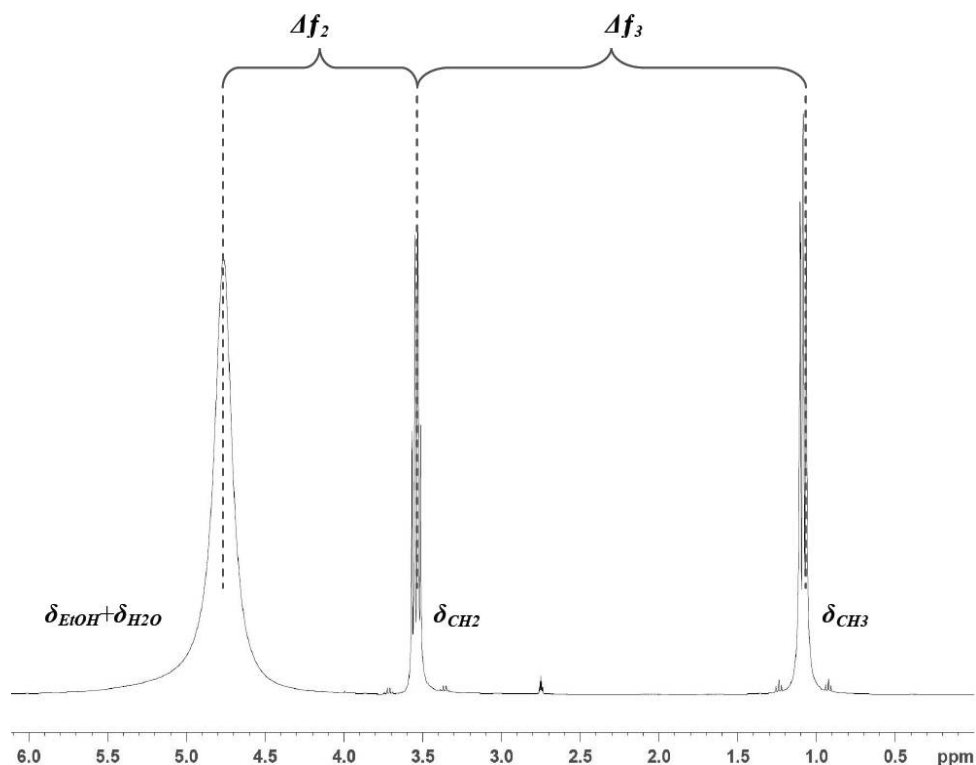


Figure 1. 1H NMR spectra of proton groups of vodka (sample №1): CH_3 ; CH_2 ; $EtOH+H_2O$

Analysis of 1H NMR spectra of methyl group's protons CH_3 in vodkas allows to state the following: methyl group of protons in each sample is located in a strong field and represented as a triplet (*t*) with a relative intensity (1:2:1). The average value of the chemical shift of the methyl group for the 12 samples is within $\delta_{CH_3}=1,07-1,09$ ppm. The distance between each components of the triplet (spin-spin coupling constant) is 8 Hz.

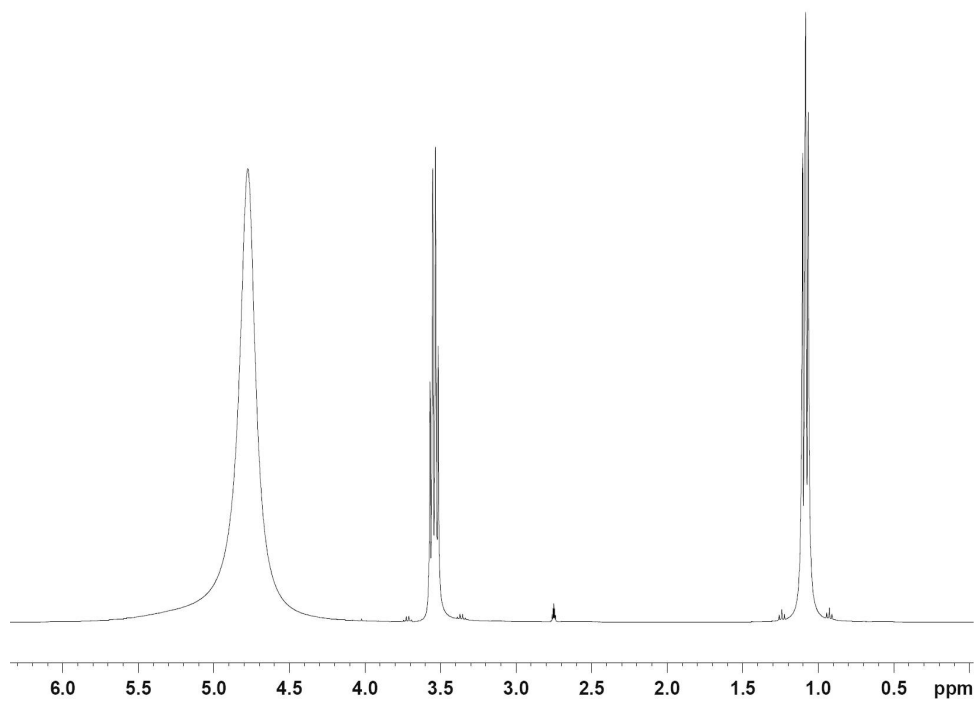


Figure 2. ^1H NMR spectra of proton groups of vodka (sample №2)

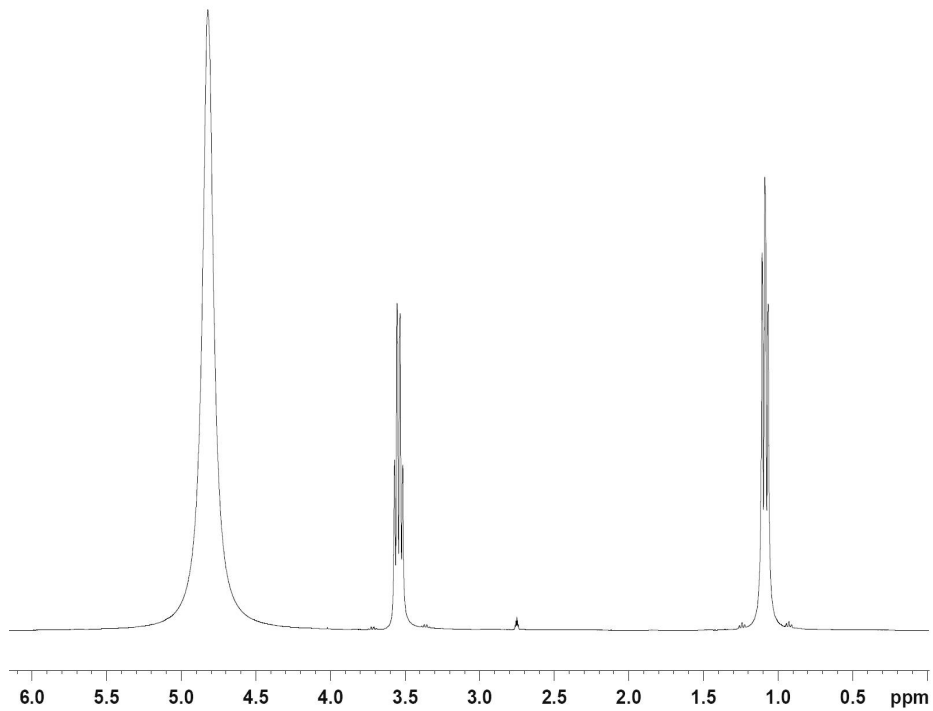


Figure 3. ^1H NMR spectra of proton groups of vodka (sample №3)

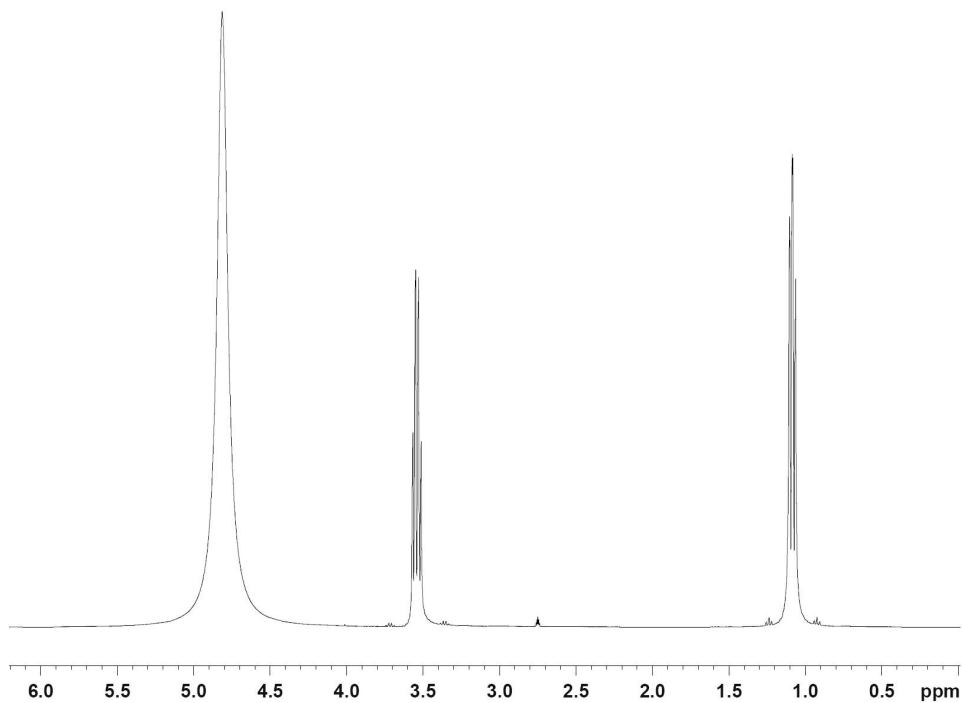


Figure 4. ^1H NMR spectra of proton groups of vodka (sample №4)

