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Selected papers of the V International Conference on European Dimensions of Sustainable Development present peer-reviewed articles based on the reports of the Conference, which had place on June 1-2, 2023 at National University of Food Technologies, Kyiv, Ukraine in terms of the ERASMUS+ projects Jean Monnet EU Centre for the Circular and Green Economy JM ECO (620627-EPP-1-2020-1-UA-EPPJMO-CoE), EU renewable energy strategy as a roadmap for Ukraine (101085755 – JM RE – ERASMUS-JMO2022-HEI-TCH-RSCH) and European Union policies and best practices in academic project management (101085243 – ProEU – ERASMUS-JMO-2022-HEI-TCHRSCH). The Selected Papers cover economic, environmental and social aspects of sustainable development of the European Union and Ukraine; new technologies for the sustainable development; as well as European Union Studies on sustainable development.

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APPLICATION OF AN IMPROVED TECHNIQUE FOR MEASURING THE MASS FRACTION OF ALCOHOL-CONTAINING RAW MATERIALS IN COSMETIC PRODUCTS

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Abstract. *An improved technique for measuring the mass fraction of ethyl alcohol in water-alcohol solutions using gas-liquid chromatography with a vapour-phase sampler has been proposed. The principle of the method consists in the transfer of volatile components, including ethyl alcohol, from the solution to the vapor phase, its introduction into the chromatograph, the separation of the mixture on a capillary column, followed by the registration of the signal on the flame ionization detector.*

The prepared sample, the working solutions of the mixtures and the mixture for checking the retention time are heated in a stoppered vial. This allows you to balance the content of volatile components present in the liquid and in the vapor phase. Part of the equilibrium sample of the steam is introduced into the gas chromatograph column.

The static vapor phase sampler provides the possibility of introducing 3 ml of the vapor phase (volatile substances) of the sample directly to the analytical column, increasing the sensitivity of the technique and extending the resolution of the column.

The mass fraction of ethyl alcohol is calculated by the external standard method according to the ratio of the areas of the chromatographic peaks of ethyl alcohol from the mass fraction of ethyl alcohol in solution.

This technique makes it possible to test cosmetic products for the content of ethyl alcohol in water-alcohol and gel solutions, as well as to confirm the quality and safety of alcohol-containing raw materials in accordance with the requirements of the Technical Regulations for cosmetic products.

Introduction. Ethyl alcohol is widely used as an industrial raw material in the perfumery and cosmetics industry. According to the International Cosmetic Ingredient Dictionary and Handbook, ethanol acts as an defoamer, a perfume, an binder, an antimicrobial component and an ingredient that reduces the viscosity of cosmetic products.

During the outbreak of COVID-19, an emergency occurred the demand for basic hygiene products that caused them critical deficit and numerous falsifications (inconsistencies in quality). Alcohol-based hand rubs (ABHRs) formulated with technical-grade ethanol were temporarily permitted in Canada and the U.S beginning April 2020 to meet the current demand due to COVID-19. ABHRs formulated with technical-grade ethanol are low risk for general use. Overall, the highest risks were associated with methanol (for its toxicity), ethyl acetate (skin defattening), and acetaldehyde (carcinogenic and teratogenic). For these reasons, Health Canada and the United States Food and Drug Administration have issued recalls on products containing some of these

contaminants. More vigilant policing by regulatory agencies and general product users are required to ensure compliance, safety, and efficacy of these new products (Tse et al., 2021).

Typically, ethanol used for hand sanitizer must adhere to specific monographs (e.g. Food Chemicals Codex; FCC and the United States Pharmacopeia; USP), and are regulated by governmental agencies (e.g. Health Canada; HC, and the United States Food and Drug Administration; US-FDA). To ensure that process contaminants are minimized, ABHRs are normally formulated using raw materials conforming with USP or FCC guidelines. The USP monograph combines colorimetric tests and analytical chromatography to determine purity of the ethanol. Common contaminants naturally coproduced during grain fermentation include, methanol, acetates, aldehydes, butanols, amyl alcohols, propanols, and pentanols (Onuki et al., 2016).

