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Thermoanalysis supported by principal component analysis (PCA) in quality assessment of essential oil samples

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Abstract

As exemplified by the analysis of 25 essential oil samples from three different species, the usefulness of thermoanalytical techniques in quality control has been estimated. Nine thermoanalytical parameters derived for each sample were used as variables for further characterization by a chemometric procedure. Principal component analysis was applied to the differentiation of samples from different sources and obtained by different technologies.

INTRODUCTION

Essential oils are complex mixtures of flavour and fragrance substances originating in plants. They have found comprehensive commercial application in the pharmaceutical, food and cosmetics industries. From the chemical viewpoint the majority of essential oils are mixtures of mono- and sesquiterpenoids, containing only minor amounts of compounds belonging to other classes. A second rather large group of essential oils consists mainly of aromatic compounds, including phenols [1]. The quality and identity control of essential oils includes sensory and chemical analysis. Commonly the oils are characterized by physical constants, such as density, refractive index and optical rotation. These investigations are increasingly supplemented by modern instrumental techniques, among which gas chromatography plays the most important role [2–5]. In general, the chemical analysis of essential oils is a difficult task because of their variability, complexity and wide range of possible impurities. Hence, there is a need for the extension of available analytical methods.

Thermoanalytical methods are widely used in analysis of complex mixtures of natural origin, although reports on the use of such methods in

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essential oil chemistry are limited. Nevertheless, they have been successfully applied in the quality control of vegetable oils. Hannewijk and Haighton [6] showed that the DTA curves are very useful in studying the melting behaviour of various stabilized and unstabilized natural oils. Hassel [7] used the DTA technique to evaluate the relative oxidative stabilities of vegetable oils. This method offer the advantages of good quality control time, requiring limited equipment and operator expertise. Moreover, Nieschlag et al. [8] proved that the TG technique provides data which can be useful for estimating the relative keeping qualities of different samples of the same oil. Complicated changes in chemical composition and thermal transformations occurring under an atmosphere of air made classical interpretation of the results of the thermal decomposition of natural products difficult. Based on an analysis of the shape of the TG and DTG curves, the characteristic parameters for these products can be indicated, such as the temperatures of the initial, the final and the successive mass losses [9].

The many parameters which have to be considered produce a multivariate problem. This work is an attempt to resolve these problems using principal component analysis (PCA) [10–12]. PCA provides an approximation of a data matrix ($\boldsymbol{X}$) in terms of the product of two small matrices $\boldsymbol{T}$ and $\boldsymbol{P}$. These matrices capture the essential data patterns of $\boldsymbol{X}$. Plotting the columns of $\boldsymbol{T}$ gives a picture of the dominant object patterns of $\boldsymbol{X}$. Similarly, plotting the rows of $\boldsymbol{P}$ shows the complementary variable patterns.

In our previous work [13] we have applied the thermoanalytical method for the analysis of a number of essential oils from different species. Using the PCA method, the essential oils can be divided into three groups: oils containing terpenoids and sesquiterpenoids without a predominant compound, oils with a single predominant compound of low molecular weight, and oils with esters as the main fraction. These results also suggest that thermal analysis might be a very useful method for quality assessment of essential oils, particularly those belonging to the first group. Therefore this work is an attempt to apply this method in the quality control of essential oils.

EXPERIMENTAL

Samples for testing

The essential oils were prepared from the following species of plants: *Pinus sylvestris* L. (pine), *Abies alba* Mill. (silver fir) and *Coriandrum sativum* L. (coriander). Plant material of *P. sylvestris* and *A. alba* species was collected from the forests of various parts of Poland. Two pine needle oils (nos. VI and XII) and two silver fir oils (nos. II and IV) were

