ELSEVIER

Thermochimica Acta 398 (2003) 175–183

thermochimica acta

www.elsevier.com/locate/tca

Quality assessment of medicinal cod-liver, edible and technical fish oils based on derivative thermogravimetry data

Marek Wesołowski*, Magdalena Czerwonka

Department of Analytical Chemistry, Medical University of Gdańsk, Al. Gen. J. Hallera 107, L 80-416 Gdańsk, Poland

Received 18 February 2002; received in revised form 7 June 2002; accepted 14 June 2002

Abstract

The quality of medicinal cod-liver, edible and technical fish oils was evaluated on the basis of chemical and thermal analyses. The most substantial chemical variables, viz. density, refractive index as well as saponification, iodine and acid numbers were determined. The two groups of thermal variables were determined based on TG and DTG curves of the thermal decomposition of studied fish oils. The onset and end temperatures as well as successive mass losses were read from the TG curves, whereas the temperature range of peak, peak temperature, peak height and peak width at a half of peak height were read from the DTG curves. To find the relation between the chemical and the TG and DTG variables, regression and principal component (PCA) analyses were applied. Good linear relations were found between a majority of chemical and thermal variables. The results of PCA indicate that the TG and DTG techniques are very useful to determine the degree of deterioration of fish oil samples.

Keywords: Density; Refractive index; Saponification; Iodine and acid numbers; Medicinal cod-liver; Edible and technical fish oils; Principal component analysis; Quality evaluation; DTA; TG and DTG measurements

1. Introduction

Thermoanalytical techniques such as DSC, DTA and TG are widely used in the study of fatty acids, triglycerides, vegetable oils and animal fats [1]. They are mostly applied in the analysis of solid–liquid phase transitions, e.g. melting and solidification in lauric, oleic, palmitic and stearic acids, in their binary and ternary mixtures [2,3] and in milk fat fractions [4]. These techniques are also applied to examine the thermal behavior of saturated, long chains fatty acids which are used as pharmaceutical excipients [5], to evaluate the kinetic parameters of induction periods for non-isothermal oxidation processes of unsaturated fatty acids and vegetable oils [6–8], and to differentiate and quality control of olive, soybean and rapeseed oils [9–11] as well as of single and double frozen fish products [12].

Recently interesting studies were performed which showed that DSC is a fast, specific and reliable method to determine the oil content in dried olive pulp of Cassanese and Carolea tree cultivars [13]. DSC has also been successfully applied to detect coating agents on apple surfaces—beswax, candelilla wax, carnauba wax and shellac [14]. These results indicate that paraffins, montanic acid esters and polyethylene wax oxides which are not approved for coating apples can be detected in the same way.

It is well known from common practice that identification of samples requires a comparison of thermo-

* Corresponding author. Fax: +48-58-349-3124.
E-mail address: marwes@eniac.farmacja.amg.gda.pl (M. Wesołowski).

0040-6031/03/$ – see front matter
PII: S0040-6031(02)00363-5

analytical curves [15]. The curves may be compared by fitting or by determination of quantities describing the shape of the curve. In the case of DTA curve, the evaluation consists of peak-related data (width, height, area and shape index) and temperature (onset, extrapolated onset, peak and final temperature) characteristics [16]. On the other hand, TG curves are characterized by plateau, initial and final temperature, and reaction interval. A little is known, however, about analytical application of DTG curves. The relative rate constants obtained from DTG curves were used in the comparative evaluation of the thermal stabilities of materials [17]. The correlation between the area of DTG or DTA peaks and the amount of sample showed that linearity is verified in the entire investigated range for DTG peak, whereas for DTA one, a discontinuity was observed [18]. These results make preferable to use DTG curves for kinetic measurements [18,19].

The present study proposes to assess the degree of rancidity of fish oil samples by comparing the results of chemical, TG and DTG analyses of oils rancid to a different degree. Because the full evaluation of the fish oils quality on the basis of large datasets produces a multivariate problem, this work is an attempt to resolve this question by using principal component analysis (PCA) [10,11]. The primary scope of this method is to get an overview of the dominant patterns or major trends in a large data matrix which contains the results of many relevant measurements.

2. Experimental

2.1. Materials

In this study medicinal cod-liver, edible and technical fish oils were analyzed. The medicinal cod-liver oils were prepared from fresh livers of the Baltic cod and other fish of the *Gadid* family. The other oils had been produced from a middle-quality (edible fish oils) or a poor-quality (technical fish oils) raw material in processing the fish flesh to folder fish meal.

The samples for testing were prepared in accordance with the Polish Standard [20]. Up to time of analysis they were stored in a dark place at 277 K. They were thoroughly mixed before each analysis.

2.2. TG and DTG measurements

The DTA, TG and DTG curves of thermal decomposition of fish oils were recorded using the OD-103 derivatograph (MOM, Budapest, Hungary). All measurements were carried out under the same conditions. A 200 mg sample of oil in an open platinum crucible was heated under the furnace atmosphere at a heating rate of $5\,\mathrm{K\,min^{-1}}$ up to a final temperature of 973 K. α-Al_2O_3 was used as reference material.

