Thermochimica Acta, 155 (1989) 327–337
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

APPLICATION OF PRINCIPAL COMPONENT ANALYSIS AND THERMOANALYTICAL METHODS IN EVALUATION OF EDIBLE FISH OILS

HENRYK LAMPARCZYK and MAREK WESOŁOWSKI
Medical Academy, Faculty of Pharmacy, K. Marksa 107, Pl 80-416 Gdańsk (Poland)
(Received 10 April 1989)

ABSTRACT

Using the example of 54 samples of edible fish oils and 43 samples of medicinal cod liver oils, the usefulness of thermal analysis techniques and classical analysis for the quality control of fish oils was compared. The data were processed using principal component analysis. The results indicate that this multivariate statistical method greatly assisted the analysts in the assessment of the quality of edible oils particularly in connection with thermal analysis. Some preliminary suggestions concerning selection of the thermoanalytical data are described.

INTRODUCTION

It is known from common practice that the quality assessment of edible oils on the basis of their physicochemical properties requires considerable labour. In this respect an investigation was undertaken to utilize the changes taking place in the course of the degradation of oils, which should be reflected by the thermal decomposition curves, for the quality assessment of fish oils [1–3].

The chemical compounds formed in the course of the rancidification of edible fish oils change the shapes of the thermal decomposition curves of the oils. 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 base line 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. Further investigation has indicated the existence of relationships between the temperature of the beginning of mass loss and the density, refractive index, saponification, iodine and acid numbers over the entire range of values [4,5].

Nevertheless, full evaluation of the edible oils on the basis of classical methods, as well as using thermoanalysis, produce a multivariate problem.

0040-6031/89/$03.50

Hence this work is an attempt to resolve these problems using principal component analysis (PCA) [6,7].

PCA provides an approximation of a data matrix (**X**) in terms of the product of two small matrices **T** and **P**. These matrices contain the essential data patterns of **X**. Plotting the columns of **T** gives a picture of the dominant object patterns of **X**. Similarly, plotting the rows of **P** shows the complementary variable patterns.

EXPERIMENTAL

Samples for testing

In this study, refined edible fish oils (EF) and medicinal cod-liver oils (MCL) were used. The EF samples had been produced from the middle-grade raw material in processing the fish flesh to fodder fish meal. The MLC samples were prepared from fresh livers of the Baltic cod and other fish of the *Gadid* family. The samples had been accumulated in 1972–1982 and received either from the Fish Processing Works in Gdynia (EF) or from the Galenic Laboratory of The Pharmaceutical Provision Enterprise in Gdańsk (MCL).

The samples for testing were prepared in accordance with the Polish Standard PN76/A-86911 [8]. Until analysis, they were stored in a dark place at a temperature of 277 K.

Testing procedure

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

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

The density of the fish oils was determined using a pyconometer of volume 10 ml at a temperature of exactly 293 K. For the determination of the refractive indices, an Abbe refractometer (Carl Zeiss, Jena, GDR) was used. The measurements were made at a temperature of exactly 293 K using a sodium discharge lamp of wavelength 589 nm.

The determinations of the saponification and acid numbers were conducted in accordance with the method described in FP IV [9]. The iodine number was determined by the Rosenmund method [10].

The analytical results together with a more precise description of the analytical procedures are published elsewhere [4,5].

Calculations

A data matrix **X**, consisting of $K = 1, 2, \ldots, k$ variables and $N = 1, 2, \ldots, n$ objects, was the starting point for futher chemometric investigations. Two sets of variables were used. For classical methods these were the acid, saponification and iodine numbers together with densities and refractive indices, and for thermoanalytical methods these were the temperatures T_0, T_1, T_5, T_{15}, T_{30}, T_{50}, T_{75} and T_{100} (which represent respective mass losses). From the data matrix **X**, its standarized version **Z** and correlation matrix **R** were calculated. The correlation matrix **R** was used as a starting matrix in principal component analysis. Principal components (PC) were determined by considering eigenvalues and associated eigenvectors. For plotting purposes only, two first principal component score vectors (t_1 and t_2) and corresponding loading vectors (p_1 and p_2) were used. These account for over 90% of variability in each case. In this way, five variables (classical method) and eight variables (thermoanalytical method) were reduced to two principal component scores t_1 and t_2.

For evaluation of the data, software developed in our laboratory for IBM-PC compatible microcomputers was used.