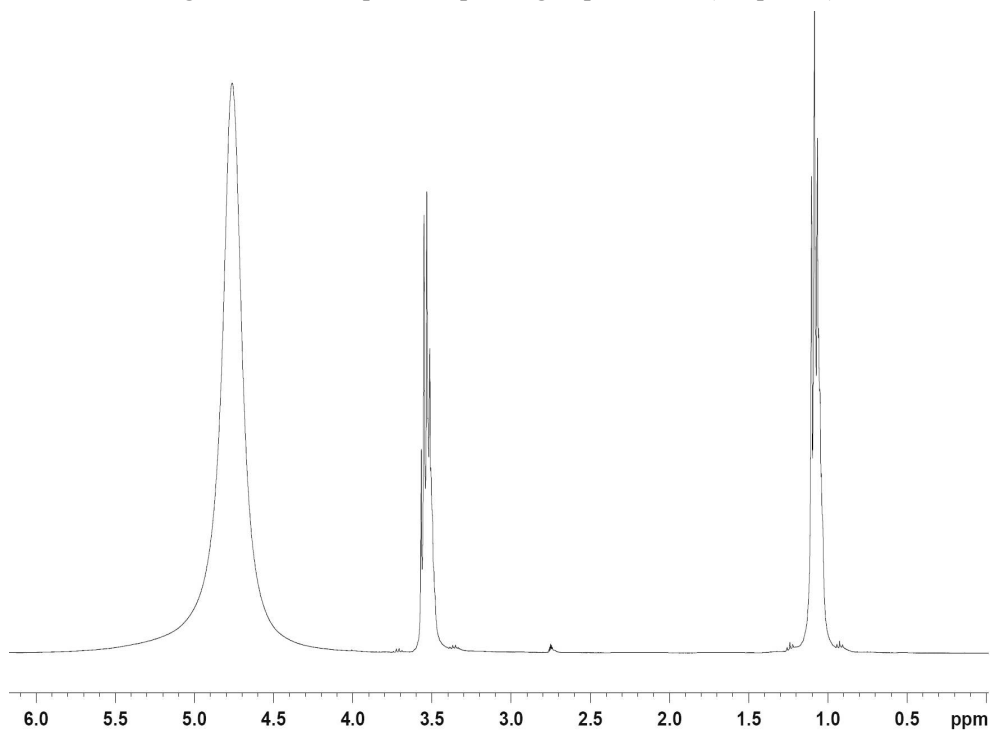


Figure 5. ^1H NMR spectra of proton groups of vodka (sample №5)

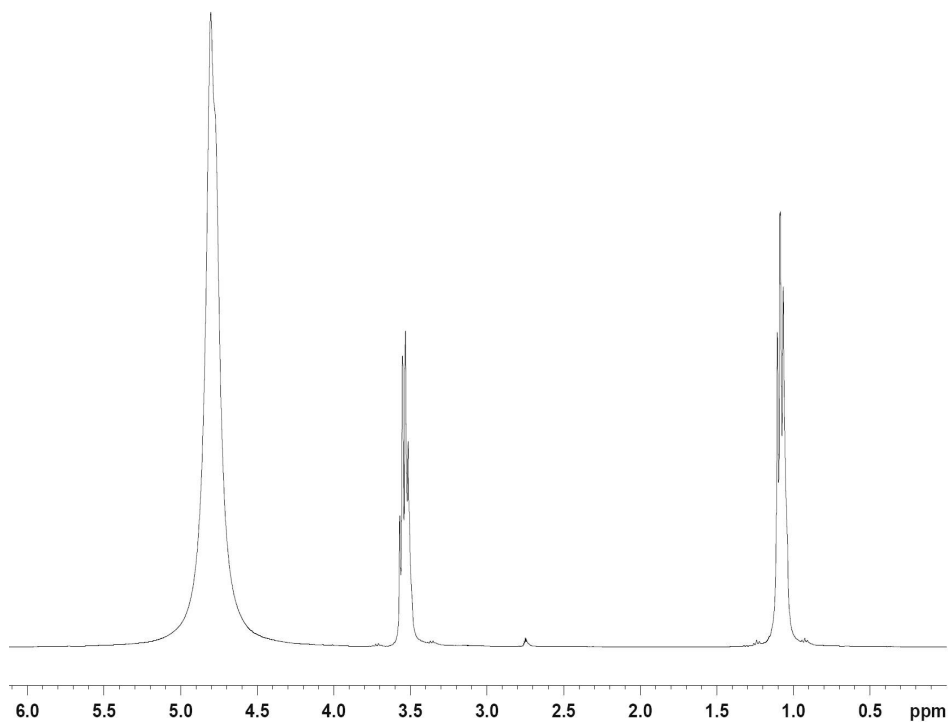


Figure 6. ^1H NMR spectra of proton groups of vodka (sample №6)

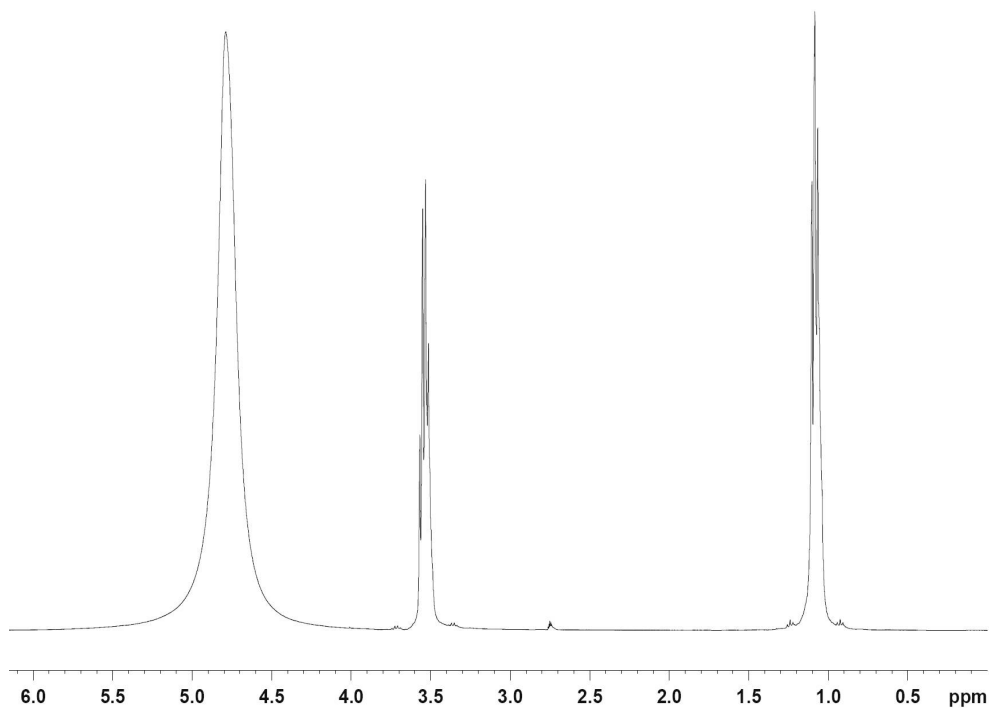


Figure 7. ^1H NMR spectra of proton groups of vodka (sample №7)

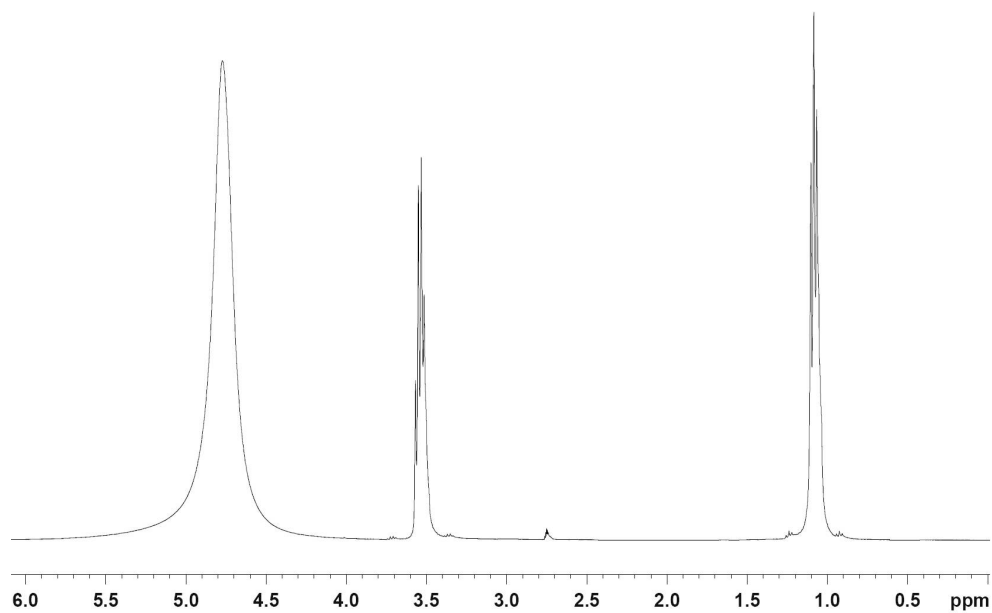


Figure 8. ^1H NMR spectra of proton groups of vodka (sample №8)

