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Thermal analysis in quality assessment of rapeseed oils

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Abstract

The evaluation of the applicability of thermoanalytical methods to the assessment of the quality of refined rapeseed oils was performed. Density, refractive index, and saponification, iodine and acid numbers of rapeseed oils were determined as part of the study. By correlating the data obtained with the temperatures of initial, final and successive mass losses determined from the thermogravimetric curves, strong relations were observed. The possibility of a practical utilization of regression equations for the assessment of the quality of refined rapeseed oils was indicated. The results of principal component analysis indicate that thermogravimetric techniques are very useful in defining the quality of rapeseed oils compared with chemical analyses.

Keywords: Chemical analysis; Differential thermal analysis; Principal component analysis; Quality assessment; Rapeseed oils; TG and DTG analysis

1. Introduction

The use of thermal methods of analysis in the study and characterization of oils and fats is receiving increasing interest. These methods rapidly furnish stability data which are important for application purposes.

Differential scanning calorimetry (DSC) is a useful tool for qualitative examination of human fat. Bore et al. [1] have shown that DSC data are correlated with other physico-chemical characteristics of human fat, especially with the proportion of unsaturated fatty acids in the whole fatty acids fraction. According to Odlyha [2], oxidative degradation studies of aged paint films by DSC have revealed that it is possible to distinguish between linseed, walnut and poppyseed oils. The oil type can provide information on the provenance of a painting. The observed difference can assist in the interpretation of data relating to the study of the ageing properties of paint media by the DSC method. Shelef and Garti [3], using the DSC technique, have studied the effect of the presence of impurities such as hydrogenated palm oil derivatives and surfactants on the polymorphic transitions of hydrogenated low erucic acid rapeseed oil at various stages of hydrogenation. They concluded that fully hydrogenated oil does not differ significantly from a mixture of tristearin and tripalmitin.

Rapeseed, sunflower and soybean oils, for possible use as collectors in the flotation of magnesite ores, were investigated by Bubanec and Sopkovă [4] using thermogravimetric (TG), derivative TG (DTG), and differential thermal analysis (DTA) techniques. These methods helped to differentiate the oils according to

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different properties of the component with a lower boiling point.

These examples do not exhaust the wide range of possibilities of employing thermal methods for examining oils and fats. The present study is designed to evaluate the quality of rapeseed oils from results of chemical analyses and thermal decomposition. Because full evaluation of a rapeseed oil's quality on the basis of chemical and thermal analyses is a multivariate problem, this work attempts to resolve this question by using principal component analysis (PCA).

2. Experimental

2.1. Material for testing

Commercial refined rapeseed oils (48 samples) manufactured by various agricultural co-operatives in Poland were analyzed. Before testing, the samples were prepared in accordance with the Polish Standard [5]. Until analysis, they were stored in a dark place at 277 K and were protected against dust.

2.2. Chemical analysis

The density of the oils was determined at 293 K with a pycnometer of 10 ml volume. The refractive index at 293 K was determined with an Abbe refractometer (Carl Zeiss, Jena, Germany) using a sodium-vapour lamp (589,3 nm). The determination of saponification, iodine and acid numbers was conducted in accordance with the methods described in the Polish Pharmacopoeia [6]. At least two values were averaged to provide the result of the analysis.

2.3. Thermal analysis

The thermal decomposition of oils was performed using an OD-103 derivatograph (MOM, Budapest, Hungary), a TG, DTG and DTA instrument. A 200-mg oil sample was heated in a platinum crucible in an air atmosphere at a rate of 5 K min^{-1}, up to the final temperature of 873 K. α-Al_2O_3 was used as reference. Each thermogram was measured at least three times.

The initial (T_0) and final (T_{100}) temperatures of the thermal decomposition of each oil sample were read from the TG and DTG curves, whereas the temperatures for the 1, 5, 15, 30, 50 and 75% mass losses (T_1, T_5, T_{15}, T_{30}, T_{50} and T_{75}) were read only from the TG curves.

2.4. Calculations

A data matrix **X**, consisting of k variables and n objects, was the starting point for the principal component analysis (PCA) [7,8]. Two matrices were constructed. In the first, the results of the determination of density and refractive index as well as saponification, iodine and acid numbers were used as variables. In the second, the results of thermal analysis (T_0, T_1, T_5, T_{15}, T_{30}, T_{50}, T_{75} and T_{100}) were used. The samples of refined rapeseed oils were objects.

For each data matrix **X**, its standardized version and correlation matrix **R**, were calculated. After further calculations, two new matrices – principal component scores (**P**) and principal component loadings (**W**) were obtained. The new matrix **P** reflects main relations among objects and makes possible a classification of the oils tested, whereas matrix **W** illustrates main relations among variables and enables their selection.

