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RELATION BETWEEN THERMAL DECOMPOSITION OF MEDICINAL HERBS AND THEIR NON-METALS CONCENTRATION

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Abstract

The studies on the concentration of total nitrogen, phosphorus, sulphur, chlorine, iodine and boron as well as on the thermal decomposition of commercial raw plant materials used in medicine were performed. The 50 independent samples of herbs originating from 25 medicinal plant species collected in 1986–92 were analysed. The content of non-metallic elements was determined spectrophotometrically after previous mineralization of plant sample. The thermal decomposition was performed using the derivatograph with the application of 100 mg samples and heating rate of 5°C min^{-1}. In order to obtain more clear classification of the analysed plant materials principal component analysis (PCA) was applied. Interpretation of PCA results for two databases (non-metals and thermoanalytical data sets) allows to state, that samples of herbs from the same plant species in majority of cases are characterized by similar elemental composition and similar course of their thermal decomposition. In this way the differences in general chemical composition of medicinal plants raw materials can be determined.

Keywords: DTA TG DTG, medicinal herbs, non-metals determination, principal component analysis (PCA), raw plant materials

Introduction

The herbs consist of the dried entire plants or the dried leaves and the flowering tops, which include smaller steams, leaves, flowers and fruits [1, 2]. There are some other consisting of all parts of the plant growing above the ground level. Herbs are the oldest drugs used in medicine. Their chemical composition is different depending on plant species and geographic region, from which these materials originated.

The thermoanalytical methods play an important role in the solution of a variety problems in the field of plant materials. The utility of DTA, TG and DTG methods has been documented in a number of studies. They are useful for characterization of fresh and archeological samples of wood [3, 4], for determination of the heat of combustion of different types of wood, bark and foliage [5, 6] as

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well as for taxonomical investigations in order to establish the systematic membership of certain species of alge [7]. As a result, the aim of the present study is to establish, if any relations exist between the chemical composition of herbs and the thermal decomposition of these raw materials originating from the same plant species.

Experimental

Materials

In the study 50 independent samples of herbs from 25 species were used. The samples were collected in years 1986–92 by Medicinal Plants Works 'Herbapol' at various factories in Poland. These herbs are as follows (numbers of the samples are given in the parentheses); Herba Absinthii (1, 2 and 3), Herba Anserinae (4 and 5), Herba Boraginis (6 and 7), Herba Cichorii (8), Herba Cnici benedicti (9, 10 and 11), Herba Dracunculi (12), Herba Equiseti (13 and 14), Herba Euphrasiae (15), Herba Herniariae (16 and 17), Herba Hyperici (18 and 19), Herba Hyssopi (20 and 21), Herba Ledi palustrae (22 and 23), Herba Leonuri (24), Herba Meliloti (25 and 26), Herba Millefolii (27, 28 and 29), Herba Melissae (30, 31 and 32), Herba Origani (33 and 34), Herba Polygoni avicularis (35), Herba Rutae (36 and 37), Herba Serpylli (38 and 39), Herba Solidaginis (40), Herba Thymi (41), Herba Urticae (42, 43 and 44), Herba Violae tricoloris (45, 46 and 47) and Herba Visci (48, 49 and 50).

Chemical analysis

The content of non-metals was determined after previous mineralization of plant sample [8, 9]. The method of nitrogen determination (N as NH_4^+) was based on the reaction between ammonia and Nessler reagent in alkaline environment. The determination of phosphorus (P as PO_4^{3-}) consisted of the measurement of its concentration by phosphomolybdenum blue complex using iron(II) as a reducer. Sulphur (S as SO_4^{2-}) was measured turbidimetrically. The $BaCl_2$ was used as an agent making turbidity. Chlorine (Cl as Cl^-) was determined basing on the reaction with $Hg(SCN)_2$, in which the equivalent amount of thiocyanate ions reacts with iron(III) giving red complex. The specific reaction of iodine (I as I_2) with starch was used to measure the iodine concentration. The content of boron (B as BO_2^-) was determined based on its reaction with Azomethine H.

Thermal analysis

The DTA, TG and DTG curves of the thermal decomposition of plant materials were recorded using the OD-103 Derivatograph. A 100 mg sample was heated in a platinum crucible under the furnace atmosphere at a heating rate of 5°C min^{-1} up to a final temperature of 900°C. The α-Al_2O_3 was used as reference material.