RESULTS AND DISCUSSION

Differentiation of EF samples

The data matrix for EF samples was taken from ref. 4. For the evaluation of oil samples on the basis of classical methods, it consists of 54 objects (oil samples) and 5 variables. Two data classes are present: high quality oils and rancid oils. The classification problem is clear: can we distinguish between these two categories on the basis of the data from classical analysis?

Table 1 lists the PC score values. Figure 1 shows the PC score plot for all 54 samples. Ten samples are clearly distinguished on the right-hand side of the plot. These correspond to the rancid oils. Therefore it can be concluded that the classification problem can be resolved using classical methods. To illustrate which variables are responsible for the separation of the two classes (high quality and rancid oils) the loading vectors p_1 and p_2 were plotted. The respective loading plot is shown on Fig. 2. The trends in Fig. 2 correspond directly to the trends in Fig. 1. The horizontal direction on Fig. 1

TABLE 1

First two principal component scores (t_1 and t_2) for edible fish oil samples

Sample	Classical method		Thermoanalytical method	
	t_1	t_2	t_1	t_2
1	−1.957	−0.359	2.169	0.217
2	3.318	−0.073	−2.102	3.079
3	−1.611	0.381	3.007	1.348
4	−1.073	0.359	0.720	−0.647
5	−0.985	0.331	1.592	0.673
6	−1.303	−0.268	0.766	−0.960
7	−1.400	−0.803	0.488	−1.998
8	0.338	−0.320	0.431	0.797
9	−0.493	0.059	1.417	−0.151
10	−1.324	−0.221	3.800	1.001
11	−0.884	−0.020	2.127	1.209
12	−1.179	0.018	1.410	1.551
13	−1.750	−0.719	1.824	0.431
14	−1.539	−0.444	2.022	−0.844
15	−0.479	−0.037	1.592	0.673
16	−1.415	0.424	0.684	−0.909
17	3.925	−0.447	−2.459	2.674
18	4.160	1.113	−3.624	1.903
19	−1.173	−0.047	1.077	−0.137
20	−0.935	0.312	1.993	1.572
21	−1.331	−0.082	1.281	−0.222
22	−0.904	0.646	2.095	2.071
23	0.049	1.023	−1.407	−0.076
24	0.414	0.613	0.302	0.218
25	−1.531	−0.622	1.235	−0.390
26	−1.483	−0.163	2.622	1.549
27	−1.550	−0.047	0.377	−1.323
28	−1.259	−0.406	0.468	−0.657
29	−0.738	0.158	1.990	1.339
30	2.550	−0.976	−3.092	0.011
31	−0.498	0.028	−0.696	−1.351
32	−1.507	−0.194	−0.330	−0.792
33	4.623	−0.048	−4.800	0.560
34	4.722	−0.631	−4.264	1.678
35	−1.376	−0.333	−0.249	−1.090
36	−0.372	−0.179	−1.636	−2.253
37	4.879	−1.107	−4.221	1.932
38	0.665	0.539	−1.694	−2.755
39	0.406	0.477	−0.336	−0.110
40	3.014	0.829	−3.219	0.500
41	−1.241	0.481	1.542	0.043
42	−1.691	0.296	1.021	−0.731
43	−0.980	0.360	−0.774	−2.325
44	−1.322	−0.270	2.426	1.415
45	−0.759	0.090	0.536	−0.959
46	−0.909	0.526	−0.412	−1.142

TABLE 1 (continued)

Sample	Classical method		Thermoanalytical method	
	t_1	t_2	t_1	t_2
47	−1.586	−0.116	2.306	0.352
48	0.553	0.419	−0.131	−0.004
49	4.497	−0.070	−4.305	−0.079
50	−1.224	−0.103	−1.354	−2.212
51	−1.396	−0.527	1.020	−1.919
52	0.506	0.124	−1.253	−2.677
53	5.611	0.201	−5.231	0.700
54	−1.075	0.671	1.250	−0.791

separates the oils into two classes. Variables far from zero in the horizontal direction are those responsible for this. Therefore, it can be concluded that acid and iodine numbers are most informative.