The temperature range of DTG peak (ΔT) was determined as the temperature interval between the points of departure from and return to the baseline. The peak temperature (T_p) represents the temperature of maximum height of DTG peak, whereas the peak height (h) was read as the distance between the baseline of DTG curve and the peak tip. The peak width at a half of peak height ($w_{1/2}$) denotes width of the peak at a half of its height.

2.3. PCA calculations

A data matrix $\boldsymbol{X}$, consisting of $\boldsymbol{K} = 1, 2, \ldots, k$ variables and $\boldsymbol{N} = 1, 2, \ldots, n$ objects, was the starting point for PCA calculations [21,22]. Three sets of variables (chemical, TG and DTG) for three types of objects (medicinal cod-liver, edible and technical fish oils) were used. Those for chemical methods were the density, refractive index, and saponification, iodine and acid numbers; those for TG analysis were the temperatures of onset (T_0) and end (T_{100}) of thermal decomposition and the temperatures for 1, 5, 15, 30, 50 and 75% mass losses (T_1, T_5, T_{15}, T_{30}, T_{50} and T_{75}); and those for DTG analysis were the temperature range of DTG peak (ΔT), peak temperature (T_p), peak height (h) and peak width at a half of peak height ($w_{1/2}$).

From the data matrix $\boldsymbol{X}$ its standardized version and correlation matrix $\boldsymbol{R}$ were calculated. After further calculations, columns in two new matrices $\boldsymbol{P}$ and $\boldsymbol{W}$ were obtained, which were called principal components (PC). New matrix $\boldsymbol{P}$ reflects main relations among objects and makes possible classification of oil samples, whereas matrix $\boldsymbol{W}$ illustrates main relations among variables and enables their selection. Principal components were determined by considering eigenvalues and associated eigenvectors.

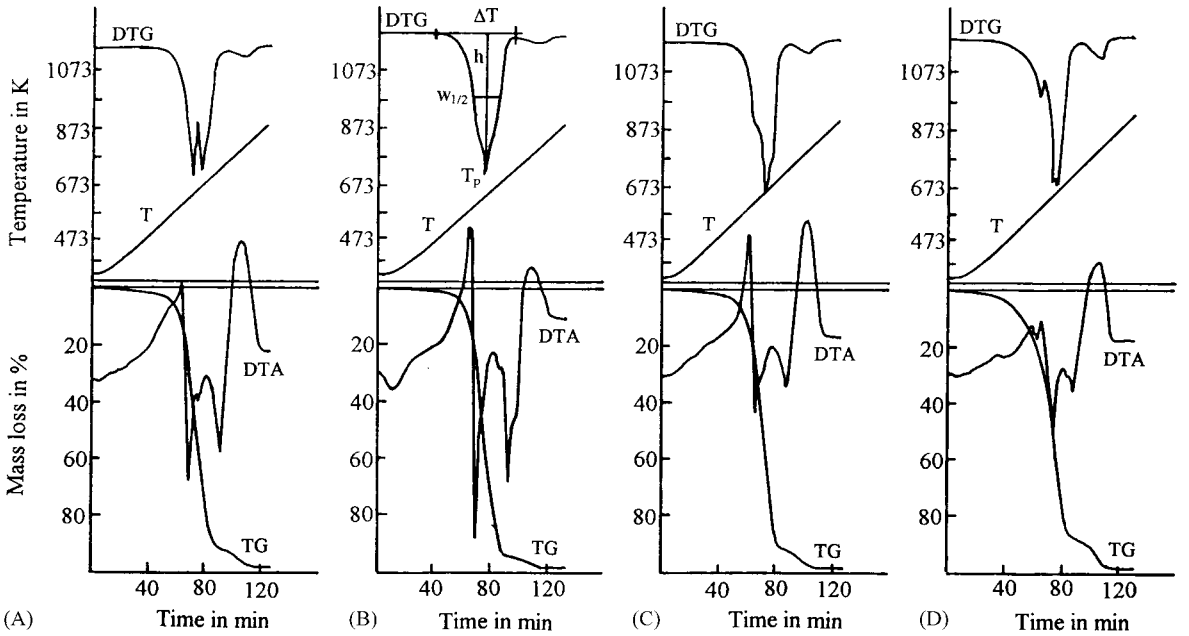


Fig. 1. DTA, TG and DTG curves of the thermal decomposition of medicinal cod-liver oils, which are arranged according to increasing values of the saponification number (the first value in the parenthesis) and decreasing values of the iodine number (the second value in the parenthesis)—(A) low (188.8; 159.7), (B) middle (196.2; 149.3), (C) middle (207.2; 123.2) and (D) high (241.2; 83.5) degree of sample deterioration.

