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THERMOANALYTICAL AND GAS CHROMATOGRAPHIC EVALUATION OF WOOL WAX ALCOHOLS SUPPORTED BY PRINCIPAL COMPONENT ANALYSIS

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ABSTRACT

Three commercial and three non-commercial samples of wool wax alcohols were analysed using thermoanalytical and gas chromatographic techniques. For further characterisation using a chemometric procedure, concentrations of 28 individual components and 14 thermoanalytical parameters were considered. The data were processed using principal component analysis. Our results demonstrate the comparable classification ability of gas chromatographic and thermoanalytical methods. However, in the case of thermal analysis the sample patterns are more complex. This suggests that the thermoanalytical data contain additional information on the contents of non-volatile compounds which cannot be determined by gas chromatography.

INTRODUCTION

Wool wax alcohols (WWA) derive from the saponification of wool wax. Consisting of aliphatic monoalcohols, alkane-1,2-diols, cholesterol, triterpene alcohols and small amounts of hydrocarbons [1], they have comprehensive commercial application in the pharmaceutical and cosmetics industries as non-ionic water–oil emulsifiers and stabilisers for oil–water emulsion systems.

Quality control of WWAs includes classical and instrumental chemical analyses. Specific gravity, viscosity, acid, iodine, hydroxyl and saponification values are usually determined using classical methods. These investigations are increasingly supplemented by modern instrumental techniques. Among these, gas chromatography [2,3] and thermal analysis [4,5] are the most

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important. Lórant [4] has performed differential thermal analysis (DTA) of lanolin, hydrated lanolin and alcohol fractions of lanolin, such as cholesterol and lanosterol. Except for cholesterol, all the compounds show only one or, rarely, two endothermic effects on the DTA curve. Srćić et al. [5] have investigated the thermal decomposition of four lanolin alcohols. Degradation of alcohols was more complicated in air than in an argon atmosphere. An exothermic effect was observed on the DTA curve only in an air atmosphere. For each alcohol, reaction order and activation energy have higher values in an argon atmosphere. Complicated chemical compositions and heat transformations in an air atmosphere make classical interpretation of the results of the thermal decomposition of natural products difficult. Based on an analysis of the shape of the thermogravimetry (TG) and differential thermogravimetry (DTG) curves, the characteristic parameters for these products can be determined, e.g. the temperatures of the beginning, the end and the successive mass losses [6].

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) [7,8]. 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**. Similarily, plotting the rows of **P** shows the complementary variable patterns. Recently, PCA has been used for processing thermoanalytical data in order to control the quality of edible fish oils [9] and lube oils [10]. In this work, we intend to study thermal decomposition of WWAs and compare the classification ability of thermoanalytical methods with the results obtained from gas–liquid chromatography (GLC). The PCA method was used as the statistical tool for this classification and comparison.

EXPERIMENTAL

Samples for testing

In this study, three commercial WWA samples were investigated. These are marked HT1 and HT2 for Super-Hartolan obtained from Croda, and WW for Wollwachs-Alcohole product of Schadstoffarm, H.E. Wagner GmbH. The rest of the samples denoted A, E, F are non-commercial laboratory samples obtained from Pollena Cosmetic Enterprise, Gdańsk, Poland.

Testing procedure

The DTA, TG and DTG curves for the thermal decomposition of WWA samples were determined using the OD-103 derivatograph (MOM, Buda-

