Available online www.jsaer.com

***Journal of Scientific and Engineering Research*, 2018, 5(7):163-172**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Effective Spectrometry of Position Isomers of Triglicerides in Animal Fats and Plant Oils

Andrei Kalinin*[1], Vladimir Titov[2]

[1]Institute for Spectroscopy of Russian Academy of Science, Russia, 142190, Moscow, Troitsk
[2]National Medical Research Center of Cardiology, Ministry of Health of the Russian Federation, Russia, 121552, Moscow

Abstract Rapid identification and assessment of the content of animal fats and plant oils in the food and blood of patients are possible, as is known, using Raman spectrometry. On the other hand, the applicability of IR spectrometry for quality control of fat and oil products is well known. It is important to simplify and reduce the cost of these applications for practical use. The aim of the work was to test the applicability of near-infrared (NIR) spectrophotometers for the differentiation and analysis of fat-oil products, taking into account the isomeric forms of triglycerides. Using the method of projection on latent structures, Raman and NIR spectrometers were calibrated to determine the proportion of milk fat and palm oil and the fractions of 7 fatty acids in fat and oil mixtures. It was found that the prediction parameters of calibration (reliability, accuracy and selectivity) for the proportions of milk fat and palm oil, both using the Raman spectra and the NIR absorbance spectra, is much better than the determination of the same fat and oil proportions calculated from the content of 7 fatty acids. This fact reflects the sensitivity of prediction both using the Raman spectra and the NIR absorbance spectra not only to the length of the carbon chain and the degree of unsaturation of the fatty acid, but also to different positional isomers of triglycerides. The data obtained were used to formulate the technical requirements for the use of a portable NIR spectrometer for express analysis of fat-oil products.

Keywords triglyceride position isomers, spectrometer calibration

Introduction

All natural fats and oils consist of approximately 98.5% of triglycerides (TG) - esters of different fatty acids (FAs) with trihydroxyl alcohol glycerol. The FAs are characterized by the number of carbon atoms in the chain, the degree of unsaturation - the number of double bonds (C = C), and their position between carbon atoms. In addition, TG FAs are differing in positional isomerism, i.e., the bond place between the FA and the C atoms of glycerol: the primary ester bonds are at sn-1 and sn-3 positions and the secondary ester bond is at sn-2 position (Figure 1).

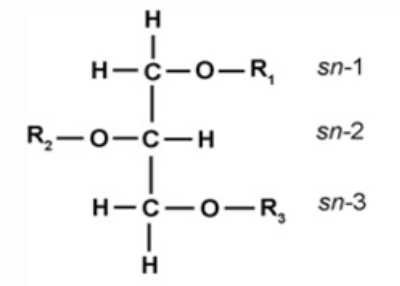

Figure 1: Triglyceride with R_1, R_2 and R_3 – the radicals of FAs in positions sn-1, sn-2 and sn-3

The person consumes vegetable oils obtained by pressing fruits (olive), seeds of cereals (corn), oilseeds (sunflower, flaxseed), legumes (soybean, peanuts), mustard crops (canola oil). All vegetable oils are liquid;, unsaturated FA predominates in position sn-2 of TG, mainly olein monounsaturated ω-9, cis C18: 1(MUFA). On the other hand, in hard fats of animal origin, for example, in milk fat, the palmitic saturated C16: 0 FA (SFA) is dominated in position sn-2 [1]. In the pork fat of an epiploon in sn-2 position the myristic C14: 0 SFA predominates. They can also be characterized by the composition of the positional isomers of TG; they mainly esterified myristic, palmitic SFA that have a melting point of + 63 ° C and a stearic SFA with a melting point of + 73 ° C, in the form up to unphysiological positional isomers of TG, such as palmitoyl-palmitoyl-palmitate (PPP) or stearyl-stearyl-stearate (SSS). Palmitic, stearic and myristic TGs (myristoyl-myristoyl-palmitoleate) give the fat a firm consistency; bovine, mutton fat, fat of marine animals, for example, whale, are solid. These TGs have a high melting temperature and a low rate of all metabolic reactions, including lipolysis, of the release of FAs from TG as free fatty acids (FFA) into the intercellular medium [2]. We divide TG into palmitic, oleic, stearic, linoleic, etc. types depending on which FA is esterified in position sn-2 with the secondary alcohol group of glycerol.

It is known [3-5] that the body cells assimilate positional isomers of TG from food by specific enzymes and hormonal mediators that activate them and FAs are most fully absorbed from the position of sn-2. So, pancreatic lipase, hydrolyzing exogenous TGs from food, shows a pronounced positional specificity. It hydrolyses the ester bond, primarily from the position sn-1, then from sn-3 and cannot hydrolyze the bond from the sn-2 position. Therefore, in the hydrolysis of TG palm oil in the small intestine, the entire palmitic SFA is released from TG in the form of FFA, and all oleic MUFA enterocytes are absorbed in the form of 2-glyceryl monooleate.