Principal components (PC) were determined by considering eigenvalues and associated eigenvectors. For plotting purposes, only the two first principal component score vectors (PC1 and PC2) were used.

3. Results and discussion

The refined rapeseed oils have not only to meet the specific organoleptic requirements, such as transparency, consistency, taste and odour, but also the specific physico-chemical requirements, such as density, refractive index, and saponification, iodine and acid numbers [9–11]. These values largely reflect the disadvantageous changes in chemical composition of the oils in the course of their deterioration. Analysing the data listed in Table 1, poorer quality corresponds to increases in density, refractive index, and saponification and acid numbers, and a decrease of the iodine number.

The TG, DTG and DTA curves for thermal decomposition of the samples denoted by numbers 25, 40 and 20, characterized by differing degrees of deterioration, are shown in Fig. 1. The temperatures of the initial,

Table 1
Results of the chemical analyses of the refined rapeseed oils (48 samples)

Sample	Density	Refractive index	Saponification number	Iodine number	Acid number
1	0.9227	1.4735	193.6	106.9	1.62
2	0.9265	1.4740	193.0	98.6	1.93
3	0.9217	1.4738	192.1	104.8	1.51
4	0.9310	1.4753	197.1	90.8	3.00
5	0.9228	1.4733	193.9	107.5	1.59
6	0.9270	1.4745	194.2	102.8	2.29
7	0.9173	1.4730	190.8	111.5	1.22
8	0.9325	1.4750	197.5	97.7	3.13
9	0.9293	1.4748	195.9	101.3	2.37
10	0.9391	1.4760	200.9	91.9	3.19
11	0.9239	1.4740	193.3	105.5	1.47
12	0.9322	1.4748	197.8	94.6	2.92
13	0.9219	1.4735	192.2	104.9	1.48
14	0.9278	1.4748	195.9	101.4	2.60
15	0.9243	1.4738	197.1	100.0	1.64
16	0.9390	1.4758	199.4	89.9	3.42
17	0.9140	1.4725	192.0	110.0	1.46
18	0.9307	1.4750	198.0	98.9	2.50
19	0.9305	1.4740	195.8	101.2	2.96
20	0.9325	1.4745	198.5	89.9	3.25
21	0.9168	1.4728	191.3	116.6	0.98
22	0.9277	1.4748	196.1	95.7	3.23
23	0.9206	1.4735	190.8	108.5	1.51
24	0.9302	1.4740	197.6	97.1	2.82
25	0.9178	1.4723	189.8	111.7	1.13
26	0.9282	1.4733	196.8	94.9	1.93
27	0.9100	1.4728	189.2	113.1	1.19
28	0.9319	1.4741	196.0	96.9	2.53
29	0.9233	1.4738	193.8	103.0	1.39
30	0.9245	1.4743	195.4	108.2	1.32
31	0.9169	1.4728	192.0	111.9	1.23
32	0.9252	1.4738	194.0	107.9	1.90
33	0.9176	1.4735	190.8	111.5	1.21
34	0.9207	1.4733	192.3	105.9	1.62
35	0.9170	1.4730	191.8	113.6	1.04
36	0.9207	1.4728	191.2	102.6	1.20
37	0.9152	1.4733	194.1	96.4	1.26
38	0.9294	1.4740	196.9	95.2	2.02
39	0.9169	1.4733	192.4	110.9	1.35
40	0.9207	1.4733	192.1	108.9	1.78
41	0.9184	1.4735	193.9	114.4	1.26
42	0.9218	1.4738	192.5	106.1	1.33
43	0.9213	1.4733	192.9	105.8	1.28
44	0.9263	1.4748	197.3	103.2	2.26
45	0.9198	1.4730	191.7	108.3	1.31
46	0.9225	1.4735	193.3	105.8	1.38
47	0.9295	1.4744	196.6	101.4	2.18
48	0.9330	1.4746	196.4	103.0	2.24

final and successive mass losses for thermal decomposition of all of the oils are given in Table 2. By comparing these values with the data summarized in Table 1, it has been found that the changes in the values of chemical variables of the products examined are reflected in the course of their thermal decom-