The FDA discovered serious safety concerns with some hand sanitizers during testing. This includes some hand sanitizers that: are contaminated with potentially toxic types of alcohol, do not contain enough active ingredient (ethyl alcohol or isopropyl alcohol), have labels containing false, misleading, or unproven claims (FDA, 2023).

There are many types of alcohol. Only ethyl alcohol and isopropyl alcohol (also known as 2-propanol) are acceptable alcohols in hand sanitizer. Other types of alcohol, including methanol and 1-propanol, are not acceptable in hand sanitizer because they can be toxic to humans. Recent FDA safety testing discovered some hand sanitizers contaminated with these potentially toxic types of alcohol.

The alcohol content is the most important parameter that must be controlled in the manufacture of disinfectants. Optimum germicidal activity occurs at concentrations between 60–95% of either ethanol, isopropanol or n-propanol. Moreover it has been found that the disinfectant for hands with an alcohol concentration below 60% (vol/vol) is ineffective and may even put the user at greater risk of infection (WHO, 2009). Alcohol concentrations of 60% to 95% (vol/vol) kill 3.4 to 5.8 log 10 CFU in 30 seconds, with higher concentrations having better antibacterial activity. However, concentrations of greater than 95% are less potent because water is essential for protein denaturation (Trampuz et al., 2004).

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In the conditions of high competitiveness of commercial spirits both in the domestic and foreign sales markets, in today's conditions, the determining indicators of its quality are the concentration of ethanol and the content of microcomponents (aldehydes, esters, fusel oils, namely isopropyl alcohol and methanol) in the finished products. The composition of alcohol-containing raw materials and products is difficult to analyze, and for this reason scientists usually choose gas chromatography methods. Thanks to a wide selection of extraction methods and detectors, qualitative and quantitative analysis of many chemical compounds with different functional groups can be provided (Kostic et al., 2021; Sirhan et al., 2019; Wiśniewska et al., 2014).

A more advanced method is headspace gas chromatography, the principle of which is the preliminary extraction of volatile components from a liquid or solid sample (formation of a vapor phase) and their subsequent introduction into the gas chromatograph system. This makes it possible to increase the sensitivity of determining volatile components in the sample and significantly expands

the capabilities of the gas chromatographic system. In research (Panasenko et al., 2018) two methods suggested in the State Pharmacopoeia of Ukraine for determination of methanol and propanol-2 contents in liquid medicines were used, specifically: head-space gas-chromatography and classic gas chromatography with common injection technique. However, it has bee shown that classic gas chromatography is not able to give information about amounts of propanol-2 in substances, while head-space chromatography has determined concentration of this compound in all examined tinctures.

Ethyl alcohol for the perfumery and cosmetic industry of EU countries and most other countries of the world is denatured and exempt from excise duty (Denatured Alcohol), which is defined by the EEC Council Directive 92/83. Denatured alcohol is included as an ingredient in the European database of cosmetics and their ingredients COSMILE Europe. According to the International Nomenclature of Cosmetic Ingredients (INCI), ethyl alcohol is designated as Alcohol Denat and under this name it can be found in the list of cosmetic ingredients. Since 2004, alcohol denatured for the perfumery and cosmetics industry in Ukraine was subject to excise tax, which made the products made from it non-competitive. Alcohol-containing raw materials for perfumery and cosmetic products were imported or produced in Ukraine of dubious quality and origin. Consumption of ethyl alcohol in the industry fell from 200,000 decalitres a year to almost zero. The output of alcohol-containing perfumery and cosmetic products was decreased sharply.

The joint efforts of interested organizations and enterprises (State Enterprise «UKRSPYRT», Ltd. «SUPERMASH», the Ukrainian Association of Perfumery and Cosmetics, Ministry of Agrarian Policy and Food of Ukraine and other) for more than 12 years have led to the adoption of a number of laws that allow unblocking the production and circulation of denatured alcohol in Ukraine:

- it has been allowed to dispense denatured alcohol for the production of perfumery and cosmetic products (Article 229 of the Tax Code of Ukraine) since 2019,
- a list of denaturing additives for alcohol denaturation has been defined (Decree of the Cabinet of Ministers of Ukraine of 14.08.2019 No. 722), including for perfumery and cosmetic products,
- it is allowed to record denatured ethyl alcohol and products from it with mass flow meters in kilograms (Article 230 of the Tax Code of Ukraine).