TABLE 1

Results of thermogravimetric analysis of essential oil samples

	Sample	Temperatures of successive mass losses (°C)							h (mm)	T_m (°C)
		T_5	T_{30}	T_{70}	T_{80}	T_{90}	T_{95}	T_{100}		
1	Silver fir I	50	110	140	145	150	160	465	163	145
2	Silver fir II	60	105	135	140	150	155	455	69	145
3	Silver fir III	50	90	120	130	140	145	490	85	135
4	Silver fir IV	75	120	150	160	175	220	515	62	145
5	Coriander I	85	135	160	165	170	180	480	197	160
6	Coriander II	85	140	165	170	175	180	480	190	170
7	Coriander III	85	140	165	170	175	180	480	180	170
8	Coriander IV	70	130	170	230	370	470	550	118	135
9	Coriander V	90	130	160	165	170	175	480	102	180
10	Coriander VI	70	105	145	155	165	175	480	70	140
11	Coriander VII	50	100	130	140	155	170	540	57	125
12	Coriander VIII	80	130	160	165	180	190	515	88	265
13	Coriander IX	70	120	150	160	165	170	450	81	165
14	Pine needle I	70	115	140	145	155	180	530	185	140
15	Pine needle II	50	110	145	150	155	160	520	167	155
16	Pine needle III	50	100	130	135	140	150	470	175	135
17	Pine needle IV	50	100	130	135	140	150	460	185	140
18	Pine needle V	55	100	130	135	140	145	460	109	140
19	Pine needle VI	80	125	160	170	190	235	525	71	160
20	Pine needle VII	60	100	135	140	145	155	470	111	150
21	Pine needle VIII	65	110	140	145	150	155	490	117	150
22	Pine needle IX	80	110	135	140	145	150	475	117	140
23	Pine needle X	50	100	125	130	140	160	510	119	135
24	Pine needle XI	60	110	135	140	150	185	510	87	140
25	Pine needle XII	60	100	160	195	270	390	530	55	130

imported from North Korea. Because the exact species yielding those oils are unknown they are designated as *Pinus* sp. and *Abies* sp. respectively. Plants of *C. sativum* L. were cultivated on plantations in Poland. The essential oils were obtained by the steam distillation process in Herbapol Enterprise, apart from the oils obtained from Korea. A full list of the oils investigated is given in Table 1. Roman numbers following the oil name denote different production outputs of the same oil.

Testing procedure

The DTA, TG and DTG curves in the thermal decomposition of essential oils were determined using the OD-103 derivatograph (MOM, Budapest, Hungary). All measurements were carried out under the same conditions. A weighed sample of 200 mg of oil in a platinum crucible was heated under the atmosphere of the furnace at a temperature increase rate of 5°C min^{-1} up to the final temperature of 700°C. α-Al_2O_3 was used as reference material. Each curve was recorded at least three times. The temperatures of the end of thermal decomposition (T_{100}) were read from the TG and DTG curves, whereas the temperatures for 5%, 30%, 70%, 80%, 90% and 95% losses in mass (T_5, T_{30}, T_{70}, T_{80}, T_{90} and T_{95}) were read exclusively from the TG curves. DTG peak height (h) was read as the distance between the baseline of the DTG curve and the peak apex. T_M represents the temperature of maximum height of the DTG peak.

The density of the essential oils was determined using a pyknometer of 5 ml volume at a temperature of exactly 20°C. For the determination of the refractive indices an Abbé refractometer (Carl Zeiss, Jena, Germany) was used. The measurements were made at a temperature of exactly 20°C using a sodium discharge lamp of 589 nm wavelength. The specific optical rotation was determined using a polarimeter (Carl Zeiss, Jena) equipped with a sodium discharge lamp of 589 nm wavelength.

Calculations

A data matrix $\boldsymbol{X}$, consisting of $K = 1, 2, \ldots, k$ variables and $N = 1, 2, \ldots, n$ objects, was the starting point for further chemometric investigations. As variables, used the temperatures which represents respective mass losses (T_5, T_{30}, T_{70}, T_{80}, T_{90}, T_{95} and T_{100}), the DTG peak height (h) and the temperature of maximum height of the DTG peak (T_m). From the data matrix $\boldsymbol{X}$, its standardized version $\boldsymbol{Z}$ and correlation matrix $\boldsymbol{R}$ were calculated. The correlation matrix $\boldsymbol{R}$ 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, three or two first principal component score vectors ($\boldsymbol{t}_1$, $\boldsymbol{t}_2$ and $\boldsymbol{t}_3$) were used. These account for over 80% of the variability in each case. In this way eight variables were reduced to three or two principal component scores.

RESULTS AND DISCUSSION

Thermal decomposition of essential oils

The results of the thermal decomposition of essential oils are listed in Table 1. The great similarity of the shape of the DTA, TG and DTG curves and the approximate temperature ranges of the particular thermal processes indicate that the chemical compositions and the resulting chemical transitions which occur are closely similar. This makes it impossible to identify the reaction responsible for the appearance of definite endo- and exo-thermic effects. On the other hand, it is not feasible to identify the weight loss associated with the decomposition of a definite component of an essential oil.