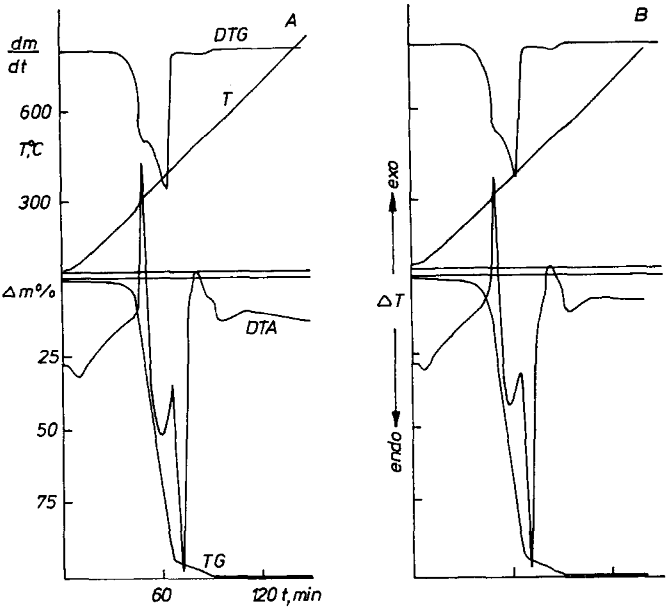

Fig. 1. DTA, TG and DTG curves of the thermal decomposition of laboratory sample E (A) and commercial Super-Hartolane sample 2 (B).

pest, Hungary). All measurements were carried out under the same conditions. A weighed sample of 200 mg of oil in a platinum crucible was heated in the furnace atmosphere 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 onset (T_0) and the end (T_{100}) of thermal decomposition were read from the TG and DTG curves, whereas the temperatures for 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. DTG peak height (h_{DTG}) was read as the distance between the base line of the DTG curve and the peak tip. T_{mDTG} represents the temperature of maximum height of the DTG peak. T_{mexo1}, T_{mexo2}, T_{mendo1} and T_{mendo2} are the temperatures of maximum deviation of the DTA curve from the base line. Examples of the thermal decomposition of WWA samples are shown in Fig. 1.

The percentage composition of WWA samples based on the peak areas was determined by gas chromatography (GC). The system used was a Hewlett–Packard gas chromatograph series HP 5890 and HP 3396A integrator. The column was HP-1 crosslinked methylsilicone (equivalent to OV-1) fused silica capillary (10 m, 0.53 mm i.d.). The experimental conditions were as follow; column temperature, 170–270 °C at 7 °C min^{-1}, 270 °C for 4 min, then up to 290 °C at 7 °C min^{-1}; injector and detector temperatures, 280 °C; carrier gas, argon; injection mode, splitless; detection, flame ioniza-

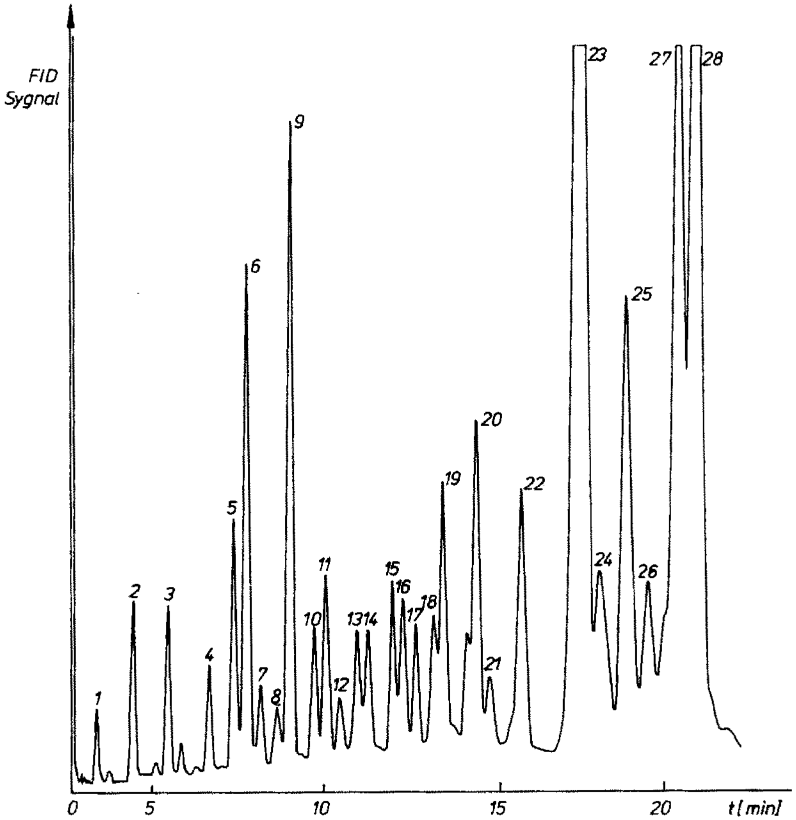

Fig. 2. Chromatogram of a wool-wax-alcohol sample. Peaks which were considered for principal component analysis are numbered.

tion. Before injection the samples were dissolved in acetone. An example of a chromatogram is given in Fig. 2.