If oleic TGs such as OOO or, to a lesser extent, OOP dominate in the olive oil, then oleic positional isomers of TGs such as POO, OOP and POP, dominate in palm oil, therefore the entire palmitic SFA is esterified with primary alcohol groups of glycerol in sn-1 or sn-3 positions; and only oleic MUFA is esterified with the secondary alcohol group in the sn-2 position [6]. Since cells in vivo absorb the entire palmitic SFA from TGs of cow's milk, the enterocytes cannot absorb from palm oil most of the palmitic SFA in the form of FFA and a significant part of SFA is lost with intestinal contents [7].

It is known that the addition of palm oil with a high content of palmitic SFA (≈40%) to food increases the cholesterol (CH) content in the blood plasma. However, the content of cholesterol in low-density lipoprotein (LDL) in volunteers is four times less pronounced (only 27%), compared with the addition of milk fat [7]. With such a small increase in LDL cholesterol when palm oil is consumed, there is no reason to regard it as a risk factor for the pathology of the cardiovascular system, atherosclerosis and atheromatosis either on the basis of clinical observations [8] or from the experimental data [9].

Such a pronounced difference in the content of LDL in the blood plasma when we add equal amounts of butter and palm oil to the food depends, we believe, on two factors: a) the physico-chemical difference of the positional isomers of TG in plant palm oil and animal fat of milk; b) features of the steric (positional) specificity of the enzyme - pancreatic lipase and its cofactors - bile acids, active endogenous detergents. As a result, since palm oil has a positional isomerism of plant oil (oleic MUFA C18: 1 at position sn-2), its SFA from positions sn-1 and sn-3 are not intended for metabolism in vivo and is not practically absorbed by humans. On the other hand, oleic MUFA and small amounts of unsaturated and polyunsaturated FAs hydrolyzed from sn-1 and sn-3 positions of milk TGs, do not enter into the physical and chemical reactions with the contents of the small intestine, in contrast to palmitic SFA [5], but enterocytes from heterogeneous micelles absorb the palmitic SFA of milk in the form of 2-glyceromonooleate; they reesterify the SFA into the same TGs and include them into the chylomicrons (XM). XM with palmitic TGs of milk reaches the liver in the flow of lymph, blood. Further, hepatocytes, after optimizing the exogenous FAs, structure palmitic TGs into the same-named lipoproteins of very low density; in them exogenous palmitic SFAs are absorbed by primarily insulin dependent cells, by apoE / B-100 endocytosis [6]. Thus, how much palmitic SFAs contain fatty cow milk, fatty dairy products (sour cream and cheeses), cream fat, as many of them, according to physico-chemical and biological patterns, will be absorbed by the cells.

It should be noted that palm oil in food, as a rule, contains trans fats that arise during its industrial processing. Therefore, American regulations do not allow its use in food.

The different role of plant and animal TG in the metabolic processes of the human body leads to the need to control the isomeric forms of TG in food and blood, in particular, in patients of cardiac clinics.

In a number of works [10-12], the possibility of identifying and quantitatively determining positional isomers of TGs using the spectra of Raman scattering of laser light and the regression on projections of latent structures (PLSR) was established. In the work of M. Motoyama [12], variations in the Raman spectra of mixtures of two standard positional isomers of triglycerides of major oleic and palmitic FAs have been studied in detail, please, see, Fig. 2. It has been shown that it is possible to distinguish between fats and oils by comparing their isomorphic forms using Raman spectroscopy, but no natural fats and oils have been studied.