Determination of the volume fraction of ethyl alcohol is carried out in accordance with DSTU 7457:2013 "Water-alcohol solutions. Methods of determining the content of ethyl alcohol" using glass hydrometers for alcohol or pycnometers, that is, the methods are based on the dependence of the density of the water-alcohol solution on the content of ethyl alcohol. Earlier studies (Kyziun et al., 2005) showed a significant effect of the presence of denaturing additives on the density of water-alcohol solutions and, accordingly, on the readings of alcohol meters when determining the volume fraction of ethyl alcohol. The measurement of the volume of ethyl alcohol according to the current regulatory documents is possible only during the measurement of the batch of alcohol that is sent for denaturation. After the denaturation process is completed, i.e. after adding denaturing additives and mixing the prepared batch of denatured alcohol, accounting for ethyl alcohol denatured according to the current methods, with accuracy in accordance with the current regulatory documentation, is impossible, for example, during the release of a part of the manufactured batch. The gas-liquid chromatography method has an undeniable advantage over other methods. Therefore, the improving of a technique for measuring the mass fraction of ethyl alcohol in water and water-alcohol solutions is relevant.

The aim of the research is to improve the technique for measuring the mass fractions of ethyl alcohol and microcomponents (aldehydes, esters, methanol, fusel oils, including propanols and butanols) in aqueous and aqueous-alcoholic solutions using gas chromatography with a vapor phase sampler.

Materials and Methods. The conducted scientific and research work was carried out in accordance with the priority direction of activity of the Scientific and Methodical Laboratory of Chromatographic Research, namely the improvement of measurement methods according to the direction of the laboratory's activity, the field of accreditation and production tasks. The proposed methodology for determining the mass fraction of alcohols was improved on the basis of the methodology according to the DFU (State Pharmacopoeia of Ukraine, 2014).

The research was carried out on an HP 6890 Plus gas chromatograph with a flame ionization detector, equipped with an automatic device for introducing a static vapor phase HP 7694 Headspace Sampler manufactured by Agilent Technologies Inc. (USA); using a capillary analytical column HP-624 (part No. 19091V-413, length 30 m, inner diameter 0.32 mm, film thickness of the stationary phase 1.8 μm) manufactured by Agilent Technologies Inc. (USA). When measuring the mass fraction of ethanol in water-alcohol mixtures, propanol is used as an internal standard. If it is necessary to determine other alcohols, fusel oils or denaturing additives, then propanol is not used as an internal standard, and calculations are made according to the calibration characteristic, where each point of the calibration characteristic is the arithmetic mean of two observation results. The calculation of the grading characteristic, which describes the dependence of the area of the chromatographic peak on the mass concentration, is performed by the method of least squares.

Research objects: hand sanitizers. The research was carried out at the request of the applicants for the compliance of the samples with labelling and detection of falsification by the State Enterprise "UKRMETRTESTSTANDART".

Results and Discussion. The principle of this technique consists in the transfer of volatile components, including ethyl alcohol, from the solution to the vapor phase, its introduction into the chromatograph, the separation of the mixture on a capillary column with subsequent registration of the signal on the flame ionization detector. The grading characteristic was set according to 5 mass concentration values of ethyl alcohol. Each point of the calibration characteristic is the arithmetic mean of two observation results. The calculation of the grading characteristic, which describes the dependence of the area of the chromatographic peak on the mass concentration, is performed by the least square method. The grading characteristic is considered satisfactory if the correlation coefficient satisfies the condition $r \geq 0.99$. If the value of the correlation coefficient is $r < 0.99$, then the calibration characteristic is considered unsatisfactory, the cause is found and eliminated, after which the procedure for constructing the calibration characteristic is repeated.