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 further chemometric investigations. Two sets of variables were used: those for thermoanalytical methods were the temperatures T_1, T_5, T_{15}, T_{30}, T_{50} and T_{75}, which represent respective mass losses, the DTG peak height, h_{DTG}, and the temperature of maximum height of the DTG peak, T_{mDTG}; and, from the DTA curve, the temperatures of maximum deviation, T_{mexo1}, T_{mexo2}, T_{mendo1} and T_{mendo2}. Hence, the total number of variables obtained from thermoanalytical methods was 14. In the case of chromatographic investigations, the variables used were peak area percentages calculated for 28 chromatographic peaks. Therefore the total number of variables was 28. From the data matrix, **X**, its standardised version, **Z**, and correlation matrix, **R**, were calculated. The correlation matrix, **R**, was used as a starting matrix in PCA. Principal components were determined by considering eigenvalues and associated eigenvectors. For plotting purposes only, two or three first principal component score-vectors (t_1, t_2 and t_3) were used. These account for over 80% of the variability in each case. In this way, 14 variables (thermoanalytical method) and 28 variables (chromatographic method) were reduced to two or three principal component scores.

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

RESULTS AND DISCUSSION

Thermal decomposition of WWAs

Because WWAs constitute a multicomponent mixture of organic compounds of similar physico-chemical properties, the DTA, TG and DTG curves of their thermal decomposition are plots of the physico-chemical phenomena which occur in the sample during heating. Thermal effects on the DTA curve result from the superposition of endothermic and exothermic effects due to transitions of particular components. This creates great difficulties for the identification of the reactions responsible for the appearance of a definite thermal effect. On the other hand the loss in weight on the TG (DTG) curves is the total of the weight losses associated with the thermal decomposition of components contained in the product examined. Thus it is not feasible to identify the weight loss associated with the decomposition of a definite component of WWAs.

Figure 1 shows the DTA, TG and DTA curves of the thermal decomposition recorded for laboratory sample E (A) and commercial sample HT2 (B). The thermal decomposition of all WWA samples is preceded by the phase transitions of their components. Because the thermoelectrical voltage curve of Pt/Pt–Rh thermocouples is flat below 200 °C, it is not possible to investigate these processes in more detail. The endothermic effect reflecting them is shallow and broad and, in addition, it occurs over a temperature range of a few tens of degrees.

In general, the thermal decomposition of WWA samples proceeds in two stages. In the first stage, thermal degradation of the alcohol components takes place; this is confirmed on the DTA curve by a narrow, sharp exothermic peak. Decomposition of the products is preceded by the vaporization of the more volatile fractions. The exothermic effect is followed by two overlapping endothermic effects related to the distilling alcohol volatile fraction, the volatile product of the thermal decomposition, and to the desorbing of gaseous decomposition products out of the system. Analysis of the shape of the TG and DTG curves has shown that it is impossible to

TABLE 1

Results of chromatographic analysis of wool wax alcohols expressed as peak-area percentages

