THE CHANGE OF THE HYDROXYL PROTONS IN AQUEOUS ALCOHOLIC MIXTURES UNDER THE PROCESS OF MAKING VODKAS

O. Kuzmin, S. Sujkov*, V. Topol'nik

Donetsk National University of Economics and Trade named after Mykhailo Tugan-Baranovsky; *L.M. Litvinenko Institute of Physical-Organic Chemistry and Coal Chemistry NAS Ukraine, Ukraine
kuzmin_ovl@mail.ru

Annotation

The aim of this work is the investigation of transformation mechanisms of hydrogen bonds nets of ethanol and water in the process of making aqueous alcoholic mixtures. The methods used in the work: ^{1}H NMR spectroscopy of aqueous alcoholic mixtures, evaluation methods of physicochemical and organoleptic characteristics of water, ethanol, aqueous alcoholic mixtures. Experimental evidence depending speed and nature of thermodynamic equilibrium, and optimum organoleptic characteristics vodka according to the method of water treatment and contact time components aqueous alcoholic mixtures. Based on this study identified fundamental difference in the behavior of the aqueous alcoholic mixtures received alcohol and water, held various treatments. We obtained the system steady and unsteady balance hydroxyl protons in aqueous alcoholic mixtures, which are different in the organoleptic properties.

Introduction

Nowadays nuclear magnetic resonance (NMR) spectroscopy has worthily gained popularity among physical methods of research, that is more adopted in science, 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.

The most wide-spread is NMR spectroscopy on nuclei of hydrogen isotope [1]H ([1]H–protons). They account for 90% of all the studied NMR spectra.

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 under placing them in a strong magnetic field and, that allows to identify nuclei in different chemical environment.

Bloch F. obtained ^{1}H NMR spectra with "low-resolution" of H_2O (fig. 1, a) for the first time in 1946 (Bloch et al. 1946), and in 1951 Arnold J.T. for the first time obtained ^{1}H NMR spectra with "high-resolution" of ethanol C_2H_5OH (fig. 1, b) (Arnold et al. 1951). Up to now, many scientists (Zhunke, 1974; Ionin et al, 1983; Silverstein et al, 1977; Nose et al, 2005; Khausser, Kaltbitzer, 1993; Richards, Hollerton, 2011; Roberts, 2002; Hu et al, 2010) bring ethanol NMR spectrums as the simplest and best understood from the analytical point of view of the substance.
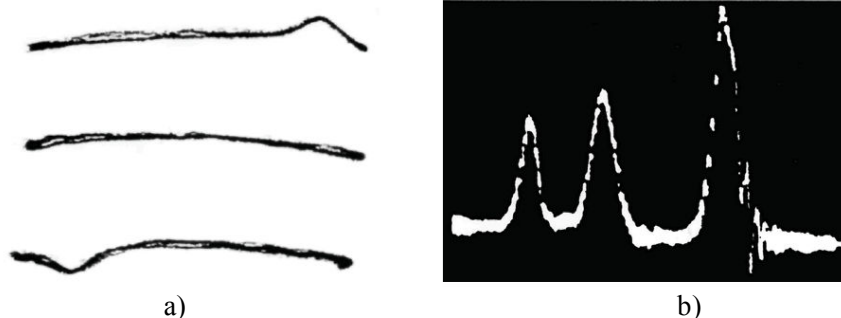

a)   b)

Figure 1 - ^{1}H NMR spectra: a - H_2O (Bloch et al. 1946); b - C_2H_5OH (Arnold et al. 1951) – (from left to right) protons of hydroxyl (OH), methylene (CH_2) and methyl (CH_3) groups

The usage of NMR spectroscopy is followed by a number of difficulties connected with the spatial orientation of nuclei, chemical exchange, chemical shift anisotropy, spin-spin interaction. However, these same effects are unique information about the processes in chemical systems. The use of ^{1}H NMR spectroscopy is important while studying hydrogen bonds of the OH-proton of water, aqueous alcoholic mixtures (AAM) and alcoholic systems that are the strongly dependent on external factors.

The aim of this work is the investigation of transformation mechanisms of hydrogen bonds nets of ethanol and water in the process of making AAM.

An ethanol molecule consists of 6 protons arranged in 3 magnetic nonequivalent groups: methyl (CH_3), methylene (CH_2), hydroxyl (OH) with the relative intensity – 3:2:1.

Chemical shift (δ) is a nondimensional parameter that determines position of a signal in the spectrum (Ionin et al, 1983; Khausser, Kaltbitzer, 1993; Richards, Hollerton, 2011), the unit of measurement is 1 part per million (ppm; parts per million; per mille) either of the field strength or of the resonance frequency relative to zero conditional – of a reference connection signal.

Spectrum position of spectrum components on nondimensional scale as usual characterizes in the terms low or high field (Khausser, Kaltbitzer, 1993): when signals are arranged in the left side they are in a "weaker (lower) field", the deshielding effect is observed; when signals are in the right side they are in a "stronger (higher) field", the shielding effect is observed.

For the overwhelming number of organic and unorganic compounds, proton signals in the ^{1}H spectra are in the range of δ=0-15 ppm.

^{1}H NMR spectra of water. Water in a liquid form (T_{sample}=300K; without solvent) – chemical shift of the proton δ_{H2O}=4,7 ppm, water in a vaporous form – δ_{H2O}=3,4 ppm. For liquid water (solvent acetone–d_6) – δ_{H2O}=2,84 ppm.

Ethanol ^{1}H NMR spectra in liquid form (T_{sample}=300K; nonaqueous; without solvent) (Roberts, 2002): methyl (CH_3) - δ_{CH3}=1,2 ppm; methylene (CH_2) - δ_{CH2}=3,7 ppm; hydroxyl (OH) - δ_{OH}=5,3 ppm. For vaporous ethanol: δ_{CH3}=3,6 ppm; δ_{CH2}=6,0 ppm; δ_{OH}=2,8 ppm. Liquid nonaqeous ethanol, solvent acetone-d_6 – chemical shift for the proton group: δ_{CH3}=1,12 ppm; δ_{CH2}=3,57 ppm; δ_{OH}=5,39 ppm.

There are nuclear spin-spin interactions (Roberts, 2002) between 3 ethanol proton-containing groups that have different resonance frequencies, thereby n equivalent protons of one group (spin 1/2) split proton resonance of the neighboring group into (n+1) lines with intensity according to Pascal's triangle (Silverstein et al, 1977; Khausser, Kaltbitzer, 1993; Richards, Hollerton, 2011). The possibility of observing of the spin-spin interactions depend on the including in the presence of intermolecular exchange of protons (fast, slow). It should be noted that, compared with other types of spectroscopy NMR - slow method, the time constant of the order of seconds and tens of seconds.

