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INFLUENCE OF THE ELEMENTAL COMPOSITION OF MEDICINAL FRUITS ON THE RESULTS OF THEIR THERMAL ANALYSIS

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Abstract

Studies on the thermal decomposition and on the elemental composition of commercial raw plant materials used in medicine were performed. 16 independent samples of fruits originating from 12 medicinal plant species collected in 1988–92 were analysed. The thermal decomposition was performed using the derivatograph. The content of non-metallic (N, P, S, Cl, I and B) and metallic (Ca, Mg, Fe, Mn, Cu and Zn) elements was determined by spectrophotometric techniques after previous mineralization of sample. In order to obtain more clear classification of the analysed plant materials principal component analysis was applied. The interpretation of PCA results for three databases (thermoanalytical, non-metals and metals data sets) allows to state, that samples of fruits from the same plant species in the 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: determination of non-metals and metals, differential thermal analysis, fruits used in medicine, principal component analysis, raw plant materials, thermogravimetry

Introduction

Application of the thermoanalytical methods in the solution of a variety problems in the field of plant materials has been shortly presented by Prosiński *et al.* [1] and Kośik [2]. In the last years, the thermal decomposition of various woods and wood components was studied by simultaneous DSC, TG and DTG methods [3–8]. As a result distinct differences were found between the thermoanalytical curves of each hemicellulose and lignin samples. On the other hand, wood species could not be separated thermally, but hardwood and softwood curves differed because of the hemicellulose degradation pattern. The DTA, TG and DTG methods were also used for characterization of fresh and archeological samples of wood [9, 10] as well as for determination of the heat of combustion of different types of wood, bark and foliage [11, 12]. Recently, a preliminary study has been performed which indicates that oxyreactive thermal analysis can be used for taxonomical investigations in order to establish the systematic membership of certain species of alge based on fragments of thallus [13].

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As it is shown there is not much information about the application of thermoanalytical methods in the study of raw plant materials, such as herbs, leaves, flowers and fruits. Their chemical composition is different depending on plant species and geographic regions, from which these materials originated [14, 15]. Taking this into account, the aim of the present study is to establish, if any relations exist between the elemental composition of fruits and the thermal decomposition of these raw materials originating from the same plant species.

Experimental

Materials

In this study 16 independent samples of fruits from 12 species were used. The samples were collected in the years 1988–92 by Medicinal Plants Works 'Herbapol' at various factories in Poland. These fruits are as follows (numbers of the samples are given in the parentheses): Fructus Anisi (1), Fructus Carvi (2), Fructus Coriandrii (3), Fructus Crataegi (4), Fructus Foeniculi (5, 6 and 7), Fructus Lupuli (Strobili Lupuli) (8), Fructus Myrtilli (9), Fructus Phaseoli sine semine (Pericarpium Phaseoli) (10 and 11), Fructus Rosae (12), Fructus Sorbi (13 and 14), Semen Lini (15) and Semen Sinapis albae (16).

Thermal analysis

The DTA, TG and DTG curves of the thermal decomposition of raw plant materials were recorded using the OD-103 Derivatograph. A 100 mg plant sample was heated in a platinum crucible under 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.

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 three successive exothermic effects, for the second, third and fourth stage. In case of the TG analysis, the mass losses (Δm) in four 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.

Chemical analysis

The content of non-metals was determined after previous mineralization of plant sample [16, 17]. The method of nitrogen determination (N as NH_4^+) was based on the reaction between ammonia and Nessler reagent. The determination of phosphorus (P as PO_4^{3-}) consisted of the measurement of its concentration by phospho-molybdenum blue complex. Sulphur (S as SO_4^{2-}) was measured turbidimetrically. Chlorine (Cl as Cl^-) was determined basing on the reaction with $Hg(SCN)_2$. 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.

The determination of metal content was also preceded by mineralization of raw plant materials. The samples of fruits were heated at 220–240°C for 3 h. The partly dry-ashed samples were evaporated to dryness with a small volume of mixture of concentrated HNO_3 and H_2O_2. Nextly, the residue was dry-ashed at 450°C for 5 h and finally, the ash was dissolved in 0.1 mol l^{-1} HCl and diluted with redistillated water.

The iron, manganese, copper and zinc concentrations were determined directly from the solution by AAS using Philips PU 9100 instrument, calcium and magnesium were also determined by AAS after appropriate dilution of the solution. To check for matrix interference, mixed standards containing trace metals were analysed.