For the evaluation of oil samples on the basis of thermoanalytical methods, the data matrix **X** with dimensions 54×8 was applied. The principal component scores are listed in the last two columns of Table 1. Figure 3 shows the t_1 versus t_2 plot. Comparing Fig. 1 and Fig. 3, it can be concluded that the separation between high quality and rancid oils on the basis of classical methods and on the basis of thermoanalytical methods is

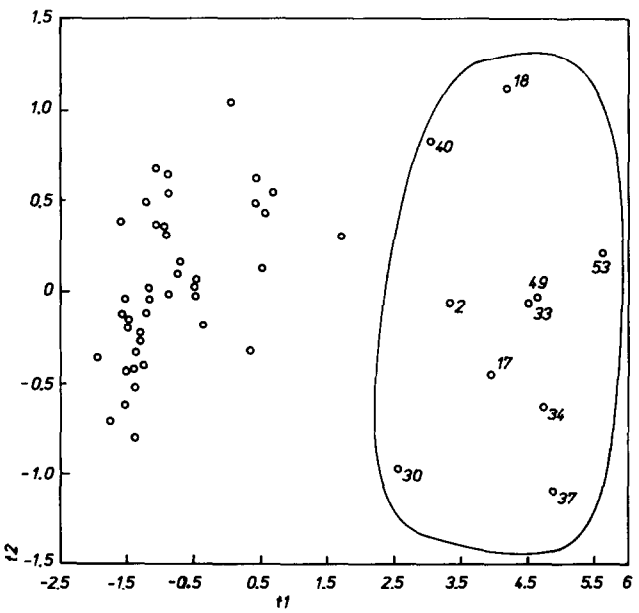

Fig. 1. Principal component scores plot derived from edible fish oil analysis. Classical methods were used. The rancid oils are numbered and circled. A full list of PA scores is given in Table 1.

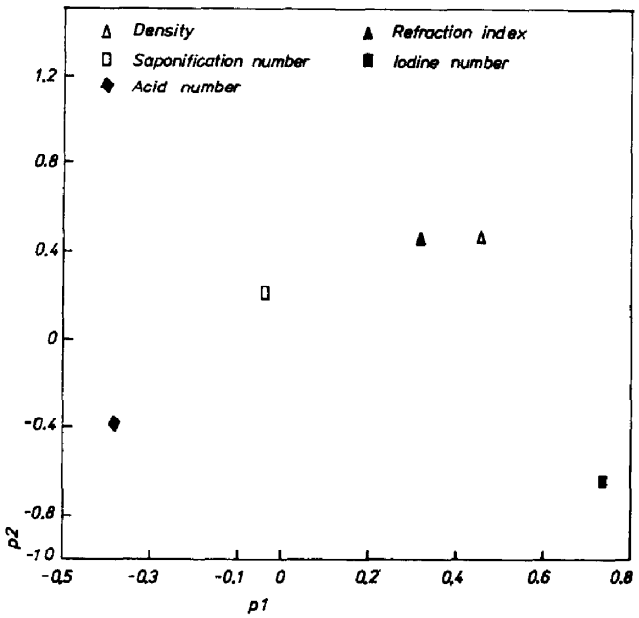

Fig. 2. Loading plot corresponding to Fig. 1.

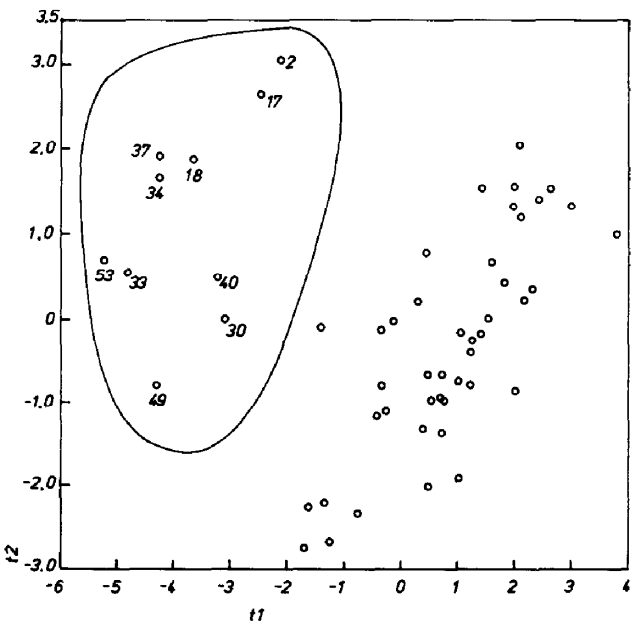

Fig. 3. Principal component scores plot derived from edible fish oil analysis. Thermoanalytical methods were used. The rancid oils are numbered and circled. A full list of PA scores is given in Table 1.

