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THERMAL DECOMPOSITION OF MEDICINAL PLANT RAW MATERIALS BASED ON PRINCIPAL COMPONENT ANALYSIS*

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Abstract

Studies on the thermal decomposition of commercial raw plant materials used in medicine were performed. 144 independent samples of plant materials – herbs, leaves, flowers, inflorescences, fruits, roots, rhizomes and barks, collected by Medicinal Plant Works 'Herbapol', were analyzed. Thermal decomposition was performed using OD-103 Derivatograph. As a result of analysis, it was established, that thermal decomposition of majority of samples proceeds through three stages. The analysis of fruits revealed, that their thermal decomposition proceeds in four stages. In order to obtain a more clear classification of the analyzed plant materials principal component analysis (PCA) was applied. Interpretation of the PCA results allows to state, that samples of raw materials from the same plant species in majority of cases are characterized by similar course of thermal decomposition due to similar chemical composition. In this way the differences in general chemical composition of medicinal plants raw materials can be determined.

Keywords: barks, DTA-TG-DTG, flowers, fruits, herbs, inflorescences, leaves, principal component analysis (PCA), raw plant materials, rhizomes, roots

Introduction

Thermoanalytical methods, particularly DSC, DTA, TG and DTG have also found an application in the investigation of material of biological origin [1]. Their utility comes from the possibility of the phase analysis as well as the qualitative and quantitative control of chemical compositions. In literature one can find many examples for the application of these techniques in the investigation on wooden pulp used in paper industry, however, there is a limited number of publications concerning the application of thermoanalytical methods for studies of raw plant materials, especially of plant materials used in medicine [2, 3].

Reviews of thermal methods applied to the wood analysis were done by Prosiński and Zakrzewski [4] and Košik [5]. From the major methods, DSC, DTA, TG and DTG, also combined techniques DTA-TG-DTG are described in these works. The process of combustion of wood, bark and leaves of trees was also investigated by

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Shafizadeh [6]. It was established, that the differentiation of the chemical composition of studied samples influence the course of their thermoanalytical curves, and also their values of the heat of combustion. Moreover, Kaloustian *et al.* [7–9] showed, that the decomposition of the plant is mainly dependent on the cellulose level. This degradation is also slightly dependent on the lignin level, mainly if the lignin present in the plant is less stable. On the other hand, Cebulak and Pliński [10] applied thermal analysis for the differentiation of chemical composition of algae. High similarity was found in the course of thermal decomposition of two samples of sea grass originating from the same plant species, but collected from different places. A similar situation was observed for algae belonging to different species, but collected in the same area. It can suggest a greater effect of the environment on the chemical composition of algae, than fact that samples originated from plant of the same taxonomical group. The possibility to use thermal analysis for a quick characterization of chemical changes in the organic matter of composted materials was also tested by Dell'Abate *et al.* [11].

Taking this into account, the aim of the study is to establish, if any relations exist between the chemical composition of raw plant materials and the thermal decomposition of these samples, originating from the same plant species. It could also help to answer the question, if thermoanalytical techniques can be used as methods, which support chemical analysis of plant materials, especially during standardization of raw materials available in a pharmaceutical market.

Experimental

Materials and methods

The total number of 144 medicinal plant materials – herbs, leaves, flowers, inflorescences, fruits, roots, rhizomes and barks, collected by Medicinal Plant Works 'Herbapol' at various factories in Poland, were analyzed. Their thermal decomposition was performed using OD-103 Derivatograph (MOM, Hungary), with α-Al_2O_3 as a reference material. 100 mg plant samples were heated under air atmosphere at a heating rate of 5°C min^{-1} up to a final temperature of 900°C. For example, the DTA, TG and DTG curves of the thermal decomposition of selected plant samples were shown in Fig. 1.

Interpretation of the DTA curves consists of designating of the onset (T_i) and peak (T_p) temperatures of an endothermic effect for the first stage of decomposition as well as T_i and T_p for two consecutive exothermic effects, for the second and third stage. In the case of TG analysis, the mass losses (Δm) in three consecutive stages of decomposition were determined. On the grounds of DTG curves, the temperature range of DTG peak (ΔT), peak temperature (T_p) and peak height (h) were designed.