The presence of proton exchange between water and ethyl alcohol is quite a known fact (Roberts, 2002). The proton exchange can be speeded up or slowed down due to the change of the solution's pH level (changing the quantitative ratio of H^+ и OH^- ions) by adding acid, alkali, water (Roberts, 2002).

Hydroxyl proton (OH) of ethanol can exchange with free hydrogen ions that are generated by the added water or by the trace quantities of the acid, alkali or dissociated ethanol. The exchange speed will be proportionate to the concentration of free ions in the matrix. Exchange with the acidic and basic impurities also affects the position of signal-averaged water. NMR spectra of AAM protons are of different shapes according to the pH level.

Under neutral conditions, pH=7 and the slow OH exchange (lifetime less than 1 second) (Ionin et al, 1983; Khausser, Kaltbitzer, 1993; Richards, Hollerton, 2011; Roberts, 2002):

- protons of the methyl (CH_3) group splits the signal of the methylene (CH_2) group in a quartet (q) of intensity ratio 1:3:3:1;

- protons of the methylene (CH_2) group splits the signal of the methyl (CH_3) group in a triplet (t) of intensity ratio 1:2:1;

- proton of the hydroxyl (OH) group splits each component of the methylene (CH_2) group quartet in 2 components (doublets) or in a double quartet;

- protons of the methylene (CH_2) group splits the signal of the hydroxyl (OH) group in 3 components in a triplet (t) of intensity ratio (1:2:1).

Under acidic environment conditions, pH<7, conditions of the fast OH exchange (Ionin et al, 1983;

Silverstein et al, 1977; Khausser, Kaltbitzer, 1993; Richards, Hollerton, 2011; Roberts, 2002):

- protons of the methyl (CH_3) group splits the signal of the methylene (CH_2) group in 4 components in a quartet (q) of intensity ratio 1:3:3:1;

- protons of the methylene (CH_2) group splits the signal of the methyl (CH_3) group in 3 components in a triplet (t) of intensity ratio 1:2:1;

- no observed effect of the spin-spin interaction between methylene (CH_2) and hydroxyl (OH) groups due to the chemical exchange, as a result, the triplet signal of the hydroxyl (OH) group turns into a single narrow signal, rarely widened singlet (s), positioned in the weak field that corresponds to 4-6 ppm; the signal of the methylene (CH_2) group remains a quartet.

Adding of water (Roberts, 2002) as proton solvent into pure ethanol in the small quantity brings to relatively slow proton exchange, that is why, separate signals for OH and H_2O protons can be registered. If the part of water increases, the exchange speeds up, separate resonance OH peaks merge and get the weighted average position that are defined by the shifts of the OH groups and the relative concentration of ethanol and water.

Adding of acid (Silverstein et al, 1977; Richards, Hollerton, 2011) into AAM catalyzes fast exchange of the hydroxyl (OH) proton of alcohol and water, that leads to the disappearance of the splits OH signal and turns it to a singlet. Its exchange speed is quite fast by the standards of NMR (less than 10^{-6} sec.) in order to "average" the electron environment of the proton and reduce to zero the ability to monitor of the spin-spin interaction with the neighboring CH_2 group. The exchange speed in AAM can be slowed down due to the processing of solution by the soda ash (Na_2CO_3), alumina or zeolites.

Adding of alkali (Ionin et al, 1983) catalyzes the OH group proton exchange, which occurs so often, that effect of the spin-spin interaction is averaged and instead of thin structure the single peak is observed. Adding of alkali reduces the lifetime of the proton in each of these states and makes separate signals merge into one resonance peak that takes intermediate position.

^{1}H NMR spectra of compounds with moving hydrogen atoms (i.e. OH groups of ethanol) depend on external factors a lot (Zhunke, 1974; Ionin et al, 1983): nature of the solvent, substrate concentration, temperature, pH level of the environment. As compared to OH-protons, CH-protons have chemical shift is much more resistant to external factors.

Dependence of the hydroxyl (OH) proton and its chemical shift on the nature of the solvent is explained by formation of hydrogen bonds (Zhunke, 1974; Ionin et al, 1983; Silverstein et al, 1977; Roberts, 2002). Hydrogen bond decreases electron density around the hydroxyl proton that leads to weakening of shielding and signal shifting to the weak field. Degree of the intermolecular interaction due to hydrogen bond formation decreases with the dilution by inert solvent. Polar solvents complicate the hydrogen bond because they can form it by themselves. Intramolecular hydrogen bonds are less susceptible to the influence of environment than intermolecular hydrogen bonds.

In the spectrum of pure ethanol hydroxyl proton is developed as a narrow triplet at δ_{OH}=5,35 ppm. In nonpolar solvent (deuterochloroform) at the concentration of about 5-20%, the chemical shift of hydroxyl proton is in the range of δ_{OH}=2-4 ppm. When extrapolating to the infinite dilution or to the gas phase, this signal is shifted to the stronger field to δ_{OH}=0,5 ppm. Using of another solvent shifts signals of the hydroxyl proton (Silverstein et al, 1977).

Substrate concentration dependence (Zhunke, 1974; Ionin et al, 1983; Silverstein et al, 1977). Unlike OH-protons, chemical shifts of protons with strong C-H bonds are poorly dependent on concentration. When dissolving the solution by the "inert" solvent, signal of the hydroxyl proton is shifted as diluting the solution to high fields because of intermolecular hydrogen bonds break. By increasing the degree of association, this signal is shifted to weak fields.

Temperature dependence (Zhunke, 1974; Ionin et al, 1983; Silverstein et al, 1977). Chemical shifts of protons with C-H bonds are almost unchanged with temperature changes. Temperature influences essentially on the position of "moving" proton signals that can create hydrogen bonds. Temperature change influences upon the creation of associates and thereby on the chemical shift. When temperature rises, signal of the hydroxyl proton is often shifted to higher fields because of intermolecular hydrogen bond break and equilibrium shift to monomer.

Dependence on pH level of environment (Khausser, Kaltbitzer, 1993). According to the law of mass

action, chemical equilibrium can be described by equilibrium constant pK that determines concentration ratio of forms that are in equilibrium. In most cases, protoning-deprotoning reactions are fast in the NMR scale of time, that is, the averaged value of the chemical shift δ is observed, its value is determined in the simplest case by the pH value as to the modified Henderson-Hasselbalch equation:

$$\delta = \delta_i + \sum_{i=1}^{N} (\delta_{i+1} - \delta_i) \frac{10^{pH-pK_i}}{1+10^{pH-pK_i}} \,.$$

Different charge states of molecules bring to the difference in the electron distribution what influences the values of chemical shifts δ_i and δ_{i+1} in the corresponding forms. When measuring ^{1}H NMR for different pH values in the range of fast exchange, we observe the signal, the chemical shift of which changes in accordance with the concentration of hydronium ions (Khausser, Kaltbitzer, 1993).

