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APPLICATION OF CHEMOMETRICALLY PROCESSED CHEMICAL AND THERMOANALYTICAL DATA FOR QUALITY CONTROL OF SOYBEAN OILS

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Abstract

The quality assessment of commercial soybean oils was evaluated on the basis of chemical and thermal analyses. The most substantial chemical parameters, viz. the density, refractive index and saponification, iodine and acid numbers were estimated. The thermal parameters were determined on the grounds of the TG and DTG curves. There are temperatures for the onset, end and successive mass losses. To find the relation between the chemical and thermal parameters, regression and principal component analyses were applied. The results of principal component analysis indicate that the TG and DTG techniques are at least in equal degree useful in defining the quality of soybean oils, as compared with the chemical analyses.

Keywords: chemical analysis, DTA, principal component analysis, quality assessment, soybean oil, TG and DTG analysis

Introduction

It is well recognized that the thermoanalytical techniques play an important role in the solution of a variety problems in the field of essential and plant oils as well as animal fats. The utility of differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) in that fields has been documented in a number of studies. They are useful for investigation of the phase transitions and determination of their thermodynamic constants [1–5], for examination of the thermal stability and kinetics of the thermooxidative decomposition [6–11] as well as for quality control of commercial oils and fats [9, 10, 12–14].

It is well known from common practice that identification of a sample (e.g. oil sample) and estimation of their physicochemical parameters requires a comparison of thermoanalytical curves [15]. In the former case the differences between the shape of experimental curves are evaluated, in the latter, the theoretical curve most similar to the measured one is searched. The curves may be compared by fitting or by means of quantities describing the shape of the curve. Taking above into account, this study designs to assess the quality of soybean oils by comparing the mass losses read from the TG and DTG curves [16]. Because of the fact that full evaluation of the oils on the basis of chemical as well as TG and DTG analyses produces a mul-

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tivariate problem, this work is an attempt to resolve these problems by using chemometric analysis. The primary scope of these methods is to get an overview of the dominant patterns or major trends in a large data matrix containing the results of many relevant measurements [17–19].

Experimental

Materials

In the study the commercial soybean oils were used. The samples were manufactured by various agricultural co-operatives in Poland and originate from consumer goods shops. Until to time of analysis they were stored in a dark place at a temperature of 298 K. They were protected against dustiness.

Determination of chemical parameters

The densities, refractive indices and saponification, iodine and acid numbers of the soybeam oils were determined according to the procedures given in the literature. The analytical results together with more precise description of the analytical procedure are published elsewhere [10].

Determination of thermal parameters

The thermal decomposition of oils was performed using OD-103 derivatograph (MOM, Budapest, Hungary). All measurements were carried out under the same conditions. 200 mg oil samples in a platinum crucible were heated in the furnace atmosphere at a rate of temperature increase of 5 K min^{-1}. α-Al_2O_3 was used as reference.

The temperatures of the onset (T_o) and end (T_{100}) of the thermal decomposition 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 solely from the TG curves. The detailed thermoanalytical results are published elsewhere [10].

Calculations

The principal component analysis (PCA) was used for interpretation of the chemical and thermoanalytical results for soybean oils [17–19]. The data matrix **X** with dimensions **n*k**, where **n** is the number of observations (rows) and **k** is the number of variables (columns), was standardized and correlation matrix **R** was calculated. It was recalculated in two new matrices – **W** and **P**. The principal component loadings are included in matrix **W** with dimensions **k*p**, while principal component scores are set in matrix **P** with dimensions **n*p**, where **p** is the number of orthogonal principal components calculated for a given set. **p** is at most equal to the number of variables **k**, and in fact it is much less than **p**. The practical conclusion, which comes from this condition is that the number of principal components is much less than the number of experimental variables **k**.