Peak No.	Sample					
	WW	HT1	HT2	A	E	F
1	0.19	0.24	0.25	0.38	0.29	0.35
2	0.56	0.72	0.74	0.91	0.83	0.98
3	0.54	0.51	0.54	0.81	0.83	0.98
4	0.54	0.52	0.54	0.61	0.57	0.74
5	0.95	0.54	0.57	1.27	1.39	1.60
6	2.35	2.57	2.68	3.06	3.08	3.45
7	0.37	0.42	0.45	0.41	0.48	0.53
8	0.31	0.10	0.16	0.02	0.36	0.43
9	3.31	3.62	3.74	3.94	3.85	4.38
10	0.66	0.32	0.34	0.61	0.73	0.80
11	1.07	1.06	1.11	1.36	1.18	1.30
12	0.33	0.39	0.40	0.02	0.39	0.42
13	0.72	0.32	0.33	0.66	0.83	0.87
14	0.73	0.70	0.73	0.80	0.86	0.93
15	1.08	0.52	0.54	1.26	0.99	1.00
16	1.02	1.01	1.05	0.99	1.02	1.04
17	0.88	0.94	0.98	0.68	0.72	0.70
18	0.92	0.10	0.38	0.57	0.69	0.74
19	1.71	2.26	1.96	2.36	1.68	1.86
20	3.52	3.16	3.27	3.30	3.14	2.86
21	0.71	0.10	0.83	0.02	0.02	0.52
22	3.21	3.03	3.15	2.71	2.55	2.30
23	33.43	35.98	36.87	31.26	30.72	29.46
24	2.36	0.10	1.83	1.55	1.88	2.05
25	5.72	6.83	6.25	4.81	4.84	4.85
26	1.79	1.56	0.93	1.03	1.18	1.24
27	11.52	9.93	8.81	10.92	10.64	10.31
28	17.29	16.89	15.30	23.27	21.12	20.50

determine the boundary between the two endothermic processes. On the TG curve, this stage is accompanied by a rectilinear segment of mass loss within the narrow temperature range.

In the second stage of the decomposition, carbon originating from the coking of the sample is burnt. This is confirmed by a rounded exothermic DTA effect and a flat DTG peak. The great similarity of the shape of the DTA, TG and DTG curves of the thermal decomposition of WWAs, and the approximate temperature ranges of the particular thermal processes, are reflected in Table 1. These values indicate that the chemical compositions and the resulting chemical transitions which occur are closely similar.

PCA differentiation of WWA samples based on chromatographic data

The data matrix, **X**, is listed in Table 1; it consists of 6 objects (WWA samples) and 28 variables. The following sequence of positive eigenvalues

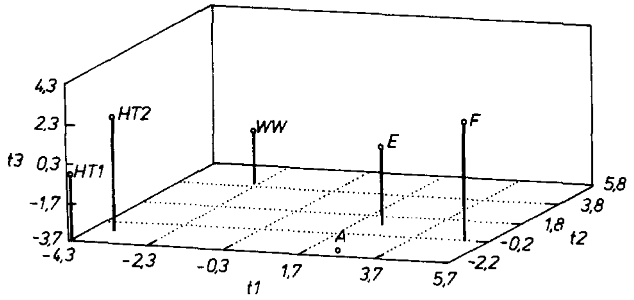

Fig. 3. Principal component scores plot derived from chromatographic data.

was calculated: 15.29, 5.29, 5.01, 1.72, 0.67 and 23 values less than 10^{-12}. From the sequence of the eigenvalues it can be seen that the first three PC score values are the most important. These explain over 90% of the total variance. In this way, 28 variables were reduced to three PC scores. Figure 3 shows the PC score plot for WWA samples. Along the t_1 axis, the samples can be clearly differentiated into two classes: commercial samples (HT1, HT2 and WW) and laboratory samples (A, E, F). Also it can be seen that the two different Hartolan samples have very similar qualitative and quantitative compositions which differ from the Wagners Woolwachs sample (WW). The commercial samples possessed excellent emulsifying properties, in contrast to the laboratory samples (A, E, F). Hence, it can be concluded that gas chromatography supported by principal component analysis is suitable for quality control of the WWA samples.