If compounds contain protons at heteroatoms and acquisition of the spectrum in the solvent that provides fast exchange of active protons (in water), all active protons will give one common signal in the spectrum. Its position depends on the pH value of environment. The signal is in a weaker field the less it is.

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) 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 ^{1}H NMR spectroscopy, IR Fourier transform spectroscopy, Raman spectroscopy. The results of the ^{1}H NMR and IR Fourier transform spectroscopy researches show that in water there are hydrates with the structure of EtOH*(5,3 ± 0,1)H_2O, that are observed either in AAM or in vodka. Authors (Hu et al, 2010) connect this hydrate proportion EtOH*(5,3 ± 0,1)H_2O and influence on the following organoleptic indicators of vodka.

In the work by Nose A. and others (Nose et al, 2005) 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) it is set that admixture bonds influence on molecular dynamics in the process of ethanol hydration.

In the work (Hu et al, 2010) the notion "structurability" is introduced – that is "ability to structuring" – a parameter that determines the ability (of alcoholic products) of vodka to order molecules of water in its structure.

In the work (Hu et al, 2010) great attention is given to ^{1}H NMR spectra of the OH proton of water and alcohol. Protons of water in all the samples is given as a long narrow signal with the chemical shift on the 5 ppm. Spectra also show that in some samples there appears the second widened peak of the OH signal that is on the 5,5 ppm level. That is the low-field peak of OH-ethanol that parted from the conditionally high-field signals of OH-water. Absence of the separate OH ethanol signal in the samples (according to the opinion of the authors (Hu et al, 2010)) points out weak hydrogen bonds of ethanol.

To achieve our aim, the experimental studies of ethanol and process water in making of AAM were carried out.

Method

The relevancy of the given studies is confirmed by the scientific-research work (SRW №681/2011 from 15.09.2011) "Optimization of technological processes of making vodka using electrochemical activation and control methods of quality indices" that was concluded between Donetsk National University of Economics and Trade named of Mykhailo Tugan-Baranovsky and LLC "Liquor-vodka factory "Altera". As a result of the experimental industrial tests, the social and scientific and technical effect – increase of the scientific-methodical level of control, improvement of the technological process and quality of finished production is received.

The research data were carried out under laboratory conditions on the certified equipment at the following enterprises: LLC "Donetsk liquor-vodka factory "Lik"; Institute of Physical-Organic Chemistry and Coal Chemistry named after L.M. Litvinenko NAS Ukraine (Donetsk city); Donetsk regional test center of water, communal enterprise "Company "Voda Donbassa".

Used devices (fig. 2) and materials, reagents and glassware:

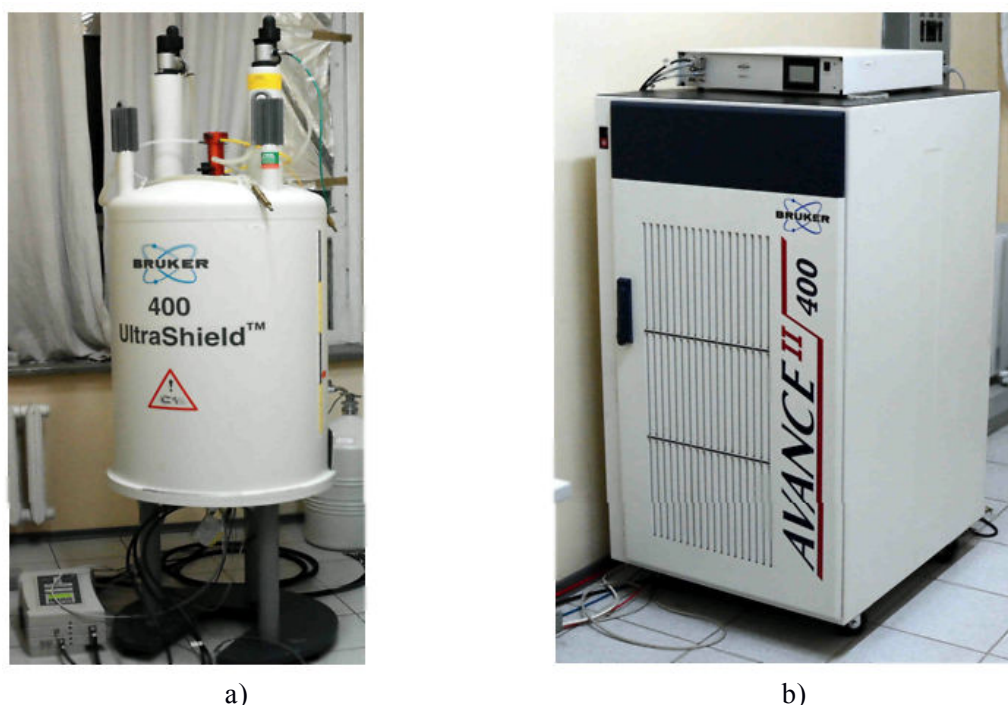a)   b)

Figure 2 – Surface appearance of the Fourier NMR spectrometer Bruker Avance II (400 MHz): a –block magnet; b – electronic equipment console

- Fourier NMR spectrometer Brucker Avance II (400 MHz) (fig. 2): magnetic field intensity – 9,4 T; operating frequency on [1]H – 400 MHz; measuring inaccuracy of chemical shifts for [1]H ± 0,0005 ppm; sensor – broadband, inverse with automatic tuning and Z-gradient; 5 mm ampules; thermostatic system (+25°C ÷ +100°C);

- capillary special form with deuterosolvent – $(CD_3)_2CO$ (acetone-d_6, deuteroacetone, DAC; nuclear share of deuterium – 99,88%; moisture content – 0,018%; t_b=+56,3ºC; t_m= -94ºC; chemical shift of residual protons at [1]H δ=2,75 ppm);

- NMR tubes №507-HP of high accuracy for NMR spectroscopy of high resolution (frequency 400 MHz): standard length – 178 mm; outer diameter – 4,97±0,006 mm; internal diameter – 4,20±0,012 mm; curvature ±0,0006 mm;

- volumetric pipette;
- dosing device;
- ethyl alcohol rectified (EAR) of the class "Lux" according to DSTU 4221:2003 "Ethyl alcohol rectified. Specifications";
- drinking water in accordance with GOST 2874-82 "Drinking water. Hygiene requirements and quality control";
- water softened due to Na-cation exchange in accordance with SOU 15.9-37-237:2005 "Water prepared for liquor-vodka production. Specifications";
- process water – demineralized by reverse osmosis in accordance with SOU 15.9-37-237:2005 "Water prepared for liquor-vodka production. Specifications";
- AAM (control) from EAR of the class "Lux" and deionized water due to distillation;
- AAM from EAR of the class "Lux" and drinking water;
- AAM from EAR of the class "Lux" and process water – softened due to Na-cation exchange;
- AAM from EAR of the class "Lux" and process water – demineralized due to the reverse osmosis.

