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ARTIFICIAL FLAVOURING AGENTS DETECTION IN DAIRY AND MILK-CONTAINING PRODUCTS

A detection method of 1,2-propylene glycole-based artificial flavouring agents by gas chromatography has been developed. This method can be applied for testing dairy and dairy-containing products regardless of their fat content. Detection limit of this method is estimated to be 0.10 mg per 100 g. Objects of research were 37 samples of butter ranging by their fat content (69 %, 73 %, 82.5 %), production place (domestic or foreign), 10 samples of spreads, 3 samples of fermented milk drinks and 4 samples of cheeses.

It was shown that majority (27 %) of butter samples with bad organoleptic characteristics contained 1,2-propylene glycol. It should be mentioned that according to the DSTU 4399:2005 "Butter: Specification" butter should not contain any artificial flavorings. In most cases, adulteration with artificial flavoring agents was observed for samples of butter and cheese with low organoleptic characteristics and milk fat replacement.

Keywords: artificial flavorings, dairy products, gas chromatography, butter, 1,2-propylene glycol.

Розроблено спосіб виявлення штучних ароматизаторів на основі 1,2-пропіленгліколю методом газової хроматографії у молочних та молоковмісних продуктах, який надає можливість ідентифікувати 1,2-пропіленгліколь незалежно від масової частки жиру у продукті. Мінімальна межа чутливості методу становить 0,10 мг на 100 г. Було досліджено 37 зразків солодковершкового масла, що відрізнялись за вмістом жирової фази (69 %, 73 %, 82,5 %) іноземного та вітчизняного виробництва, 10 зразків спредів, 3 зразка кисломолочних напоїв та 4 зразка твердого сичужного сиру.

Встановлено, що більшість (27 %) зразків вершкового масла з низькою органолептичною оцінкою містили 1,2-пропіленгліколь. Слід звернути увагу, що згідно вимогам ДСТУ 4399:2005 *"Масло вершкове. Технічні умови" масло вершкове не повинно містити ароматизаторів. Найчастіше фальсифікація штучними ароматизаторами спостерігалась в продукції масла солодковершкового та сирів з низькою органолептичною оцінкою, що містила замінники молочного жиру.*

Ключові слова: газова хроматографія, молочні продукти, солодковершкове масло, 1,2-пропіленгліколь, штучні ароматизатори.

Разработан способ обнаружения искусственных ароматизаторов на основе 1,2-пропиленгликоля методом газовой хроматографии в молочных и молокосодержащих продуктах, который дает возможность идентифицировать 1,2-пропиленгликоль независимо от массовой доли жира в продукте. Минимальный предел чувствительности метода составляет 0,10 мг на 100 г. Было исследовано 37 образцов сладкосливочное масла, отличались по содержанию жировой фазы (69 %, 73 %, 82,5 %) иностранного и отечественного производства, 10 образцов спредов, 3 образца кисломолочных напитков и 4 образца твердого сычужного сыра.

Установлено, что большинство (27 %) образцов сливочного масла с низкой органолептической оценке содержали 1,2-пропиленгликоль. Следует обратить внимание, что согласно требованиям ДСТУ 4399:2005 "Масло сливочное. Технические условия" масло сливочное не должно содержать ароматизаторов. Чаще всего

фальсификация искусственными ароматизаторами наблюдалась в продукции сладкосливочного масла и сыров с низкой органолептической оценкой, содержащей заменители молочного жира.

Ключевые слова: газовая хроматография, искусственные ароматизаторы, молочные продукты, 1,2-пропиленгликоль, сливочное масло.

Introduction. Starting from 20 January, 2011 Regulation (EC) No 1334/2008 of the European Parliament and of the Council on flavourings and certain food ingredients with flavouring properties for use in and on foods became the binding regulation in EU, amending Regulation (EC) No 1601/91 of the Council, Regulations (EC) No 2232/96 and (EC) No 110/2008 and Directive 2000/13/EC and replacing the former Flavouring Directive 88/388/EEC. This Regulation defines the rules of the use of flavorings and food ingredients possessing food flavorings properties in food products in order to guarantee the effective functioning of the internal market of the EU to protect the health and well-being of consumers and providing truthful information. The Regulation also provides for a Community list of flavorings and source materials accepted for use in food products, conditions of flavorings and food ingredients with flavouring properties application, as well as flavorings labeling conditions. Regulation (EC) No 1334/2008 applies to flavourings manufacturers as well as manufacturers of food products and drinks. Fragrances of many natural products are unstable, quickly disappear or undergo changes during technological processing and the vast majority of source materials for food products have no flavor. That makes conditions for production and use of food flavorings. In the same time, consumers have become choosier concerning quality of food products, in particular dairy products, consequently foregrounding the requirements for methods of their quality control [1, 2].