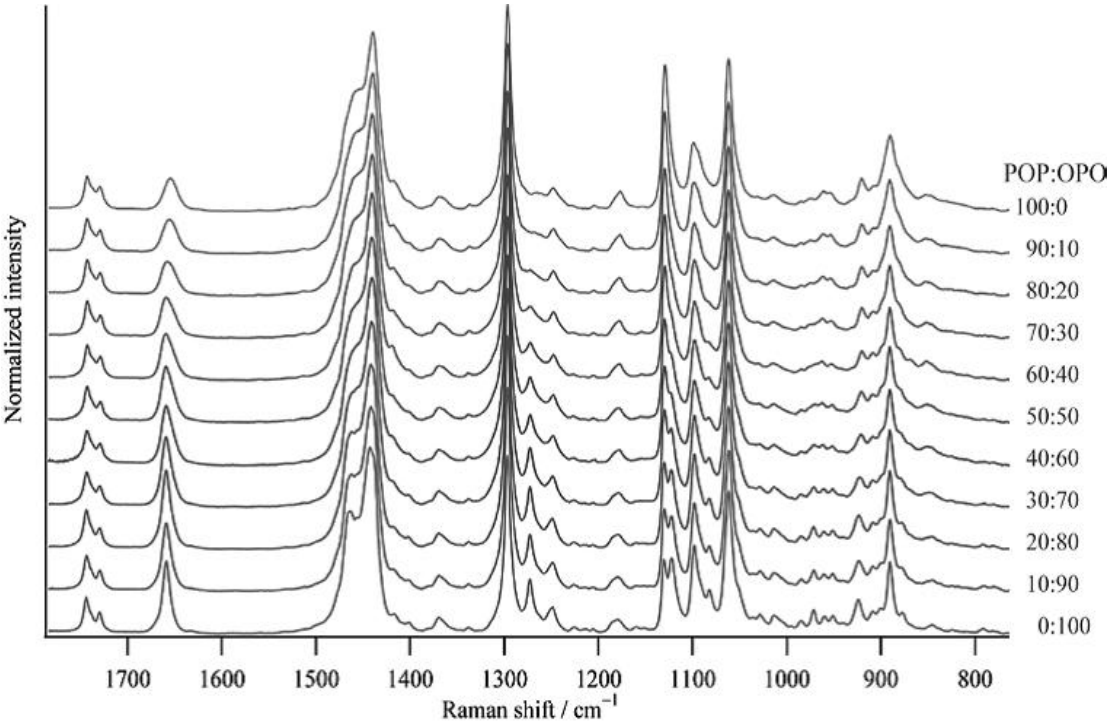

Figure 2: Raman spectra of eleven POP-OPO binary mixtures [12].

Since we previously studied mixtures of plant oils and butter with the method of spectrophotometry in the near infrared (NIR) range [13], it seems relevant to investigate correlations of NIR spectra with positional isomeric forms of oils on the basis of comparison of models using NIR spectra and Raman spectra and answer the question, whether it is possible to identify animal fats and plant oils using the NIR -spectrophotometer taking into account positional isomerism of TG FAs.

The purpose of this work was to evaluate the feasibility of analyzing the positional isomers of TGs characteristic of milk fat and palm oil, using Raman and near-IR absorption spectrometers. This problem was solved by calibrating spectrometers to determine both the content of 7 regulated FA, and the proportion of milk fat and palm oil in fat-and-oil mixtures using the projections on latent structures [14]. The second goal was to study the suitability of Raman spectrometry for the differentiation of animal fats and plant oils by the positional isomers of TGs.In addition, the efficiency of NIR spectrophotometer calibration (in terms of reliability, accuracy and selectivity) to determine the proportion of cream and palm oils was compared to the effectiveness of determining the same proportion based on analysis of 7 fatty acid contents. Also, the technical requirements and conditions for the use of a portable spectrometer for an express analysis of the quality of fat-oil products were formulated

Materials and Methods

Forming of calibration and test sets of samples

Spectrometric analysis of mixtures of organic molecules involves laborious calibration of the spectrometer for a large number of standard samples with a change in the concentrations of several (not only detectable, but also interfering components). Earlier, we described and tested the "economical" method of PLC calibration [15, 16],

which gives good parameters for determining the content of 3 components using a NIR spectrometer with a special choice of the concentration distributions of components in a batch of 35 standard calibration samples. In these studies, the preparation of lots of standard calibration and test oil mixtures was based on the inclusion in the calibration of only boundary, axial and central samples (by component concentrations). 35 calibration and 15-18 test samples, according to our data [15, 16], was suitable for obtaining suitable metrological parameters and laboriousness for determining the content of the three components.

A similar approach was carried out in the present work in the construction and testing of PLS models based on 50 batch # 1 samples for determination of the saturated C4: 0, C14: 0 and C16: 0 saturation in mixtures of milk fat (MF) and palm oil (PO), and also 51 samples of batch No. 2 to determine the content of C18: 0, C18: 1 and C18: 2 FAs in mixtures of MF, PM and small additives of olive oil in order to simulate the composition of the FAs in butter. The parameters of the samples are shown in Table. 1. To create the specified variations of the fractions of three FAs in batches of samples other than the starting materials - milk fat, palm oil and olive oil, n-octane diluent ("Fluka Analytical", Germany) was also used. The batches of standard samples were obtained by mixing the raw materials calculated in accordance with the "economical" method of weighed samples, previously measured by the FA content, using a Crystallux-4000M gas chromatograph (LLC "Interchrom", RF), in accordance with GOST R 51483-99 "Plant oils and fats . Determination by mass spectrometry of the mass fraction of methyl esters of individual fatty acids to their sum ", with a preliminary calibration of it with a mixture of standards for methyl esters of fatty acids (FAME., Mix C4-C24, Supelco, No. 18919). Then, the content of the seven FAs, named above, in two batches of calibration and test samples was checked by measurement on the same chromatograph. The samples were stored at room temperature under "soft" conditions to avoid transesterification [17] and used for spectrometry for two weeks. Before being measured in NIR spectrometers, the samples were heated to 59 ° C in a thermostat. The fraction of lauric FA C12: 0 was determined from the high correlation (0.98) with the FA C4: 0 [18].

Table 1: Ranges of variations in the fractions of FAs and oils (analytes) in 2 batches of calibration and test samples (in %)

№	Number	Analyte								
		C4:0	**C12:0**	**C14:0**	**C16:0**	**C18:1**	**C18:0**	**MF**	**PO**	**Ol**
1	35 + 15	0.5-4.2	0.5-5	6.0-14	14-33	21-42	2.5-8.5	20-80	10-60	-
2	35 + 16	0.5-3.0	0.5-4	5.0-11	14-25	24-48	2.3-3.8	20-70	20-40	0.5-20

Note: Ol – olive oil.