To prepare a perfume-cosmetic product for testing a sample of an aqueous or aqueous-alcohol solution of 1.0±0.01 g is taken into a measuring flask with a stopper with a capacity of 100 cm^3. After that, 40 cm^3 of distilled water is added to the flask. The flask is closed with a stopper, sample is stirred until complete dissolution and kept in a thermostat at a temperature of (20.0±0.1)°C for 20 minutes. Next, the sample is brought to the mark with distilled water, stoppered, and mixed thoroughly. 0.5 cm^3 of the diluted solution of the test substance is introduced into the prepared glass vial with a capacity of 20 cm^3 and the vial is stoppered. Similarly, a parallel sample is prepared. Measurements are carried out on an automatic static vapor phase introduction device HP 7694 Headspace Sampler in the following sequence (table 1):

- blank solution;
- a mixture solution for checking retention time (Mixture F);
- five grading solutions (Mixture A, Mixture B, Mixture C, Mixture D, Mixture E) (fig. 1).

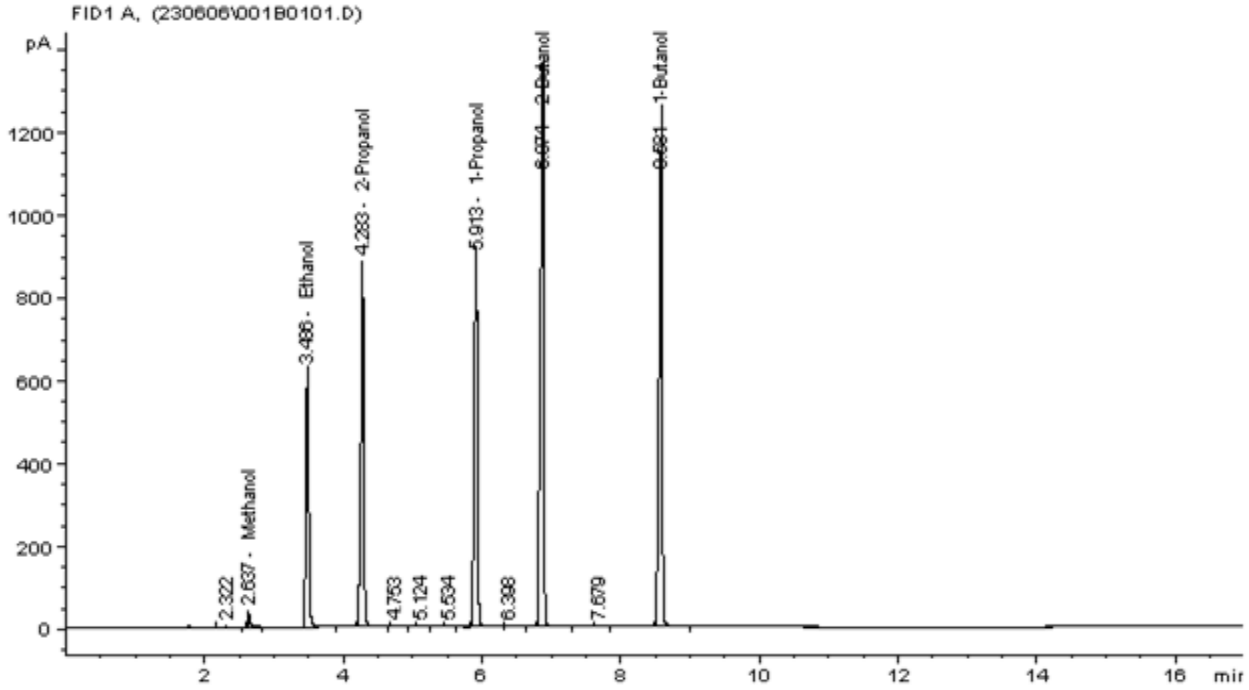

Fig. 1 Chromatogram of a standard sample of StMix alcohols (methanol, ethanol, 2-propanol, 1-propanol, 2-butanol, 1-butanol)

The sequence of placement of the grading solutions is from lower mass concentration to higher.