The interpretation of the DTA curve 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 successive exothermic effects, for the second and third stage. In the case of the TG analysis, the mass losses (Δm) in three successive stages of decomposition were determined. However, on the grounds of the DTG curves, the temperature range of the DTG peak (ΔT), peak temperature (T_p) and peak height (h) were designed.

Calculations

The (PCA) was used for complex interpretation of the experimental data sets for herbs [10, 11]. In this method high number of variables can be reduced to two or three principal components which very often illustrate relations among objects in multidimensional space. In this way problems which are difficult to imagine or interpret become easy to present in clear two or three dimensional plots.

The PCA consists of calculating of two new matrices – principal component scores and principal component loadings according to experimental data set **X** with the dimensions **np**, where **n** is a number of observations (rows) and **p** is a number of variables (columns). Principal component scores are set in matrix **P** with dimensions **nk**, and principal component loadings are contained in matrix **W** with the dimensions **pkk** is a number of orthogonal principal components calculated for the given set, it does not exceed the number of **p** variables and as a rule it is less than **p**. From the condition **k<p** one can conclude, that the number of principal components is much less than the number of the experimental variables **p**

Starting point for the calculations was matrix of the data **X**. In this study two matrices were constructed. While the first data set was established as the mean values of nitrogen, phosphorus, sulphur, chlorine, iodine and boron content in the herb samples, the second one contained data set for three stages of the thermal decomposition of herbs – T_i and T_p from DTA, Δm from TG as well as ΔT, T_p and h from DTG curves. These values were set as the columns (**p**) and were called variables. In each matrix, fifty herb samples were used as the rows (**n**), which were called objects.

Matrix **X** was at first standardized, than matrix **R** was calculated according to it. After further calculations, columns in matrices **P** and **W** were obtained, which were called principal components. New matrix **P** reflects main relations among objects and makes possible classification of the investigated samples, whereas matrix **W** illustrates main relations among variables and enables their selection.

Results and discussion

The analysis of the total concentration of non-metals in herbs shows that this material contains high amounts of nitrogen and chlorine, from several to some

tens of mg per gram of dry plant tissue [12]. The relatively high content of sulphur and phosphorus was also established, from several hundred μg to several mg per gram of dry plant tissue. On the other side, the boron and especially iodine levels are significantly lower, about several μg of iodine to some tens of μg of boron per gram of dry plant tissue.

The comparing analysis of concentration of six elements in 50 samples of herbs is subjective. In many samples there are higher contents of some elements, but concentration of the other non-metals is low. In that case, it is not clear enough, if any particular plant raw material is rich or poor in non-metals. In order to overcome these difficulties, the PCA was used. The main idea of this method is to describe major part of variability of multidimensional system by means of small amount of new variables.

The data set (matrix **X**, which has the dimension 6×50) consists of the arithmetic means of the six non-metals concentrations in fifty samples of herbs. As a result of calculations the following sequence of positive eigenvalues was obtained; 2.13, 1.18, 0.99, 0.79, 0.58 and 0.34. The first three principal components (PC1, PC2 and PC3) explain together 71.6 % of the experimental data.

The distribution of herb samples in three-dimensional space is shown in Fig. 1. On the right side of the plot, above 0.9 value in the PC1 axis, there are localized all samples of Herba Urticae (42, 43 and 44), Anserinae (4 and 5) and Boraginis (6 and 7). In these samples the highest level of investigated elements was determined. It is also worth admitting, that in one sample of Herba Boraginis (6) the lowest level of sulphur in all herbs was determined. High concentrations of non-metals were also established in the samples of Herba Violae tricoloris (45, 46 and 47), Visci (48, 49 and 50) as well as Cnici benedicti (9, 10 and 11) and Equiseti (13 and 14).

On the opposite side of the plot, below −1.1 value in the PC1 axis, samples of herbs characterized by the lowest concentrations of non-metals are grouped. There are two different samples of Herba Ledi palustrae (22 and 23), Serpylli (38 and 39), Solidaginis (40), Thymi (41), Herniariae (16 and 17) and Hyperici (18 and 19). Samples of Herba Millefolii (27, 28 and 29), Rutae (36 and 37) as well as Origani (33 and 34) are localized in the neighborhood – 1.1 value in the PC1 axis.

In central part of three-dimensional space are samples, which contained intermediate level of analysed elements, such as Herba Absinthii (1, 2 and 3), Meliloti (25 and 26), Hyssopi (20 and 21) and Melissae (30, 31 and 32).