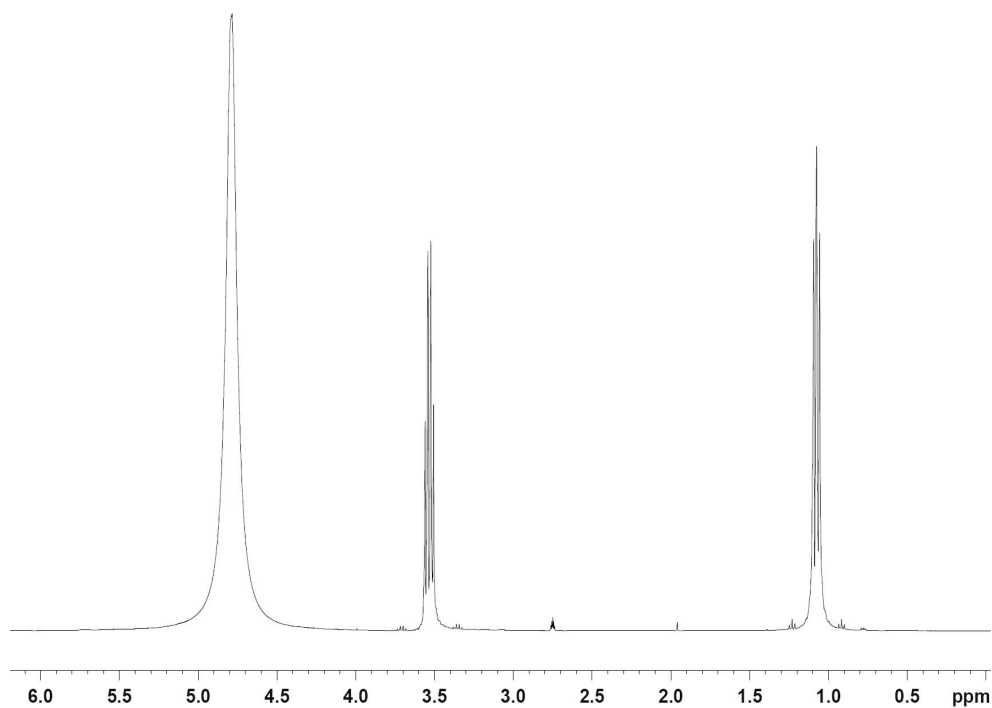


Figure 9. ^1H NMR spectra of proton groups of vodka (sample №9)

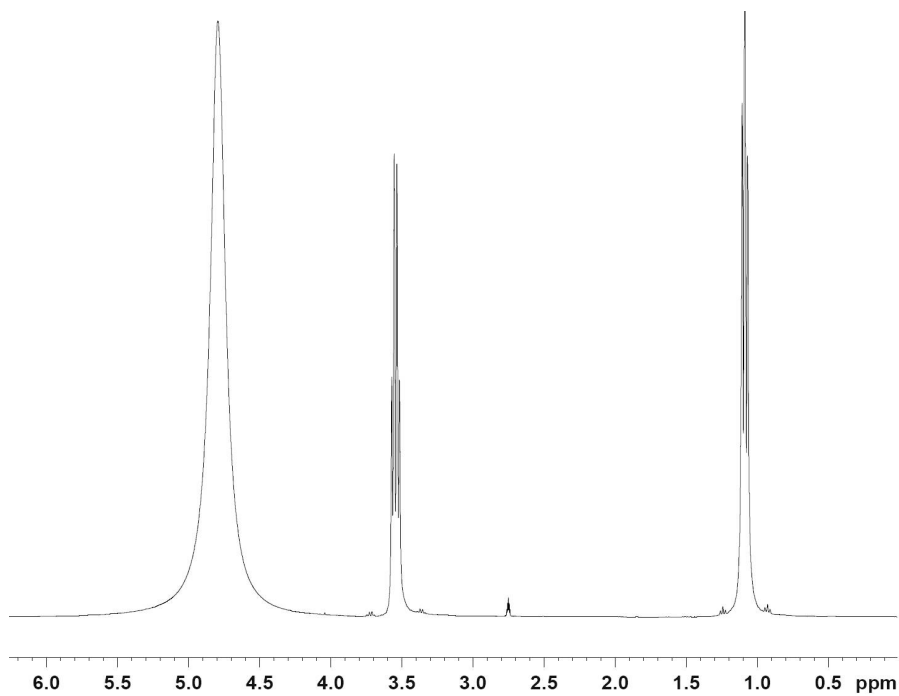


Figure 10. ^1H NMR spectra of proton groups of vodka (sample №10)

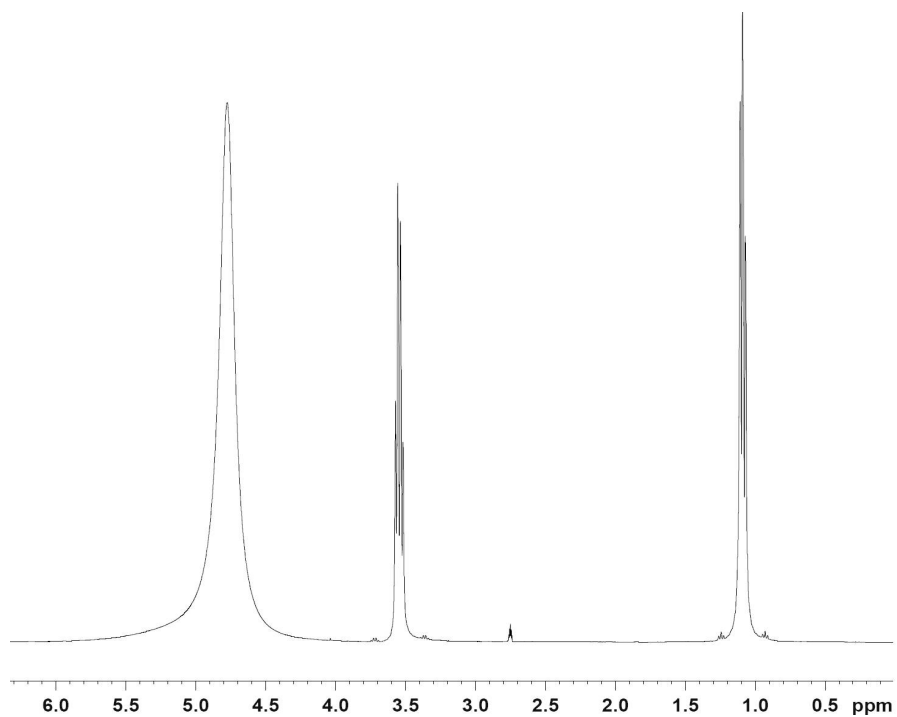


Figure 11. ^1H NMR spectra of proton groups of vodka (sample №11)

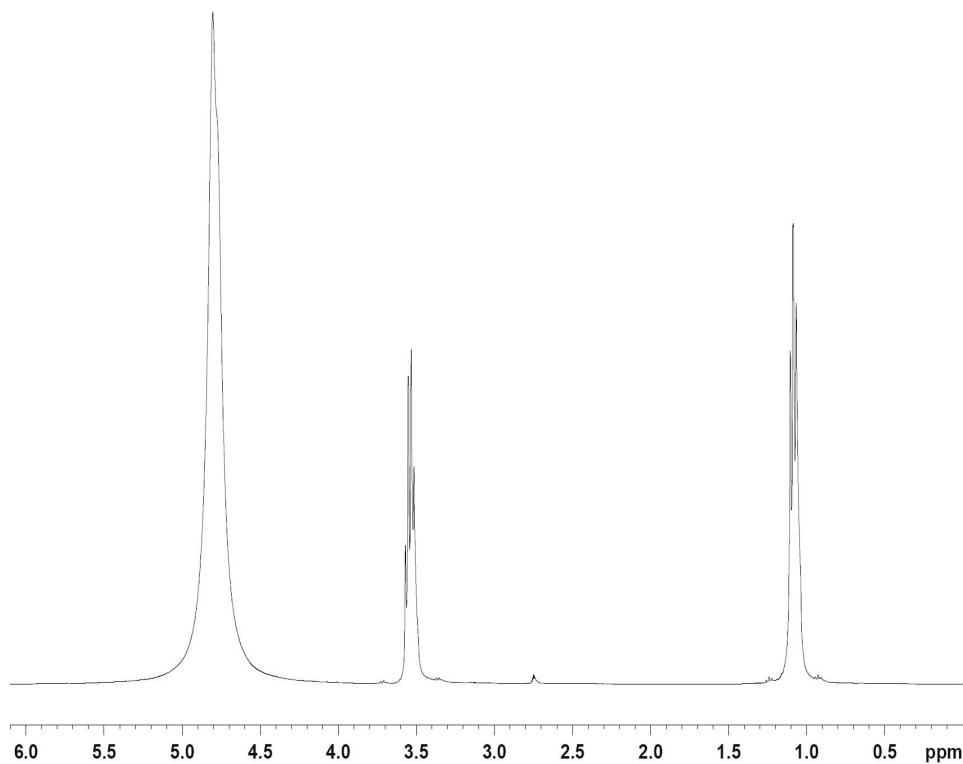


Figure 12. 1H NMR spectra of proton groups of vodka (sample №12)

The analysis of 1H NMR spectra of methylene group's protons CH_2 indicates that the group is represented as a quartet (q) with intensity (1:3:3:1), with an average value of the chemical shift $\delta_{CH_2}=3,52-3,54$ ppm. Most of the components of the methylene group have an average value of the chemical shift $\delta_{CH_2}=3,53$ ppm. The distance between each peak of quartet is also 8 Hz. The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and hydroxyl group $EtOH+H_2O - \Delta\delta_2=1,23-1,27$ ppm. The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and methyl group of ethanol (CH_3) in each sample is $\Delta\delta_3=2,45$ ppm, which specifies on stability of chemical shifts between these groups, and strong links between methyl (CH_3) and methylene (CH_2) groups.

