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# Thermoanalytical, chemical and principal component analysis of plant drugs

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**Abstract**

Thermal decomposition and elemental content of commercial raw plant materials used in medicine—roots, rhizomes and bark originating from different medicinal plant species were analyzed. 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 samples. In order to obtain more clear classification of the analyzed plant materials principal component analysis (PCA) was applied. Interpretation of PCA results for three databases (thermoanalytical, non-metals and metals data sets) allows the statement that samples of roots, rhizomes and bark 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:* Bark; Differential thermal analysis; Medicinal raw plant materials; Metals; Non-metals; Principal component analysis; Rhizomes; Roots; Thermogravimetry

## 1. Introduction

Raw medicinal plant materials are commercial products and have to be standardized. It is known from common practice, that their standardization includes humidity and ash estimation, and in case of plants which contain strong pharmacologically active substances, their determination (Farmakopea Polska, 1999; Kohlmünzer, 1993). However, there is a lack of information about the general chemical composition of raw medicinal plant materials and their physicochemical properties, for example, thermal characterization of plant materials.

The application of thermoanalytical methods may provide new information, such as phase transformations or the content of volatile and non-volatile compounds. Some examples of usefulness of these techniques in the examination of plant materials, such as different species of wood, bark and foliage, various wood components, fresh and very old samples of wood as well as medicinal herbs have been presented previously (Wesołowski et al., 2001).

Chemical content of raw medicinal plant materials may differ significantly not only for species of different origin, but also for plants belonging to the same species (Kohlmünzer, 1993; Volák and Stodola, 1986; Merian, 1991; Kabata-Pendias and Pendias, 1999). There is no doubt that genetic factors may play a crucial role, and the macro- and micro-environmental conditions, in which any plant grows are important, as

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well. Considering these facts, the target of the work is to establish, if any relations exist between the chemical composition of selected plant materials (roots, rhizomes and bark) and the thermal decomposition of these raw materials coming from the same and from different plant species. It also could help to answer the question, if thermoanalytical techniques can be used as methods, which support chemical analysis of plant drugs, especially during standardization of raw materials available in a pharmaceutical market.

## 2. Experimental

### 2.1. Materials

In this study 22 plant samples collected by the Medicinal Plants Works "Herbapol" at various factories in Poland were used, 10 samples of roots, 3 samples of rhizomes and 9 samples of bark. The plant materials were as follows (plant species and sample numbers are given in the brackets): roots—Radix Bardanae (*Arctium lappa* L., 1), Radix Cichorii (*Cichorium intybus* L., 2), Radix Hydrolapathi (*Rumex hydrolapathum* Huds., 3 and 4), Radix Inulae (*Inula helenium* L., 5), Radix Levistici (*Levisticum officinale* Koch., 6), Radix Rhei (*Rheum officinale* Baill., 7), Radix Symphyti (*Symphytum officinale* L., 8), Radix Taraxaci (*Taraxacum officinale* Web., 9) and Radix Valerianae (*Valeriana officinalis* L., 10); rhizomes—Rhizoma Agropyri (*Agropyron repens* L., 11), Rhizoma Calami (*Acorus calamus* L., 12) and Rhizoma Tormentillae (*Potentilla tormentilla* Neck., 13); bark—Cortex Frangulae (*Rhamnus frangula* L., 1 and 2), Cortex Fraxini (*Fraxinus excelsior* L., 3), Cortex Hippocastani (*Aesculus hippocastanum* L., 4), Cortex Quercus (*Quercus robur* L., 5 and 6) and Cortex Salicis (*Salix alba* L., 7–9).

### 2.2. Thermal analysis

The DTA, TG and DTG curves of raw plant materials were recorded using the OD-103 Derivatograph (MOM, Budapest, Hungary). One hundred milligram plant samples were heated in an unsealed platinum crucible at a heating rate of $5\,^{\circ}C\,min^{-1}$. The analyses were performed in air up to the final temperature of $900\,^{\circ}C$. The $\alpha$-$Al_2O_3$ was employed as reference material. Each thermogram was recorded at least three times.