The results discussed above provide evidence that there are mutual relations among concentrations of non-metals in the analysed material. In some cases PCA may also be used to gather together herb samples belonging to the same plant species.

The course of the thermal decomposition of two samples of herbs – Cnici benedicti (10) and Visci (50) is illustrated in Fig. 2. Since herbs comprise a multicomponent mixture of organic and inorganic compounds, the DTA, TG and DTG curves of their thermal decomposition are plots of the physicochemical

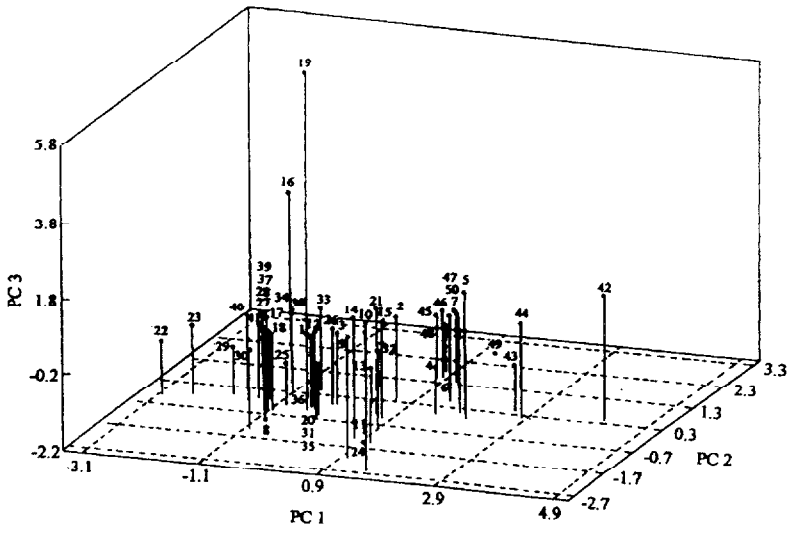

Fig. 1 Plot of the first three principal component score vectors (PC1 *vs.* PC2 and PC3) for 50 samples of herbs based on the level of six non-metallic elements

phenomena which occur in the sample when it is heated. The effects on the DTA curve result from the superposition of endo and exothermic effects due to transitions of particular components. This creates great difficulties for the identification of the reaction responsible for the appearance of a definite thermal effect. On the other side, the mass losses on the TG curve are the total loss in mass associated with the thermal decomposition of components contained in studied sample. Thus it is not feasible to identify the mass loss associated with the decomposition of a definite component of a herb.

All these facts led to general conclusion that the thermal decomposition of herbs proceeds in three stages. In the first stage a small loss in mass is observed connected with a wide and shallow endothermic effect on the DTA curve. This peak is probably due to the desorption of water from raw plant material together with the evaporation of volatile components and essential oils. Next stages of decomposition, the second and third, are accompanied with wide and strong exothermic effects on the DTA curve and high mass losses as reflected by the TG and DTG curves. There are due to the destruction and combustion of compounds contained in the herbs. The fragments of small woody stems together with tars and charred residue after the destruction of low-molecular compounds burned finally in the third stage of decomposition. Mineral residue is the final decomposition product of all the herbs.

The data set (matrix **X**, which has the dimension 18×50) consists of the results of thermal analysis for all samples of herbs. The following sequence of positive eigenvalues was calculated; 6.02, 3.11, 2.16, 1.58, 1.34, 0.76, 0.63, 0.51 and ten

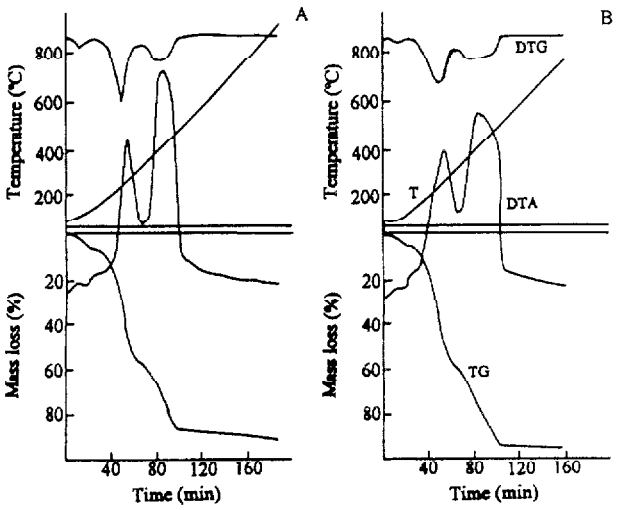

Fig. 2 DTA, TG and DTG curves of the thermal decomposition of (A) Herba Cnici benedicti (H.5.10) and (B) Herba Visci (H.25.50). The 100 mg samples were heated at a rate of 5 °C min^{-1}

values less than 0.5. The first three principal components (PC1, PC2 and PC3) explain together 62.7% of the variability. When comparing results of PCA obtained for both non-metals and thermoanalytical data sets, it can be stated that the distribution of the analysed plants in three-dimensional graph basing on higher amount of the results in the case of non-metal concentrations.