Calculations

Principal component analysis (PCA) was applied for the interpretation of thermoanalytical results [12, 13]. Two starting matrices for each studied plant parts – herbs, leaves, flowers, inflorescences, fruits and for roots with rhizomes, were created. In each matrix, raw materials were used as the rows, whereas columns were the results

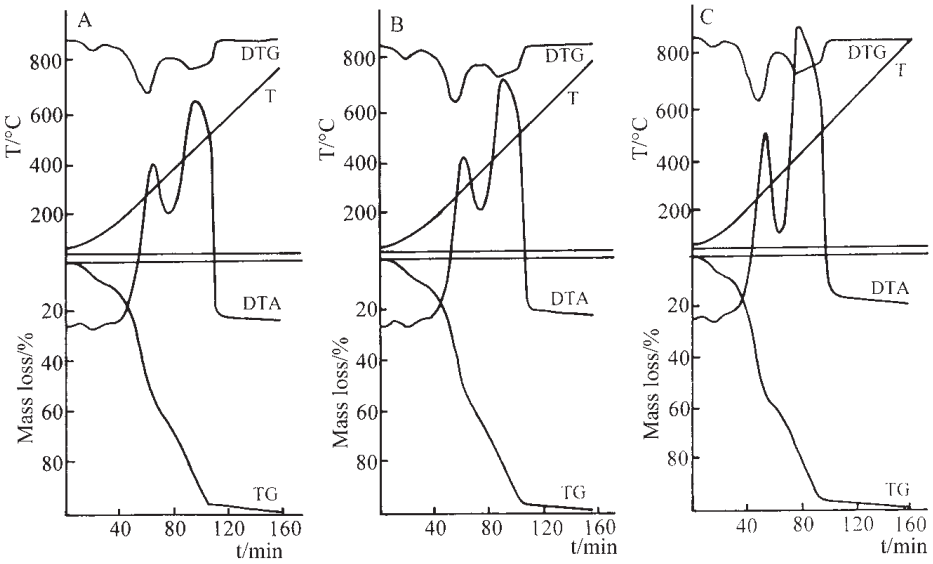

Fig. 1 DTA, TG and DTG curves of the thermal decomposition of inflorescences: A – *Inflorescentia Crataegi* (2), B – *Inflorescentia Tiliae* (9) and C – *Anthodium Chamomillae* (11). Numbers in parentheses denote plant samples compiled in Tables 1 and 2

of thermal decomposition of the raw materials. The first matrix was based on the DTA results and comprised 6 columns – T_i and T_p for consecutive DTA peaks (Table 1 for inflorescences as an example). The second matrix, based on the TG and DTG results, was built on 12 columns – Δm from TG as well as ΔT, T_p and h from DTG curves for consecutive decomposition stages (Table 2).

Table 1 Results of analysis of the DTA curves for inflorescences. There are the onset (T_i) and peak (T_p) temperatures (°C) of the DTA effects for three consecutive stages of decomposition of plant samples

Sample number	I stage		II stage		III stage	
	T_i	T_p	T_i	T_p	T_i	T_p
1	30	80	160	310	360	470
2	35	70	150	305	360	470
3	35	75	160	305	365	475
4	40	70	150	300	355	470
5	40	65	120	300	350	465
6	40	70	150	290	345	455
7	35	80	150	300	355	445
8	35	90	140	270	335	445
9	40	80	135	310	370	465
10	40	70	130	295	365	455
11	30	65	130	305	355	450
12	30	60	135	275	340	465

Table 2 Results of analysis of the TG and DTG curves for inflorescences. There are the mass losses (Δm) as well as the temperature range (ΔT), peak temperature (T_p) and height (h) of the DTG peaks for three consecutive stages of decomposition of plant samples