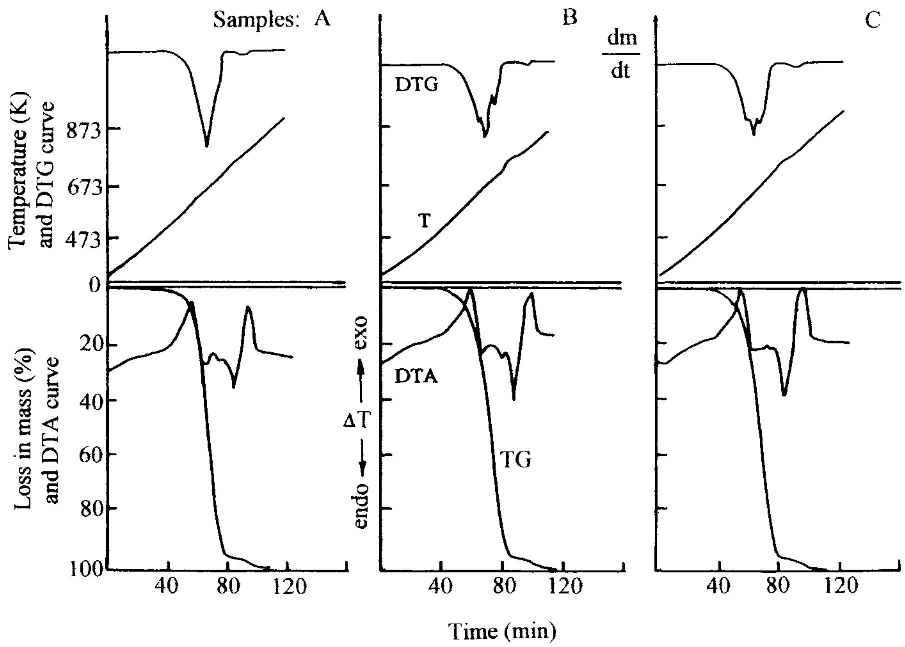

Fig. 1. TG, DTG and DTA curves for thermal decomposition of rapeseed oils characterized by differing degrees of deterioration: (A) sample # 25, (B) sample # 40 and (C) sample # 20. These samples were selected and arranged according to increasing values of density, refractive index, saponification and acid numbers and decreasing value of iodine number. The chemical and thermal variables for these oils are listed in Tables 1 and 2, respectively.

position. The higher values of the initial temperature of decomposition indicate the higher quality of the rapeseed oil. Also, this relation is observed for the temperatures of successive mass losses.

The values of correlation coefficients between the thermal and chemical variables for the rapeseed oils are listed in Table 3. Except for the iodine number, the correlation coefficients assume negative values for temperatures of successive mass losses including T_{50}. For T_{75} and T_{100}, the coefficients assume positive values. In the case of density and iodine number for the initial, final and T_1, T_5 and T_{15} temperatures, the correlation coefficients are characterized by higher values than the critical ones at the significance level of 0.01; absolute values greater than 0.368 indicate significant correlation [12,13]. For the refractive index, saponification and acid numbers, the correlation coefficients are also characterized by higher values for T_0, T_1, T_5 and T_{100} than the critical ones, except for T_{100} for the saponification number. No significant correlation coefficients are observed for the other temperatures of mass losses.

For example, the relationship between T_0 and the iodine number for oils studied is presented in Fig. 2. The plot reflects the existence of a strong relationship between both variables over the full range of their values.

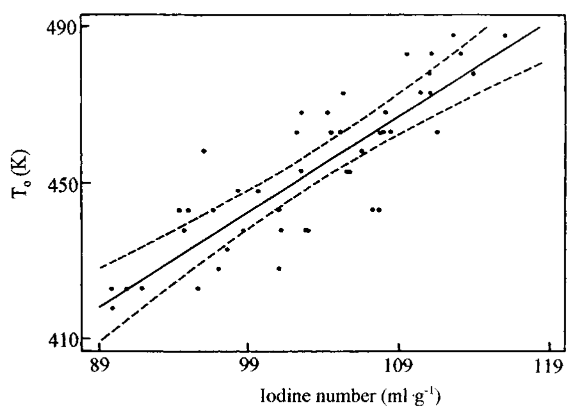

Fig. 2. Relationship between T_0, the initial temperature of thermal decomposition, and iodine number for 48 rapeseed oils tested. This relation is described by equation y=203.7+2.4x (R^2=74.30%).