Flavourings: products which are not intended to be consumed as such, which are added to food in order to impart or modify odour and/or taste. They are made or consist of the following categories: flavouring substances, flavouring preparations, thermal process flavourings, smoke flavourings, flavour precursors or other flavourings or mixtures thereof [3].

According to the Russian GOST R 52464-2005 “Food flavour additives and food flavourings. Terms and definitions” flavorings are divided into next groups: natural flavorings, nature-identical flavourings and synthetic flavorings. In the USA, and now in the European Union, the term “nature-identical” is not used. The term “synthetic flavorings” there include both artificial and nature-identical flavourings. There are about 1500 artificial flavourings approved for use, belonging to such groups as: aldehydes, acetals, ketones, acids, lactones, alcohols, compound ethers, furans, pyrazines, sulfur-containing compounds and others.

Desired and unique butter flavour depends on delicate balance of concentrations of compounds with a low odour threshold. The crucial factor is a complex interaction between volatile, non-volatile compounds and food matrix. This balance upset resulting from addition or extraction of aromatic compounds may lead to flavor bouquet flaw. Likewise, presence of undesirable aromas and tastes may indicate the decrease of nutritional quality (loss of vitamins, oxidation of unsaturated lipids) and sensory characteristics of butter that in turn may lead to significant economic losses [4].

One of the common solvents and preservatives of foodstuff is 1,2-propylene glycol (E1520), registered as a water-retaining, softening and dispersing agent and added to dairy and dairy-containing products to enhance their flavor. Food propylene glycol is a “generally recognized as safe” (GRAS) additive for foods and medications. Propylene glycol rarely causes toxic effects and mostly have no side effects. However if propylene glycol concentration in plasma rises to more than 1 g/l may cause serious damages in the organism. Cases of propylene glycol poisoning is usually associated with excessive intravenous injection of medicinal drugs containing it or accidental ingestion of a large amount of it.

Intravenous administration of large doses of propylene glycol-containing medicinal drugs may cause hypotension, bradycardia, heart failure, hemolysis and more. Increased concentration of propylene glycol in indoor air may lead to the emergence of the respiratory and immune disorders. Excessive consumption of products containing propylene glycol E1520, can lead to kidney damage. Part of it is excreted unchanged, the remainder is oxidized to lactic acid.

Acceptable daily intake (DDA) of propylene glycol is 25 mg per 1 kg of body weight per day. In the production of cottage cheese the allowed concentration of propylene glycol used as a stabilizer is up to 5 g/kg individually or in combination with other stabilizers. As a carrier-solvent it may be added to flavorings, antioxidants, dyes, emulsifiers, enzymes in concentration not exceeding 1 g/kg of product [5].

Research objective. This research aimed the development of detection method of propylene glycol-based flavorings by gas chromatography as well as monitoring investigations of food products for presence of artificial flavorings.

Materials and methods. Objects of the study were samples of butter, spreads (spread - milk/vegetable fat mixture), cheeses, fermented milk drinks of domestic and foreign production. The analyzes were conducted using gas chromatograph "Krystallux 4000M", equipped with capillary column FFAP with length of 60 m, inner diameter of 0.25 mm, stationary phase thikness of 0.25 μm. Gas chromatography settings were as follows: column oven temperature – (60 – 180) ºC, temperature increase rate – 5 ºC/min, detector temperature – 200 ºC, injector temperature – 200 ºC.

Results and conclusions. As part of the project the method of detection of artificial flavours in dairy and dairy-containing products has been developed [6].

Objects of research were 37 samples of butter ranging by their fat content (69 %, 73 %, 82.5 %), production place (domestic or foreign), 10 samples of spreads, 3 samples of fermented milk drinks and 4 samples of cheeses.

It was shown that majority (27 %) of butter samples with low organoleptic characteristics contained 1,2-propylene glycol (Table 1).

Table 1.

