

Methods For The Determination Of Fatty Acid Trans-Isomers In Palm Oil

Zafar Sadikov

Associate Professor at the Customs Institute of the Customs Committee of the Republic of Uzbekistan

e-mail:zsadikovs@mail.ru

Abstract: *the article highlights alternative ways of solving problematic situations that have arisen in the customs system and economic systems by ensuring the importation into Uzbekistan's domestic markets of goods of high quality and suitable for consumer consumption, stopping the importation of goods that pose a threat to human health and regulating the domestic market.*

Keywords: *vegetable oils, animal fats, methods of research of fat and oil products, triglycerides, sunflower oil, margarine, butter, assortment adulteration.*

Introduction

Food safety, nutrition and food security are inextricably linked. Unsafe food creates a vicious cycle of disease and malnutrition, particularly affecting infants, young children, the elderly and the sick.

Foodborne diseases are an obstacle to socio-economic development by placing an undue burden on health systems and damaging national economies, tourism and trade [1].

Food products are among the most imported goods to our country. Customs duty for these goods is also set at different rates. Therefore, an unscrupulous foreign trade participant tries to conceal the real information about the goods in order to avoid paying customs duties. Incorrect presentation of information in the documents for goods is the reason not only for applying tariff regulation measures to them, but also for incorrect application of non-tariff regulation measures. Therefore, it is important to know the different methods of examination of consumer goods, oil, meat and dairy products, their composition and ways to distinguish them from each other.

Expertise of goods, as a rule, is carried out to identify defects (to determine their significance), to establish the mechanisms of their formation, to determine the consumer characteristics of the object.

It is important to carry out customs expertise when carrying out customs control of goods. It is important to know the goals and objectives of this type of examination.

The main task of customs examination is to protect the domestic market from low-quality goods that pose a threat to human health. This is a very complex task and products need to be tested from different perspectives. Often, checking documents is only the first step, because certificates do not always fully correspond to the real quality. For this reason, some products are subject to epidemiological control. This will help prevent and detect the entry of potentially dangerous goods into the internal territory of the country.

The goals and objectives of customs examination can be called extremely complex. After all, checkpoints are the first obstacle on the way of smugglers supplying counterfeit products. Currently, the importation of counterfeit goods not only has a negative impact on the economy of the country, but also poses a serious threat to public health. This, in turn, imposes a huge responsibility on customs officers. An unscrupulous foreign trade participant may attempt to evade payment of duty or smuggle low-quality goods across the border, which requires very thorough customs control.

Methods

Food products are among the most imported goods in our country. Customs duty for these goods is also set at different rates. Therefore, an unscrupulous foreign trade participant tries to conceal the real information about the goods in order to avoid paying customs duties. Incorrect presentation of information in the documents for goods is the reason not only for applying tariff regulation measures to them, but also for incorrect application of non-tariff regulation measures. Therefore, it is important to know the different methods of examination of consumer goods, oil, meat and dairy products, their composition and ways to distinguish them from each other.

In recent years, the use of trans fats by food manufacturers has increased dramatically. Trans fats (or fatty acid trans-isomers) are a type of unsaturated fat. They are naturally present in meat and dairy products derived from ruminants (cows, sheep, goats). Trans fats in these products are naturally formed by bacteria during normal digestion in the stomach. On average, natural dairy products contain 2-6% trans fats, ruminant meat 3-9%, chicken and pork only 0-2%. The trans-isomer of the most common naturally occurring fatty acid is conjugated linoleic acid (CLA), which is found in milk fat and is considered healthy.

Artificial fats, also known as industrial trans fats or partially hydrogenated fats, are dangerous to health. An example of such trans fats is hydrogenated palm oil.

Hydrogenated palm oil is now used in the production of most food products. This, in turn, causes an increase in various diseases among the population. In particular, the fact that such trans-isomeric fats cause gastrointestinal, cardiovascular and even cancer diseases indicates the need to limit the consumption of these products.

As mentioned above, the use of trans fats, especially hydrogenated palm oil, by food manufacturers indicates the need for strict control over the importation of these products into the country.

According to the rules, the total percentage of saturated fats should not exceed 10 per cent of the total fats consumed.