3. Results and discussion

The DTA, TG and DTG curves of thermal decomposition of selected medicinal cod-liver oils are shown in Fig. 1. When using open cells, thermal decomposition is endothermic and is accompanied by gas release. It was found that along with the deterioration of an oil quality, beginning of the deflection of TG curve from the baseline is shifted towards lower temperature values and, in addition, the curve is characterized by a less steep trend. The same dependence is observed for the temperatures associated with the successive mass losses. The lower quality of fish oils is also well reflected by DTG curves. Analysis of their shape has shown that as the extent of oil deterioration increases, the temperature range of DTG peak and the peak width at a half of peak height become broader, whereas the peak temperature and the peak height become lower. This can be confirmed by comparing the DTG peak-related data—ΔT, T_p, h and $w_{1/2}$, listed in Tables 1–3 for medicinal cod-liver, edible and technical fish oils, with the results of the chemical analyses of these oils [23–25].

To express the strength of relation between the DTG and the chemical data linear correlation coefficients were calculated [26]. The values compiled in Table 4 showed that for the temperature range of DTG peak and for the peak width at a half of peak height, the correlations are characterized by higher values than the critical ones for the given number of samples at *P*-level of 0.05 for all sorts of fish oils. In the case of the peak height and the chemical variables, the correlations exists only for edible fish oils, and in the few cases for technical fish oils—for the refractive index and saponification number. On the other hand, no correlation exists between the peak temperature and the chemical variables for all sorts of fish oils. The same can be said about the correlations between the peak height and the chemical variables for cod-liver oil. It should also be mentioned that except for the iodine number, in the of majority cases the correlations assume positive values. The reverse relation is observed

Table 1
Results of the DTG analysis of the medicinal cod-liver oils

No.	ΔT (K)	T_p (K)	h (mm)	$w_{1/2}$ (mm)
1	395	643	95	18
2	290	623	100	15
3	295	653	93	18
4	395	658	107	8
5	290	638	100	17
6	395	668	94	18
7	400	658	110	10
8	320	648	116	13
9	385	648	92	13
10	290	653	118	17
11	365	638	127	10
12	365	633	128	10
13	360	663	98	12
14	280	638	106	16
15	280	643	107	16
16	295	648	108	16
17	290	648	109	15
18	310	648	95	16
19	375	653	107	15
20	400	663	113	10
21	385	668	111	10
22	295	658	110	16
23	280	653	118	14
24	305	673	98	17
25	300	648	115	15
26	275	638	102	17
27	290	653	98	17
28	275	643	112	15
29	290	653	101	17
30	290	648	105	16
31	335	663	96	16
32	270	643	86	20
33	250	643	122	13
34	280	648	90	17
35	280	643	96	15
36	275	648	100	17
37	270	643	102	17
38	265	653	115	16
39	270	643	98	18
40	270	643	137	15
41	280	638	89	20
42	275	643	99	16
43	275	633	94	20

for the peak width at a half of peak height in the case of cod-liver oils and for the peak height in the case of edible and technical fish oils.

From the practical point of view the relations between the density, refractive index, and saponification, iodine and acid numbers, and the temperature range of DTG peak and the width of peak at a half of its

Table 2
Results of the DTG analysis of the edible fish oils

No.	ΔT (K)	T_p (K)	h (mm)	$w_{1/2}$ (mm)
1	265	658	129	13
2	400	658	103	15
3	260	643	134	13
4	275	653	127	13
5	290	648	109	16
6	300	648	126	14
7	275	648	120	11
8	285	658	124	10
9	275	653	136	10
10	280	663	119	14
11	275	663	130	13
12	285	638	126	11
13	270	658	140	10
14	265	658	134	11
15	290	648	126	11
16	270	648	116	13
17	335	648	117	13
18	385	643	86	19
19	285	648	117	12
20	280	658	125	12
21	275	638	123	13
22	305	643	123	13
23	330	648	94	16
24	310	643	121	12
25	365	653	123	11
26	280	663	137	12
27	280	638	135	10
28	275	648	125	12
29	270	648	106	16
30	300	633	105	14
31	300	643	118	13
32	280	638	117	14
33	380	653	106	18
34	400	643	97	16
35	280	648	130	11
36	290	638	95	19
37	350	643	82	21
38	275	638	106	17
39	310	643	99	17
40	390	653	91	20
41	260	653	130	10
42	265	643	106	16
43	300	643	125	16
44	290	648	104	16
45	300	653	111	11
46	290	643	124	12
47	265	658	100	15
48	300	643	103	18
49	395	653	107	14
50	270	633	121	14
51	290	653	140	9
52	325	633	91	19
53	370	653	76	20
54	280	648	93	18

Table 3
Results of the DTG analysis of the technical fish oils

No.	ΔT (K)	T_p (K)	h (mm)	$w_{1/2}$ (mm)
1	270	668	137	9
2	260	658	126	11
3	245	673	128	13
4	265	648	111	13
5	255	668	138	9
6	370	658	89	17
7	285	643	99	11
8	285	638	127	11
9	270	653	121	10
10	270	623	103	16
11	380	653	117	16
12	285	653	89	18
13	270	643	132	11
14	275	648	135	10
15	255	643	120	10
16	285	638	106	16
17	250	638	120	13

height are of most significance. From the linear equation $y = a + bx$, where y is the chemical variable and x is the DTG one, the chemical data for medicinal cod-liver, edible and technical fish can be found after the temperature range and the peak height had been read from DTG curve. The exemplary equations are listed in Table 5.