Table 2
Results of the thermogravimetric analyses of the refined rapeseed oils (48 samples)

Sample	Temperatures (K) of the successive losses in mass							
	T_0	T_1	T_5	T_{15}	T_{30}	T_{50}	T_{75}	T_{100}
1	458	513	568	603	623	638	668	803
2	448	513	568	603	628	648	668	818
3	468	518	568	603	628	643	673	808
4	423	498	548	583	628	643	673	818
5	443	503	553	593	613	633	658	798
6	453	508	563	603	628	648	668	813
7	478	528	578	613	633	653	673	813
8	433	503	563	608	633	648	663	828
9	443	513	573	608	628	653	673	818
10	423	508	568	613	638	663	683	823
11	463	518	573	608	628	643	668	808
12	443	513	578	613	638	653	678	823
13	463	513	568	613	633	648	653	793
14	438	508	568	608	628	648	673	818
15	448	508	563	603	623	638	663	803
16	418	493	553	588	613	628	673	823
17	483	533	583	618	638	653	678	818
18	438	503	563	598	618	638	668	808
19	428	503	553	593	613	628	678	793
20	423	498	563	598	628	648	668	818
21	488	543	583	623	638	663	683	808
22	423	508	568	613	633	653	678	823
23	468	513	563	603	623	638	663	808
24	428	493	553	593	613	633	658	798
25	483	528	583	618	638	653	668	818
26	438	513	568	608	633	653	673	818
27	488	528	578	613	643	653	673	808
28	443	508	563	603	633	648	673	818
29	468	518	568	608	628	643	663	808
30	463	523	568	608	633	648	668	823
31	463	518	573	603	628	643	663	803
32	443	513	563	603	623	638	663	803
33	473	523	568	603	628	643	663	803
34	453	513	563	603	623	643	663	808
35	483	523	578	613	638	648	663	813
36	463	513	568	603	623	638	663	808
37	458	518	563	593	613	633	653	798
38	443	503	558	603	623	643	663	813
39	473	523	573	603	623	643	663	803
40	463	503	563	593	613	633	653	803
41	478	523	573	608	623	643	668	803
42	453	523	573	608	628	648	668	808
43	473	523	573	613	633	643	663	813
44	438	508	568	613	633	653	673	808
45	463	518	563	603	623	643	678	803
46	453	513	563	608	613	643	663	813
47	443	493	553	603	613	633	658	803
48	438	488	533	583	593	623	643	803

Table 3
Correlation coefficients between the temperatures of the initial, final and successive losses in mass and the density, refractive index and saponification, iodine and acid numbers for the rapeseed oils tested. Significant coefficients are in bold characters

Variable	T_0	T_1	T_5	T_{15}	T_{30}	T_{50}	T_{75}	T_{100}
Density	**−0.89**	**−0.78**	**−0.57**	**−0.39**	−0.25	−0.14	0.13	**0.40**
Refractive index	**−0.81**	**−0.66**	**−0.47**	−0.32	−0.14	−0.04	0.19	**0.43**
Saponification number	**−0.87**	**−0.71**	**−0.49**	−0.33	−0.21	−0.10	0.14	0.35
Iodine number	**0.86**	**0.71**	**0.49**	**0.42**	0.16	0.11	−0.11	**−0.40**
Acid number	**−0.90**	**−0.74**	**−0.48**	−0.36	−0.14	−0.07	0.25	**0.42**

From the practical point of view, the correlation coefficients between the chemical variables and T_0, T_1 and T_5 are of the highest significance. By using the equation $y=a+bx$ the value of density, refractive index, and saponification, iodine and acid numbers can be estimated from T_0, T_1 or T_5 from TG and DTG curves. The regression equations for T_0 and T_1 for the oils tested are given in Table 4.

To find the relation between the chemical and thermoanalytical variables, PCA was used. In this method, the high number of variables can be reduced to two or three principal components which very often illustrate relations among objects in multi-dimensional space. In this way, problems which are difficult to imagine or interpret become easy to present in clear two or three dimensional plots.

In the case of the chemical data, the two first principal components (PC1 and PC2) describe ca. 93% (a sufficiently high value) of the experimental data. As shown in Fig. 3, the oil samples studied can be clearly divided into two groups, according to their position on the PC1 axis. At PC1>0.5, there are low quality oils (inside the hand-drawn, continuous line). This group contains nineteen rapeseed oils, Nos. 4, 6, 8, 9, 10, 12, 14, 16, 18, 19, 20, 22, 24, 26, 28, 38, 44, 47 and 48. Within this cluster, the oil samples with PC1>2.0 (Nos. 4, 8, 10, 12, 16, 18, 20, 22 and 24) are rancidified in the highest degree. As shown in Table 1, these oils are generally characterized by higher values of density and refractive index as well as saponification and acid numbers, and decreased iodine number. There are twenty-nine rapeseed oils which meet the requirements of the standard, all located on the left side of the plot.