Table 1

Concentration of working solutions of mixtures of ethyl alcohol

Mass concentration, g/dm^3	Blank solution	Mixture A	Mixture B	Mixture C	Mixture D	Mixture E	Mixture F
	0,0	0,40	0,50	0,60	0,70	0,8	0,65
Mass of ethyl alcohol, g		0,4000 ±0,004	0,5000 ±0,005	0,6000 ±0,006	1,4000 ±0,014	0,8000 ±0,008	0,6500 ±0,007
Volume of the flask, dm^3	0,1	0,1	0,1	0,1	0,2	0,1	0,1

The blank solution was obtained from the same distilled water that was used in the preparation of standard solutions. The shelf life of solutions is 3 months, provided they are stored in a refrigerator at a temperature from +4 to +10°C.

Calculation of the mass concentration of ethyl alcohol in the solution of the prepared sample is performed according to the calibration curve. The calibration curve is set for 5 mass concentration

values of ethyl alcohol. Each point of the grading characteristic is the arithmetic mean of two observation results. The calculation of the grading characteristic, which describes the dependence of the area of the chromatographic peak on the mass concentration, is made using the method of least squares. Chromatography is performed on the prepared sequence. Identification of the ethyl alcohol peak on the chromatogram is carried out by the content time according to the table stored in the chromatographic system.

Ethyl alcohol and other volatile organic compounds are determined in a diluted solution of the test product using gas chromatography with a flame ionization detector. The prepared sample, the working solutions of the mixtures and the mixture for testing the retention time are heated in a stoppered vial. This allows to balance the content of volatile components present in the liquid and in the vapor phase. Part of the equilibrium sample of the steam is introduced into the gas chromatograph column.

The mass fraction of ethyl alcohol is calculated by the external standard method, according to the ratio of the areas of the chromatographic peaks of ethyl alcohol from the mass fraction of ethyl alcohol in solution.

Research has established the need to analyse a control sample (Mix D) in duplicate after every 10th sample and at the end of each sequence to verify calibration. The arithmetic mean of these two repetitions should be within ±10% of the value of the mass fraction of ethyl alcohol certified according to the preparation procedure. If this condition is not met, all measurements after the last acceptable control sample must be repeated.

It has been proven that all samples of the product must be measured in duplicate. The measurement results of two copies should be within ±10% of the average value of the measurement results of this sample. If this condition is not met, then the measurement must be repeated (for two samples of the product), and the results of the two new measurements must be within ±10% of the average value of the results of this sample. During the research, samples adulterated with propanol and containing toxic methanol, acetone, and methyl ethyl ketone were found in hand sanitizers (fig. 2 and fig. 3).

Figure 2 shows a chromatogram of a hand sanitizer sample in which an increased amount of toxic substances, the content of which is not indicated on the label, was found, namely, methanol-0.5 % and acetone-0.1 %.

Methanol or methyl alcohol, also known as wood alcohol, is used to make rocket fuel and antifreeze and is very toxic, since its decomposition produces toxic substances: formaldehyde, formic and lactic acids, which disrupt processes important for the normal functioning of the body. Methanol poisoning can occur after inhaling its vapors, as well as after absorbing them through the pores of the skin or when ingested. Without expertise, it is quite difficult to distinguish methanol from ethyl alcohol by appearance, smell and taste. The direct use of methanol in cosmetics is prohibited, and its impurities in life-threatening concentrations can be present in technical ethyl alcohol, denatured alcohol and its surrogates (Lanigan, 2001). According to the Technical Regulation on cosmetic products of Ukraine, it is permissible to use methanol to denature ethyl and isopropyl alcohol in an amount not exceeding 5% of the content of these alcohols.

Acetone and methyl ethyl ketone (MEK) are potentially toxic to the body through inhalation, ingestion or skin contact. People who are occupationally exposed generally complain of symptoms such as headaches, confusion, dizziness, irritation (in throat, nose and eyes) and loss of consciousness. The exposure limits are 2 mg/L and 50 mg/L for MEK and acetone respectively (Southon et al., 2020).