The group of vodkas with transitional equilibrium. This group has included 11 samples of vodkas (Fig. 13–23). The samples of vodkas with the transitional equilibrium as well as samples with unsteady equilibrium are characterized by the absence of unitary signal ($EtOH+H_2O$) therefor protons of hydroxyl group is presented by two separate picks of H_2O and $EtOH$. Signal of hydroxyl protons of ethanol ($EtOH$) in each sample is represented as a separate subtle signal of a rounded shape located in a weak field with a chemical shift $\delta_{EtOH}=5,34$ ppm. Component of proton of water (H_2O) in each sample is represented as a singlet with a chemical shift $\delta_{H_2O}=4,75$ ppm. Waveform of H_2O signals is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline. The difference between the chemical shifts of hydroxyl protons of ethanol ($EtOH$) and proton of water (H_2O) in each sample is about $\Delta\delta_1=0,59$ ppm ($\Delta f_1=236$ Hz). This may indicate that certain prerequisites are created to establish equilibrium structure (unsteady/steady equilibrium).

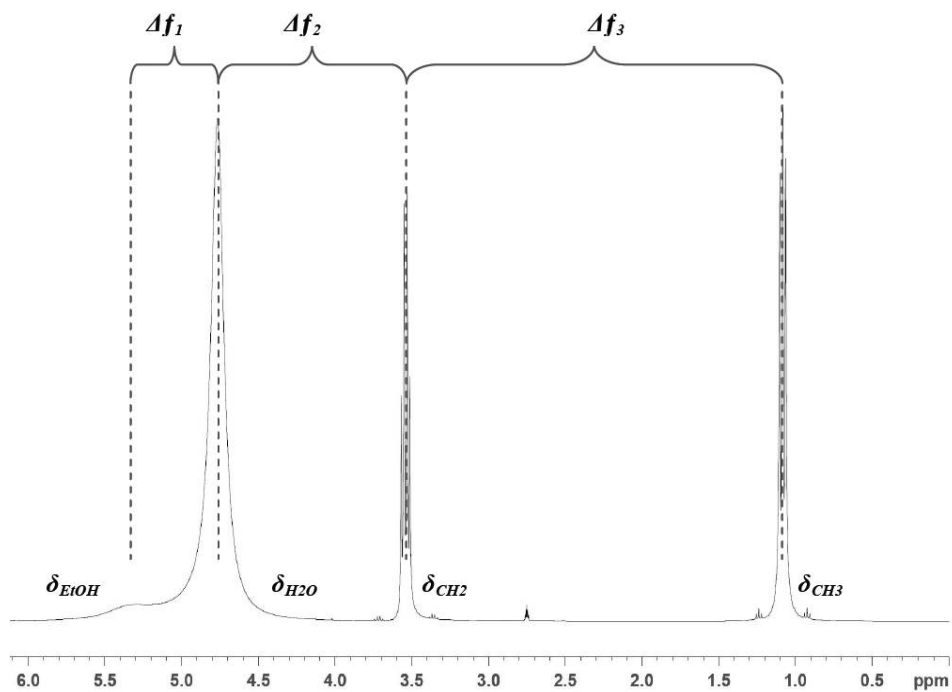


Figure 13. ^1H NMR spectra of proton groups of vodka (sample №13)

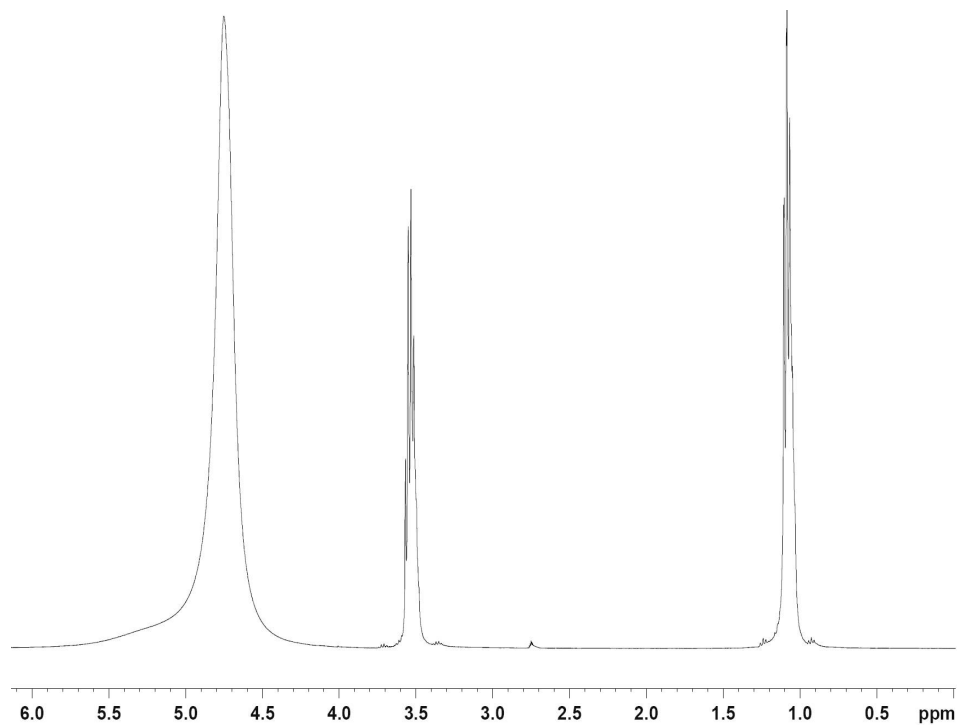


Figure 14. ^1H NMR spectra of proton groups of vodka (sample №14)

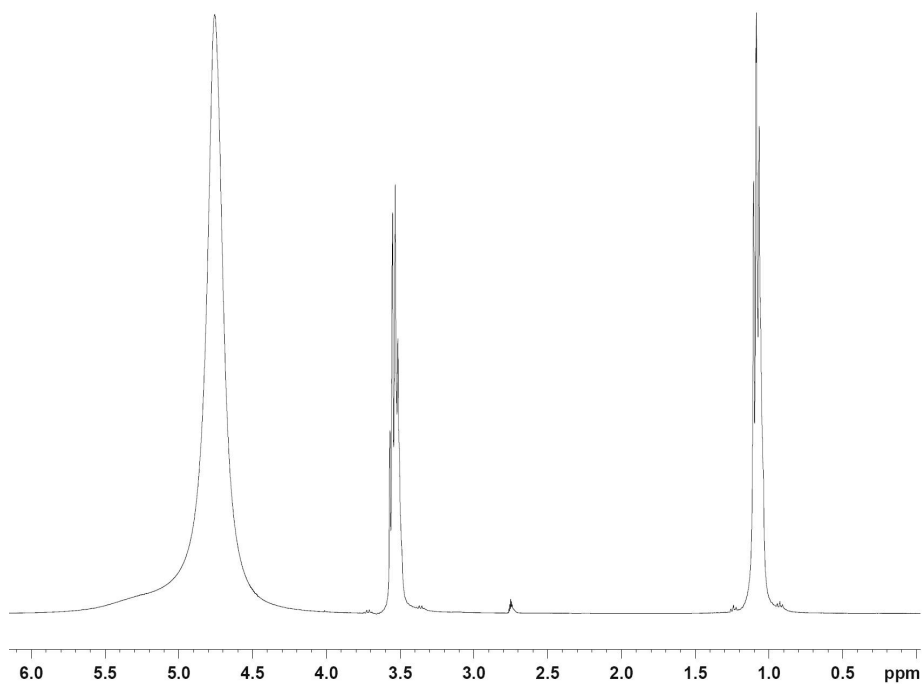


Figure 15. ^1H NMR spectra of proton groups of vodka (sample №15)

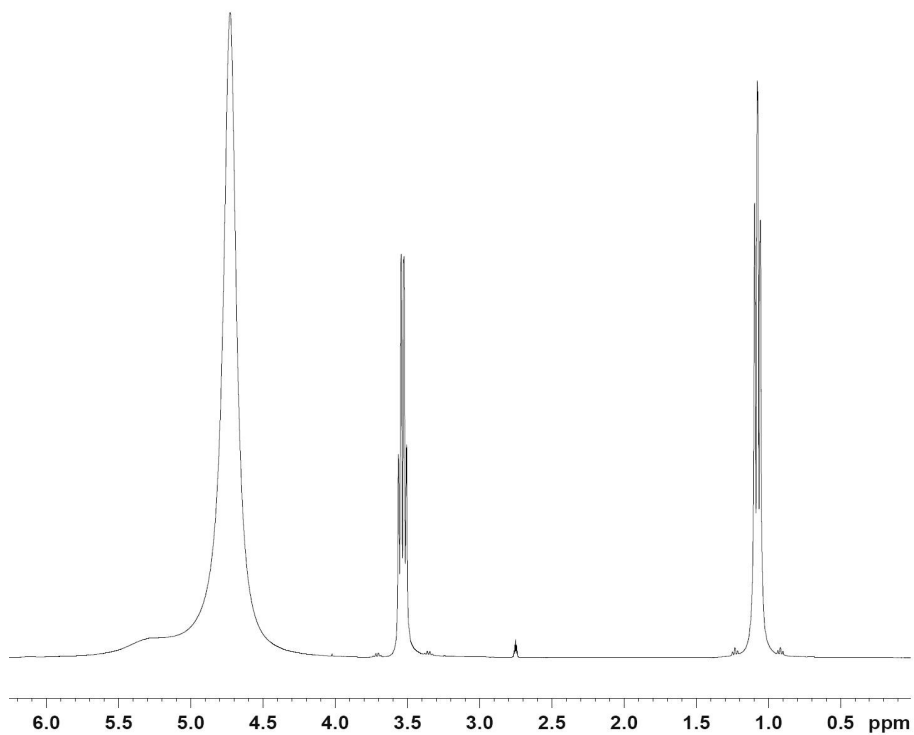


Figure 16. ^1H NMR spectra of proton groups of vodka (sample №16)