Sample number	I stage				II stage				III stage			
	Δm/ %	ΔT/ °C	T_p/ °C	h/ mm	Δm/ %	ΔT/ °C	T_p/ °C	h/ mm	Δm/ %	ΔT/ °C	T_p/ °C	h/ mm
1	8.0	95	80	8	58.0	265	280	45	30.0	170	455	22
2	9.0	100	70	9	59.5	275	280	44	26.0	145	450	24
3	8.0	100	75	9	53.5	255	275	44	33.0	190	460	24
4	8.0	95	60	8	57.0	250	265	43	30.0	195	440	24
5	8.0	100	75	10	59.0	245	270	61	31.0	165	440	26
6	10.0	80	60	7	52.0	240	255	57	32.0	180	445	27
7	8.0	100	80	10	59.0	240	265	64	29.0	180	445	28
8	6.0	75	60	7	57.0	260	250	47	29.0	160	435	26
9	9.0	110	75	10	56.0	240	280	45	32.0	185	450	26
10	9.0	100	75	9	54.0	245	260	46	32.0	180	440	23
11	8.0	90	65	10	53.0	245	265	49	34.0	205	435	29
12	10.0	90	60	8	55.0	235	255	43	33.0	200	435	26

After calculations, new columns in matrices P and W were obtained, which were called principal components. New matrix P reflects main relations among samples and enables their classification, whereas matrix W illustrates main relations among thermoanalytical data and enables their selection. Very often two or three first principal components illustrate relations among objects in multidimensional space.

Results and discussion

Thermal decomposition of raw plant materials

When trying to interpret the results of thermal decomposition of studied samples, one should realize, that medicinal plant raw materials are natural products, which are characterized by complex chemical composition [14–16]. They are mixtures of numerous chemical compounds, inorganic and organic, which occur in a very different range of concentrations. Hence, particular compounds of these natural mixtures can be found in a very different quantitative ratios. Because of this, DTA, TG and DTG curves of thermal decomposition of raw plant materials would appear as overlapping effects of all physico-chemical processes, which occur, when a sample is heated. It is also evident, that the presence of single compounds is not reflected in DTA, TG and DTG curves. However, they influence the characteristics of the obtained thermal effects, mainly on temperatures of the onset, peak and the end of the effect, its height, width in the half of height and area.

Effects related to thermal decomposition of a particular compound will be less pronounced in the curves, when the decomposition takes place in a broader range of temperatures together with possible small loss of its mass. Mineral constituents, which are not thermally decomposed in used range of temperatures, influence on the

conductivity and heat capacity of the sample and cause many other changes in thermal decomposition course of the analyzed plant raw material.

Typical curves of thermal decomposition of medicinal raw plant materials are shown in Fig. 1. Taking them and data set in Tables 1 and 2 into consideration it was established, that thermal decomposition of majority of samples proceeds through three stages. During the first stage, evaporation of volatile products of analyzed samples takes place, associated with several percent of mass loss and with the endothermic effect on the DTA curve. In the second stage, thermal degradation of components of analyzed sample occurs. It is confirmed by the exothermic effect on the DTA curve, and from several to several tens percent of mass loss on the TG curve. Charred residue after decomposition is burnt during the third stage, yielding ash residue. The last stage is associated with a large exothermic effect.

The analysis of fruits revealed, that their thermal decomposition proceeds in four stages [3]. Additional stage, not present in the case of other analyzed groups of plant materials, appeared as the effect of division of the second stage of decomposition into two new stages. In this way, the additional stage is numbered as III, and previous third stage of thermal decomposition becomes the fourth stage in the case of fruits. Such a rule was accepted after precise analysis of the temperatures of the onset and peak of the DTA and DTG effects, and ranges of temperatures with mass losses on the TG curves.

Barks are characterized by a different course of thermal decomposition from other plant materials. In general, their thermal decomposition can be treated according to the three-stage model, but large number of narrow and sharply ended exothermic peaks occurring on the DTA curves during the second stage makes impossible to create homogenous matrix. For these reasons PCA calculations for the barks cannot be performed.

PCA of the thermoanalytical results

A huge number of thermoanalytical parameters (T_i, T_p, Δm, ΔT and h) with similar numeric values, which describe thermal effects on the DTA, TG and DTG curves, causes problems during identification of the raw plant materials on the grounds of their thermal data. It is a very complicated and difficult task, especially when the interpretation has to be done based on subtle differences among similar courses of thermal decomposition of many samples. In order to overcome these difficulties, and to obtain a more clear classification of the analyzed plant samples, PCA was applied. PCA seems to be particularly useful, because one of its principal aims is to reduce the number of variables, which describe groups of similar samples. Application of PCA also helps to obtain better classification of the analyzed samples.