It can be stated in general that the thermal decomposition of essential oils proceeds in two main stages. The first stage is the distillation of the volatile oil fraction. The distillation process, which begins at ≈30°C, is common to all essential oils. As is shown in Fig. 1A (pine needle IX), a rapid loss in mass is observed in a very narrow temperature range. The high and narrow DTG effect indicates that this loss is associated with the release of a mixture of liquid components similar in physico-chemical properties. This is also confirmed by the endothermic effects on the DTA curve. The residue, which constitutes a maximum 2% of the essential oil mass, undergoes decomposition in the second stage.

The group of essentials oils for which the residue after distillation is decomposed and burnt in the second stage can be divided into two subgroups. In the first subgroup the second stage of thermal decomposition is marked by 3–10% loss in mass. This is reflected in Fig. 1B (pine needle X) by a slight deviation on the TG and DTG curves from the baseline. This process is also accompanied by a wide and shallow exothermic effect on the DTA curve. The second subgroup is represented in Fig. 1C (pine needle XII). This is an example of an essential oil which is characterized by a distinct loss in mass in the second stage. A large exothermic peak is observed at the end of the DTA curve, and a distinct effect on the DTG curve. A considerable mass loss, of about 15–30%,

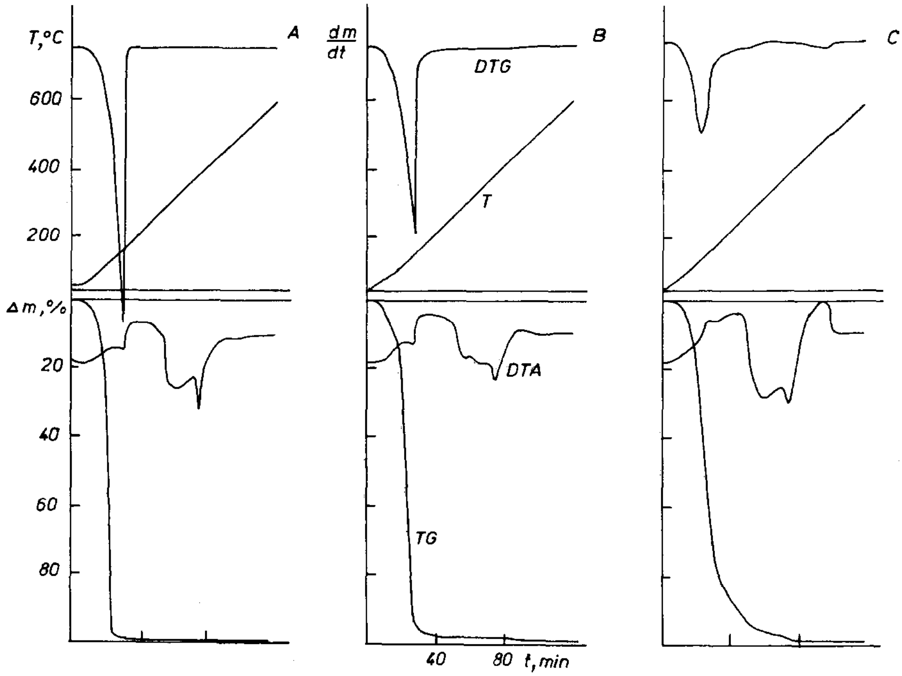

Fig. 1. DTA, TG and DTG curves of the thermal decomposition of pine needle oils: (A) No. 22, pine needle IX; (B) No. 23, pine needle X; (C) No. 25, pine needle XII.

TABLE 2

Classification of the essential oils according to type of the thermal decomposition

Essential oil	Stages of thermal decomposition		
	First	Second	
		First subgroup	Second subgroup
Loss in mass (%)	98–100	3–10	15–30
Silver fir	I–III	IV	
Coriander	I–III, V–IX		IV
Pine needle	II–V, VIII, IX	I, VII, X, XI	VI, XII

confirmed that the coked residue remaining after decomposition of the essential oils burns off slowly, so that the decomposition of the products ultimately terminates within the range 160–530°C. A classification of all the essential oils studied is presented in Table 2.