Calculations

The PCA was applied for interpretation of the results [18–20]. This method consists of calculating two new matrices – principal component scores and principal component loadings according to the experimental data set **X** with the dimensions **n**×**p**, 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 **n**×**k**, and principal component loadings are contained in matrix **W** with the dimensions **p**×**k**, where **k** is a number of orthogonal principal components calculated for the given set. **k** is at most equal to the number of variables **p**, and as a rule is much less than **p**. From this condition it can be concluded, that the number of principal components **n** is much less than the number of the experimental variables **p**.

The starting point for the calculations was matrix of the data **X**. In this study three matrices were constructed. In each matrix, sixteen medicinal fruit samples were used as the rows (**n**), which were called objects. Columns (**p**) were the results of thermal and chemical analyses of the particular raw materials and were called variables.

The first matrix contained data set for four stages of the thermal decomposition of fruits –T_i and T_p from DTA, Δm from TG as well as ΔT, T_p and h from DTG curves. The second one consisted of the mean values of nitrogen, phosphorus, sulphur, chlorine, iodine and boron content in the same fruit samples, and the third one grouped data set as the mean values of calcium, magnesium, iron, manganese, copper and zinc content in the fruits.

Matrix **X** is at first standardised, than matrix **R** is calculated according to it. After further calculations, columns in matrices **P** and **W** were obtained, which were called principal components. New matrix **P** reflects the main relations among objects and makes possible the classification of samples, whereas matrix **W** illustrates the main relations among variables and enables their selection. Very often two or three first principal components illustrate relations among objects in multidimensional space. It makes possible to present phenomena, which are difficult for imagination and interpretation, in clear two or three dimensional plots.

Results and discussion

The course of the thermal decomposition of two samples of fruits – Fructus Anisi (1) and Fructus Lupuli (8) is illustrated in Fig. 1. Since plant samples comprise a multicomponent mixture of organic and inorganic compounds, the curves of their thermal decomposition are plots of the physicochemical 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 the transitions of particular components. On the other hand, the mass losses on the TG curve are the total loss in mass associated with the thermal decomposition of components contained in the studied sample. Thus it is not feasible to identify the thermal effect and the mass loss associated with the decomposition of a definite component of a sample.

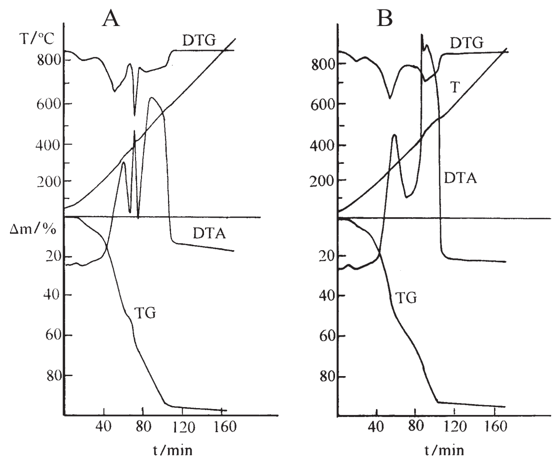

Fig. 1 DTA, TG and DTG curves of the thermal decomposition of two samples of fruits: A – Fructus Anisi (1); and B – Fructus Lupuli (8). The 100 mg samples were heated at a rate of 5°C min^{-1}

All these facts led to the general conclusion that the thermal decomposition of fruits proceeds in four 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. The next stages of decomposition, the second and third, are accompanied with strong exothermic effects on the DTA curve and high mass losses as reflected by the TG and DTG curves. They are due to the destruction and combustion of compounds contained in the fruits. Charred residue after the destruction of low-molecular compounds burned finally in the fourth stage of decomposition. Mineral residue is the final decomposition product of all the fruits.

Large number of parameters, which describe thermal effects on the DTA, TG and DTG curves is the reason for creation of huge databases with similar values of the particular thermoanalytical parameters. It also makes serious interpretative problems in case of the need to distinguish slight differences in a course of the thermal decomposition of the analysed raw materials. PCA seems to be a particularly useful tool, because one of its supreme advantage is a reduction of the number of variables describing the studied group of the experimental data.

The data set (matrix **X**, which has the dimension 24×16) consists of thermoanalytical results for all samples of fruits. The PCA calculations show that first three principal components (PC1, PC2 and PC3) explain together 65.2% of the variability. As it is illustrated in Fig. 2, the fruit samples are located in three different sectors. In the left down corner of the plot there are all fruits originating from plants belonging to *Rosaceae* family – Fructus Crataegi (4), Rosae (12) and Sorbi (13 and 14). 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, which differentiate this sample from the others [21]. In the central part of the plot there are all fruits from plants of *Umbelliferae* family located. There are Fructus Anisi (1), Carvi (2), Coriandrii (3) and Foeniculi (5, 6 and 7) among them. All of these samples are described by similar PC1 value, but are slightly differentiated by PC2 and PC3 values. Particular attention should be paid to Strobili Lupuli (8). It contains great amounts of resins – about 80%, which can be a reason for its special location [21]. Two samples of Pericarpium Phaseoli (10 and 11) can be found in the right down part of the plot. They come from the *Leguminosae* family. Similar way there are located Semen Lini (15) and Sinapis albae (16).