Assessment of butter with low organoleptic characteristics for 1,2-propylene glycol content

Taste and flavour characteristics	*1,2-propylene glycol, mg/100 g of the product*
Butter with fat content of (80.0 – 85.0) % (Extra butter)	
№3 - pronounced artificial creamy, vanilla flavour	104,0
№4 - artificial flavour of lactones, slightly creamy flavour	33,4
№6 - creamy flavour, slightly bitter off-flavour	4,5
Butter with fat content of (72.5 – 79.9) % (Peasant butter)	
№13 - pasteurization and butter oil flavour	11,5
№15 - slightly creamy flavour, butter oil flavour	3,13
№18 – milk fat replacer off-flavour, stale butter flavour	11,2
№20 - milk fat replacer off-flavour, vegetable oil flavour	11,6
№25 - stale butter off-flavour, pronounced cheesy flavour	118,8
№27 – butyric acid artificial flavour	10,8
№28 - pronounced butter oil flavour	29,6

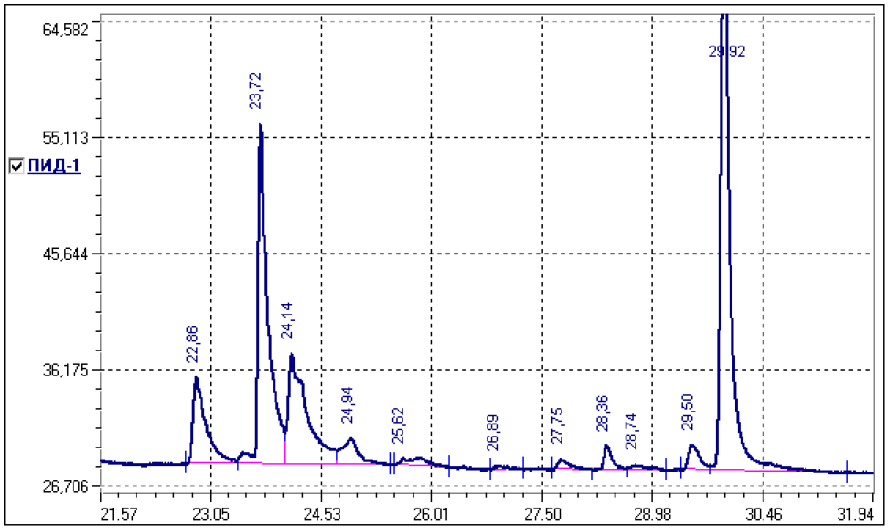
Table continuation 1

№29 - pronounced butter flavour	32,1
№ 31 - milk fat replacer off-flavour, green vegetables flavour	20,1
№ 32 – sweets and baked milk flavour	4,3

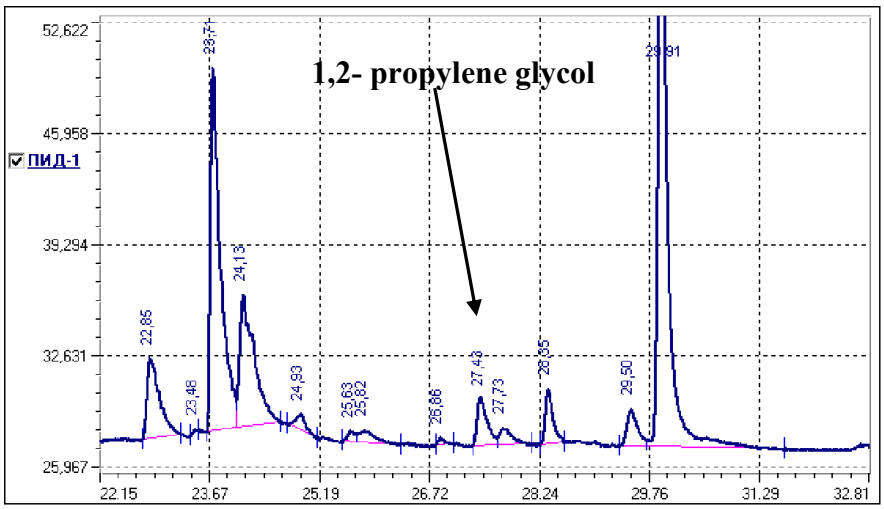
Note: Samples of butter not listed in the table contained no flavourings

It should be mentioned that according to the DSTU 4399:2005 “Butter: Specification” butter should not contain any flavorings or emulsifiers unlike the Russian GOST R 52969-2008 “Butter. Specifications”.