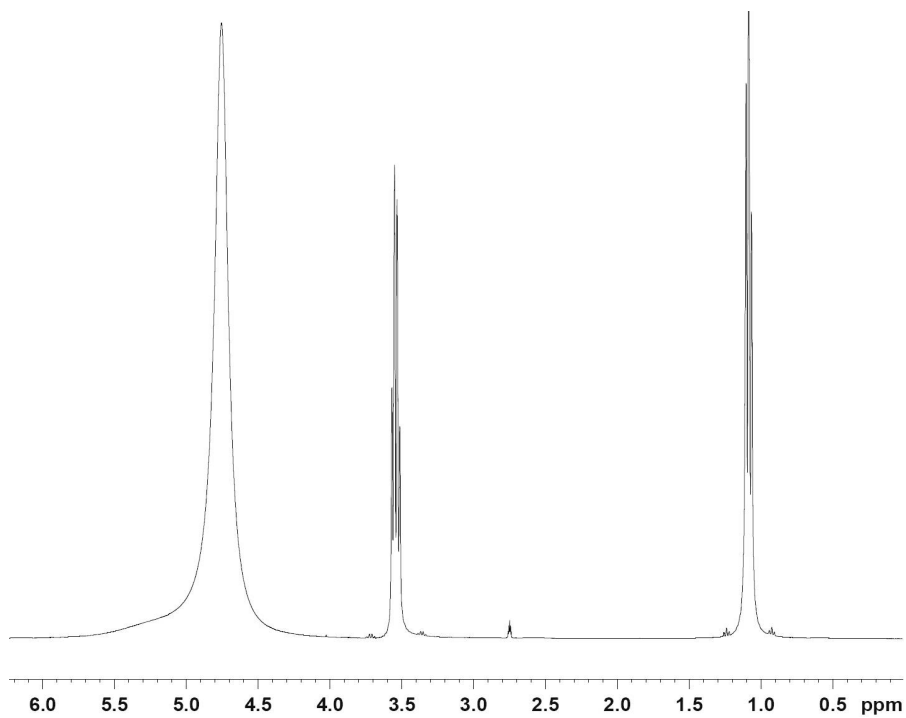


Figure 17. ^1H NMR spectra of proton groups of vodka (sample №17)

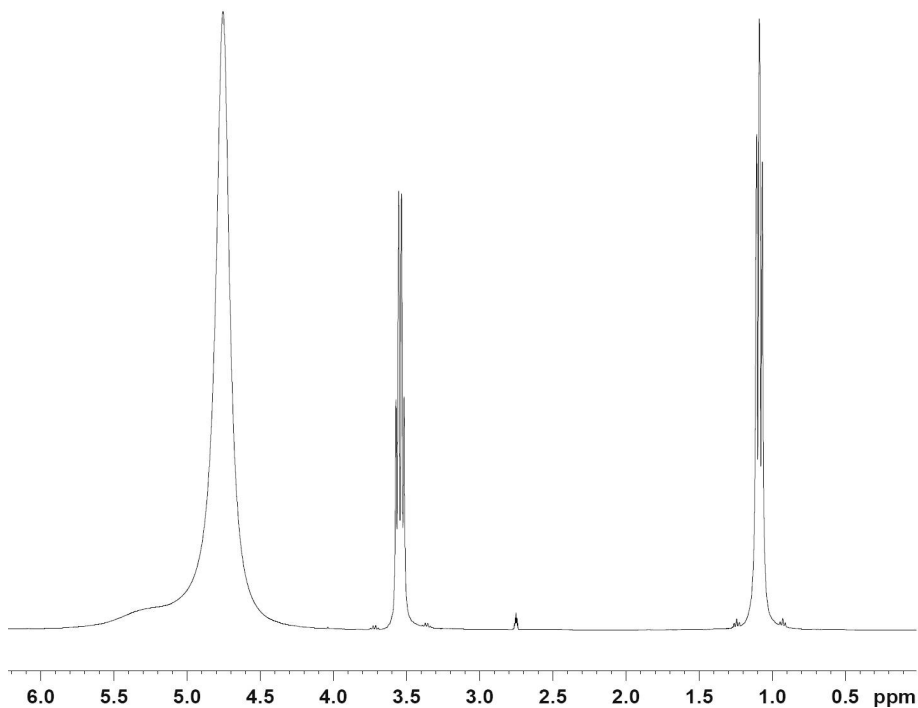


Figure 18. ^1H NMR spectra of proton groups of vodka (sample №18)

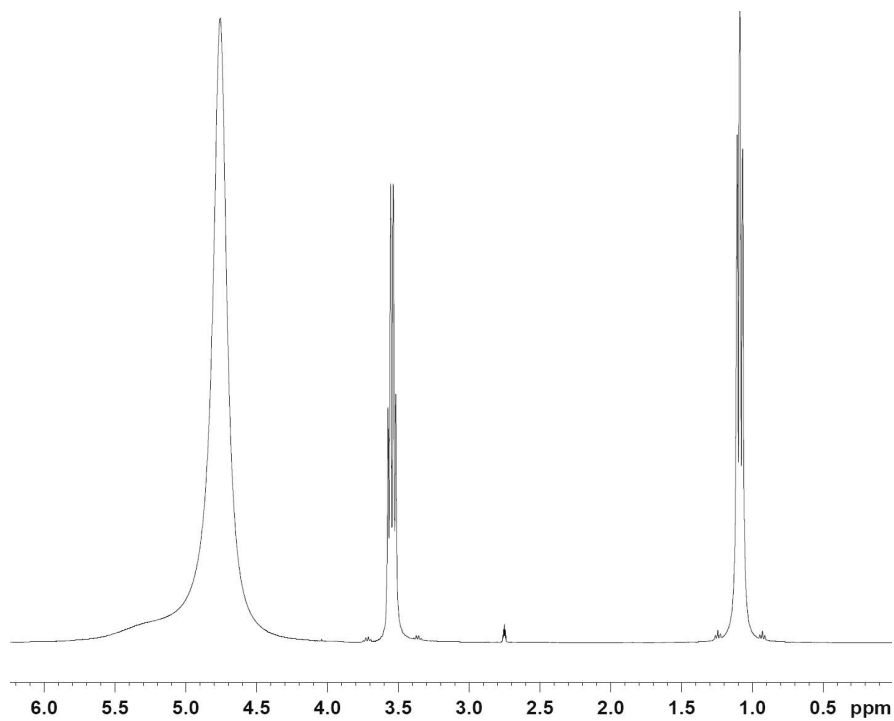


Figure 19. ^1H NMR spectra of proton groups of vodka (sample №19)

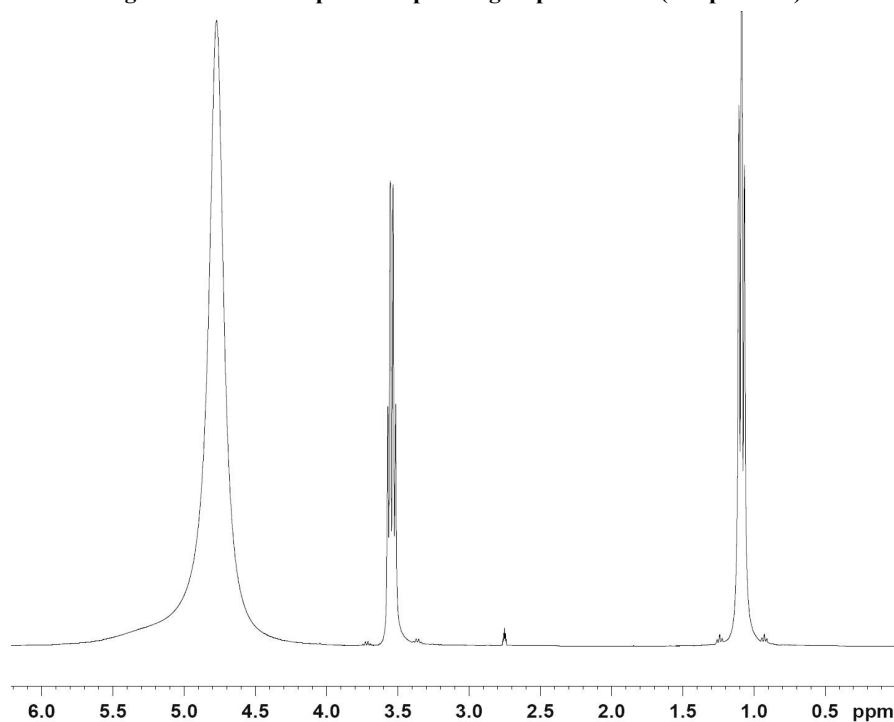


Figure 20. ^1H NMR spectra of proton groups of vodka (sample №20)