Drinking water characteristics (ionic composition) were determined using an ion chromatograph «Metrohm 792» with measurement error ± 0,1 mg/dm^3.

Characteristics of alcohol and AAM were determined using gas chromatography «Chromatec Crystal 5000.1» with measuring error of methanol ± 0,002 % vol., the rest of positions - ± 0,5 mg/dm^3.

The work order:
- preparation of alcohol-containing liquid in deuteroacetone;
- registration of the NMR ^{1}H spectrum of the alcohol-containing liquid;
- conclusions and interpretation of the results obtained.

Method for carrying out the work:
- with the help of volumetric pipette (dosimeter), the AAM with the given alcoholic strength ($40,0 \pm 0,2$) % vol. (0,3 ml) is prepared. It is necessary for the work of the LOCK system – deuterium stabilization of the NMR spectrometer - deuterosolvent (acetone-d_6), the external standard that is separated from the studied solution, poured into, soldered in the capillary of a special form and placed in the measuring NMR tube. The obvious advantage of using the external standard is that there is no interconnection between molecules of the standard substance and the studied solution;

- in accordance with registration of the NMR ^{1}H spectrum, the NMR ^{1}H spectrum of the AAM sample in deuteroacetone is registered;

- the obtained data are processed in accordance with methodical instructions for using the software complex MestRe-C 2.3a or Bruker™ TopSpin;

- studies are carried out on the Fourier NMR spectrometer Brucker Avance II with frequency of 400 MHz, 1ppm = 400 Hz.

Results

Drinking water in accordance with GOST 2874-82 "Drinking water. Hygiene requirements and quality control", with the following baseline characteristics: solid residual – 867 mg/dm^3; electrical conductivity – 1150 microS/cm; pH – 7,01; oxidation reduction potential (ORP) – "+" 271 mV; total hardness – 7,93 mM/dm^3; permanganate oxidability – 4,27 mg O$_2$/dm^3; mass concentration (MC) of sodium – 90,75 mg/dm^3; MC of potassium – 4,87 mg/dm^3; MC of ammonium – <2,0 mg/dm^3; MC of calcium – 106,03 mg/dm^3; MC of magnesium – 23,91 mg/dm^3; total alkalinity – 5,38 mM/dm^3.

Water softened due to Na-cation exchange in accordance with SOU 15.9-37-237:2005 "Water prepared for liquor-vodka production. Specifications", with characteristics: solid residual – 695 mg/dm^3; electrical conductivity – 1070 microS/cm; pH – 6,71; ORP – "+" 288 mV; total hardness – <0,05 mM/dm^3; permanganate oxidability – 2,36 mg O$_2$/dm^3; MC of sodium – 266,1 mg/dm^3; MC of potassium – <2,0 mg/dm^3; MC of ammonium – <2,0 mg/dm^3; MC of calcium – <2,0 mg/dm^3; MC of magnesium – <2,0 mg/dm^3; total alkalinity – 4,12 mM/dm^3.

Process water – demineralized by reverse osmosis in accordance with SOU 15.9-37-237:2005 "Water prepared for liquor-vodka production. Specifications", with characteristics: solid residual – 15 mg/dm^3; electrical conductivity – 20,7 microS/cm; pH – 5,05; ORP – "+" 393 mV; total hardness – <0,05 mM/dm^3; permanganate oxidability – 0,46 mg O$_2$/dm^3; MC of sodium – 11,60 mg/dm^3; MC of potassium – <2,0 mg/dm^3; MC of ammonium – <2,0 mg/dm^3; MC of calcium – <2,0 mg/dm^3; MC of magnesium – <2,0 mg/dm^3; total alkalinity – 0,15 mM/dm^3.

Ethyl alcohol rectified (EAR) of the class "Lux" according to DSTU 4221:2003 "Ethyl alcohol rectified. Specifications": content of aldehydes in anhydrous alcohol, in recalculation on acetic aldehyde – 1,3 mg/dm^3; content of fusel oils in anhydrous alcohol: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,5 mg/dm^3; content of esters in anhydrous alcohol, in recalculation on acetic-ethyl ether – 1,3 mg/dm^3; content of methanol in anhydrous alcohol – 0,0022 % vol.

AAM (control) from EAR of the class "Lux" and deionized water due to distillation: alcoholic strength – 40,03 % vol.; electrical conductivity – 1,0 microS/cm; ORP – "-" 30 mV; pH level – 6,28; content of aldehydes in anhydrous alcohol, in recalculation on acetic aldehyde – 1,3 mg/dm^3; content of fusel oils in anhydrous alcohol: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,5 mg/dm^3; content of esters in anhydrous alcohol, in recalculation on acetic-ethyl ether – 1,3 mg/ dm^3; content of methanol in anhydrous alcohol – 0,0022 % vol.; alkalinity – <0,1 cm^3 0,1 M of hydrochloric acid for titration of 100 cm^3 sorting; oxidability test – 10,5 min.; taste evaluation – 9,30 bal. (form – colourless liquid without sediment; smell – strong alcoholic; taste – sour and bitter, pungent).

AAM from EAR of the class "Lux" and drinking water: alcoholic strength – 39,94 % vol.; electrical conductivity – 183 microS/cm; ORP – "+" 37 mV; pH level – 8,32; content of aldehydes in anhydrous

alcohol, in recalculation on acetic aldehyde – 1,5 mg/dm^3; content of fusel oils in anhydrous alcohol: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,1 mg/dm^3; content of esters in anhydrous alcohol, in recalculation on acetic-ethyl ether – 1,2 mg/dm^3; content of methanol in anhydrous alcohol – 0,0022 % vol.; alkalinity – 2,5 cm^3 0,1 M of hydrochloric acid for titration of 100 cm^3 sorting; oxidability test – 13,5 min.; taste evaluation – 9,43 bal. (form – colourless liquid with sediment; smell – strong alcoholic; taste – heavy).