PCA differentiation of the whole sample set

It is without doubt that the shape of the thermoanalytical curves is conditioned by the chemical composition of the essential oil being degraded. In chemotaxonomy [14] the chemical individuals which constitute essential oils are classified as secondary metabolites. The quality and the quantity of secondary metabolites in plant species differ greatly, not only from species to species but within a species as well. The causal agent of such variations is little known [15]. In such a case, besides genetic factors, both macro- and micro-environment would be responsible for the variations in chemical composition of the essential oil. Hence it cannot be expected that the principal component analysis of the thermoanalytical data will be a reflection of the botanic system. On the other hand, thinking about essential oils as commercial products which should be standardized, some general requirements for their chemical composition are needed. The PCA examination of the whole data set may answer the question if thermoanalytical methods can support the chemical assessment of essential oils.

The data matrix for essential oil samples is listed in Table 1. It consists of 25 objects (oil samples) and nine variables. The following sequence of positive eigenvalues was calculated: 4.46, 2.07, 1.31, 0.53, 0.42, and four values less than 0.2. The number of PC scores was estimated from the sequence of the eigenvalues. Only eigenvalues greater than 1 were considered, and in this case over 86% of the total variance is explained by

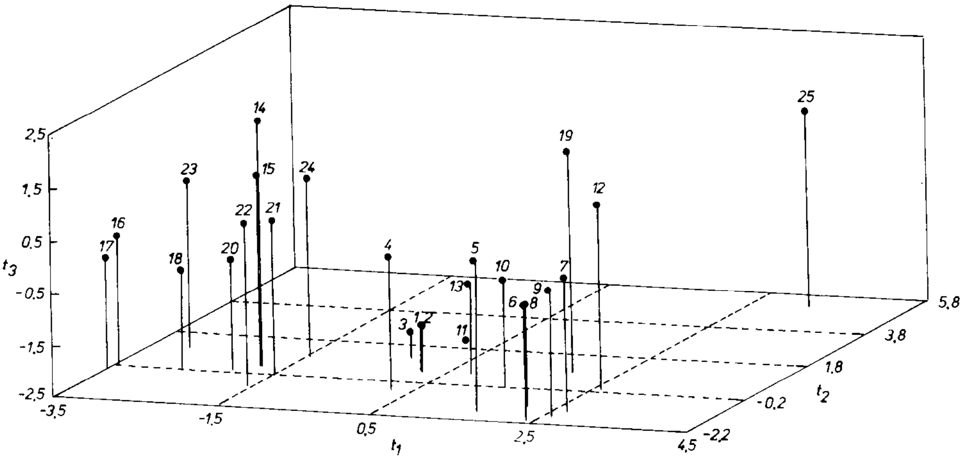

Fig. 2. Principal component scores plot derived from the thermoanalytical data for the whole sample set.

this rule. In this way nine variables were reduced to three PC scores. Figure 2 shows the PC score plot for all 25 samples. With the exception of samples 19 (pine needle VI) and 25 (pine needle XII) the samples cluster in accordance with the species from which the essential oils were derived. Moreover, samples 19 and 25 originated from North Korea and in this work the species is designated as *Pinus* sp. It should be noted, however, as it was stated in our previous work [13], that this classification is connected more with the chemical composition of an essential oil than with botanic systematics.

PCA differentiation in quality assessment of essential oils

The main aim of this work is to test the thermoanalytical technique supported by principal component analysis in quality assessment of essential oil samples. Therefore the essential oils considered were studied separately and the results were compared with the standardized assessment in accordance with the Polish Pharmacopoeia [16] and the Pharmaceutical Codex [17].

PCA analysis of pine needle oils

The data matrix for pine needle oil samples consists of 12 objects and nine variables. The following sequence of positive eigenvalues was calculated: 4.92, 2.20, 0.82, 0.60, 0.40, 0.05, and three values less than 10^{-2}. The number of PC scores was estimated from the sequence of eigenvalues. Only eigenvalues greater than 1 were considered, and in this case over 80% of the total variance is explained by this rule. The t_1 vs. t_2