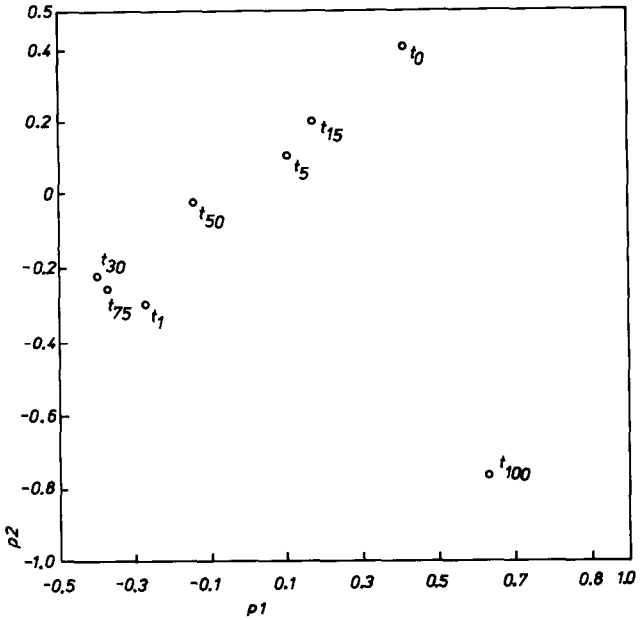

Fig. 4. Loading plot corresponding to Fig. 3.

similar. Samples 53, 33, 34, 37, 49, 18, 40, 30, 17 and 2 are clearly distinguished and can be classified as the most rotten oils. The corresponding p_1 versus p_2 plot is shown on Fig. 4. From this figure it can be seen that the t_{100}, t_0, t_{30} and t_{75} variables were mostly responsible for the separation.

Differentiation of MCL samples

The data matrices for MCL samples were taken from ref. 5. The data matrix **X** used for the evaluation of oil samples on the basis of classical methods have 43×5 dimensions. Table 2 lists the PC score values, while Fig. 5 shows the t_1 versus t_2 plot. Thirteen samples are clearly distinguished from the others. These correspond to rancid MCL samples. It confirms our earlier finding that five classical methods are suitable for full separation between the high quality and rancid oils. The plot of loadings (p_1 versus p_2) is shown on Fig. 6. In this case, acid number, density and saponification number are largely resposible for the sample classification. The comparison between Figs. 2 and 6 shows that the rank of a particular classical method depends on the nature of the oil sample. Hence, all five methods are recommended for proper classification of an unknown oil sample. Figure 7 shows the t_1 versus t_2 plot for MCL samples obtained on the basis of thermoanalytical methods. Comparison between Figs. 5 and 7 leads to the conclusion that the separation ability of classical and thermoanalytical methods is similar. Figure 8 shows the loadings plot for thermoanalytical

TABLE 2

First two principal component scores (t_1 and t_2) for medicinal cod-liver oil samples

Sample	Classical method		Thermoanalytical method	
	t_1	t_2	t_1	t_2
1	2.192	−0.530	−1.736	0.826
2	−1.172	0.126	−1.384	−2.409
3	−0.288	0.240	−0.681	−1.147
4	4.808	−1.046	−4.693	1.063
5	−1.378	0.916	−0.300	−1.879
6	1.556	−0.494	−0.569	0.807
7	2.102	−0.052	−1.564	0.935
8	0.852	0.316	−1.910	−0.943
9	4.151	0.177	−4.062	1.056
10	−1.560	−0.013	1.588	−0.633
11	4.346	0.610	−4.237	0.500
12	5.485	−0.032	−6.123	0.725
13	5.303	0.140	−3.451	2.376
14	−1.703	−0.098	−0.896	−2.297
15	−1.268	−0.182	0.345	−1.188
16	−1.287	0.455	1.557	0.456
17	−1.177	0.534	1.464	0.499
18	−0.760	0.468	2.119	1.882
19	1.158	0.358	−0.668	1.285
20	1.640	0.610	0.911	3.136
21	1.761	0.787	0.206	3.547
22	−0.831	0.254	1.890	1.246
23	−1.684	−0.683	2.528	0.992
24	0.148	−0.346	1.611	2.433
25	−1.610	0.730	2.179	1.141
26	−1.191	−0.206	0.107	−2.451
27	−1.304	0.276	2.836	2.262
28	−1.459	0.452	0.614	−1.252
29	−1.506	0.689	3.471	2.322
30	−1.426	0.340	1.359	0.167
31	2.550	−0.321	−2.222	1.121
32	−1.400	−0.282	1.312	−0.873
33	−1.229	−0.403	0.221	−2.263
34	−1.544	−0.209	1.396	−0.508
35	−1.603	−0.722	−0.244	−1.674
36	−1.073	−0.482	1.268	−0.544
37	−1.369	−0.174	0.928	−1.493
38	−1.594	−0.227	1.127	−1.560
39	−1.295	−0.162	0.711	−1.814
40	−1.076	−0.602	1.411	−0.881
41	−1.350	−0.281	0.641	−1.673
42	−1.151	−0.470	0.915	−0.896
43	−1.402	−0.463	0.028	−2.411