Comparing the results of PCA for both of the DTA and TG-DTG databases it was noticed, that in the case of herbs, leaves, flowers and roots with rhizomes, DTA describes their thermal decomposition based on a larger number of the results in the two-dimensional plot, better than TG and DTG results together in the three-dimensional plot. Distribution in space of samples of inflorescences and fruits is in the same degree

characterized by the DTA results and TG-DTG ones, both in two- as in threedimensional space. However, taking into consideration as much complex interpretation of the data as possible, the results determined from the DTA and TG-DTG curves were analyzed together. Another reason for this way of thinking was the assumption that considering more experimental results has more significant impact on elaboration of the final conclusion. The percent shares of the experimental results during description of variation in the three-dimensional relations among samples in particular groups of plant parts were given in parentheses – herbs (62.7), leaves (63.3), flowers (64.2), inflorescences (69.0), fruits (65.2) and roots with rhizomes (77.9).

Distribution of medicinal raw plant materials in three-dimensional space based on their combined DTA, TG and DTG results, can be illustrated taking inflorescences as an example. In this case, twelve samples were investigated numbered as follows – *Inflorescentia Crataegi* (1, 2, 3 and 4), *Helichrysi* (5, 6, 7 and 8), *Tiliae* (9 and 10) and *Anthodium Chamomillae* (11 and 12). Matrix for PCA, which has the dimension 18 columns × 12 rows, was constructed based on the results of their thermal decomposition set in Tables 1 and 2. As it is shown in Fig. 2, analysis of distribution of inflorescences in PCA plot gives information, that in the narrow range of PC2 and PC3 values there are *Anthodium Chamomillae* (samples number 11 and 12) and *Inflorescentia Tiliae* (9 and 10). However, two samples of each of these plant materials are differentiated by values of PC1. From the rest of plant materials of this group, only two from *Inflorescentia Helichrysi* (5 and 7) and three from *Inflorescentia Crataegi* (1, 2 and 3) are described by similar values of three first principal components – PC1, PC2 and PC3. Other samples are located in distant spaces of the plot, for example two samples of *Inflorescentia Helichrysi* (6 and 8), which are differentiated by PC2 values.

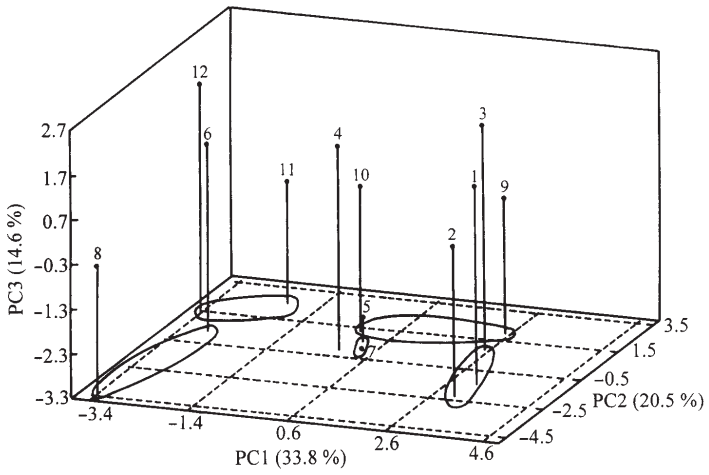

Fig. 2 Plot of the first three principal component score vectors (PC1 *vs.* PC2 and PC3) for 12 samples of inflorescences based on the combined DTA, TG and DTG results compiled in Tables 1 and 2

Distribution in PC1 *vs.* PC2 and PC3 space of herbs revealed, that samples of *Herba Anserinae*, *Herniariae*, *Ledi palustrae* and *Millefolii* are grouped in the range of similar values of PC1, PC2 and PC3, in the right area of the plot. On the opposite, there are *Herba Boraginis*. In some cases, several plant materials originating from the same plant species, such as *Herba Origani*, *Rutae* and *Visci* are differentiated only by PC1, however their values of PC2 and PC3 are the same or very close.