Sample preparation of mixtures of raw materials was performed without the use of solvents in accordance with the methods described earlier, namely [16, 19]:

a) the product was heated to 60 ° C and centrifuged at 4000 rpm for 6-18 minutes;

b) the lower aqueous fraction was drained through a hole in a test tube;

c) the upper part (sometimes with protein-containing foam) was filtered out in a thermostat at 59 ° C.

Spectral methods, instruments and measurement conditions

NIR absorption spectra of both batches of standard samples containing milk fat were measured three times (to verify reproducibility) in a 10 mm cuvette with the help of the diffractive NIR spectrometer created at the Institute of Spectroscopy of the Russian Academy of Sciences [20] in the wavelength range 1.10-1, 65 μm with a resolution of 10 nm, with an accumulation time of 40 s and a sample temperature of 59 ± 1 ° C, selected on the one hand to completely melt, and on the other, to avoid transesterification of the LCs determined. The sample was heated to 59 ° C, defended for 3 minutes, its transparency was checked, its spectrum was measured in a NIR spectrometer, and the digitized spectrum was used for calibration or analysis.

Optical density spectra are calculated from the transmission spectra of the samples and the empty cell: $Di = \log (I / I_i)$, where I is the detector signal proportional to the spectral density of the radiation flux incident on the sample, I_i is the detector signal proportional to the spectral density of the radiation flux, passed through the i-th sample. The digitized spectra are then subjected to pre-treatment: subtraction of the common baseline, Golay-Savitsky smoothing and differentiation once or twice.

The Raman spectra of the samples of the second batch were also measured three times using a Thermo Scientific Nicolet NXR FT spectrometer with excitation of a Raman laser radiation with a wavelength of 1.06 μm at a maximum power of 2 W, sample temperature of 59 ± 1 ° C, and then averaged. The accumulation time of the KR spectrum is 2.5 min.

The novelty of the work is that the portable NIR spectrometer uses multiple regression in accordance with the NIPALS algorithm [14], which we implemented in the ISCAP program [20], to improve resolution (Figure 3).

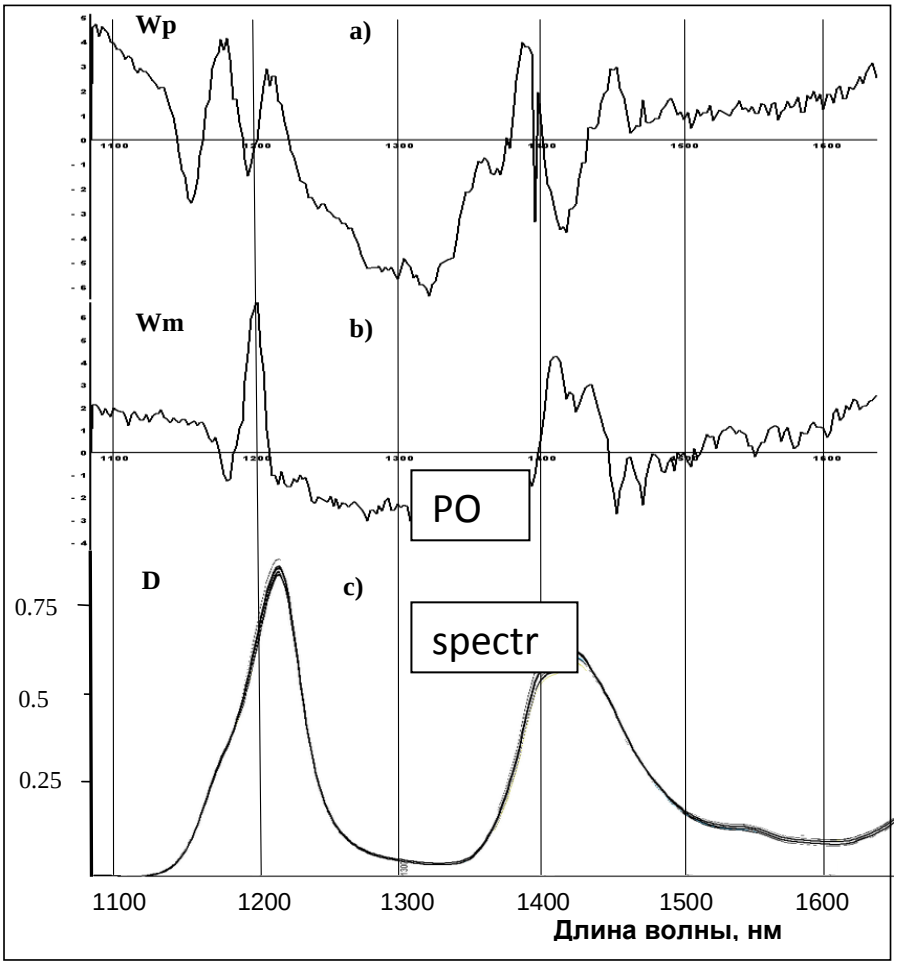

Figure 3: Spectra: a), b) - regression coefficients for the determination of MF and PM, respectively; c) - the absorbance D of 51 fat-oil mixture samples

Construction and testing of PLC calibrations

The solution of the problem of multidimensional linear calibration (regression) from the matrix equation **Y = XB + E** * for multicomponent analysis based on spectra consists of:

1. In the search for batches of calibration samples standardized for fractions of FA or fats and oils, the **Y** matrix.
2. The choice of the technical conditions of the spectral method, the measurement and processing of the spectra of a batch of samples, is the **X** matrix.
3. Creation of a calibration model - a matrix of calibration coefficients **B** for the spectra of **X** and **Y** spectra and its optimization, including:
- construction of various PLS models;
- testing (estimation of parameters of error matrix **E**, choice of models).
4. Determination of the indices ŷ in unknown samples from the measured spectrum

* The matrix values are in bold.