AAM from EAR of the class "Lux" and process water – softened due to Na-cation exchange: alcoholic strength – 39,85 % vol.; electrical conductivity – 255 microS/cm; ORP – "-" 35 mV; pH level – 7,84; content of aldehydes in anhydrous alcohol, in recalculation on acetic aldehyde – 1,3 mg/dm^3; content of fusel oils in anhydrous alcohol: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,4 mg/dm^3; content of esters in anhydrous alcohol, in recalculation on acetic-ethyl ether – 1,4 mg/dm^3; content of methanol in anhydrous alcohol – 0,0020 % vol.; alkalinity – 2,4 cm^3 0,1 M of hydrochloric acid for titration of 100 cm^3 sorting; oxidability test – 9 min.; taste evaluation – 9,49 bal. (form – colourless liquid without sediment; smell – strong alcoholic; taste – bitterish, softened).

AAM from EAR of the class "Lux" and process water – demineralized due to the reverse osmosis: alcoholic strength – 39,92 % vol.; electrical conductivity – 3,5 microS/cm; ORP – "-" 98 mV; pH level – 7,60; content of aldehydes in anhydrous alcohol, in recalculation on acetic aldehyde – 1,8 mg/dm^3; content of fusel oils in anhydrous alcohol: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,4 mg/dm^3; content of esters in anhydrous alcohol, in recalculation on acetic-ethyl ether – 1,4 mg/dm^3; content of methanol in anhydrous alcohol – 0,0021 % vol.; alkalinity – 0,4 cm^3 0,1 M of hydrochloric acid for titration of 100 cm^3 sorting; oxidability test – 9 min.; taste evaluation – 9,30 bal. (form – colourless liquid without sediment; smell – strong alcoholic; taste – sour and bitter, pungent).

Discussion

Figure 3 illustrates one-dimensional AAM proton spectra made of drinking water (GOST 2874-82 "Drinking water. Hygiene requirements and quality control") and EAR of the class "Lux" (DSTU 4221:2003 "Ethyl alcohol rectified. Specifications") according to the time of the system functioning (lifetime, hours) and the chemical shift of the proton group (ppm) are brought.

The area of hydrophilic protons of ethanol and water is represented by two separate peaks – by OH ethanol (C_2H_5OH) and water H_2O – at the initial moment of the system functioning (τ=0 hours). The multiplet component of the hydroxyl (OH) proton of ethanol (C_2H_5OH) is represented by a separate broadened singlet that is in the "weaker field" with the chemical shift of δ_{OH}=5,33 ppm. The component of water proton (H_2O) is represented by a singlet with the chemical shift of δ_{OH}=4,70 ppm. H_2O proton has a conical form with a widened base and a top of irregular form, its peak is shifted to the left relative to the axial line. The difference in chemical shifts between OH proton (C_2H_5OH) and H_2O proton at the initial moment of their "system life" (τ=0 hours) is $\Delta\delta_{OH}$=0,63 ppm, that is why, H_2O proton relative to OH proton (C_2H_5OH) is "strongly tied" with lower resonance frequency.

The second spectrum (τ=48 hours) is also characterized by two separate peaks – of OH ethanol (C_2H_5OH) and H_2O water. The multiplet component of OH proton of ethanol is represented by a separate short round-shaped singlet that is in the "weaker field" with the chemical shift of δ_{OH}=5,37 ppm. The component of H_2O proton is represented by a long singlet that is in the "weak field" with the chemical shift of δ_{OH}=4,78 ppm. H_2O proton has a distorted gauss form with a widened base and a top of irregular form, its peak is shifted to the left relative to the axial line. The difference in chemical shifts between OH proton (C_2H_5OH) and H_2O proton is $\Delta\delta_{OH}$=0,59 ppm.

The third spectrum (τ=120 hours) is characterized by one summarized peak of OH ethanol (C_2H_5OH) and H_2O water. The component of H_2O proton and OH proton C_2H_5OH is represented by a singlet with the chemical shift of δ_{OH}=4,76 ppm. The summarized H_2O+(EtOH) protons signal has a nonesymmetric shape with a widened base and a top of regular form.

The fourth spectrum (τ=192 hours) is characterized by one summarized peak – of OH ethanol (C_2H_5OH) and H_2O water represented by a symmetrical singlet at δ_{OH}=4,77 ppm. The summarized H_2O+(EtOH) protons signal has a symmetrical form with a widened base and a top of regular form.
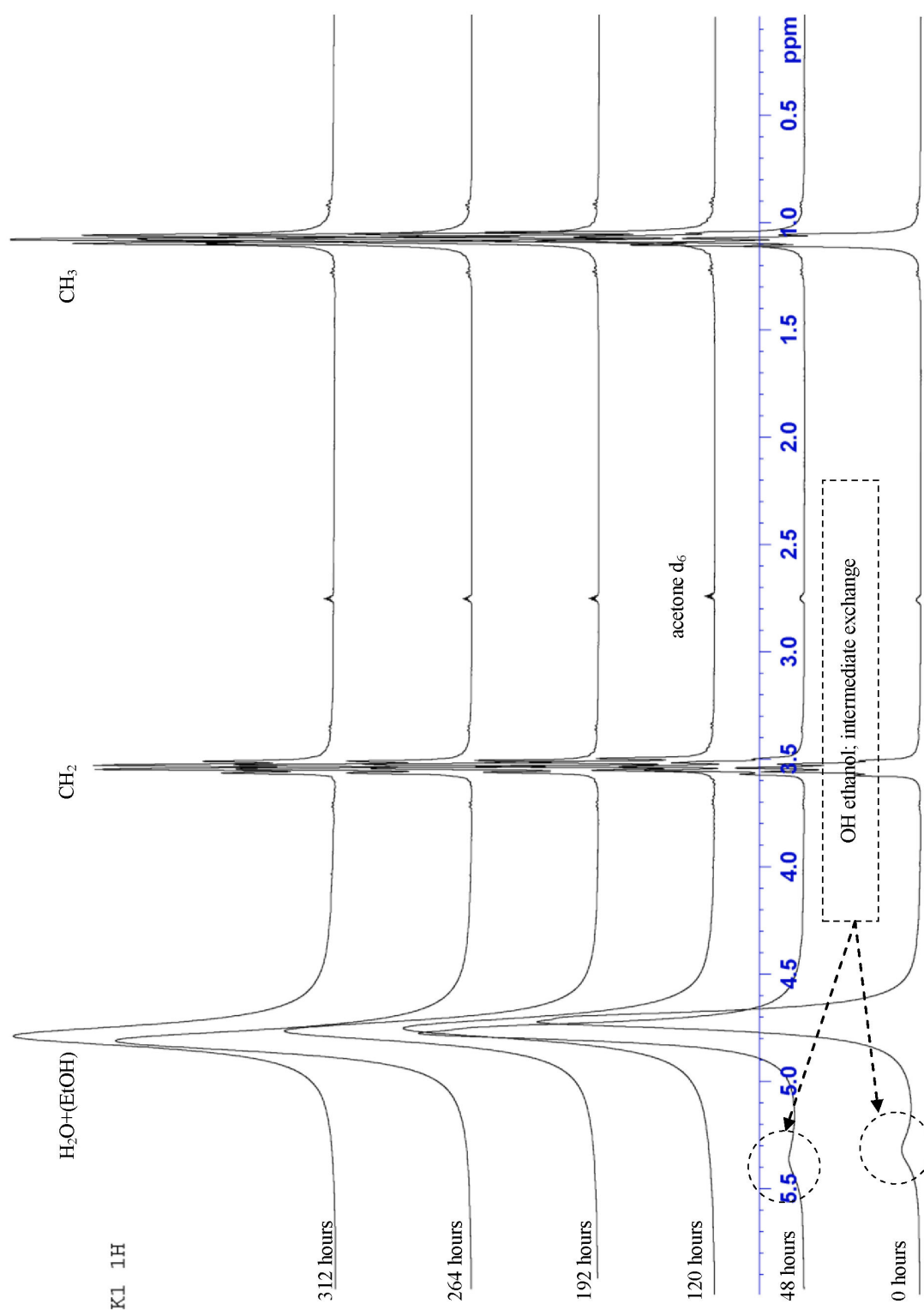
Figure 3 – Simultaneous AAM proton spectra made of drinking water (GOST 2874-82 "Drinking water. Hygiene requirements and quality control) and EAR of the class "Lux" (DSTU 4221:2003 "Ethyl alcohol rectified. Specifications") according to the time of system functioning (lifetime, hours)