Table 4
Correlation coefficients between the DTG and chemical values

Chemical variables	DTG variables			
	ΔT (K)	T_p (K)	h (mm)	$w_{1/2}$ (mm)
Medicinal cod-liver oils ($n = 43$)				
Density	0.85	0.26	0.14	−0.66
Refractive index	0.84	0.32	0.18	−0.69
Saponification number	0.80	0.25	0.08	−0.63
Iodine number	−0.81	−0.33	−0.13	0.62
Acid number	0.81	0.25	0.12	−0.65
Edible fish oils ($n = 54$)				
Density	0.86	−0.15	−0.71	0.66
Refractive index	0.79	−0.06	−0.65	0.56
Saponification number	0.84	−0.04	−0.65	0.57
Iodine number	−0.82	−0.04	0.55	−0.44
Acid number	0.71	−0.09	−0.52	0.44
Technical fish oils ($n = 17$)				
Density	0.91	−0.09	−0.42	0.60
Refractive index	0.85	−0.35	−0.59	0.65
Saponification number	0.85	−0.08	−0.56	0.60
Iodine number	−0.82	−0.12	0.40	−0.46
Acid number	0.86	0.02	−0.47	0.63

Complete evaluation of fish oils on the basis of chemical, TG and DTG measurements may be solved by using PCA. The data matrix for PCA was taken from Tables 1–3 and [23–25]. As a result of PCA calculations, two significant principal components—PC1 and PC2 are extracted in each case, which together explained at least 80% of the total variance. The remaining principal components, PC3 and the next, describe only a few or even hundredth part of percent of the total variance and there are of no importance for interpretation of the data.

As shown in Figs. 2–4, by using PCA approach to the distinction ability between good quality oils (samples which meet all quality standards) and rancid oils (samples for which the quality standards are not all fulfilled) on the grounds of the chemical, TG and DTG results can be critically compared. Taking into account medicinal cod-liver oils, the matrix for chemical dataset has dimension 43×5. After PCA calculations five new variables were obtained which eigenvalues were as follows: 4.49, 0.23, 0.17 and the last two variables with values less than 0.1. First two PC's explain together more than 97% of the total variance of the data. The localization of cod-liver oil samples on the plane determined by PC1 and PC2 axes is displayed in Fig. 2A. Comparing their positions with the chemical values listed in reference [23] and with the Polish Pharmacopoeia specifications [27,28] the degree of deterioration of oil samples can be defined. The oils which do not meet the requirements of standards are grouped on the right side of the plot. The cluster gathered fourteen medicinal cod-liver oils with numbers 1, 4, 6, 7, 8, 9, 11, 12, 13, 19, 20, 21, 24 and 31. The worse quality of oils is reflected by appreciable increase in the density, refractive index, saponification and acid numbers whereas the iodine number decreases. Good quality oils are localized on the left side of the plot.

The matrix for TG results of medicinal cod-liver oils has dimension 43×8. After PCA calculations eight new variables were obtained. Their eigenvalues were as follows: 4.46, 2.72, 0.46, 0.13, 0.12 and next three values less than 0.1. Taking into account eigenvalues that were more than 1.0, the distribution of oil samples is presented in two-dimensional pattern PC1 versus PC2, as shown in Fig. 2B. First two PCs included

Table 5
Linear regression equations for relations between the chemical values and the temperature range of DTG peaks for fish oils