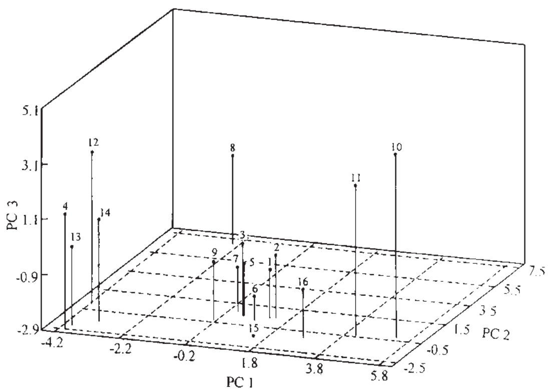

Fig. 2 Plot of the first three principal component score vectors (PC1 *vs*. PC2 and PC3) for 16 samples of fruits based on the thermoanalytical results

General rule after the PCA application to the non-metals and metals data sets can be drawn, that according to the distribution of plant materials along PC1, PC2 and PC3 axis, it is possible to separate at least three main classes of samples. They are differentiated because of their contents of elements. Medicinal fruits with low concentration of the analysed elements are located on the left side of the plot, but samples rich in elements, can be found on the opposite side. In some cases PCA may also be used to gather together fruit samples belonging to the same plant species. Similarly as in case of thermoanalytical results, in the close range of PC1, PC2 and PC3 values there can be found three samples of Fructus Foeniculi (5, 6 and 7) as well as two samples of Fructus Phaseoli sine semine (10 and 11) and Sorbi (13 and 14). In the last example, plant material is only differentiated by PC3 value.

Conclusions

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

The general conclusion can be drawn that the elemental composition together with chemical composition of fruit 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.

References

1 S. Prosiński and R. Zakrzewski, Z. Probl. Post. Nauk Rol., 185 (1976) 103.
2 M. Kośik, Z. Probl. Post. Nauk Rol., 185 (1976) 109.
3 T. Arima, Mokuzai Gakkaishi, 19 (1973) 435.
4 T. Arima, Mokuzai Gakkaishi, 19 (1973) 443.
5 T. Arima, Mokuzai Gakkaishi, 19 (1973) 475.
6 T. Arima, Mokuzai Gakkaishi, 25 (1979) 327.
7 F. C. Beall, Wood Sci. Technol., 5 (1971) 159.
8 F. C. Beall, W. Merrill, R. C. Baldwin and J. H. Wang, Wood Fiber, 8 (1976) 159.
9 C. Simionescu, A. Cernátescu-Asandei, P. Andriescu and C. S. Papadopol, Cellulose Chem. Technol., 11 (1977) 141.
10 M. Tomassetti, L. Campanella and R.Tomellini, Thermochim. Acta, 117 (1987) 297.
11 F. Shafizadeh, P. P. S. Chin and W. F. DeGroot, Forest Sci., 23 (1977) 81.
12 F. Shafizadeh, AIChE Symp. Ser., 74 (1978) 76.
13 S. Cebulak and M. Pliński, Oceanologia, 38 (1996) 99.
14 J. Volák and J. Stodola, Rośliny lecznicze (Medicinal plants), PWRiL, Warszawa 1986.
15 B. Bełdowska and J. Guzewska, Rośliny lecznicze, opis, zbiór, zastosowanie (Medicinal plants, description, harvest, application), IWZZ, Warszawa 1987.
16 M. Wesołowski and P. Konieczyński, Orient. J. Chem., 11 (1995) 1.
17 M. Wesołowski and P. Konieczyński, Orient. J. Chem., 11 (1995) 115.
18 J. C. Miller and J. N. Miller, Statistics for analytical chemistry, 2nd ed., Ellis Horwood, London 1989.
19 R. G. Brereton, Chemometrics, Applications of mathematics and statistics to laboratory systems, Ellis Horwood, London 1990.
20 R. E. Aries, D. P. Lidiard and R. A. Spragg, Chemistry in Britain, 9 (1991) 821.
21 S. Kohlmünzer, Farmakognozja (Pharmacognosy), 4th ed., PZWL, Warszawa 1993.