The fifth spectrum (τ=264 hours) is characterized by one summarized peak – of H_2O+(EtOH) ethanol and water represented by a singlet at the chemical shift of δ_{OH}=4,83 ppm. The summarized protons signal has a symmetric form with a widened base and a top of regular form.

The sixth spectrum (τ=312 hours) is characterized by one summarized peak – of H_2O+(EtOH) ethanol and water represented by a singlet at the chemical shift of δ_{OH}=4,8 ppm. The summarized proton has a symmetric form with a widened base and a top of regular form.

The first conclusion is that in the process of making AAM when mixing drinking water with the pH level = 7,01 and EAR of the class "Lux", the assorting with the pH level = 8,32, the value of which characterizes the reduced content of free H^+ ions relative to OH^- due to alkaline reaction, is received. That is why, during the first 48 hours at a constant concentration of alcohol (AAM alcoholic strength – 39,94 % vol.) and a system thermostating (t= 23,5°C), hydroxyl proton (OH) of ethanol has been in the intermediate exchange speed with water protons. At τ=48-120 hours intermediate proton exchange speed has speeded up and at τ=120-312 hours intermediate exchange has disappeared. The chemical shift value of the hydroxyl proton δ_{OH}=4,76 ppm (τ=120 hours) increases a little and shifts to "weaker fields" up to the value δ_{OH}=4,80 ppm (τ=312 hours).

Signal of the methyl (CH_3) group is represented by a triplet of the intensity ratio 1:2:1 and the chemical shift δ_{CH3}=(1,05-1,10) ppm, signal of the methylene (CH_2) group – by a quartet with the intensity ratio of 1:3:3:1 and the chemical shift δ_{CH2}=(3,50-3,57) ppm, signal of the external standard of acetone-d_6 has the chemical shift $\delta_{acetone-d6}$=2,76 ppm.

Figure 4 illustrates simultaneous AAM proton spectra made of demineralized water by reverse osmosis (SOU 15.9-37-237:2005 "Water made for liquor-vodka production. Specifications") and EAR of the class "Lux" according to the time of system functioning (hours) and the chemical shift of proton groups (ppm).

The first spectrum (τ=0 hours) is characterized by one summarized peak – of OH ethanol (C_2H_5OH) и H_2O water. The component H_2O+(EtOH) is represented by a singlet that is at δ_{OH}=4,73 ppm. The summarized H_2O+(EtOH) proton has a symmetric form with a widened base and a top of regular form.

The second spectrum (τ=48 hours) the area of hydroxyl protons of ethanol and water is represented by two separate peaks – by OH ethanol (C_2H_5OH) and H_2O water. The component of the hydroxyl OH proton of ethanol is represented by a hardly noticeable salience that is in the weaker field to water signal δ_{OH}=5,35 ppm. The component of the hydroxyl proton of water (H_2O) is represented by a symmetric singlet of with a widened base and a top of regular form that have the chemical shift δ_{OH}=4,78 ppm. The difference in chemical shifts between OH proton (C_2H_5OH) and H_2O proton at this stage (τ=48 hours) is $\Delta\delta_{OH}$=0,57 ppm, that is why, H_2O proton relative to OH proton (C_2H_5OH) is in high field.

The third spectrum (τ=120 hours) is characterized by two separate peaks – by OH ethanol (C_2H_5OH) and H_2O. The component of the OH proton C_2H_5OH is represented by a separate salience that is in the weaker field with the chemical shift δ_{OH}=5,33 ppm. The component of the H_2O proton is represented by a symmetric singlet of conical form with a widened base and a top of regular form that is also with the chemical shift δ_{OH}=4,75 ppm. The difference in chemical shifts between OH proton (C_2H_5OH) and H_2O proton is $\Delta\delta_{OH}$=0,58 ppm.

The fourth spectrum (τ=192 hours) is also characterized by two separate peaks –of OH ethanol and water. The component of the OH proton C_2H_5OH is represented by a short round-shaped singlet that is in the weaker field with the chemical shift of δ_{OH}=5,36 ppm. The component of the H_2O proton is represented by a singlet of conical form with a widened base and a top of irregular form due to salience in the left side of the spectrum at δ_{OH}=4,74 ppm. The difference in chemical shifts between OH proton (C_2H_5OH) and H_2O proton is $\Delta\delta_{OH}$=0,62 ppm.

The fifth spectrum (τ=256 hours) is also characterized by two separate peaks –of OH ethanol and water. The multiplet component of the OH proton C_2H_5OH is represented by a hardly noticeable salience that is in the weaker field with the chemical shift δ_{OH}=5,38 ppm. The component of the H_2O proton is represented by a singlet of conical form with a widened base and a top of irregular form due to the considerable salience in the left side of the spectrum at δ_{OH}=4,80 ppm. The difference in chemical shifts between OH proton (C_2H_5OH) and H_2O proton is $\Delta\delta_{OH}$=0,58 ppm.