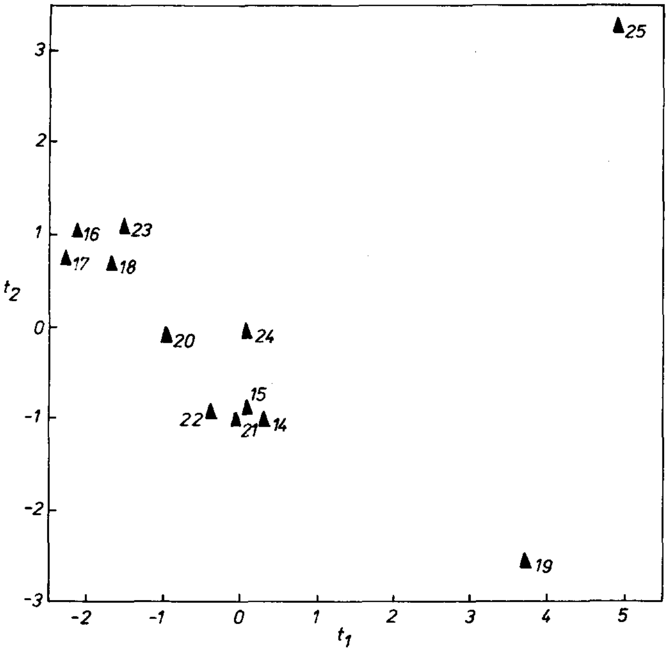

Fig. 3. Principal component scores plot derived from analysis of pine needle oils.

plot is shown on Fig. 3. Samples 19 (pine needle VI) and 25 (pine needle XII) are clearly distinguished on the right-hand side of the plot. These samples originated from North Korea. The standard requirements for pine needle oils are as follows: $d_{20}^{20} = 0.861$–0.881, $[\alpha]_D = -20°$ to $+13°$. Oils 14, pine needle I ($d_{20}^{20} = 0.922$), and 25, pine needle XII ($d_{20}^{20} = 0.911$), differ from the standard.

Although all remaining pine needle oils are in accordance with the Polish Standard it is interesting to note that the two essential oils from North Korea have left handed optical rotation coefficient ($[\alpha]_D = -3.3°$ for pine needle VI and $[\alpha]_D = -13.2°$ for pine needle XII). Other standards require also the measurement of refractive indices. As an example, the Pharmaceutical Codex [17] requires for pine needle oils that the refractive indices should range from 1.470 to 1.480. Three of the oils investigated, i.e. 14, pine needle I ($n_D^{20} = 1.484$), 19, pine needle VI ($n_D^{20} = 1.481$), and 25, pine needle XII ($n_D^{20} = 1.485$), differ from this standard. Because, all these three samples have higher t_1 values than the other oils it can be suggested that the quality control of pine needle oils can be resolved using thermoanalytical data.

In order to study whether thermoanalytical methods are suitable for controlling the technological process, a few samples (i.e. oils 21, pine needle VIII, 22, pine needle IX, and 23, pine needle X) were taken after various times of steam distillation. The principal component

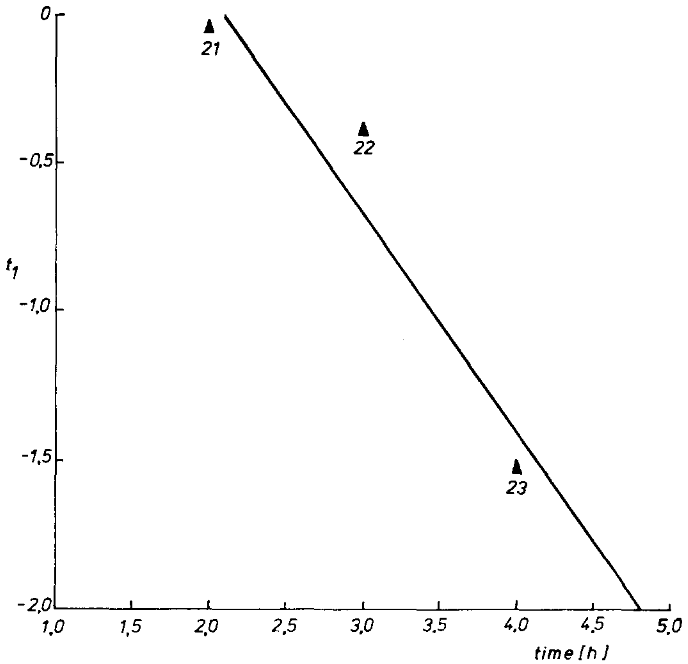

Fig. 4. Plot of the first principal component score vector (t_1) against time of distillation of pine needle oils.

score values (t) are computed such that the first value (t_1) describes, as far as possible, variations in the data. Hence the first few t values might be used as supervariables in correlation with parameters which influence the technological procedures. Figure 4 shows the plot of t_1 value vs. time of distillation up to 4 h. As can be seen, this relationship is highly linear. Moreover, sample 20, pine needle VII, is a mixture of essential oils as shown on Fig. 4. As can be seen on Fig. 3, the t_1 values for this mixture lie between the t_1 values of samples obtained after 3 and 4 h of distillation. Therefore it can be suggested that thermoanalytical methods can be used to control the quality of an essential oil during distillation.