PCA differentiation of WWA samples based on thermoanalysis

The data matrix, **X**, is listed in Table 2; it consists of 6 objects (WWA samples) and 14 variables. The following sequence of eigenvalues was found: 6.48, 3.38, 1.82, 1.36, 0.96, and nine values less than 10^{-12}. The first three t values describe 84% of the total variance. From the sequence of eigenvalues, it can be concluded that the structure of the data derived from thermal analysis is far more complex in comparison with those derived from gas chromatography. Figure 4 shows the t_1 versus t_2 versus t_3 plot. Although the commercial samples can easily be distinguished from the non-commercial, this distinction depends on all the PC score values considered. Among these, the t_1 and t_3 values seems to be most important. This plot is shown in Fig. 5. Comparing Figs. 3 and 5, it can be concluded that the discriminatory ability of gas chromatographic and thermoanalytical methods is similar. On the other hand it should be emphasized that the thermoanalytical data carry more information. There is no doubt that the shape of the thermoanalytical curves is conditioned by the chemical composition of the WWA samples being degraded. Such information can also be obtained directly from the

TABLE 2

Results of the thermal decomposition of wool wax alcohols. The h_{DTG} parameter is expressed in mm, the remaining parameters in °C

Parameter	Sample					
	WW	HT1	HT2	A	E	F
T_0	160	145	150	150	150	170
T_1	220	205	210	205	210	225
T_5	270	265	260	255	265	270
T_{15}	305	300	305	300	325	310
T_{30}	330	320	330	320	330	330
T_{50}	355	350	355	350	350	355
T_{75}	380	380	380	375	380	385
T_{100}	610	590	630	600	620	600
T_{mDTG}	380	385	385	375	385	385
h_{DTG}	85	85	92	90	95	90
T_{mexo1}	310	310	315	305	305	310
T_{mexo2}	520	520	495	495	490	505
T_{mendo1}	355	355	360	355	355	365
T_{mendo2}	520	520	495	495	490	505

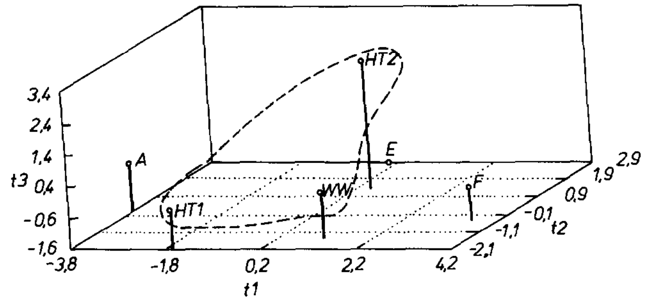

Fig. 4. Principal component scores plot derived from thermoanalytical data. The commercial samples are circled.

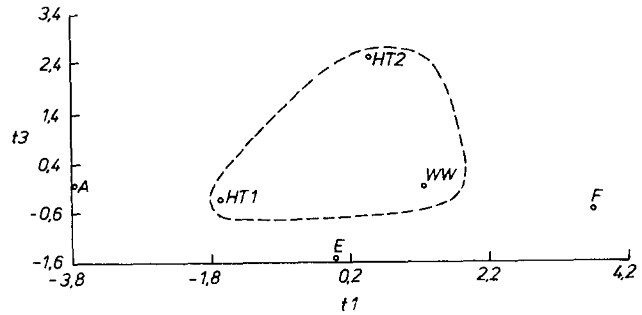

Fig. 5. Two principal component scores (t_1 vs. t_3) plot derived from thermoanalytical data. The commercial samples are circled.

chromatographic data. This information, however, is incomplete because it is restricted to only volatile compounds. Moreover, the phase transitions of WWA constituents do not influence the chromatographic data. Thus it can be suggested that in addition to a differentiation comparable to GC, thermoanalytical methods also reflect some other differences in the quality of the WWA samples. However, in this initial work it is premature to make a definitive statement concerning the nature of these differences.

CONCLUSIONS

Our results indicate that thermal analysis might be a useful supplement in the analytical determination of the quality of WWA samples. In particular, it allows the detection of non-volatile impurities which cannot be determined using gas chromatography. PCA greatly assists in the handling of the data. Using this method, the multivariate problem can be effectively reduced to two or three variables. In quality assessment, our results demonstrate the comparable classificatory ability of chromatographic and thermoanalytical methods. However, in the thermal analysis some other, as yet unknown, properties of WWA samples can also be detected.

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