Animal and vegetable fats and oils, products of their decomposition, finished edible oils; waxes of animal and vegetable origin are included in Group III of Section 15 of the current Commodity Nomenclature of Foreign Economic Activity of the Republic of Uzbekistan, and hydrogenated palm oil is classified in commodity position 1516 of this group. In the above commodity position all types of palm oil are classified irrespective of their physical state (liquid, solid and solid) and whether they are crude or refined. The melting point of palm oil is 33-56°C, depending on whether it is crude or refined (partially or fully hydrogenated). Therefore, it is advisable to detail them at the level of specific commodity sub-items in the nomenclature of foreign economic activity of the Republic of Uzbekistan, and at the same time to restrict the import of oils containing trans-isomers into the territory of the country. Restrictions on import of these goods will increase the number of cases of disguised import of such goods with similar goods. Therefore, the examination of imported processed palm oil is an important process.

In order to identify processed palm oils, their organoleptic and physico-chemical indicators as well as physical properties are studied. The physical indicators used for identification are density, refractive index, melting point and solidification temperature.

The melting point is the temperature at which the fat changes from a solid to a liquid state, and it depends on the ratio of fatty acids in the triglyceride molecule. As the amount of low molecular weight and unsaturated fatty acids increases, the melting point decreases.

Solidification temperature is the temperature at which the oil changes from liquid to solid.

Iodine number - characterises the amount of unsaturated compounds in 100 g of oil and is equal to the reactant consisting of halogens bound to the oil, expressed in grams of iodine. Iodine number characterises the quality and degree of saturation of the oil.

The acid number represents the quantitative content of free fatty acids in the oil; their increase causes the hydrolytic breakdown of glycerides.

The measurement of melting point is one of the most important parameters in the analysis of palm oil. Measurement checks are carried out based on the requirements of GOST ISO 6321-2019.

Method for determining the melting point of palm oil or its fractions

Essence of the method. The essence of the method for determining the melting point is to measure the temperature at which palm oil or a fraction thereof changes from a solid to a liquid state. The method is applicable in the melting point measurement range from 12 °C to 70 °C.

Methods for the determination of fatty acid trans-isomers

Chromatographic, spectral and hybrid methods of analysis are often used for fatty acid trans-isomers [6].

Chromatographic methods for the determination of hydrogenated fatty acids

The most promising chromatographic methods for the determination of hydrogenated fats are capillary gas-liquid chromatography (GCLC) [7,8,9-13], high-performance liquid chromatography (HPLC) and silver-ion HPLC [14-17], because any hybrid methods are much more expensive.

At present, satisfactory analytical results for acids of fats containing trans fatty acids are obtained by gas chromatography (GC) using capillary columns with an extremely polar cyano-silicone stationary phase. In capillary gas chromatography methods, a key limitation has been the incomplete separation of trans isomers from its cis acid; however, improvements in separation are achievable with the use of 100-metre columns. These columns, allow for insignificant overlap between cis and trans isomers.

Trans-fatty acids in food are often analysed by gas-liquid chromatography (GLC) as methyl esters [7-9]. However, this method is fraught with distorted results due to insufficient separation of cis- and trans-isomers. Separation can be optimised by preceding Ag⁺ thin layer chromatography (Ag-TLC), but this is time consuming. An efficient method for separating 18-carbon fatty acid trans-isomers has been developed by combining GC of LC methyl esters with GC of fatty acid derivatives of 4,4-dimethylloxazoline compounds. The combination of GLC determinations of methyl ester derivatives and fatty acid derivatives of 4,4-dimethylloxazoline compounds improves the quantification of 18-carbon fatty acid isomers and possibly replaces the difficult and time-consuming Ag-TCA [10,11].

Silver ion HPLC is commonly used for the separation and determination of trans 18:1 isomers in partially hydrogenated oils and milk fats [14,15]. The application of HPLC with Ag^{*} ions for the separation of isomers of unsaturated monoenic and polyenoic fatty acids is considered. The influence of the type of chemical derivatisation of LCs on the efficiency of their separation is discussed and it is noted that the most optimal for the analysis are specific aromatic derivatives of LCs. The achievements of Ag-HPLC for the determination of octadecenoic and actadecadienoates with conjugated triple bonds in partially hydrogenated oils and milk fat are described [16-17].

Spectroscopic methods of hydrogenated fats determination

A large number of works are devoted to the identification and determination of hydrogenated fats by spectral methods: infrared spectroscopy, Fourier infrared spectroscopy, the method of disturbed total internal reflection (TIR) infrared spectroscopy.