Chemical variable	Linear regression equation
Medicinal cod-liver oils ($n = 43$)	
Density	8.91×10^{-1} $(7.51 \times 10^{-3}) + 2.47 \times 10^{-4}$ $(2.39 \times 10^{-5})\Delta T$ (72.21)
Refractive index	1.47 $(1.27 \times 10^{-3}) + 4.05 \times 10^{-5}$ $(4.05 \times 10^{-6})\Delta T$ (70.94)
Saponification number	113.81 (10.65) $+ 2.85 \times 10^{-1}$ $(3.39 \times 10^{-2})\Delta T$ (63.26)
Iodine number	247.51 (12.90) $- 3.59 \times 10^{-1}$ $(4.11 \times 10^{-2})\Delta T$ (65.10)
Acid number	-72.19 (9.64) $+ 2.70 \times 10^{-1}$ $(3.07 \times 10^{-2})\Delta T$ (65.30)
Edible fish oils ($n = 54$)	
Density	9.03×10^{-1} $(4.87 \times 10^{-3}) + 1.97 \times 10^{-4}$ $(1.60 \times 10^{-5})\Delta T$ (74.53)
Refractive index	1.47 $(1.01 \times 10^{-3}) + 3.12 \times 10^{-5}$ $(3.32 \times 10^{-6})\Delta T$ (62.94)
Saponification number	125.35 (6.75) $+ 2.52 \times 10^{-1}$ $(2.22 \times 10^{-2})\Delta T$ (71.31)
Iodine number	237.53 (10.89) $- 3.65 \times 10^{-1}$ $(3.58 \times 10^{-2})\Delta T$ (66.65)
Acid number	-46.09 (7.25) $+ 1.75 \times 10^{-1}$ $(2.38 \times 10^{-2})\Delta T$ (50.89)
Technical fish oils ($n = 17$)	
Density	9.00×10^{-1} $(7.41 \times 10^{-3}) + 2.20 \times 10^{-4}$ $(2.62 \times 10^{-5})\Delta T$ (82.48)
Refractive index	1.46 $(3.16 \times 10^{-3}) + 7.05 \times 10^{-5}$ $(1.12 \times 10^{-5})\Delta T$ (72.73)
Saponification number	92.18 (17.58) $+ 3.94 \times 10^{-1}$ $(6.21 \times 10^{-2})\Delta T$ (72.83)
Iodine number	276.66 (27.21) $- 5.43 \times 10^{-1}$ $(9.61 \times 10^{-2})\Delta T$ (68.02)
Acid number	-63.94 (11.24) $+ 2.54 \times 10^{-1}$ $(3.97 \times 10^{-2})\Delta T$ (73.13)

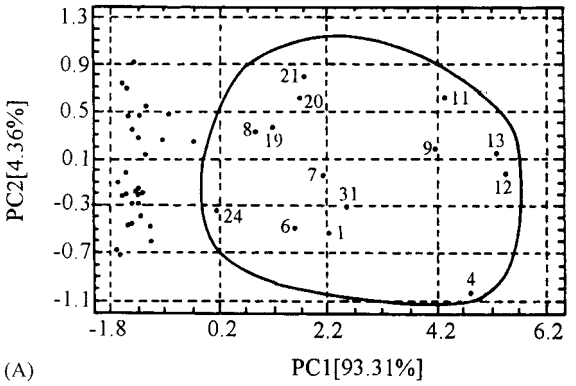
The standard errors of the estimation of intercept (s_a) and slope (s_b) of the equation $y = a + bx$, and the R-squared (R^2) are indicated in the parentheses.

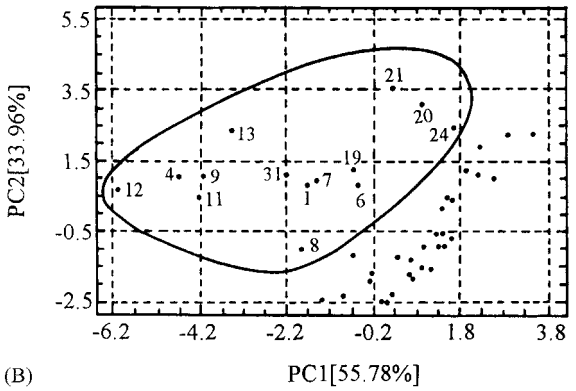
more than 89% of the total variance of the data and displayed difference in the degree of deterioration of examined oil samples similarly as in the case of the chemical values. The same fourteen, rancid cod-liver oils are grouped in clear cluster.

The last matrix for medicinal cod-liver oils with dimension 43 × 4 was constructed on the dataset compiled in Table 1. As a result of PCA calculations, four new variables were obtained which were characterized by consecutive eigenvalues—2.01, 1.23, 0.58 and 0.18. Two first PCs account for more than 80% of the DTG data. After considering the eigenvalues, the distribution of oil samples is illustrated in two-dimensional plot. As it is shown in Fig. 2C, all of the oil samples that are of worse quality are located on the right side of the plot. Comparison of the results achieved from the chemical, TG and DTG measurements leads to the conclusion that the discrimination ability obtained by these methods is very similar. Samples numbered 1, 4, 6, 7, 8, 9, 11, 12, 13, 19, 20, 21, 24 and 31, which represent the rancid cod-liver oils, are clearly separated from the others on each plot.

The graphical presentation of PCA results for edible fish oils is illustrated in Figs. 3A–C. There are clear clusters on each plot which gathered ten samples with numbers 2, 17, 18, 30, 33, 34, 37, 40, 49 and 53, which represent the most highly rancid oils. In the case of PCA data for DTG measurements, samples 17 and 30 are included into the group of good quality oils. This is not in agreement with their values of density, refractive index, and saponification, iodine and acid numbers, which do not meet the requirements of standards [27,28]. Therefore, it can be concluded, that the classification problem can be resolved using DTG technique when compared with the chemical and TG examinations.