The results of PCA are illustrated in Fig. 3. The samples of Herba Anserinae (4 and 5), Herniariae (16 and 17), Ledi palustrae (22 and 23) as well as Millefolii (27, 28 and 29) 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 (6 and 7). In some cases, it appeared to be, that several raw materials originating from the same plant species, such as Herba Origani (33 and 34), Rutae (36 and 37) and Visci (48, 49 and 50) are differentiated by PC1 only, however the values of PC2 and PC3 are in fact the same or very similar.

As it can be concluded from literature data, large group of herbs contain aether oils [13]. From the point of PCA, their presence, however is not a crucial factor, which influence the shape of thermoanalytical curves of herbs leading them to group along similar values of PC1, PC2 and PC3. Perhaps it is caused by low contents of essential oils, amounting to about ten parts of percent. There is a similar situation in the case of plant materials containing tars and flavonoids. On the other side, fact that some plant materials contain several percent of tars, may influence the distribution of herbs along PC2 axis. All of the samples, which are rich in tars, such as Herba Anserinae (4 and 5), Hyperici (18 and 19), Melissae (30, 31 and 32) and Thymi (41) are located in the range of PC2 values from –2.3 to 1.7. Moreover, plant materials containing silicon compounds, Herba Equiseti

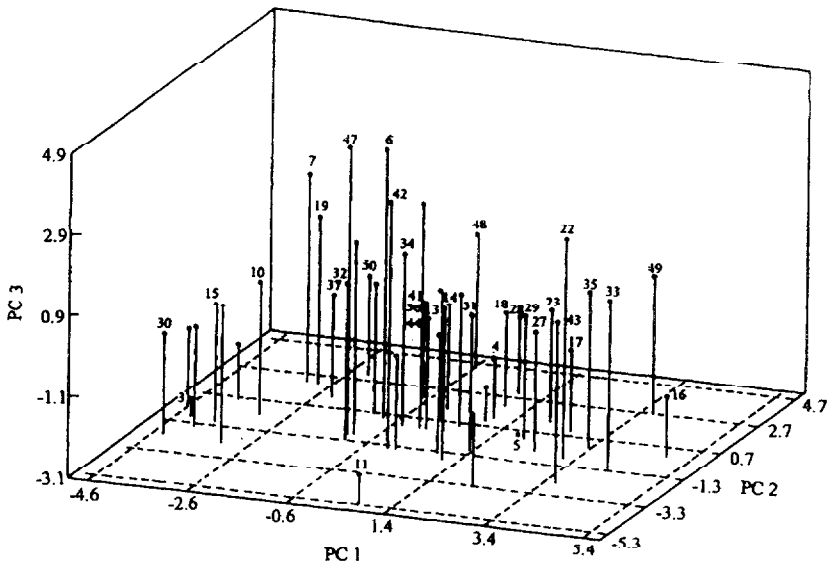

Fig. 3 Plot of the first three principal component score vectors (PC1 *vs.* PC2 and PC3) for 50 samples of herbs based on the thermoanalytical results

(13, 14), Polygoni avicularis (35) and Urticae (42, 43 and 44) can be found in the central part of the plot.

Conclusions

The results of PCA calculations for two matrices containing chemical and thermoanalytical data sets for herbs revealed that there are mutual relations between the results of thermal analysis and chemical composition of analysed material. The distribution of investigated plant material in the three-dimensional space indicates, in some cases, similarity in the course of thermal decomposition of the particular plant belonging to the same plant species. It reflects the close relation between the shape of DTA, TG and DTG curves of a herb and its chemical composition, which depends on plant species.

The general conclusion can be drawn that the elemental composition together with chemical composition of herb samples reflected by the results of their thermal analysis can be taken into consideration as a factor, which could support the chemotaxonomy of medicinal plants.

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