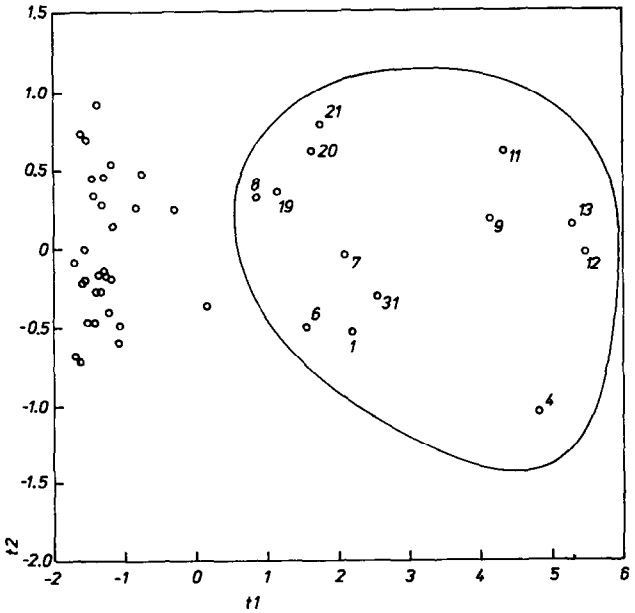

Fig. 5. Principal component scores plot derived from medicinal cod liver oil analysis. Classical methods were used. The rancid oils are numbered and circled. A full list of PA scores is given in Table 2.

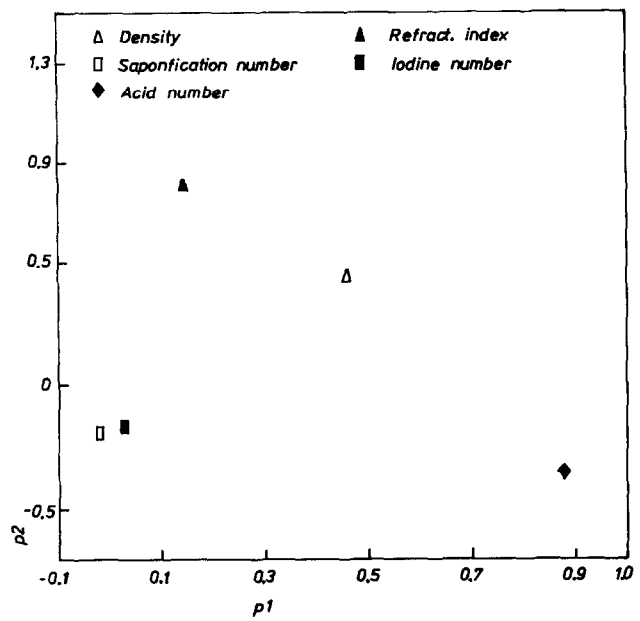

Fig. 6. Loading plot corresponding to Fig. 5.