The distribution of technical fish oils in two-dimensional space PC1 versus PC2 is presented in Figs. 4A–C. Comparing the results of PCA calculations it can be concluded that the separation between two groups of oils on the grounds of the chemical, TG and DTG data is very similar. In the group of rancid oils, three oil samples with numbers 6, 11 and 16 are separated on the left or right side of plot. There are most of all rancid oil samples. Moreover, samples numbered 7, 8, 10 and 12 are of intermediate quality and have been found on the border region of both groups of oils. The values of majority of the chemical





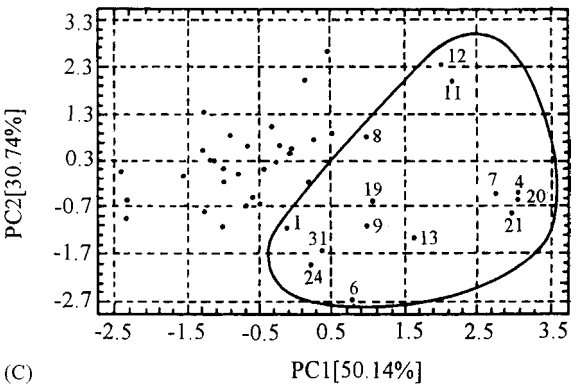
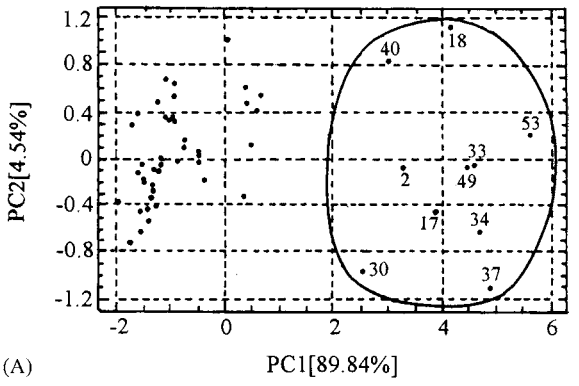
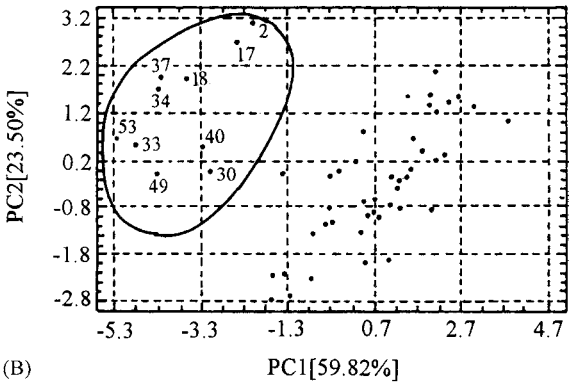


Fig. 2. Scatterplots of the first two principal component vectors (PC1 vs. PC2) for medicinal cod-liver oils. Classification of 43 samples according to the—(A) chemical, (B) TG and (C) DTG analyses. Low quality oil samples are circled.





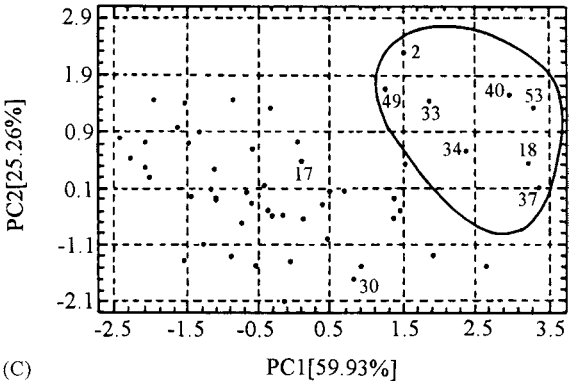
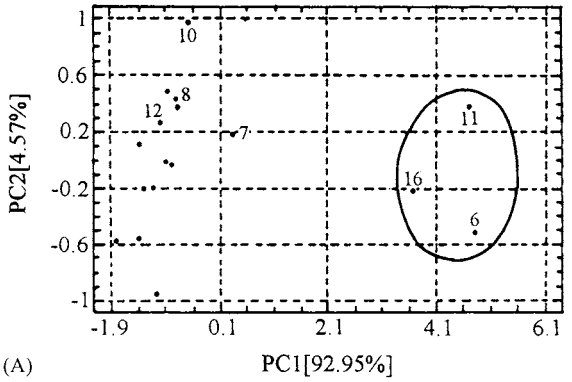
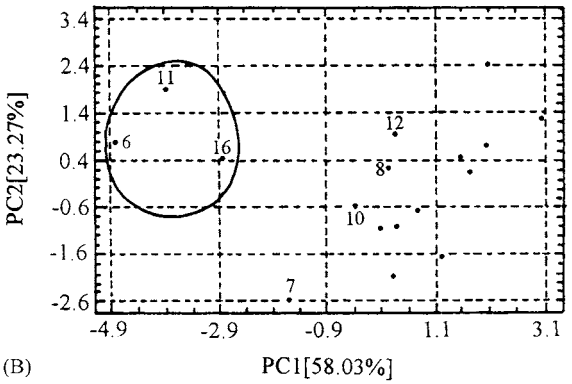


Fig. 3. Scatterplots of the first two principal component vectors (PC1 vs. PC2) for edible fish oils. Classification of 54 samples according to the—(A) chemical, (B) TG and (C) DTG analyses. Low quality oil samples are circled.

variables for these oil samples meet the specifications [27,28], but density (samples 8 and 10), refractive index (10), saponification number (7) and acid number (12) are higher than the requirements of standard, whereas the iodine number (7) is lower than that of standard.