PCA analysis of coriander oils

The data matrix for coriander oil samples consists of nine objects and nine variables. The following sequence of positive eigenvalues was calculated: 4.30, 3.73, 0.53, 0.33, 0.09, 0.02, and three values less than 10^{-2}. Considering only eigenvalues greater than 1, a two PC scores model which explains over 88% of the total variance was adopted. In this way, nine variables were reduced to two PC scores. The t_1 vs. t_2 plot is shown in Fig. 5. The standard requirements for coriander oils are as follows: $d_{20}^{20} = 0.864–0.877$, $[\alpha]_D = +8°$ to $+13°$ and $n_D^{20} = 1.462–1.472$. Oil 8, coriander IV ($d_{20}^{20} = 0.977$, $n_D^{20} = 1.474$ and $[\alpha]_D = +3.2°$), differs markedly

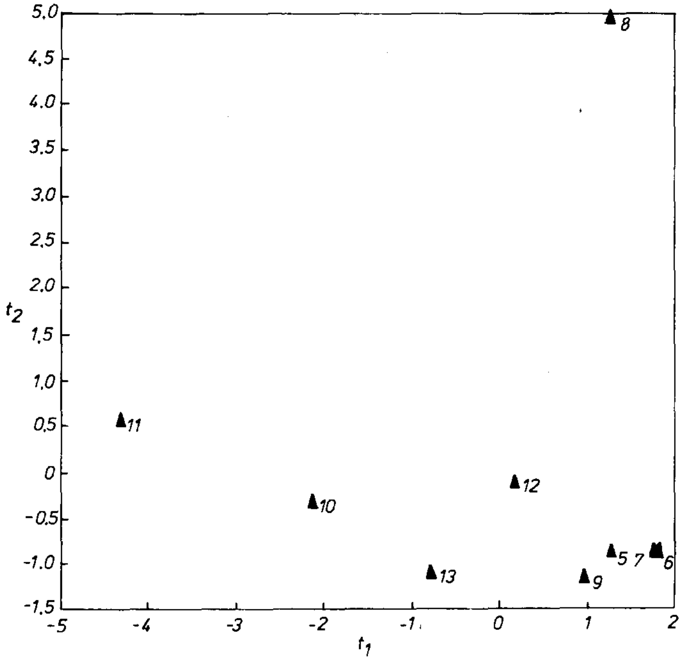

Fig. 5. Principal component scores plot derived from analysis of coriander oils.

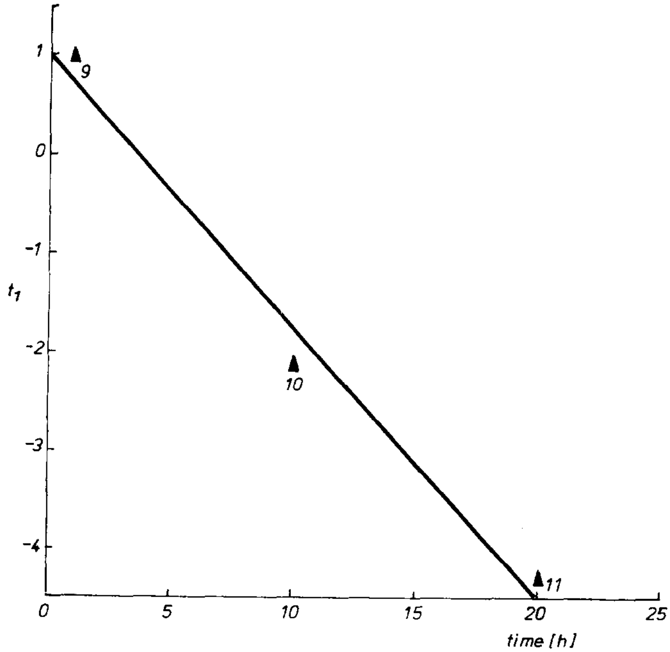

Fig. 6. Plot of the first principal component score vector (t_1) against time of distillation of coriander oils.