The matrix **B** from the equation **Y = XB** is found by the method of least squares: by minimizing the sum of the squared deviations of the values obtained on the standards **(Y - XB) ^{t} (Y - XB)**, we find estimates of the coefficients of the matrix **B: B = (X^{t} X) $^{-1}$ X^{t}Y**.

The main mathematical problem is the inversion of the matrix **X^{t}X**. Obviously, if the number of standard samples is less than the number of variables in **X**, then the inverse matrix does not exist.

Moreover, even for a sufficiently large number of samples, the inverse matrix may not be due to a significant (up to linear) similarity (collinearity) of the spectra.

The tool against collinearity is the compression of data by the principal component method (PCA).

In the Principle Component Analysis, new variables $t_a = p_{a1}x_1 + p_{a2}x_2 + ...$ (a = 1, ..., A) are formed, called the main components (LS), so that: **X = TP^{T} + E**

HA, or scores, make up the matrix **T**, together with the loadings matrix **P**, they reproduce the matrix **X** quite accurately, and in the remainders of **E,** only an error remains. Wherein:

1) the variables **T** are orthogonal;

2) they are much less than in the matrix **X**, that is, the similarity of the spectra is overcome and **T** can be used instead of **X** to construct the regression.

In the method of PLS regression:

- compresses both matrices, **X** and **Y**;
- HA factors are calculated in turn by the NIPALS algorithm [14];
- receive 2 scores of **T, U** and loads **P, Q** plus the load-weights matrix **W**;
- iteratively improves the model to maximize cov (**T, U**);
- fulfill the prediction:

$\hat{\mathbf{Y}} = \mathbf{Xnew\ B}$

$\mathbf{B = W\ (P^{T}W)^{-1}Q^{T}}$

The constructed models (matrices **B**) were tested by a batch of standards not used for calibration, and models with the best reliability indicators are selected - the r^2p multiple correlation coefficient, complexity n - the HA number and the error - the random component of the standard deviation SEP for the prediction of each analyte in the samples tested batch.

The algorithms for determining the fraction and error of MF in a mixture with vegetable oils were:

1. Using the content of FAs, regulated in GOST 32261-2013:

a) identify the MF by the oil C4: 0 fraction of the oil. If the MF is present (the proportion of MF is more than 0.5%), then:

b) identify the PO from the measured C12: 0, C14: 0, C16: 0, C18: 0 and C18: 1 FAs ratios, comparing them with the reference values (from Codex Alimentarius, Codex Standard for Named Vegetable Oils (CODEX-STAN 210- 1999), please, see the Protocol in Figure 4. If there is a PO (the shares of the FAs occupy an intermediate position between the reference values for the MF and the PO), then:

c) Calculate the percentage of MF, $D_{M,}$ and the probable standard error, SE, for the fractions of FAs, using the equations: $D_{м} = \frac{1}{7}\sum_{i=1}^{7} D_{iM}$ и $SE = 0{,}14\sqrt{\sum d_i^{\,2}}$ and, where d_i are the possible variations in the proportion of MF in the sample for each of the 7 FAs. For this purpose, the lines of the measured value of the i-th FA content in the sample intersect, first, to determine the D_M, with the line of the average reference MF share in the mixture with the PO and, secondly, to determine the SE, with the lines of the maximum and minimum reference values i-th FA for different ratios of MF and PO. It should be borne in mind that the share of the i-th FA in the sample consists of the contributions of PO and MF, the shares and variations of which are regulated by GOST R 53776-2010 "Palm oil refined deodorized for the food industry. Technical conditions " and GOST 32261-2013 "Butter. Technical conditions".

2. Using the calibration of the MF and PO parts.

Since the calibration and test samples were made from samples of MF, PM and olive oil, it is possible to build and test models for the direct determination of the proportions of these fats and oils using the ISCAP program.