The sixth spectrum (τ=312 hours) is characterized by one summarized peak – of H_2O+(EtOH) represented by a long singlet that is in the "weak field" with the chemical shift δ_{OH}=4,82 ppm. The summarized proton has a conical form with a widened base and a top of regular form.
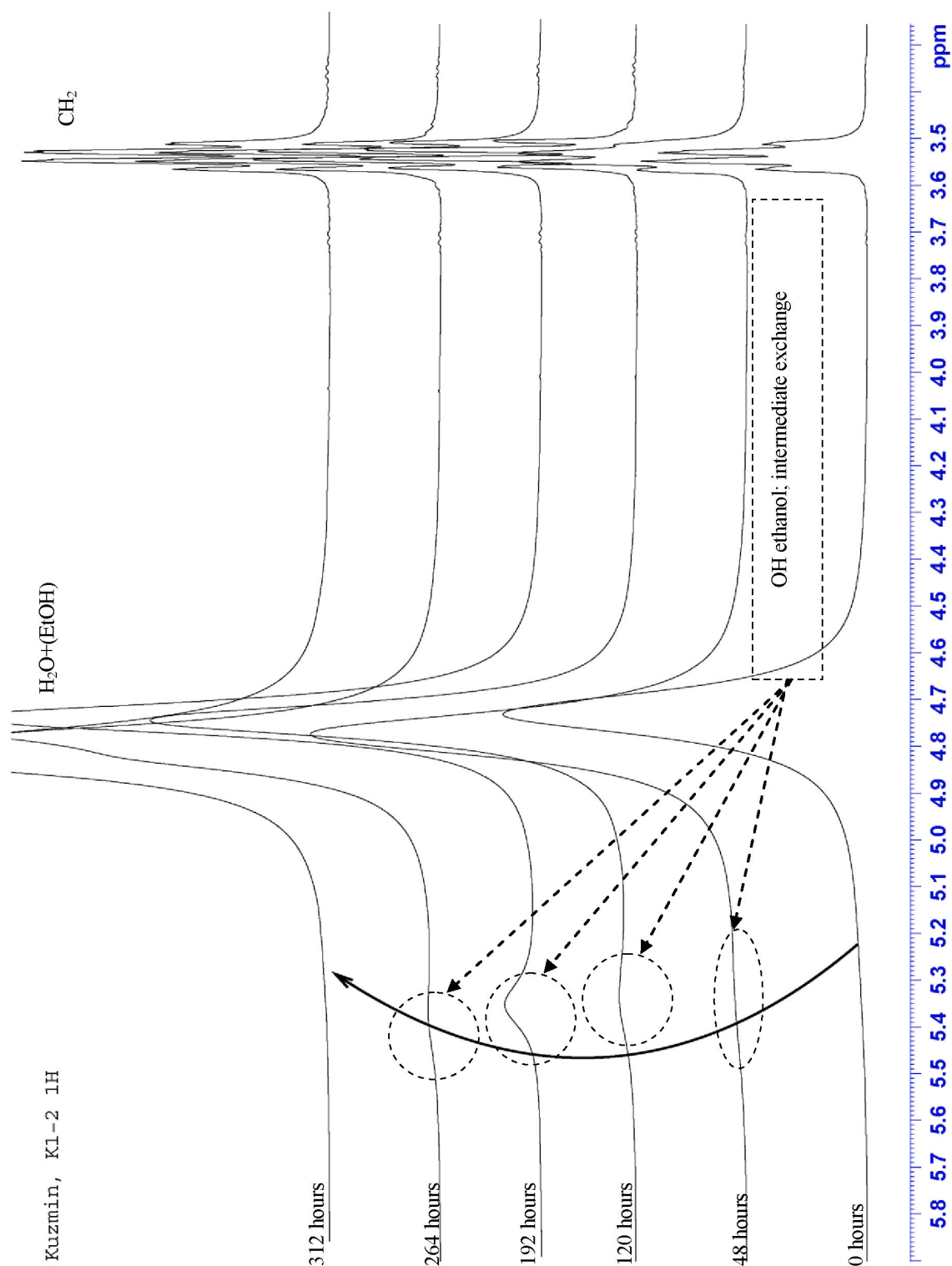
Figure 4 – Simultaneous AAM proton spectra made of demineralized water by reverse osmosis (SOU 15.9-37-237:2005 "Water made for liquor-vodka production. Specifications) and EAR of the class "Lux" (DSTU 4221:2003 "Ethyl alcohol rectified. Specifications") according to the time of system functioning (lifetime, hours). The chemical shift of the proton group expressed in parts per million (ppm)

The observed pattern of evidence of the complex dynamics of the processes to achieve equilibrium in the solution obtained for AAM when mixing it with demineralized water by reverse osmosis with the pH level = 5,05 and EAC of the class "Lux", the assorting with the pH level=7,60, the value of which characterizes the decreased content of free H^+ ions relative to OH^- due to alkaline reaction is received.

In the time interval from 48 to 264 hours after mixing, at a constant concentration of alcohol (AAM fortress – 39,92% vol.) and thermostating system (t = 23,5ºC), there is a "restoration" of the provisions of the hydroxyl proton signal (OH) ethanol first "lame duck" out of the water signal, and then undergoes evolution is usually observed for the alcohol/water (figure 3). It can be assumed that the initial separation of the signals associated with the process of restoring the structure of water, broken in desalination by reverse osmosis. Further, there is already a regular operation the formation of a stable system of alcohol/water with a high degree of socialization of protons and its characteristic data rates. The low exchange rate (remote monitoring signals hydroxyl and water) can be associated with significant microheterogeneity of the system and the appropriate barrier effect, reducing the effective rate of proton exchange.

Signal of the methyl (CH_3) group is represented by a triplet with the intensity ratio of 1:2:1 and the chemical shift δ_{CH3}=(1,06-1,10) ppm, signal of the methylene (CH_2) group – by a quartet with the intensity ratio of 1:3:3:1 and the chemical shift δ_{CH2}=(3,52-3,58) ppm, signal of the external standard of acetone-d_6 has the chemical shift $\delta_{acetone-d6}$=2,76 ppm.

Figure 5 illustrates one-dimensional proton spectra of AAM made of softened water due to Na-cation exchange (SOU 15.9-37-237:2005 "Water made for liquor-vodka production. Specifications") and EAR of the class "Lux" (DSTU 4221:2003 "Ethyl alcohol rectified. Specifications") according to the time of system functioning (hours) and the chemical shift of the proton group (ppm).