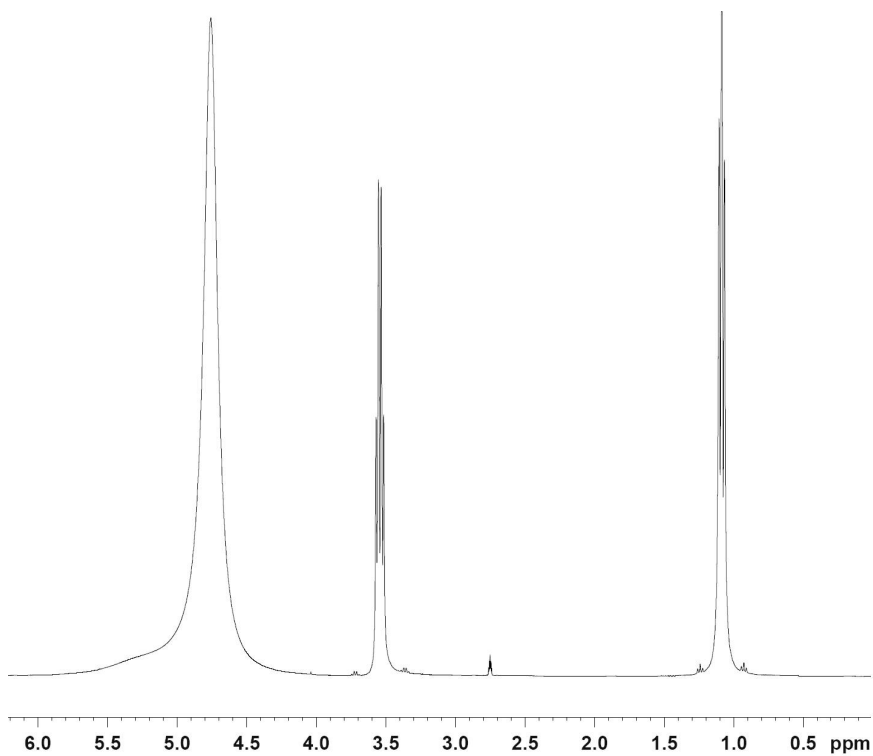


Figure 21. ^1H NMR spectra of proton groups of vodka (sample №21)

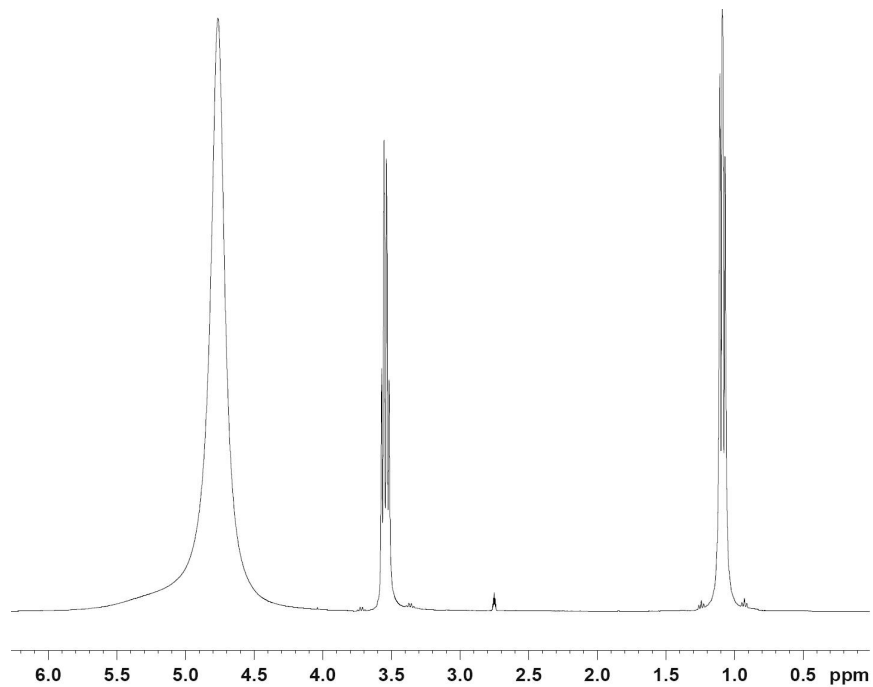


Figure 22. ^1H NMR spectra of proton groups of vodka (sample №22)

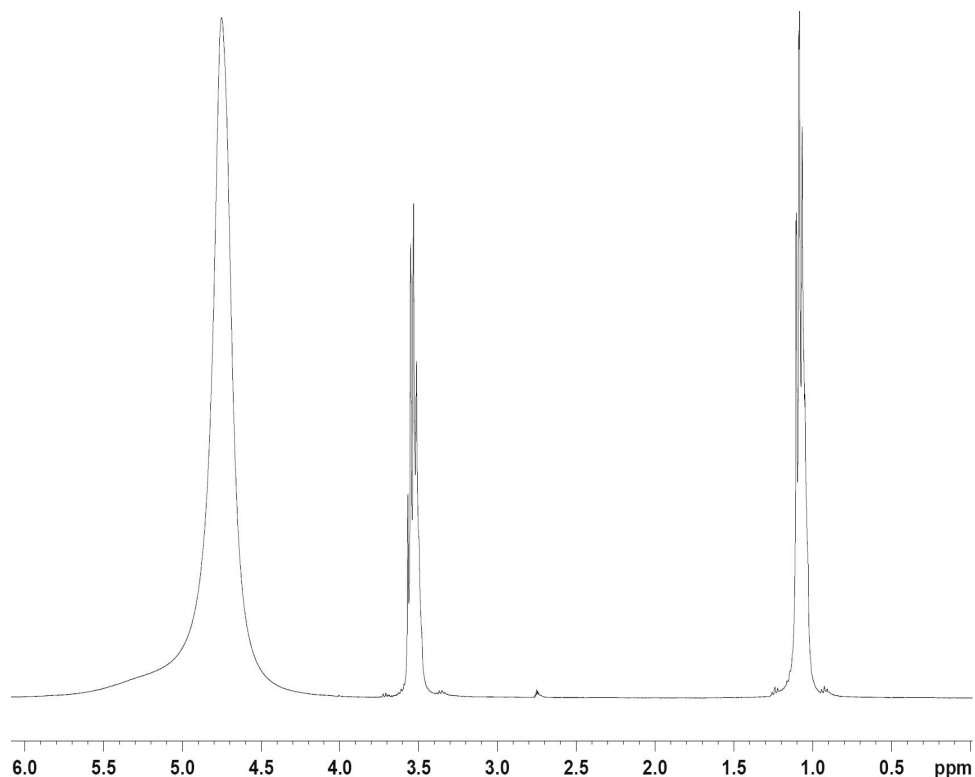


Figure 23. ^1H NMR spectra of proton groups of vodka (sample №23)

Methyl group of protons (CH_3) in each sample is located in a strong field and represented as a triplet (t) with a relative intensity of (1:2:1). The average value of chemical shift is $\delta_{\text{CH}_3}=1,08$ ppm. The distance between each peak of quartet is 8 Hz.

^1H NMR spectra of proton's methylene group (CH_2). The group is represented as a quartet (q) with intensity ratio of (1:3:3:1) and average value of chemical shift of $\delta_{\text{CH}_2}=3,53$ ppm. The distance between each peak of quartet is 8 Hz. The difference between the chemical shifts of ethanol's protons of methylene group (CH_2) and hydroxyl group of water (H_2O) in each sample is $\Delta\delta_2=1,22$ ppm ($\Delta f_2=488$ Hz). The difference between the chemical shifts of ethanol's protons of methylene group (CH_2) and methyl group of ethanol (CH_3) in each sample is $\Delta\delta_3=2,45$ ppm ($\Delta f_3=980$ Hz).

The group of vodkas with unsteady equilibrium. This group has included 8 samples. Figure 24–31 shows one-dimensional proton spectra of vodkas for the following groups of protons: CH_3 ; CH_2 ; H_2O ; EtOH .

The selected samples of vodkas with unsteady equilibrium characterized by the absence of single signal ($\text{EtOH}+\text{H}_2\text{O}$), therefore hydroxyl group of protons is represented by two separate peaks of ethanol (EtOH) and water (H_2O). The signal of ethanol's hydroxyl protons (EtOH) in each sample is represented as a single broad singlet (s) with a rounded shape, located in a weak field with a chemical shift $\delta_{\text{EtOH}}=5,34$ ppm. The signal of water proton (H_2O) in each sample presented as singlet (s) with a chemical shift $\delta_{\text{H}_2\text{O}}=4,72$ ppm.

Waveform of H_2O protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline. The difference between hydroxyl protons of ethanol (EtOH) and water (H_2O) in each sample is $\Delta\delta_1=0,62$ ppm ($\Delta f_1=248$ Hz). This may indicate that conditions for the formation of water structure with hydroxyl proton of alcohol were not yet set, therefore we can state that thermodynamic equilibrium didn't appear in any of the samples.

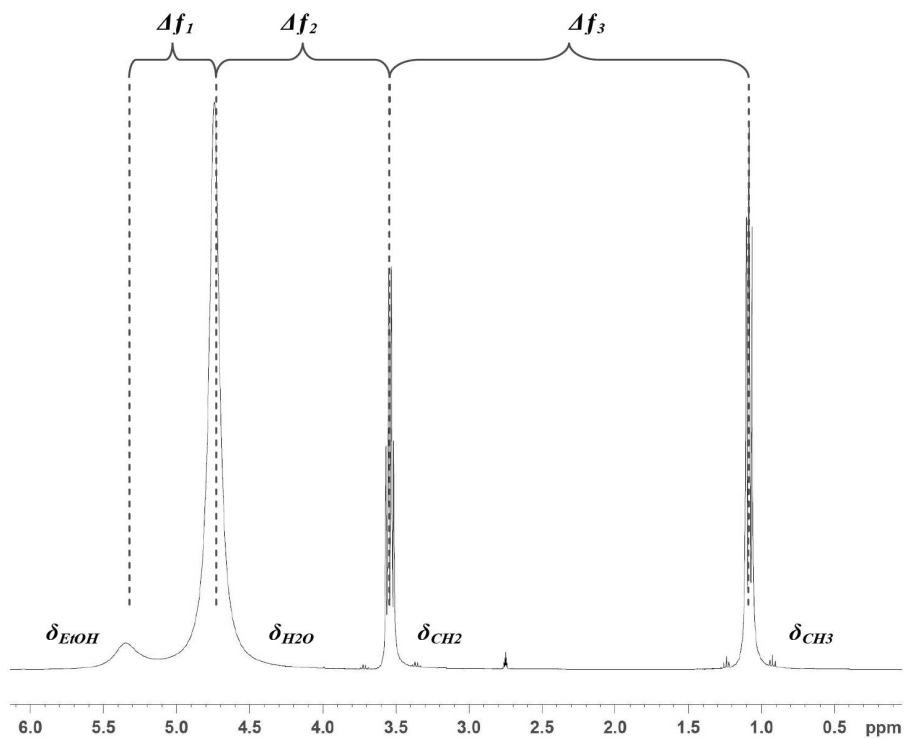


Figure 24. ^1H NMR spectra of proton groups of vodka (sample №24): CH_3 ; CH_2 ; H_2O ; EtOH