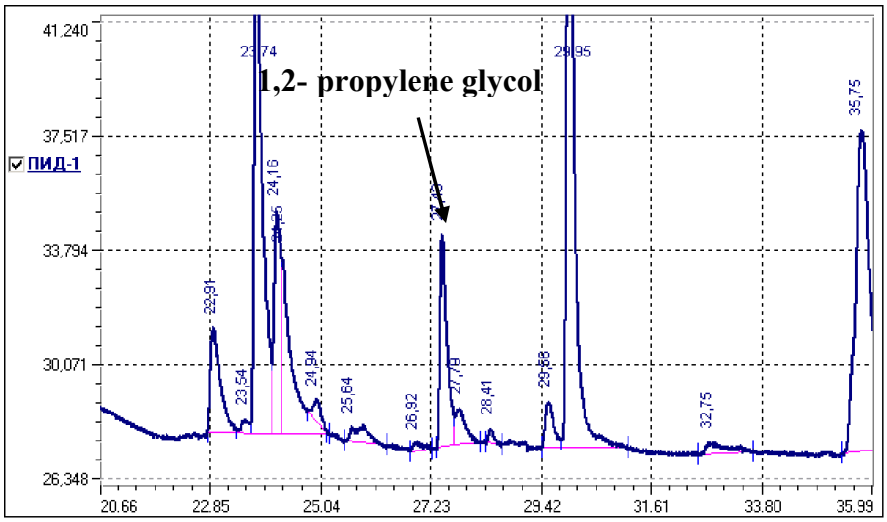
After storing the butter samples at a temperature of -18 °C for 75 days the content of 1,2-propylene decreased by about (40 – 70) % (Picture 1).



a) no flavorings



b) with flavourings



c) with flavourings

Picture 1. Chromatograms of peasant butter.

At Fig. 1a one can see a chromatogram of butter with good organoleptic characteristics. Comparison of this chromatogram with a standard chromatogram of propylene glycol has provided the evidence of artificial flavorings absence. The peak corresponding to propylene glycol with retention time of 27.28 min is not found at the chromatogram, that attests to the fact that propylene glycol-based artificial flavourings are not present in this butter. By comparison, Figures 1b-1c provides chromatograms of peasant sweat cream butter samples containing propylene glycol peaks.

Other dairy products such as spreads, fermented milk drinks and hard rennet cheese were investigated in order to verify the identification of flavorings based on propylene glycol. Table 2 shows the results of the study of products with low organoleptic characteristics.

Table 2.

Assessment of dairy and dairy-containing products with low organoleptic characteristics for 1,2-propylene glycol content

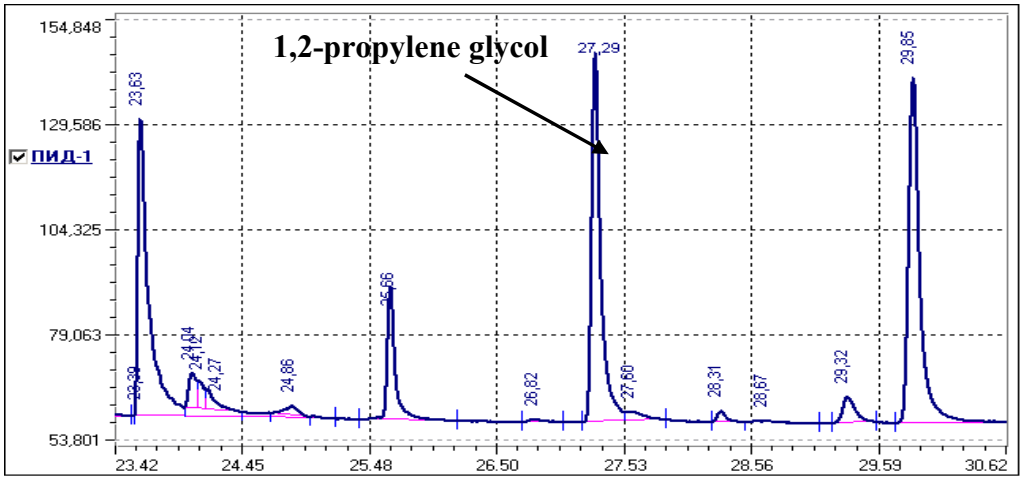
Taste and flavor characteristics	*1,2-propylene glycol, mg/100 g of the product*
Spreads with fat content randing from 50 % to 85 %	
№1 – weak creamy flavour	10.0
№2 – intense creamy flavour	81.5
№3 – pronounced diacetyl off-flavour	30.0
№4 – milk fat replacer off-flavour, weak creamy flavour	8.7
№5 – weak creamy flavour	12.0
№6 – pronounced butyric acid flavour	50.5
№7 – milk fat replacer off-flavour, pronounced green vegetabls	34.6
№8 – butter oil flavour	26.3
№9 – milk fat replacer off-flavour, weak creamy flavour	15.2
№10 – milk fat replacer off-flavour, weak creamy flavour	25.2
Fermented milk drinks with fat content randing from 1.5 % to 2.5 %	
№1 - pronounced sweets flavour	6.5
№2 - slight fruity flavor, diacetyl off-flavour	108.0