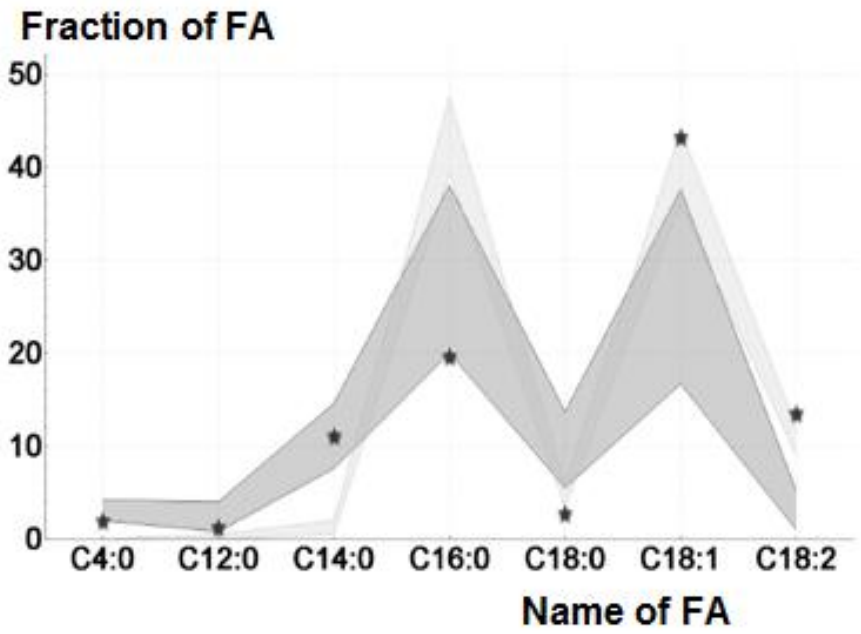

Figure 4: The reference values of the shares of 7 FAs in the MF are in the dark gray zone, the same values for PM (according to Codex Alimentarius, 2009, Brussell) - in the light gray zone; stars - the values of FAs in the sample No. 85.

Results and Discussion

According to NIR spectra and the values of the mass fractions of FAs: C 4: 0, C14: 0, C16: 0, C18: 0, C18: 1 and C18: 2, the proportion of MF and PO on 35 standards of both batches, and according to the Raman-spectra of 35 samples of the second batch (selected models are presented in Table 2), ISCAP regressions were constructed using the PLC program. In total, about 100 calibration models were constructed that differed in ranges, methods for preprocessing spectra, composition of samples in a calibration lot, and composition of analytes. Then the models were tested by the 15th-16th standards of each batch, the errors in the determination of the MF (by the coefficients of multiple correlation, r^2_p , SEP and selectivity) were calculated and the models were compared by samples of another batch (made from other raw materials).

Table 2: Parameters of the PLS-models on Raman and NIR-spectra by the results of testing: Raw - untreated spectra; Rb - the common baseline of the spectra was deleted; GSDer - the spectra are smoothed over Golay-Savitsky and differentiated; 2GSDer - the spectra are twice smoothed over Golay-Savitsky and differentiated.

Models with Raman spectra												
	Pretreatment of the spectra											
	Raw			**Rb**			**SmDer**			**2SmDer**		
Analyte	n	r^2_p	SEP	n	r^2_p	SEP	n	r^2_p	SEP	n	r^2_p	SEP
C4:0	5	0.72	2	5	0.7 3	1.7	5	0.71	1.4	5	0.7 6	1.3
C14:0	6	0.84	1.8	5	0.84	1.8	5	0.91	1.4	5	0.91	1.4
C16:0	4	0.95	1.6	4	0.97	1.4	3	0.92	1.1	3	0.91	1.2
C18:0	5	0.83	1.6	5	0.83	1.5	4	0.84	1.3	4	0.81	1.4
C18:1	5	0.86	1.3	5	0.86	1.2	4	0.85	1.3	5	0.81	1.2
C18:2	6	0.91	1.2	6	0.94	1.3	5	0.94	1.2	5	0.86	1.3
MF	4	0.94	1.1	3	0.92	1.0	3	0.97	0.9	3	0.87	0.8
PO	6	0.81	1.5	4	0.81	1.2	3	0.82	1	3	0.81	0.9
Ol+PO	4	0.93	1.0	5	0.94	0.8	3	0.95	0.8	4	0.91	0.8
Models with NIR spectra												

C4:0	7	0.82	1.2	7	0.83	1.3	6	0.91	1.3	6	0.91	1.3
C14:0	6	0.84	1.8	5	0.84	1.8	5	0.91	1.4	5	0.91	1.4
C16:0	5	0.85	1.6	5	0.87	1.4	5	0.92	0.9	5	0.91	0.9
C18:0	6	0.83	1.6	6	0.83	1.5	5	0.94	1	5	0.91	1
C18:1	5	0.86	1.4	5	0.86	1.4	4	0.95	0.9	5	0.91	0.9
C18:2	7	0.81	1.2	7	0.84	1.4	5	0.91	1	5	0.91	1
MF	6	0.89	1.5	4	0.89	1.1	4	0.96	0.8	5	0.91	0.8
PO	7	0.86	1.6	6	0.86	1.3	5	0.92	0.9	5	0.91	0.9

Then, for a batch of 15 randomly selected reference samples, the values of the MF share were compared by the models for the NIR and Raman spectra by the FA fraction of the calculation method described in the Materials and Methods section and by the MF and PO models. It should be noted that the share of PO from the data of Table 2 is significantly worse than the proportion of MF, which is probably due to a greater variation in the fatty acid composition of PM from different sources of supply.