Two matrices were constructed. For the first assigned data set the chemical analysis of soybean oils [10]. Fifty three oils were used as the observations (rows), whereas the densities, refractive indices and saponification, iodine and acid numbers were written as the variables (columns). The second one contained data set for the thermal analysis of oils [10]. Just as previously, fifty-three oils were used as the observations (rows), while the T_0, T_1, T_5, T_{15}, T_{30}, T_{50}, T_{75} and T_{100} were used as the variables (columns).

Results and discussion

The chemical compounds formed in the course of the rancidification of edible oils change the shapes of their thermal decomposition curves. It has been found that along with the deterioration of an oil's quality, the beginning of the deflection of the TG curve from the baseline is shifted towards lower temperature values and, in addition, the curve is characterized by a less steep course. The same dependence is observed for the temperatures associated with the successive mass losses. That way it can be concluded, that the estimation of the degree of deterioration of soybean oil should be carried out for the temperatures associated with the initial segment of the mass loss in the TG curve.

Further investigation has indicated the existence of a certain relationships between values of the T_0, T_1, T_5, T_{15}, T_{30}, T_{50}, T_{75} and T_{100} and values of the density and reflective index as well as the saponification, iodine and acid numbers [10]. From the practical point of view the correlations between the chemical parameters and T_0, T_1 and T_5 are of most significance. Taking into account the linear regression equations, the temperature ranges may be determined to which the beginning of thermal decomposition of soybean oils and the 1 and 5% mass losses should correspond so that it could be estimated whether the oil met the standard. On the other hand, by virtue of the T_0, T_1 and T_5 values read from TG curves, the above mentioned chemical parameters can be determined.

To find the relation between the chemical and thermal parameters, PCA was applied. As a results of calculations two matrices were obtained, both for chemical and thermoanalytical data set. The matrix **P** reflects main relations among oil samples and allows their classification, whereas the matrix **W** illustrates main relations among variables, which makes their selection possible.

For the describing of the relations among empirical results that first principal components (PC) should be chosen, which have big variations and differ one from another on certain level. In that case it is possible to obtain proper and sufficiently adequate description of total data set of studied oils. Because of this, the distribution of the analysed soybean oil samples is illustrated in the two-dimensional plot.

Taking into account the results of chemical analyses, the calculated PC1 and PC2 explain together 81.2% of the studied variability. As it is shown in Fig. 1, all studied oil samples can be divided into two major groups. The first one, on the right-hand side of the plot, gather twenty oils with numbers 1, 8, 10, 13, 14, 15, 18, 19, 20, 21, 22, 24, 26, 29, 32, 35, 38, 44, 48 and 50. These oils are rancid and have been characterized by higher values of the density, refractive index and saponification number. On the other hand, the iodine number is lowering. The second one, on the left-hand side of the plot, contain oils which met requirements of the standard.

The distribution of soybean oil samples by virtue of thermoanalytical results is shown in Fig. 2. This plot was obtained according to the first two 'eigenvalues'. PC1 and PC2 cover 83.7% of the total variability, it is more than those for chemical results. Comparing Fig. 1 and Fig. 2, it can be concluded that the separation between two groups of oils on the grounds of chemical and of thermoanalytical data is very similar. In the group of rancid oils, eight oil samples is separated on the left-hand side of Fig. 2. There are most of all rancid oil samples. These oils cannot be distinctly separated in Fig. 1. That confirms higher ability of the thermoanalytical techniques in classification of oils than in the case of chemical methods. The oils

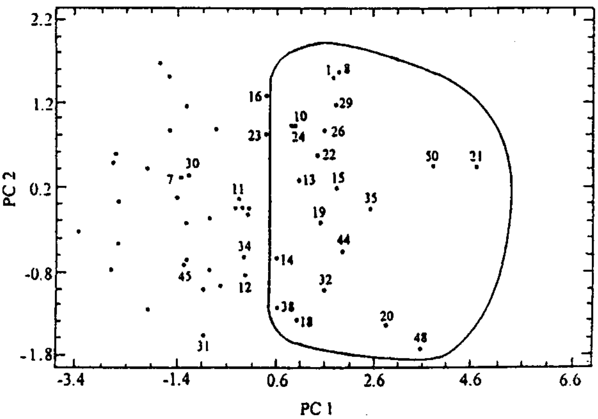

Fig. 1 Two-dimensional plot PC1 *vs.* PC2 for 53 soybean oil samples on the grounds of chemical data. The rancid oils are circled and numbered