Table continuation 2

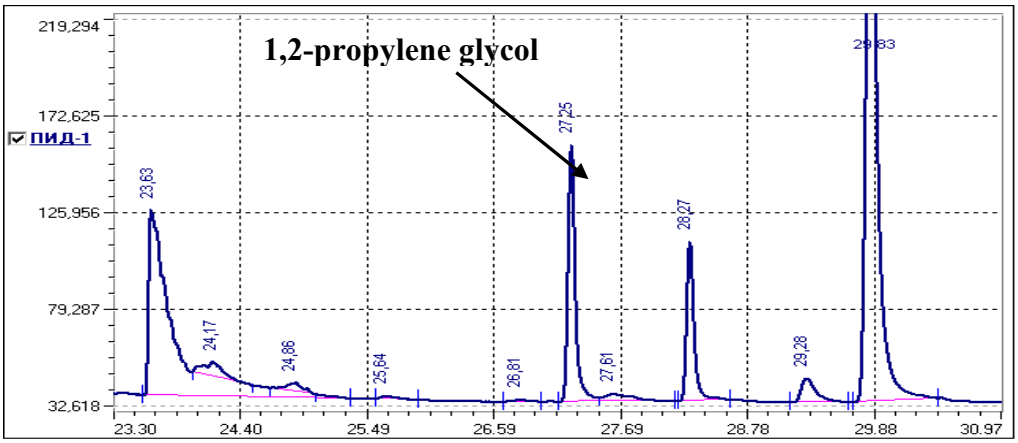
№3 – pronounced floral aroma	21.2
Hard rennet cheese with fat content of 45 %	
№1 – pronounced baked milk flavour	54.8
№2 – milk fat replacer off-flavour, weak creamy flavour	36.7
№3 - pronounced baked milk flavour	60.3
№4 - pronounced cheesy flavour	12.2

Note: All samples contained flavourings.

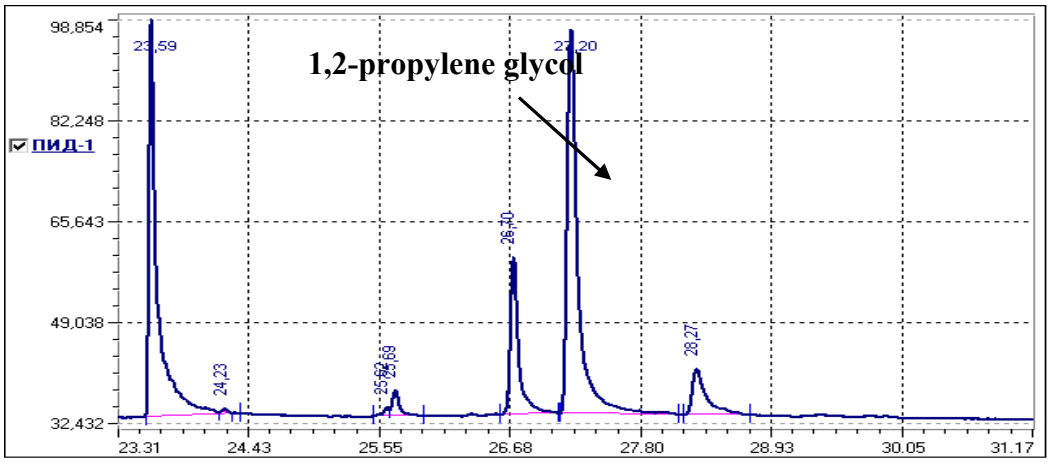
Dairy products analyses argue for the possibility of detection of flavourings based on 1,2-propylene glycol. It has been shown that flavourings of this type are widely used in manufacturing of spreads, fermented milk drinks and cheeses. Comparison of chromatograms of spread, yogurt and hard rennet cheese with the standard chromatogram of propylene glycol identified the presence of artificial flavorings in concentration of (8.7 – 81.5) mg/100 g, (6.5 – 108.0) mg/100 g, (12.2 – 60.3) mg/100 g, correspondingly (Figure 2).



a) spread



b) fermented milk drink



в) hard rennet cheese

Figure. 2. Chromatograms of spread, yogurt and hard rennet cheese, containing 1,2-propylene glycol.

Conclusions

It has been demonstrated that capillar gas chromatography method can be applied for testing dairy and dairy-containing products regardless of their fat content and minimum detection limit of this method is 0.10 mg per 100 g. Therefore this is a potent, valid, cost-efficient and convenient method for identification of artificial flavourings which may be applied for food products quality assessment.

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