However, many plant materials originating from the same plant species are located at different values of three first principal components. The reason for this could be the diversity of their chemical composition. As it can be read from literature, a large group of herbs contains aether oils [14–16]. From the point of PCA, their presence does not appear as a crucial factor, which influences the shape of thermoanalytical curves of herbs. One of the reasons, can also be the low concentration of essential oils, about ten parts of percent. The similar tendency can be seen, when one take the contents of tans and flavonoids, into consideration. On the other hand, it is a fact, that some plant materials contain several percent of tans, may influence their distribution along PC2 axis. As examples, *Herba Anserinae*, *Hyperici*, *Melissae* and *Thymi* can serve, because they are located in the range of PC2 values from –2.3 to 1.7. Also, herbs containing silicon compounds, like *Herba Equiseti*, *Polygoni avicularis* and *Urticae* can be found in the central area of the PCA plot.

From the analysis of samples of leaves in the PCA plot, one can notice, that lack of great differences in their chemical composition, is the reason for distant distribution in three-dimensional space of samples, which originated from the same plant species [14–16]. All plant materials containing bigger amounts of tans, from 5 to 19%, are located in the central part of the plot. There can be found *Folium Fragariae*, *Melissae*, *Menthae piperitae*, *Menyanthidis*, *Rubi fruticosi* and *Uvae-ursi*. In similar way samples, which have aether oils, like *Folium Betulae*, *Rosmarini*, *Salviae*, and also plant samples containing both aether oils and tans – *Folium Melissae* and *Menthae piperitae*, are distributed. Four samples of *Folium Farfarae*, a plant material rich in mucilage, are located in three-dimensional space along very distant values of PC1, PC2 and PC3. Very small amounts of mucilage contain also *Folium Plantaginis lanceolatae* and *Sennae*, which spatial distribution is similar to the samples described above. So it is possible to say, that the content of mucilage does not influence the thermal decomposition of plant material to such a degree, which could distribute samples in the range of similar values of three first PCs.

In three-dimensional plot of PC1 *vs.* PC2 and PC3 for samples of analyzed flowers one can find, that particular plant materials originating from the same plant species are located according to very close values of PC1 and PC3. The differentiating factor in this case is PC2. The exceptions are two samples of *Flos Lamii albae*, which have the same PC2 value, but are characterized by different values of PC1 and PC3.

The distribution of fruit samples in a PCA plot can be characterized by the division of analyzed plant materials into three different sectors. In the left down corner of the plot there are all fruits originating from plants belonging to *Rosaceae* family – *Fructus Crataegi*, *Rosae*, and *Sorbi*. They are described by very similar values of PC1 and PC2, and with the exception of *Fructus Rosae*, PC3 value. Besides *Fructus*

Rosae is rich in vitamin C, and this differs that sample from the other. In the central part of the plot there are all fruits from plants of *Umbelliferae* family located. Examples are *Fructus Anisi*, *Carvi*, *Coriandrii* and *Foeniculi*. Particular interest on *Fructus Lupuli* should be focused, because this plant material contains great amounts of resin – about 80%, which can be reason for its distant location in the PCA plot. Two samples of *Percarpium Phaseoli* can be noticed in the right down part of the plot and they belong to plants originating from *Leguminosae* family. In similar way *Semen Lini* and *Synapis albae* are located.

The last analyzed group of plant materials, roots and rhizomes are distributed in one area of three-dimensional PCA plot. The only exception is the sample of *Rhizoma Tormentillae*, located in a certain distant from other samples, which are distributed in a narrow range of values in PC1 axis. The majority of roots are differentiated by PC2 and PC3 values. The two of root samples, which come from the plant originating from the same plant species – *Radix Hydrolapathi*, are located along the same PC1 and PC2 values, as two other rhizomes – *Rhizoma Agropyri* and *Calami*, do.

Conclusions

PCA calculations revealed, that the distribution of samples of raw plant material in three-dimensional space indicates, in some cases, similarity in the course of thermal decomposition of the particular plant samples belonging to the same plant species. It reflects the close relation between the shape of DTA, TG and DTG curves of a raw plant material and its chemical composition, which depends on plant species.

Moreover, it has been confirmed that application of the thermoanalytical methods for investigation of plant material in order to try to classify them to the taxonomical group is still at the beginning of studies, and because of it, they can only be treated as supporting tools. Using the thermal methods of analysis could also provide new information, for instance on phase transitions, which take place in plant materials, or about their volatile components and mineral ash contents.

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