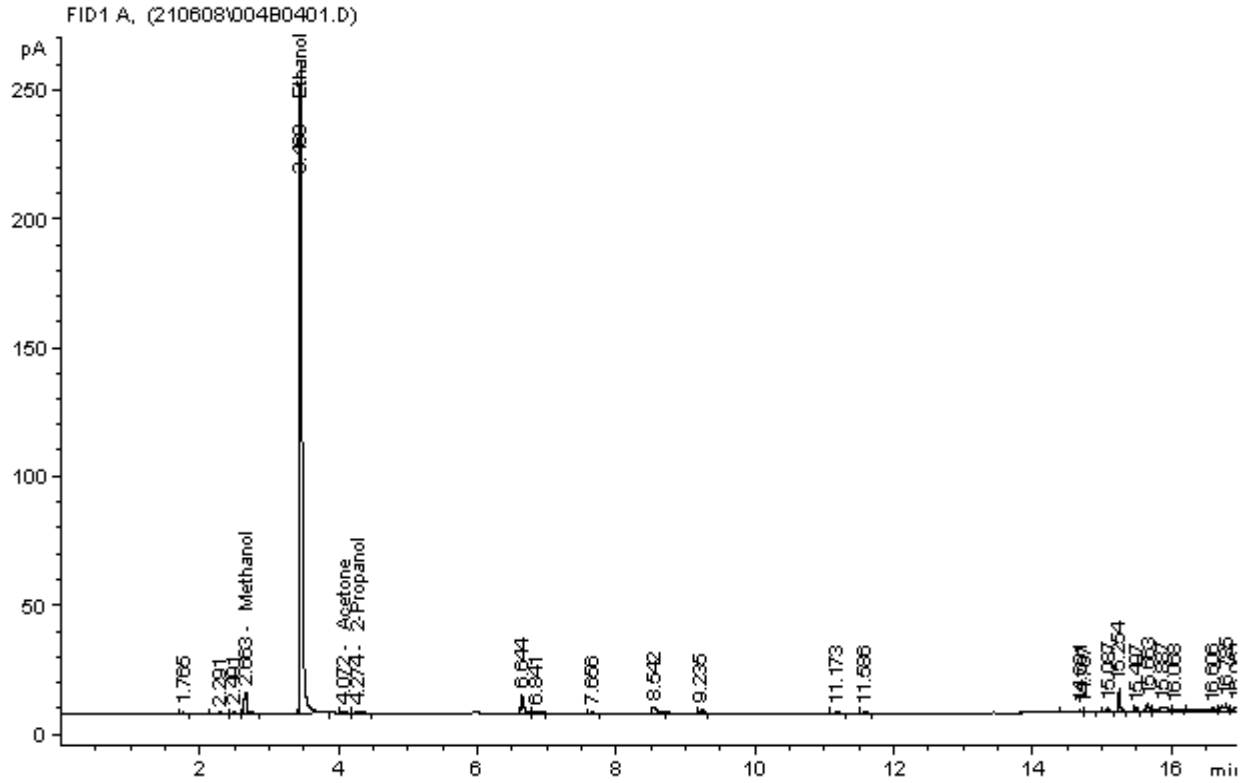

Fig. 2 Chromatogram of a sample of a water-alcohol solution of a hand sanitizer (ethanol – 87 %, methanol – 0.5 %, acetone – 0.1 %, 2-propanol – 0.5 %).