The MF share can be calculated from the values of seven measured FAs. The calculation example is presented in Table 3 for sample No. 85. In sample No. 85, for example, the share of MF was determined by means of oil fraction calibration (according to the GSDer model with the NIR spectra: n = 4 - number of latent variables, r^2p = 0.97 - multiple correlation coefficient, SEC = 0.8%,- the random component of the root-mean-square error). For sample No. 85, the MF share, D_M, was obtained: D_M = 0.45 ± 0.005 % mass, which agrees well with the MF share obtained from the 7 FA fractions (see Table3), but more reliably and accurately.

Table 3: The MF share,$D_{M,}$ calculated from the values of 7 FAs in sample No. 85: Z_i – the share (% mass) of the i-th FA; D_{iaM} is the average share of the i-th FA in MF; D_{iaP} is the average share of the i-th FA in PO, δc = /D_{iaM} - D_{iaP}/, δ = /Z_i - D_{iaM}/, D_{Mi} =δ / δc.

FA	**Z_i**	**D_{iaM}**	**D_{iaP}**	**δc**	**δ**	**D_{Mi}**
C4:0	1.8	3	0	3	1.2	0.4
C12:0	1.1	2.2	0.2	2	1.1	0.55
C14:0	10	11	1.2	9.8	1	0.1
C16:0	19	29	42	13	10	0.77
C18:0	8.5	10	5	5	1.5	0.3
C18:1	39	27	39	12	12	1.0
C18:2	1.4	4	10	6	2.6	0.43
				ΣD_{Mi} /7	0.460 ± 0.025	

Parameters of models from Raman spectra for the prediction of MF-PO fractions: r^2p = 0.93; SD = 2.5 % mass. were much better than for the models calculated from the shares of the 7th Fas: r^2p = 0.69; SD = 9.5 % mass.

The model indices from the NIR absorption spectra for the prediction of MF-PO fractions: r_2p = 0.91; SD =1 % mass compared to the models calculated from the 7-n FA fractions were also significantly better, albeit to a lesser extent: r^2p = 0.79; SD = 5.4 %mass.

It was found that the selectivity of oleic FA C18:1 determination (namely, independence from the change in the fraction of the nearest analogue, stearic FA C18:0) was 86% if only the length of the carbon chain and the number of double bonds C = C are used, but when using the model by MF and PO fractions, i.e., taking into account the difference in the isomeric forms of TG, the selectivity was more than 96%. This analogy of the properties of models on Raman spectra and on NIR absorption, with allowance for the known sensitivity of Raman spectra to positional isomers, confirms the correlation of NIR absorption spectra with TG isomers. This conclusion is also confirmed by an increase in the selectivity of the determination of oleic C18: 1FA, taking into account the difference in the isomeric forms of PO and MF.

Conclusion

According to the phylogenetic theory of general pathology [21], among the seven biological functions in vivo, the biological function of trophology, the function of nutrition, is more influenced by the aphysiological

influence of environmental factors. Violation of the biological function of trophology is an important factor in the pathogenesis of metabolic pandemics: metabolic arterial hypertension, atherosclerosis with atheromatosis, metabolic syndrome - pathologies of insulin-independent visceral fat cells, insulin resistance, obesity - pathology of insulin-dependent subcutaneous adipocytes and non-alcoholic fatty liver disease.

From the standpoint of general biology, adults, especially the elderly, are advised not to consume butter and reduce the content of foods rich in palmitic FA: beef, sour cream, fatty cheeses. This is a real step in the prevention of metabolic pandemics (atherosclerosis and atheromatosis, metabolic syndrome, insulin resistance, obesity). Still a large population of people who, with the optimal amount of food, persist in vivo for a long time an increased amount of exogenous palmitic FA in blood plasma in the form of an unesterified (free) FAs. This is always the basis for the formation of insulin resistance syndrome, hyperinsulinemia and conditions for the potential development of diabetes mellitus. The portable NIR spectrometer described in the present and previous work [22] can be used to intensify the mass operative control of the content of vegetable oils and animal fats in patients' food.

Acknowledgment

The authors are grateful to Mrs. E.A. Yurova, the head of Technochemical Control Laboratory of the All-Russian Scientific Research Institute of Dairy Industry for the chromatography measurements of batches of samples and discussions. Special thanks the authors express to A.P. Sviridov, DrP., from Center for Laser Research, Russian Academy of Sciences for organizing the measurement of the Raman spectra of the batches of samples.

Financing

The research was carried initially without any financial support.

Conflict of interest

The authors state that there is no conflict of interest.

References

[1]. Titov V.N. (2008). *Klinicheskaya biokhimiya hzirrnyh kislot, lipidov i lipoproteinov (Clinical biochemistry of fatty acids, lipids and lipoproteins)*, Publisher «Triada»Ltd, Moscow – Tver, 1st Ed., 87-112, (in Russian).

[2]. Lasa A., Schweiger M., Kotzbeck P., Churruca I., Simón E., Zechner R., Portillo M.P., (2012), Resveratrol regulates lipolysis via adipose triglyceride lipase. *J. Nutr. Biochem,* 23(4): 379 - 384.

[3]. Yao M., Lien E.L., Capeding M.R., Fitzgerald M., Ramanujam K., Yuhas R., (2014). Effects of term infant formulas containing high sn-2 palmitate with and without oligofructose on stool composition, stool characteristics, and bifidogenicity. *J. Pediatr. Gastroenterol. Nutr.*; 59(4): 440 - 488.