It is known to determine the mass fraction of isolated trans-isomers of fatty acids by the method of disturbed total internal reflection (TIR) [8,18]. The method is designed for express (about 5 min) determination of the mass fraction of isolated trans-isomers in fat products with the level of trans-isomers 1% and more. The method is not applicable to products: containing high levels (more than 5%) of conjugated unsaturated bonds (e.g., tung oil); containing functional groups that change the intensity of C-H deformation double bonds in trans-configuration (e.g. castor oil containing ricinoleic acid or its geometric isomer, ricinelaic acid (12-hydroxy-E-otadecenoic acid)); representing mixed triglycerides having long- and short-chain radicals (like diacetostearin); any other containing components having functional groups that give absorption bands close enough to the C-H band of a strained isolated double bond in the trans configuration with a frequency (wave number) of 966-968 cm⁻¹.

A new and rapid (5 min) Fourier-IR spectroscopy method for the determination of total isolated trans fatty acids that absorb at 966 cm⁻¹ was developed, co-researched and applied to food products containing 1-50% trans fat (as a percentage of total fat) [6].

Quantitative and qualitative assessment of trans fatty acid isomers is difficult because of the wide range of positional mono-, di- and trieno fatty acid isomers that is present in hydrogenated oils.

The possibility of using the method of Fourier transform infrared spectroscopy for rapid simultaneous determination of cis- and trans-isomers, iodine number and saponification number of edible oils was shown. Measurements were carried out in the near infrared spectrum 10000-4000 cm⁻¹ with processing of the obtained data with the help of application software package. Using the method of least squares 2 calibration graphs were obtained - for hydrogenated soybean oils and for oils of different types. The method is recommended for wide application at the enterprises of food industry [19].

Hybrid and combined methods of hydrogenated fats determination

A new group of promising methods of analysis are hybrid and combined methods, which allow to reduce the limits of determination, increase selectivity, and expand the area of application.

Hybrid methods are used: the method of gas chromatography combined with thin-layer chromatography [20-23] with mass spectrometric detection after preliminary methyl transesterification of fatty acids [23-27].

Conclusion

The choice of method depends on the specific objectives of the study, the resources available and the specificity and sensitivity required. The optimal approach often involves a combination of different methods to achieve the best results in the analysis of fatty acid trans-isomers in palm oil.

References

1. www.who.int
2. Методичка по экологии продуктов питания. www.ncbi.nlm.nih.gov/pubmed
3. Riya Ganguly, Grant N. Pierce. The toxicity of dietary trans fats. Food and Chemical Toxicology, V. 78, 2015, P.170-176.
4. В.Вишнякова. Что такое гидрогенизированное пальмовое масло и стоит ли его бояться? www.journal.tinkoff.ru
5. Екатерина Соловьева. Транс-жиры и пальмовое масло. www.azbyka.ru
6. Ф.А.Чмиленко, Л.П.Сидорова, Н.П.Минаева. Методы и объекты химического анализа. 2010, Т.5, №3, с.106-117.
7. ГОСТ Р 51483-99. Масла растительные и жиры животные. Определение методом газовой хроматографии массовой доли метиловых эфиров индивидуальных жирных кислот к их сумме.
8. ГОСТ Р 52677-2006. Масла растительные и жиры животные и продукты их переработки. Методы определения массовой доли транс-изомеров жирных кислот.
9. Study of individual trans- and cis-16:1 isomers in cow, goat and ewe cheese fats by gas-liquid chromatography with emphasis on the trans-delta3 isomer / Destailats F, Wolff RL, Precht D. Molkentin J. // Lipids. - 2000. - vol. 35(9). - P. 1027-1032.
10. Rapid analysis of the isomers of trans-octadecenoic acid in milk fat/ Dietz Prechta, Joachim Molkentime // International Dairy Journal. - 1996. - vol. 6(8). -P.791-809.
11. Determination of trans octadecenoic acids by silver-ion chromatography-gas liquid chromatography: an intercomparison of methods // Buchgraber, M; Ulberth, F // J. Amer oil Chem. Soc. Int. - 2001. - vol. 84(5). - P. 1490-1498.
12. Precision of low trans fatty acid level determination in refined oils. Results of a collaborative capillary gas-liquid chromatography study / Bruggen, F., Duchateau, G., Mooren, M., Oosten, H. // J. Amer oil Chem. Soc. -1998. - vol. 75(4). - F. 483-488.
13. Analysis of cis- and trans- fatty acid isomers in hydrogenated and refined vegetable oils by capillary gas-liquid chromatography / G. S. M. J. E.Duchateau, H. J. van Oosten, M.A. Vasconcellos // J. Amer Oil Chem. Soc. - 1996. - vol. 73(30). - P. 275-282.
14. Utilisation of reversed-phase high-performance liquid chromatography as an alternative to silver-oin chromatography for the separation of cis- and trans-C13:1 fatty acid isomers / Pierre Juaneda // Journal of Chromatography A. - 2002. -vol. 954(2). -P.285-289.
15. Trans-free margarine from highly Saturated Soybean Oil / Li Lee Kok, Walter R Fehr, Earl G. Hammond and others // J. Amer Oil Chem. Soc. - 1999, - vol. 76(10). -P.1175-1180.