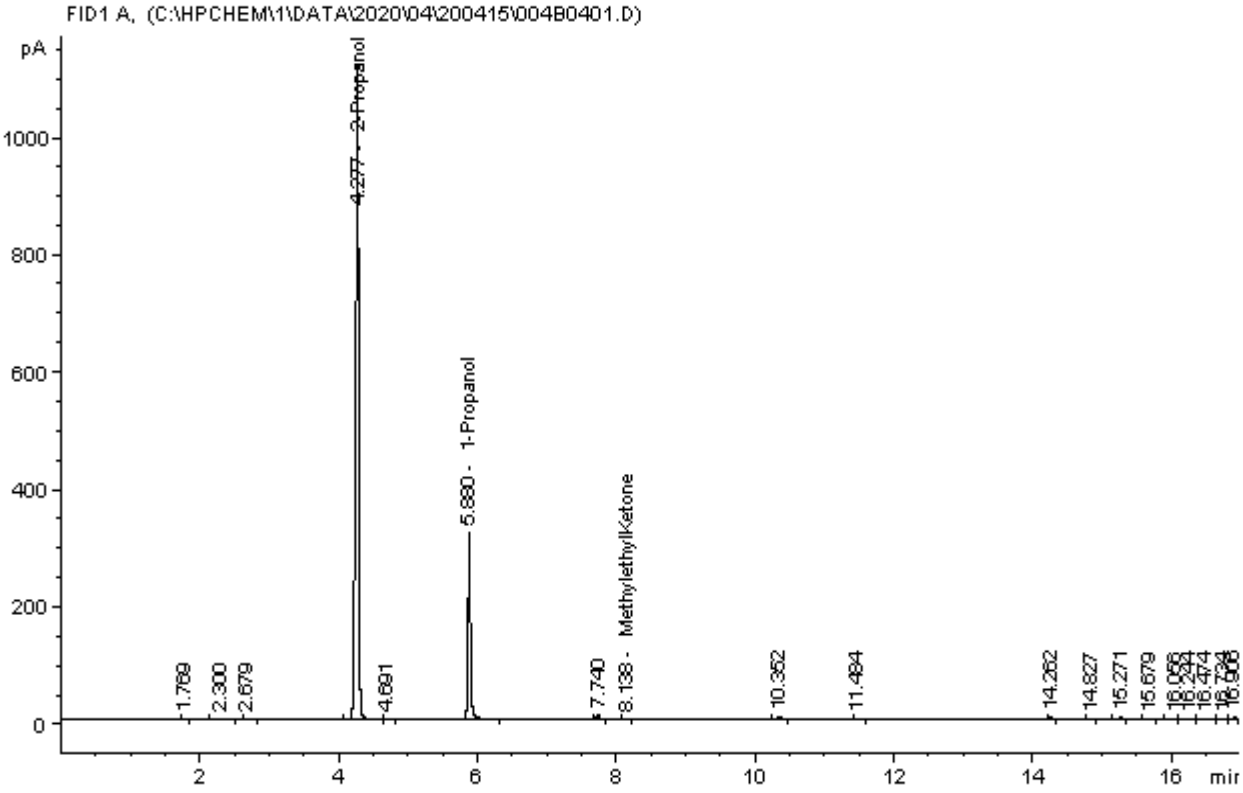

Fig. 3 Chromatogram of a falsified sample of a hand sanitizer (2-propanol – 76%, 1-propanol – 15%, MEK – 0,01%, no ethanol according to the label)

Figure 3 shows a chromatogram of a hand sanitizer sample falsified with propanol alcohols, with an ethyl alcohol content of 85% declared when labeling. Instead, the sample contains alcohol 2-Propanol in the amount of 76% and toxic substances, namely, 1-propanol in the amount of 15% and MEK in the amount of 0.01%.

Isopropanol (2-propanol) is routinely used as an active ingredient in hand sanitizers and surface disinfectants and is regulated as a separate product (Mahmood et al., 2020) with its own risks. In the current context of technical-grade ethanol as an ingredient, Health Canada identifies and controls isopropanol as an "impurity" and places a limit of 1000 ppm (Timothy et al. 2021). Isopropanol can cause hypotension and coma. The content of 2-propanol in medicinal products should not exceed 0.05% (State Pharmacopoeia of Ukraine, 2014).

1-Propanol or 1-propyl alcohol is used to make industrial solvents (a type of cleaner) and can be toxic to humans when swallowed. Hand sanitizer with 1-propanol contamination can irritate skin (or eyes, if exposed) and cause allergic reactions. According to the Technical Regulations on cosmetic products of Ukraine, the content of 1-propanol should not exceed 2.0%.

Conclusions. The improved technique makes it possible to control raw materials based on denatured alcohol and to test cosmetic products for the content of ethyl alcohol in water-alcohol and gel solutions, which will allow to confirm its quality and safety in accordance with the requirements of the Technical Regulation of cosmetic products. The technique is fast, reliable and requires no sample pre-treatment. Based on the results of studies of the composition of hand sanitizers, the effectiveness of an improved technique for determining the mass fraction of ethyl alcohol and microimpurities has been proved.

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