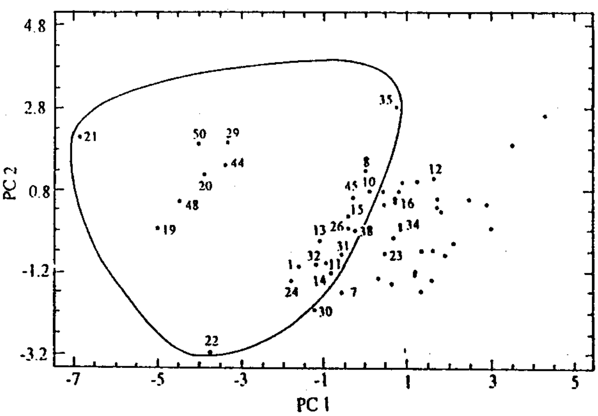

Fig. 2 Two-dimensional plot PC1 *vs.* PC2 for 53 soybean oil samples on the grounds of thermoanalytical data. The rancid oils are circled and numbered

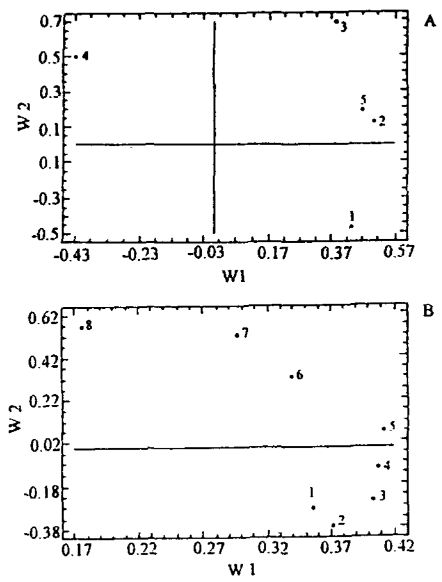

Fig. 3 Two-dimensional plot W1 *vs.* W2 for: (A) chemical and (B) thermoanalytical data. Numbers in Fig. 1A denotes - the density (1), refractive index (2) and saponification (3), iodine (4) and acid (5) numbers, whereas in Fig. 1B - T_0(1), T_1(2), T_5(3), T_{15}(4), T_{30}(5), T_{50}(6), T_{75}(7) and T_{100}(8)

with numbers 11, 31 and 45 are intermediate quality and have been found on the border line of both groups of oils.

By plotting the first two component loading factors (W1 and W2), the graph shows the complementary variable patterns that reveals information about relationships between variables. As it is shown in Fig. 3A and B, all the chemical and TG variables (with exception of T_{75} and T_{100}) are the most useful in the quality assessment of soybean oil samples. All these variables have a high loading in the PC1, only iodine number has a negative sign.

Conclusions

Based on the investigations performed it has been stated that the TG and DTG techniques can be applied for the quality defining of soybean oil.

The PCA makes possible to reduce a large number of variables (determination of 5 chemical and 8 thermoanalytical parameters in 53 soybean oil samples) to a smaller number of uncorrelated (orthogonal) factors which account at least of 80% of the total variance. This analysis proved, that it is the fruitful approach in the assessment of the quality of soybean oil samples which differ in the deterioration. The PCA very good reflects relationship between the degree of deterioration of oils as measured by different way, because it enables the comparable classification ability of chemical and thermoanalytical methods.

It should also be emphasized that the information by PCA cannot be immediately deduced from the classical mathematical treatment and classical diagrams.

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