In the case of the thermoanalytical results, the two first principal components (PC1 and PC2) explain more than 84% of the variation. As shown in Fig. 4 by the hand-drawn line, oil samples of high and low quality are also clearly separated in this plot. The cluster marked by the line includes 20 samples of low quality including the same nineteen oils as in the previous plot plus the addition of sample No. 2. This oil and sample No. 15 are characterized by a high acid number and for this reason have been classified as oils of average quality. As in the case of chemical analyses data, oils rancidified in the highest degree are clearly separated and have PC2>1.8.

Scatterplots of the first two principal component loading factors show all the chemical and thermoanalytical variables are useful for differentiating oil quality. Strong relations exist between the chemical variables and PC1, except for the iodine

Table 4
Linear regression equations for the relation between the chemical variable and T_0, the initial temperature of thermal decomposition, or T_1, the temperature of 1% loss in mass, for refined rapeseed oils. The standard error of the estimation of intercept (S_a) and slope (S_b) of the linear equation $y=a+bx$, and R^2 (in percentage) are indicated in parentheses

Chemical variable	T_0	T_1
Density	$1.060\ (1.0\times10^{-2})-2.99\times10^{-4}(2.2\times10^{-5})T_0$ (79.35%)	$1.154\ (2.7\times10^{-2})-4.49\times10^{-4}(5.3\times10^{-5})T_1$ (60.50%)
Refractive index	$1.490\ (1.7\times10^{-3})-3.54\times10^{-5}(3.8\times10^{-6})T_0$ (65.25%)	$1.499\ (4.3\times10^{-3})-4.97\times10^{-5}(8.4\times10^{-6})T_1$ (43.45%)
Saponification number	$250.5\ (4.7)-0.12(1.0\times10^{-2})T_0$ (75.42%)	$283.6\ (13.1)-0.17(2.5\times10^{-2})T_1$ (50.41%)
Iodine number	$-36.14\ (12.12)+0.31(2.7\times10^{-2})T_0$ (74.30%)	$-118.6\ (33.0)+0.43(6.4\times10^{-2})T_1$ (49.68%)
Acid number	$17.02\ (1.11)-3.33\times10^{-2}(2.4\times10^{-3})T_0$ (80.30%)	$26.15\ (3.26)-4.73\times10^{-2}(6.4\times10^{-3})T_1$ (54.58%)

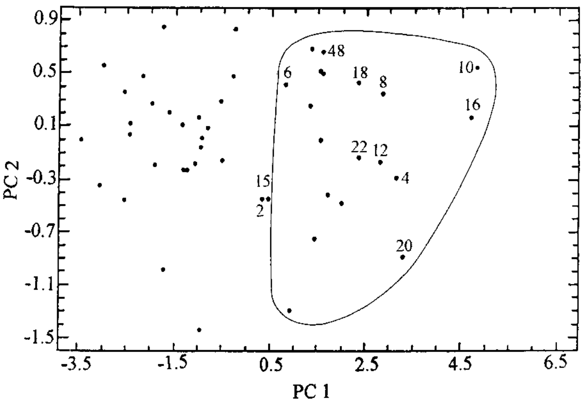

Fig. 3. Plot of the first two principal component score vectors (PC1 vs. PC2) for 48 samples of refined rapeseed oils based on the chemical analyses data listed in Table 1. The cluster marked by the hand-drawn line includes the low quality oils.

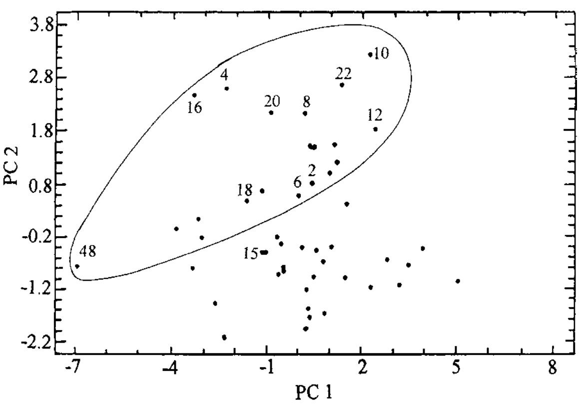

Fig. 4. Plot of the first two principal component score vectors (PC1 vs. PC2) for 48 samples of refined rapeseed oils based on the thermoanalytical data listed in Table 2. The cluster marked by the hand-drawn line includes the low quality oils.

number, but no relations were found for PC2. Density, saponification and acid numbers are similarly useful in the classification of rapeseed oils. All the thermoanalytical variables are highly correlated with PC1. In the case of PC2, correlations exist only for T_{75} and T_{100}.

4. Conclusions

PCA accurately reflects oil rancidity. Discrimination between oils using thermal methods of analysis is as good as that achieved by chemical analysis. Consequently, thermal methods of analysis can be applied for defining the quality of refined rapeseed oils.

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