Scatterplots of the first two principal component loading factors W_1 and W_2 show the complementary





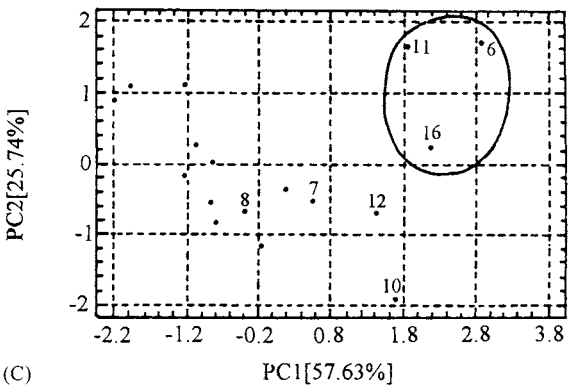
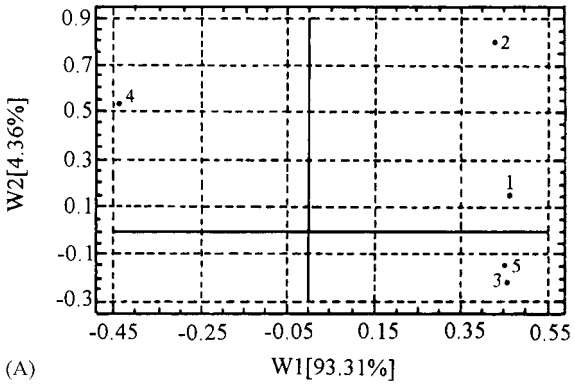
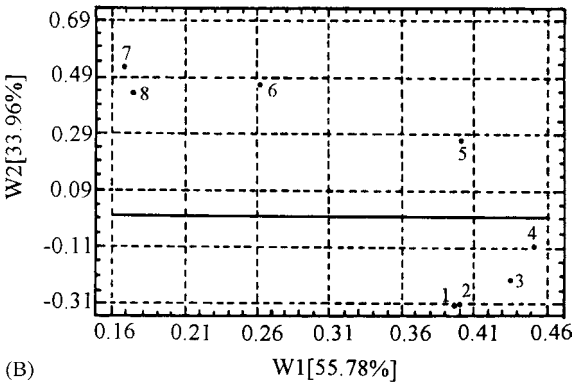


Fig. 4. Scatterplots of the first two principal component vectors (PC1 vs. PC2) for technical fish oils. Classification of 17 samples according to the—(A) chemical, (B) TG and (C) DTG analyses. Low quality oil samples are circled.





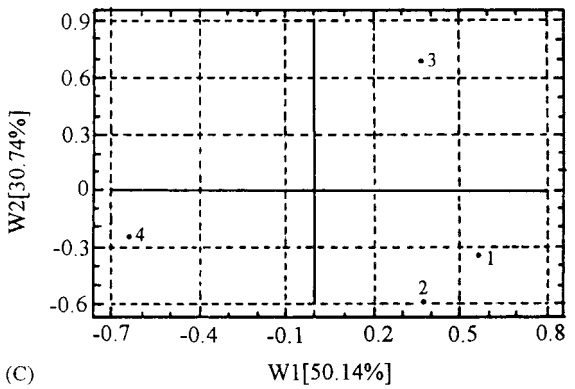


Fig. 5. Scatterplots of the first two principal component loadings factors (W_1 vs. W_2) for edible fish oils. (A) chemical variables—(1) density, (2) refractive index, and (3) saponification, (4) iodine and (5) acid numbers; (B) TG variables—(1) T_0, (2) T_1, (3) T_5, (4) T_{15}, (5) T_{30}, (6) T_{50}, (7) T_{75} and (8) T_{100}; (C) DTG variables—(1) ΔT, (2) T_p, (3) h and (4) $w_{1/2}$.

variable patterns which reveal information about relationships between variables. As presented in Fig. 5A and B for medicinal cod-liver oils as an example, all the chemical and TG variables, with exception of T_{50},

T_{75} and T_{100}, are the most useful in the quality assessment of all sorts of fish oil samples. All these variables have a high loading in the PC1, only iodine number has a negative sign. On the other hand, the density and iodine number, as well as the T_{50}, T_{75} and T_{100} have a high loading in the PC2, which classification ability is very low as compared with the PC1, especially in the case of chemical variables. Considering Fig. 5C, it can be recognized that all the DTG variables have a high loading in the PC1, only $w_{1/2}$ has a negative sign. The PC2 is strongly loaded by the peak height and the peak temperature, but in the latter case correlation has a negative sign.