[4]. Lopez C., Cauty C., Guyomarc'h F., (2015). Organization of lipids in milks, infant milk formulas and various dairy products: role of technological processes and potential impacts. *Dairy. Sci. Technol*.; 95(6): 863 - 893.

[5]. Giammanco A., Cefalu A.B., Noto D., Averna M.R. (2015). The pathophysiology of intestinal lipoprotein production. *Front. Physiol*.; 6: 61 - 70.

[6]. Sun Y., Neelakantan N., Wu Y., Lote-Oke R., Pan A., van Dam R.M. (2015). Palm oil consumption increases LDL cholesterol compared with vegetable dils low in saturated fat in a meta-analysis of clinical trials. *J. Nutr*.; 145(7): 1549 -1558.

[7]. Bourlieu C., Michalski M.C. (2015). Structure-function relationship of the milk fat globule. *Curr. Opin. Clin. Nutr. Metab. Care*.; 18(2): 118 - 127.

[8]. Odia O.J., Ofori S., Maduka O. (2015). Palm oil and the heart: areview. *World J Cardiol.*; 7(3): 144 - 14 9.

[9]. Nowacki J., Lee H.C., Lien R., Cheng S.W., Li S.T., Yao M. et al. (2014). Stool fatty acid soaps, stool consistency and gastrointestinal tolerance in term infants fed infant formulas containing high sn-2

palmitate with or without oligofructose: a double-blind, randomized clinical trial. *Nutr J.*; 13: 105 – 111.

[10]. Bresson S., El Marssi M, Khelifa K. (2006). Konformational influences of the polymorphic forms on the C=O and C–H stretching modes of five saturated monoacid triglycerides studied by Raman spectroscopy at various temperatures. *Vibrat. Spectroscopy*.; 40: 263–269.

[11]. Da Silva E, Bressonb S, Rousseaua D. (2009). Characterization of the three major polymorphic forms and liquid state of tristearin by raman spectroscopy. Chem. Phys. Lipids; 113 –119.

[12]. Motoyama M., (2012). Structure and phase characterization of triacylglycerols by raman spectroscopy. *Bull NARO. Inst. Livest. Grassl. Sci*.; (12): 19-68.

[13]. Kalinin A.V., Krasheninnikov V.N. (2017). Detection of fatty product falsifications using a portable near Infrared spectrometer. *EPJ. Web. Conferences*.; 132, DOI:10.1051/epjconf/201713202009.

[14]. Wold S., Sjostrom M., Eriksson. (2001). PLS regression: a basic tool of chemometrics, *Chem. Intelligent. Lab. Syst*; 58(7): 109 – 130.

[15]. Kalinin A., Krasheninnikov V., Sadovskiy S., Yurova E. (2013). Determining the composition of proteins in milk using a portable near infrared spectrometer. *J. Near. Infrared. Spectrosc.;* 21(5): 409 - 416.

[16]. Kalinin A., Tarabukin I., Yurova E. (2013). Determination of the milk fat in fat-oil mixture using portable NIR spectrometer. *In Proceedings of 16th International Conference on Near Infrared Spectroscopy*, la Grande-Motte, France. publ. France Institut National de recherche en sciences et technologies pour l'environnement et l'agriculture, part 3: 38 – 45,.

[17]. Orlova T.I., Ukolov A.I., Savel'eva E.I., Radulov A.S. (2015). Determination of free and esterified fatty acids in blood plasma by gas chromatography with mass-selective detection. *Analitika i kontrol*; 19(2): 183-188. (in Russian)

[18]. Rudakov O.B., Ponomarev A.N., Polyanskiy K.K., Lobar' F.V. (2005). Zhiry, khimicheskiy sostav i ekspertiza kachestva (Fats, chemical composition and quality examination), Pub, Deli Print, Moscow; (in Russian).

[19]. Cabassi G, Povolo M, Pelizzola V., Monti L., Genorini E. Contarini G. (2013). Development of a near infrared method for the quantification of the main classes of fatty acids obtained from raw milk by solvent-free extraction. *J. Near Infrared Spectrosc*.; 21(5): 395-403.

[20]. Kalinin A., Krasheninnikov V., Sadovskiy S., Denisovich E., Yurova E., (2008). Calibration models for multi-component quantitative analyses of dairy with the use of two different types of portable near infrared spectrometer. *J. Near. Infrared. Spectr.;* 16(3): 343 –34 8.

[21]. Titov V.N. (2014). Phylogenetic theory of general pathology. The pathogenesis of metabolic pandemics. Diabetes. [Filogeneticheskaya teoriya obschey patologii. Patogenez metabolicheskih pandemiy. Saharniy diabet]. Pub. INFRA-M., Moscow, 314 pages, (in Russian).

[22]. Kalinin A.V., Krasheninnikov VN., Sviridov A.P., Titov V.N. (2015). Determination of the content of diagnostically significant fatty acids and individual triglycerides in biological media based on infrared spectrometry. *Klinicheskaya laboratornaya diagnostika*.; 60(11): 13 - 20. (In Russian)