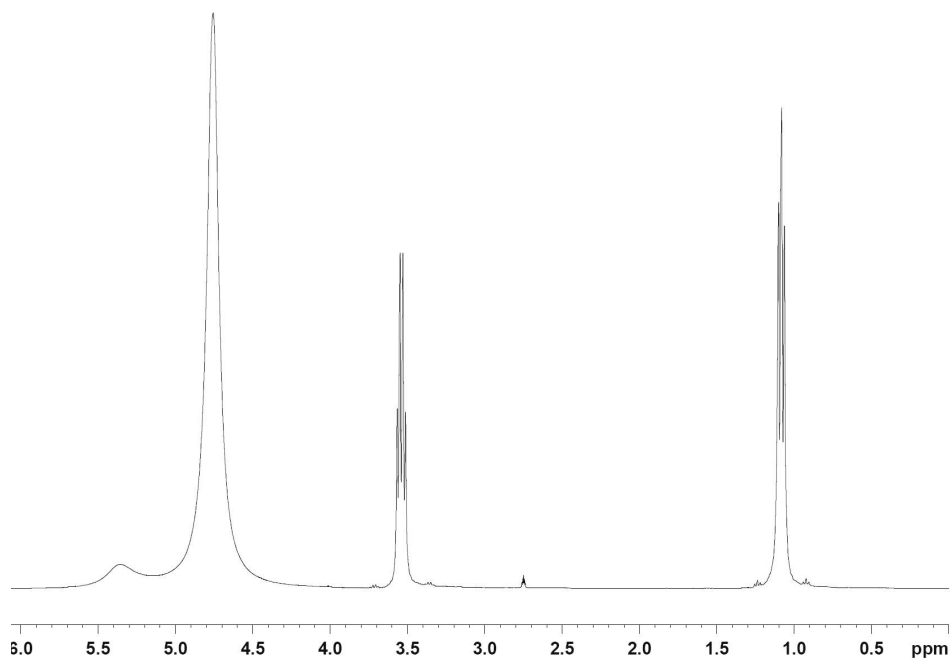


Figure 25. ^1H NMR spectra of proton groups of vodka (sample №25)

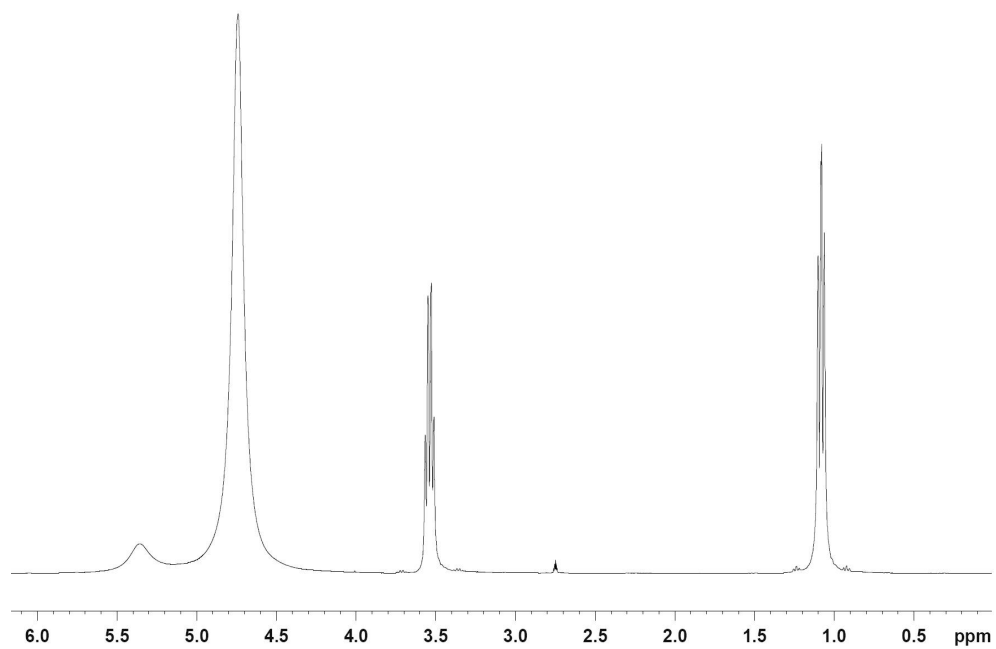


Figure 26. ^1H NMR spectra of proton groups of vodka (sample №26)

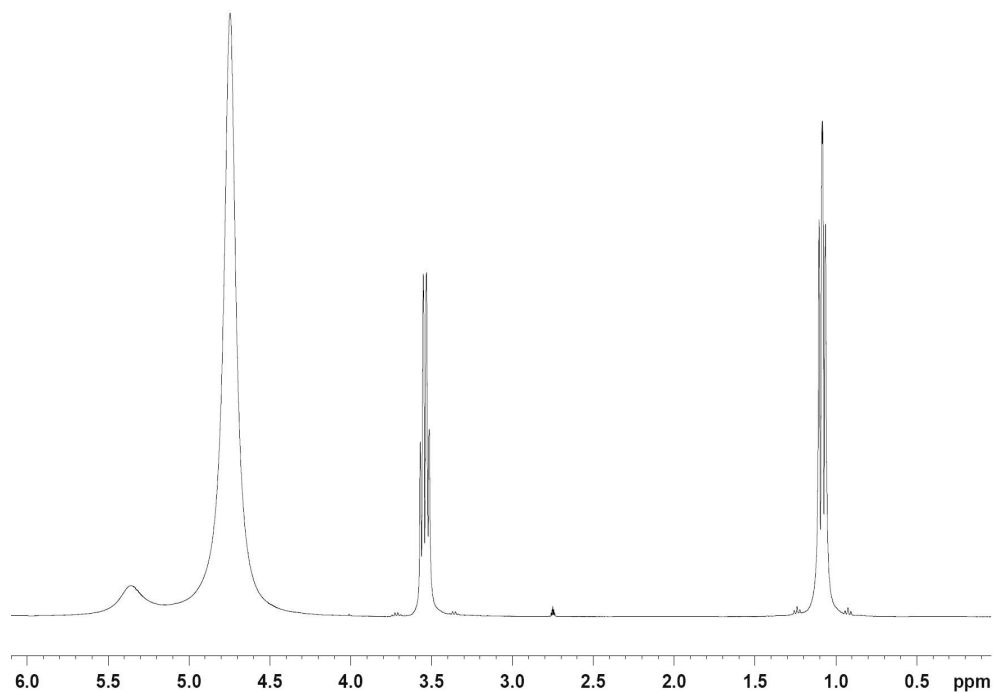


Figure 27. ^1H NMR spectra of proton groups of vodka (sample №27)

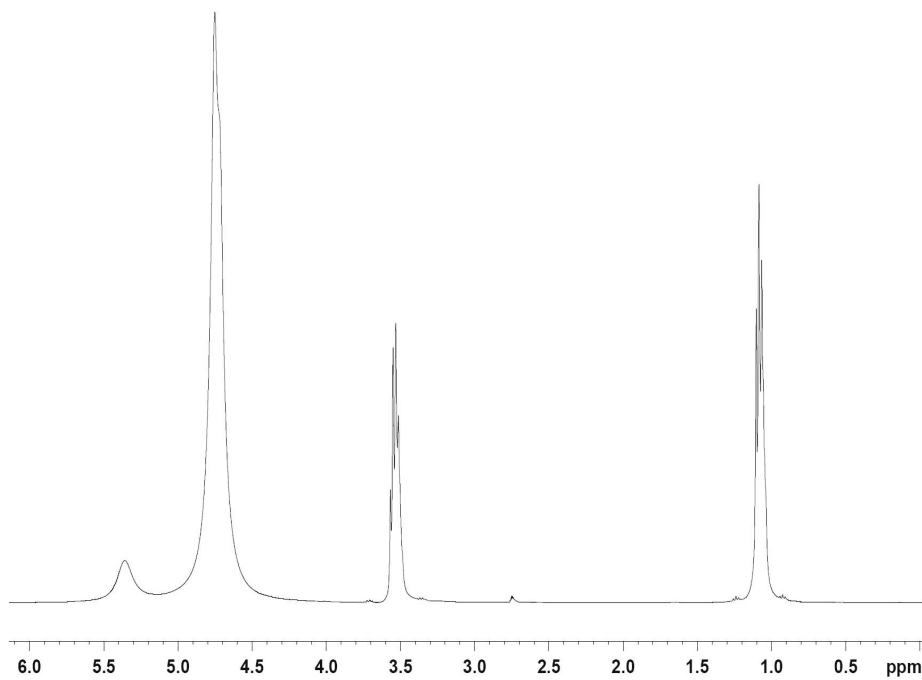


Figure 28. ^1H NMR spectra of proton groups of vodka (sample №28)