Taking all above into account the chemical, TG and DTG variables can be extracted, which are the most useful in the quality assessment of studied oil samples. In the case of chemical analysis there are the density, refractive index, and saponification, iodine and acid numbers; the T_0, T_1, T_5, T_{15} and T_{30} for the TG data, and for the DTG measurements there are the ΔT and $w_{1/2}$. The usefulness of theT_{50}, T_{75} and T_{100}, as well as the T_p and h is doubtful.

4. Conclusions

PCA studies confirm that the distinction ability between good quality oils (samples which meet all quality standards) and rancid oils (samples for which the quality standards are not all fulfilled) on the grounds of the DTG measurements is as good as that achieved by the chemical and TG measurements. Therefore, it can be concluded that the classification problem can be resolved using DTG technique when compared with the chemical data. The PCA and DTG is the valuable approach in the quality assessment of fish oil samples which differ in the degree of rancidity. They reflect in a very good way relationship between the degree of deterioration of oil samples as measured by different techniques.

The regression analysis indicates that by using appropriate linear regression equations, the density, refractive index, and saponification, iodine and acid numbers for examined oils can be found based on the temperature range of DTG peak and the peak width at a half of peak height. Moreover, thermal methods of analysis have some advantages as an useful tool for the examination of oils. They are rapid and relatively simple, besides very small quantities of samples are required and by applying automatic recording of the TG and DTG curves, the time-consumption for the determination may be reduced.

References

[1] Setaram Group, Vademecum of Application in Thermal Analysis, Caluire, France, 1995.
[2] F.O. Cedeno, M.M. Prieto, A. Espina, R. Garcia, Thermochim. Acta 369 (2001) 39.
[3] J.-J. Zhang, J.-L. Zhang, S.M. He, K.-Z. Wu, X.-D. Liu, Thermochim. Acta 369 (2001) 157.
[4] B. Schäffer, S. Szakály, D. Lőrinczy, B. Schäffer, J. Thermal Anal. Cal. 64 (2001) 659.
[5] S. Li, K.S. Alexander, Thermochim. Acta 340/341 (1999) 271.
[6] P. Šimon, L. Kolman, J. Thermal Anal. Cal. 64 (2001) 813.
[7] G. Litwinienko, J. Thermal Anal. Cal. 65 (2001) 639.
[8] E. Rudnik, A. Szczucińska, H. Gwardiak, A. Szulc, A. Winiarska, Thermochim. Acta 370 (2001) 135.
[9] D. Martinez, M.A. Revilla, A. Espina, J.R. Garcia, Thermochim. Acta 349 (2001) 147.
[10] M. Wesołowski, B. Suchacz, Fresenius J. Anal. Chem. 371 (2001) 323.
[11] M. Wesołowski, B. Suchacz, J. Thermal Anal. Cal. 68 (2002) 893.
[12] R. Schubring, Thermochim. Acta 337 (1999) 89.
[13] N. Iannotta, C. Oliviero, G.A. Ranieri, N. Uccella, Eur. Food Res. Technol. 212 (2001) 240.
[14] B. Ritter, J. Schulte, E. Schulte, H.-P. Thier, Eur. Food Res. Technol. 212 (2001) 603.
[15] G. Pokol, S. Gál, E. Pungor, Thermochim. Acta 92 (1985) 89.
[16] R.C. Mackenzie, C.J. Keattch, D. Dollimore, J.A. Forrester, A.A. Hodgson, J.P. Redfern, Talanta 19 (1972) 1079.
[17] P.K. Dávid, E. Zelenyánszki, J. Thermal Anal. 5 (1973) 337.
[18] G. Siracusa, V. Cucinotta, Thermochim. Acta 23 (1978) 185.
[19] F.W. Wilburn, Thermochim. Acta 340/341 (1999) 77.
[20] PN-76/A-86911, Tłuszcze roślinne jadalne, Metody badań, Przygotowanie próbek do analizy (Eatable vegetable fats, testing methods, Preparation of samples for analysis).
[21] E. Aries, D.P. Lidiard, R.A. Spragg, Chem. Brit. 9 (1991) 821.
[22] R.G. Brereton, Chemometrics, Applications of Mathematics and Statistics to Laboratory Systems, Ellis Horwood, London, 1990.
[23] M. Wesołowski, Sci. Pharm. 54 (1986) 11.
[24] M. Wesołowski, Fat Sci. Technol. 89 (1987) 111.
[25] M. Wesołowski, Seifen, Öle, Fette, Wachse 112 (1986) 231.
[26] K. Doerffel, Statystyka dla chemików analityków (Statistik in der Analytische Chemie), WNT, Warszawa, 1989.
[27] Farmakopea Polska IV (IVth Polish Pharmacopoeia), Vol. 2, PZWL, Warszawa, 1970.
[28] Farmakopea Polska V (Vth Polish Pharmacopoeia), Vol. 1, PZWL, Warszawa, 1990.