16. Silver ion HPLC for the analysis of positionally isomeric fatty acids / Nikolova-Damyanova B., Momchilova Sv. J. // *Liq. Chromatogr. and Relat Technol.* 2002. 25, №13-15. P.1947-1965.
17. Wolff, R.L. Content and Distribution of trans-18:1 Acids in Ruminant Milk and Meat Fats. Their importance in European Diets and Their Effect on Human Milk // *J. Amer. Oil. Chem. Soc.* - 1995, -vol. 72(3). -P.259-272.
18. Fourier transform infrared spectroscopy: a newly developed, non-invasive method to measure body fat: non-invasive body fat content measurement using FT-NIR // Azizian H. // *Lipids.* 2007. -vol. 6. -P.154-160.
19. Simultaneous determination of iodine value and trans content of fats and oils by single-bounce horizontal attenuated total reflectance Fourier transform infrared spectroscopy / Sedman J., Van de Voort F.R., Ismail A.A. // *J. Amer Oil Chem. Soc.* 2000. 77, №4, -P.399-403.
20. Methods for analysis of conjugated linoleic acids and trans-18:1 isomers in dairy fats by using a combination of gas chromatography, silver-ion thin-layer chromatography/gas chromatography, and silver-ion liquid chromatography / Cruz-Hernandez Cristina, Zeyuan Deng, Jianqiang Zhou and others // *J. Amer oil Chem. Soc. International.* - 2004. - vol. 87(2). - P. 545-562.
21. Quantification of trans fatty acids in food products by GC. ATR-FTIR and FT-NIR methods / Hormoz Azizian. John K.G. Kramer, Anthony R Kamalian and others // *Lipid Technology.* - 2004. - vol. 16(10). -P. 229-231.
22. Detection of trans-fatty-acids content in margarine - an intercomparison study of GLC, GLC+TLC, FT-IR, and optothermal window / D Bicanic, M. M Chirtoc, Jp Favier and others // *Analytical Chemistry.* - 1999. -vol. 68(5). - P.00729-00733.
23. Trans fatty acids (TFA): analysis, occurrence, intake and clinical relevance / Steinhart H, Rickert R, Winkler K. // *Eur. J Med Res.* - 2003. - vol. 8(8). - P.358-362.
24. Gas chromatography - mass spectrometry determination of metabolites of conjugated cis-9, trans-11, cis-15 18:3 fatty acid / Frederic Destailatsa, Jean-Louis Sebediob, Olivier Berdeauxb and others // *Journal of Chromatography B.* - 2005. - vol. 820(1). - P.15-22.
25. A simple method for the analysis of trans fatty acid with GC-MS and ATTM-Silar-90 capillary column / Zhiliang Huang, Baowu Wang, Aneesha A. Grenshawa // *Food Chemistry.* - 2006. - vol. 98(4). - P.593-598.
26. Recent developments in instrumental analysis for food quality / André Müller, Hans Steinhart // *Food Chem.* 2007. 101, №3, P.1136-1144.
27. Analysis of isomeric long-chain hydroxy fatty acids by tandem mass spectrometry Application to the diagnosis of long-chain 3-hydroxyacyl CoA dehydrogenase deficiency / Jonson D. W., Trinh M.U // *Rapid Commun. Mass Spectrometry*, 2003. 17, №2, P.171-175.