from the standard and also this oil is an outlier on Fig. 5. Oil 12, coriander VIII, was obtained using different technology by distillation of aromatic water. This oil differs from the standard in its optical rotation ($[\alpha]_D = -1.6$) and density ($d_{20}^{20} = 0.889$). As can be seen from Fig. 5, oil 12, coriander VIII, has the most similar t_1 and t_2 values to oil No. 8, coriander IV. All remaining coriander oils are in accordance with the Polish Standard. Therefore it can be suggested that the quality control of coriander oils can be achieved using thermoanalytical data.

In order to study where thermoanalytical methods are suitable for controlling the technological process, a few samples (i.e. oils 9, coriander V, 10, coriander VI, and 11, coriander VII) were taken after various times of steam distillation. Figure 6 shows the plot of t_1 value vs. time of distillation up to 20 h. This relationship seems to be highly linear. Moreover, sample 13, coriander IX, is a mixture of essential oils as shown on Fig. 6. As can be seen from Fig. 5, the t_1 values for this mixture lie between the t_1 values of samples obtained after 1 h and 10 h of distillation. Therefore it can be suggested that the thermoanalytical method can be used to control the quality of an essential oil during distillation.

PCA analysis of silver fir oils

The data matrix for silver fir oil samples consists of four objects and nine variables. The following sequence of positive eigenvalues was

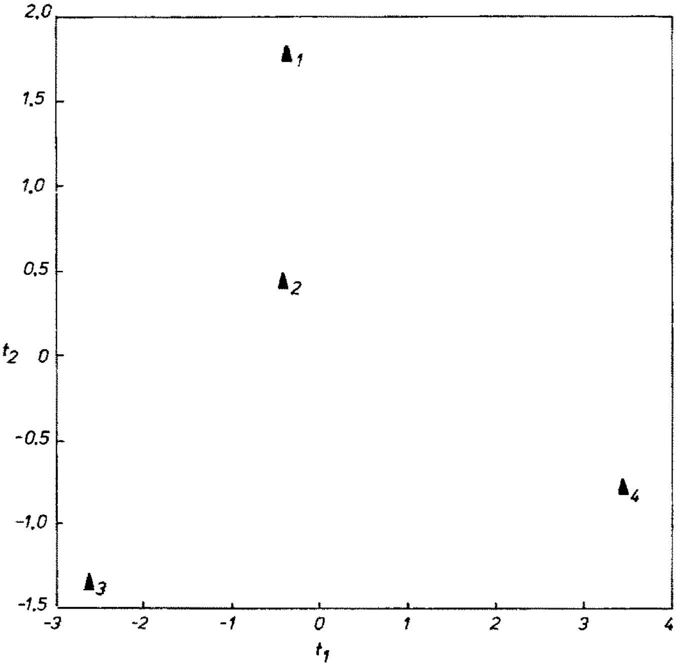

Fig. 7. Principal component scores plot derived from analysis of silver fir oils.

calculated: 6.37, 1.91, 0.72, and six values less than 10^{-15}. The t_1 vs. t_2 plot is shown in Fig. 7. Although the number of objects studied in this case is very limited, the oils cluster into two groups, i.e. oils 1, silver fir I, 3, silver fir III, and oils 2, silver fir II, 4, silver fir IV. The groups differ in their country of production. Samples 1 and 3 originate from Poland whereas samples 2 and 4 are from North Korea. The standard requirements [17] for silver fir oils are as follows: $d_{20}^{20} = 0.867$–0.878, $[\alpha]_D = -67°$ to $-34°$ and $n_D^{20} = 1.470$–1.475. The density of the oils from North Korea differs from standard; $d_{20}^{20} = 0.885$ and 0.923 for samples 2 and 4 respectively. As established previously, the results indicate that the thermoanalytical method is suitable for the quality control of silver fir oils.

CONCLUSIONS

The principal component method of data handling is a fruitful approach in the assessment of the quality of essential oil samples from different sources.

Using thermoanalytical procedures in combination with chemometric methods of data handling, it was found that the quality of essential oils depends strongly on the duration of steam distillation of the raw material.

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