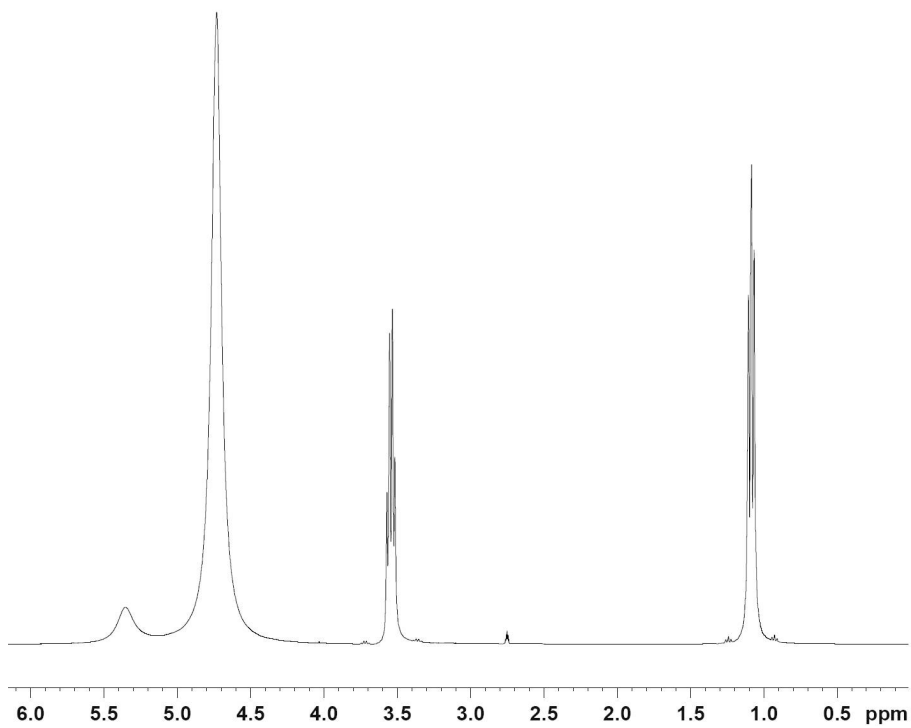


Figure 29. ^1H NMR spectra of proton groups of vodka (sample №29)

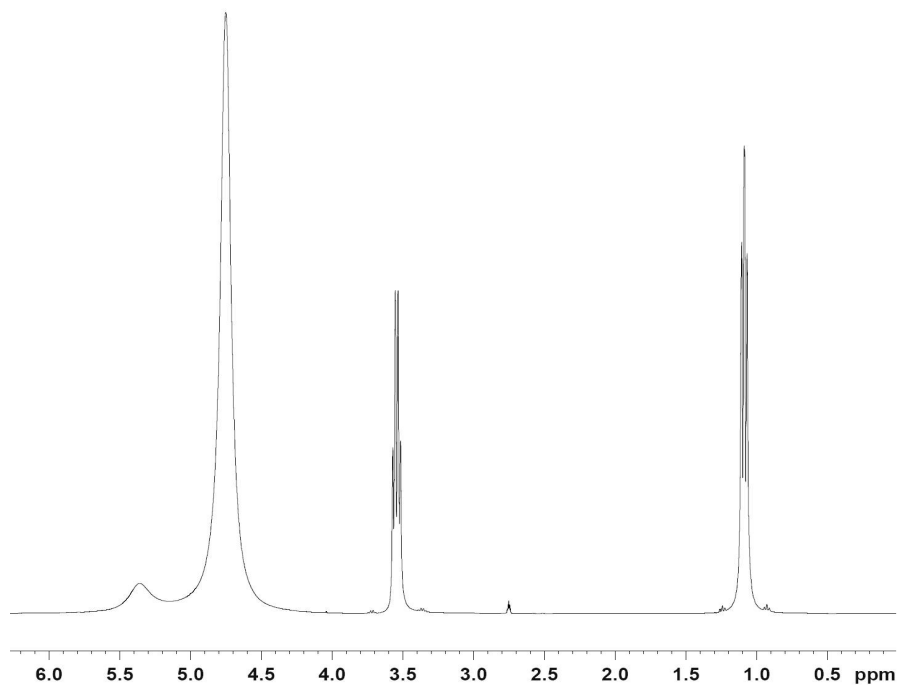


Figure 30. ^1H NMR spectra of proton groups of vodka (sample №30)

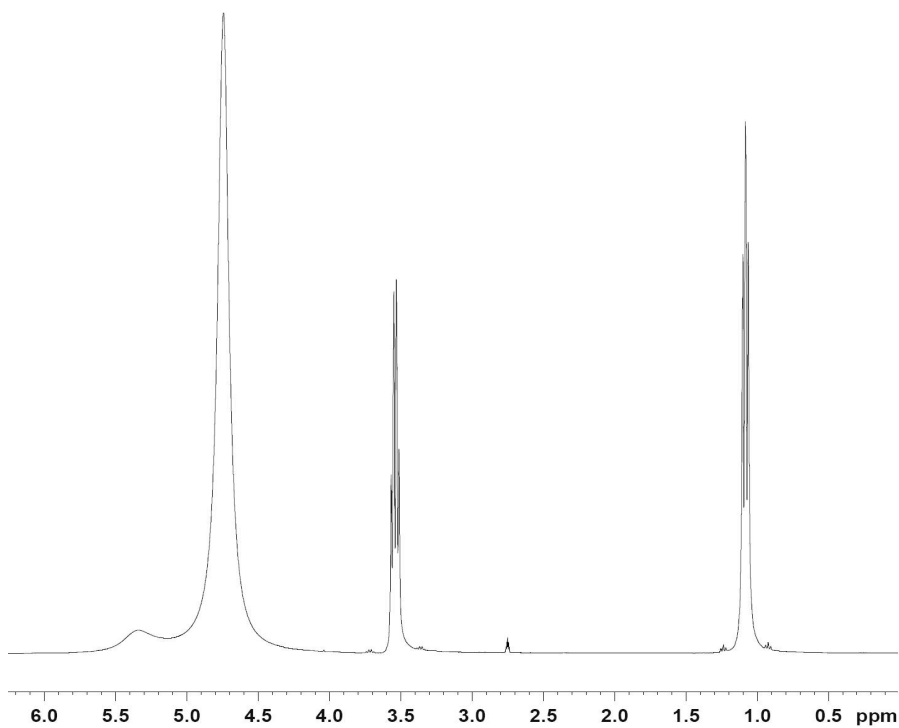


Figure 31. ^1H NMR spectra of proton groups of vodka (sample №31)

Analysis of 1H NMR spectra of methyl group's protons CH_3 in vodkas allows to state the following: methyl group of protons in each sample is located in a strong field and represented as a triplet (t) with a relative intensity (1:2:1). Based on spin-spin interaction of groups of protons, the methyl group's signals (CH_3) must be split by neighboring protons of the methylene group (CH_2) into a triplet (t), in accordance with Pascal's triangle with intensity ratio of (1:2:1). Thus, methyl group of protons (CH_3) is located in a strong field with an average value of chemical shift $\delta_{CH_3}=1,08$ ppm. The distance between each peak of quartet is 8 Hz.

The analysis of 1H NMR spectra of methylene group's protons CH_2 indicates that the group is represented as a quartet (q) with intensity (1:3:3:1). This is confirmed by the spin-spin interaction of protons of methyl (CH_3) group. This group has to split signal of the methylene group (CH_2) into four components and form a quartet (q) with intensity ratio of 1:3:3:1. In turn, the protons of hydroxyl (OH) groups should split every component of methylene (CH_2) group's quartet into two components and form a double quartet. The absence of observable spin-spin interaction between hydroxyl (OH) and methylene (CH_2) groups should make signal of methylene (CH_2) group a quartet. At the same time methylene group of protons (CH_2) is located in a weak field, with an average value of chemical shift $\delta_{CH_2}=3,53$ ppm. The distance between each peak of quartet is 8 Hz. The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and hydroxyl group of water (H_2O) in each sample is $\Delta\delta_2=1,19$ ppm ($\Delta f_2=476$ Hz). The difference between chemical shifts of protons of methylene group of ethanol (CH_2) and methyl group of ethanol (CH_3) in each sample is $\Delta\delta_3=2,45$ ppm ($\Delta f_3=980$ Hz).

Conclusions

We will draw conclusions on establishing of equilibrium hydroxyl proton of ethanol and water in vodka by 1H NMR spectroscopy. We identified three groups of samples based on the equilibrium of the hydroxyl groups of protons of ethanol ($EtOH$) and water (H_2O): steady; transitional; unsteady.

Steady equilibrium is characterized by a presence in hydroxyl group combined unitary signal of $EtOH+H_2O$. The component of protons of $EtOH+H_2O$ in each sample presented as singlet (s), located in a «weak field» with a chemical shift, which is in a range $\delta_{EtOH+H_2O}=4,75-4,80$ ppm. Waveform of $EtOH+H_2O$ protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

Transitional equilibrium characterized by a presence of hydroxyl groups two separate signals of $EtOH$ ($\delta_{EtOH}=5,34$ ppm) and H_2O ($\delta_{H_2O}=4,75$ ppm). The difference between the chemical shifts of hydroxyl protons of ethanol ($EtOH$) and proton of water (H_2O) in each sample is $\Delta\delta_1=0,59$ ppm ($\Delta f_1=236$ Hz). Transitional equilibrium is characterized by the presence of hydroxyl proton, which is barely noticeable, which characterizes the transition from steady equilibrium to unsteady equilibrium. This may indicate that certain prerequisites have not yet been created to establish equilibrium structure (unsteady/steady equilibrium).

Unsteady equilibrium characterized by a presence of hydroxyl groups two separate signals of ethanol ($EtOH$) ($\delta_{EtOH}=5,34$ ppm), which is obvious and H_2O ($\delta_{H_2O}=4,72-4,75$ ppm). The difference between $EtOH$ and H_2O – $\Delta\delta_1=0,62$ ppm ($\Delta f_1=248$ Hz).

The conducted researches set a fundamental difference of behavior of hydroxyl proton of ethanol and water in vodkas, using 1H NMR spectroscopy. Established criteriums of the systems equilibrium allow to improve the technological process of vodka on distillery enterprises, to stabilize quality of finished product.

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