All six spectra are characterized by one summarized peak – of OH ethanol (C_2H_5OH) and H_2O water. In all the spectra the H_2O+(EtOH) component is expressed by a singlet that is in the weak field with the chemical shift: τ=0 hours - δ_{OH}=4,76 ppm; τ=48 hours - δ_{OH}=4,81 ppm; τ=120 hours - δ_{OH}=4,79 ppm; τ=192 hours - δ_{OH}=4,78 ppm; τ=264 hours - δ_{OH}=4,82 ppm; τ=312 hours - δ_{OH}=4,80 ppm. The summarized proton has a conical from with a widened base and a top of irregular form. The top has the main peak and additional high-field OH peak that has been separated from the low-field signal. When increasing the systems lifetime, this branch is merged with the main peak and creates a distortion zone in that place. Thus, in the process of creating the AAM made of softened water due to Na-cation exchange, with a pH = 6,71 and EAR of the class "Lux" obtained sorting with pH = 7,84 that is slightly alkaline reaction. The rate of proton exchange in the system initially high and separate the signals of hydroxyl and water are not observed even after mixing.

Signal of the methyl (CH_3) group is represented by a triplet with the intensity ratio of 1:2:1 and the chemical shift δ_{CH3}=(1,04-1,08) ppm, signal of the methylene (CH_2) group – by a quartet with the intensity ratio of 1:3:3:1 and the chemical shift δ_{CH3}=(3,50-3,55) ppm.

Based on this study identified a fundamental difference in the behavior of the AAM received alcohol and water, held various treatments. System with non-stationary equilibrium for: AAM from EAR of the class "Lux" and drinking water with significant organoleptic properties – taste evaluation – 9,43 bal. (form – colourless liquid with sediment; smell – strong alcoholic; taste – heavy); AAM from EAR of the class "Lux" and demineralized due to reverse osmosis with the taste evaluation – 9,30 bal. (form – colourless liquid without sediment; smell – strong alcoholic; taste – sour and bitter, pungent). System with the steady-state equilibrium is typical for AAM from EAR of the class "Lux" and process water softened due to Na-cation exchange that has the best organoleptic properties with the highest taste evaluation – 9,49 bal. (form – colourless liquid without sediment; smell – strong alcoholic; taste –bitterish, softened).

Thus, in the experimental evidence obtained according as the speed and nature of the thermodynamic equilibrium and optimum organoleptic characteristics of vodka water treatment process and the contact time of components AAM.

It is shown that in order to obtain high performance vodka products derived from the use of reverse osmosis water is necessary to conduct additional studies in order to find the optimal parameters postprocessing AAM.
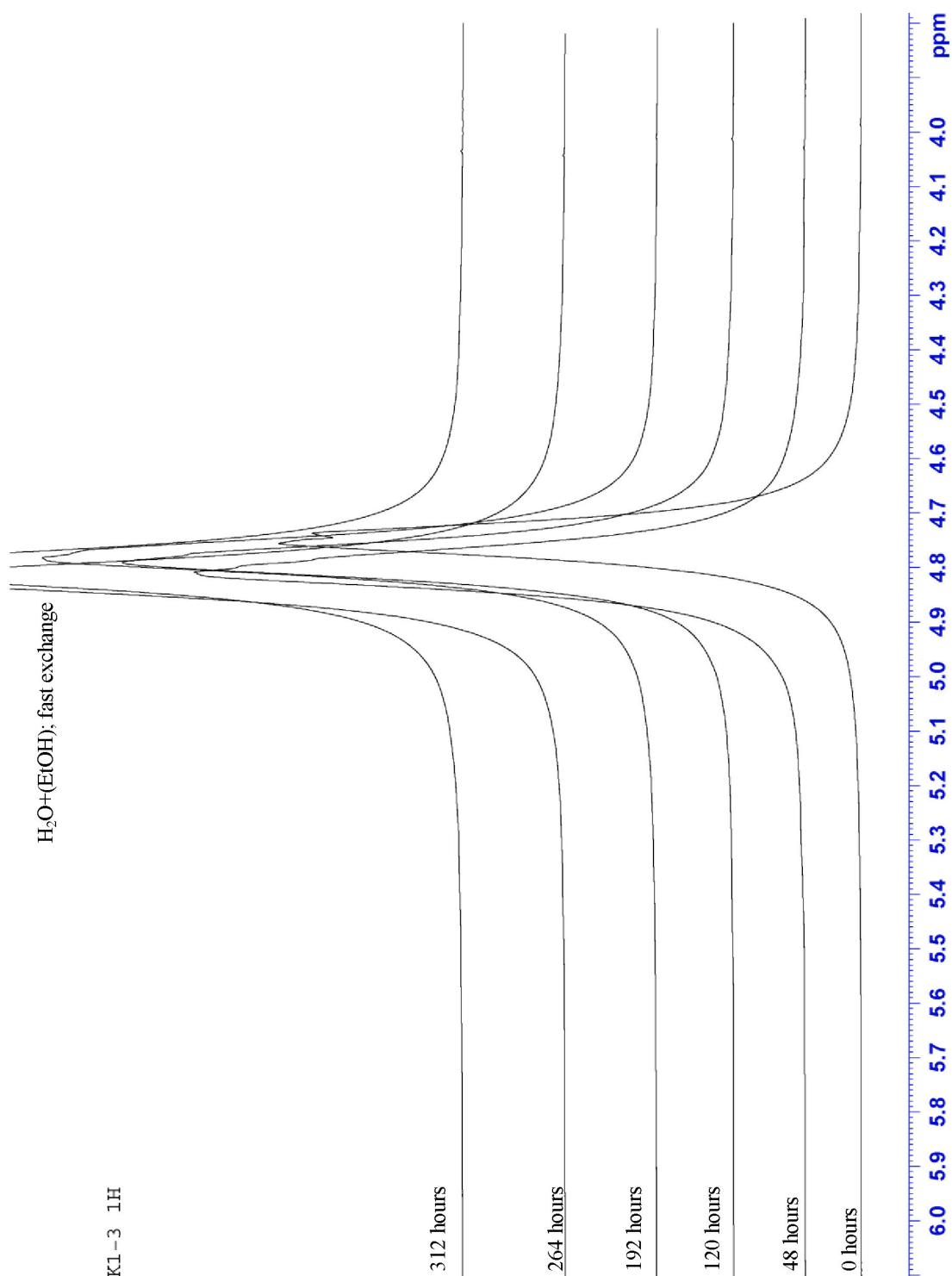
Figure 5 – Simultaneous proton spectra of AAM made of softened water due to Na-cation exchange (SOU 15.9-37-237:2005 "Water made for liquor-vodka production. Specifications) and EAR of the class "Lux" (DSTU 4221:2003 "Ethyl alcohol rectified. Specifications") according to the time of system functioning (lifetime, hours). The chemical shift of the proton group (ppm)

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