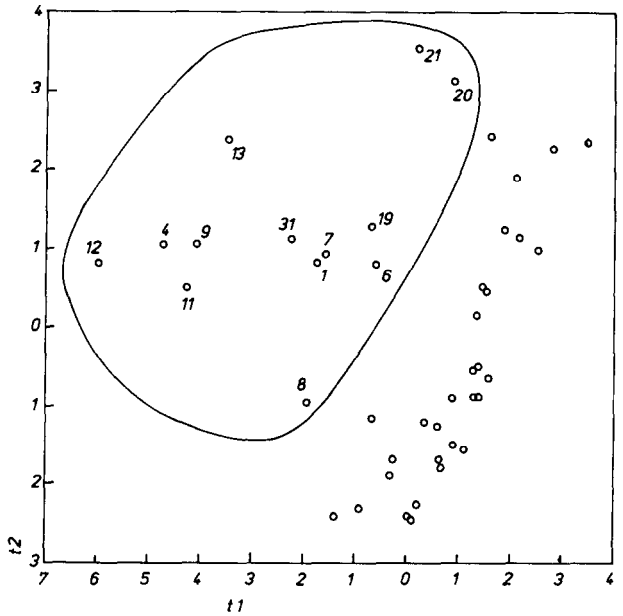

Fig. 7. Principal component scores plot derived from medicinal cod liver oil analysis. Thermoanalytical methods were used. The rancid oils are numbered and circled. A full list of PA scores is given in Table 2.

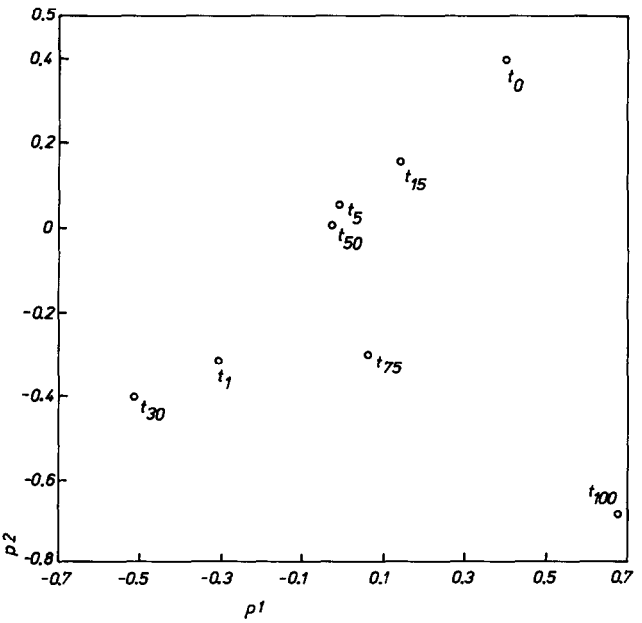

Fig. 8. Loading plot corresponding to Fig. 7.

methods. This figure shows the prevalent influence of variables T_{100}, T_0 and T_{30} for the MCL oils classification. It is noteworthy that the variables rank is similar to those observed in the case of the EF oils. This suggests further possible reductions in thermoanalytical data required for proper oil classification. Moreover, the classification procedure can be based on only thermoanalysis and computerized data transformation. In this work, the classical methods were used only for comparison. Hence, our results suggest the possibility of the construction of equipment for automated oil evaluation based on a derivatograph coupled with a microcomputer.

CONCLUSIONS

Our results indicate that principal component analysis greatly assisted the analysts in the assessment of the quality of edible oils. Using this method, the multivariate problem can be effectively reduced to two variables. Our results demonstrate the comparable classification ability of classical and thermoanalytical methods. However, in the case of thermal analysis of different oils, the variable rank seems to be stable. This suggests a possible reduction of the measured thermoanalytical data required for proper oil evaluation.

REFERENCES

1 I. Buzas, J. Simon and J. Holló, J. Therm. Anal., 12 (1977) 397.
2 I. Buzas, E. Kurucz-Lusztig and J. Holló, Acta Alimentaria, 7 (1978) 335.
3 I. Buzas, E. Kurucz and J. Holló, J. Am. Oil Chem. Soc., 56 (1979) 685.
4 M. Wesołowski, Fett. Wissenschaft Technol., 89 (1987) 111.
5 M. Wesołowski, Sci. Pharm., 54 (1986) 11.
6 S. Wold, Pattern Recognition, 8 (1976) 127.
7 B.R. Kowalski, Anal. Chem., 52 (1980) 112R.
8 Polish Standard PN-76/A-86911, Tłuszcze roślinne jadalne, Metody badań, Przygotowanie próbek do analizy (Edible vegetable fats, testing methods, preparation of samples for analysis).
9 Farmakopea Polska IV (IVth Polish Pharmacopoeia), PZWL, Warsaw, Vol. 2, 1970, p. 359.
10 Z. Stolzmann, Podręcznik do ćwiczeń z chemii fizjologicznej (Laboratory Textbook of Physiological Chemistry), PZWL, Warsaw, 3rd edn., 1954, p. 72.