Analysis of the DTA curves consists of designating the onset ($T_i$) and peak ($T_p$) temperatures of an endothermic effect for the first stage and for the two successive exothermic effects, for the second and the third stage of decomposition. In the case of the TG analysis, the mass losses ($\Delta m$) in three successive stages of decomposition were determined. However, the temperature range of the peak ($\Delta T$), peak temperature ($T_p$) and peak height ($h$) were obtained from the corresponding DTG curves. Peak height is given as an intensity indicator. These data are presented in Tables 1 and 2.

### 2.3. Chemical analysis

The content of non-metals and metals was determined after previous mineralization of plant samples. The method of nitrogen determination (N as $NH_4^+$) was based on the reaction between ammonia and Nessler reagent in the alkaline environment (Nowosielski, 1974). The determination of phosphorus (P as $PO_4^{3-}$) consisted of the measurement of its concentration by phospho-molybdenum blue complex using iron(II) as a reducer (Ganowiak et al., 1990). Sulphur (S as $SO_4^{2-}$) was determined turbidimetrically (Nowosielski, 1974). Barium chloride was used as an agent producing turbidity. Chlorine (Cl as $Cl^-$) was determined basing on the reaction with mercury(II) thiocyanate, in which the equivalent amount of thiocyanate ions reacts with iron(III) giving red complex (Nowosielski, 1974; Williams, 1979). The specific reaction of iodine (I as $I_2$) with starch was used to measure the iodine concentration (Ayiannidis and Voulgaropoulos, 1988; Marczenko, 1979). The content of boron (B as $BO_2^-$) was determined based on its reaction with Azomethine H (Gestring and Soltanpour, 1981; Ciba and Chruściel, 1992). Spectrophotometer Spekol-11 (Carl Zeiss, Jena, Germany) was used for all measurements.

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 the matrix interference, mixed standards containing trace metals were analyzed.

Table 1
Results of the thermal decomposition of roots (samples 1–10) and rhizomes (samples 11–13)

| Sample number | I stage | | | | | | II stage | | | | | | III stage | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | DTA | | TG and DTG | | | | DTA | | TG and DTG | | | | DTA | | TG and DTG | | | |
| | $T_i$ (°C) | $T_p$ (°C) | $\Delta m$ (%) | $\Delta T$ (°C) | $T_p$ (°C) | $h$ (mm) | $T_i$ (°C) | $T_p$ (°C) | $\Delta m$ (%) | $\Delta T$ (°C) | $T_p$ (°C) | $h$ (mm) | $T_i$ (°C) | $T_p$ (°C) | $\Delta m$ (%) | $\Delta T$ (°C) | $T_p$ (°C) | $h$ (mm) |
| 1 | 45 | 85 | 9.5 | 85 | 85 | 12 | 125 | 280 | 52.0 | 230 | 260 | 42 | 345 | 440 | 31.5 | 215 | 420 | 25 |
| 2 | 35 | 85 | 8.5 | 80 | 60 | 9 | 160 | 285 | 57.5 | 245 | 285 | 30 | 355 | 485 | 33.0 | 225 | 480 | 24 |
| 3 | 45 | 75 | 8.0 | 75 | 55 | 11 | 175 | 305 | 58.0 | 305 | 275 | 40 | 365 | 485 | 31.0 | 320 | 465 | 28 |
| 4 | 50 | 85 | 8.5 | 90 | 85 | 14 | 185 | 320 | 56.5 | 270 | 295 | 53 | 355 | 485 | 33.0 | 370 | 465 | 28 |
| 5 | 55 | 90 | 9.0 | 85 | 90 | 10 | 180 | 290 | 54.0 | 240 | 290 | 30 | 350 | 490 | 34.5 | 215 | 430 | 24 |
| 6 | 50 | 80 | 8.0 | 100 | 80 | 9 | 170 | 295 | 57.0 | 260 | 275 | 51 | 345 | 470 | 32.0 | 210 | 440 | 23 |
| 7 | 55 | 90 | 8.0 | 100 | 80 | 11 | 180 | 310 | 47.0 | 220 | 280 | 41 | 360 | 500 | 42.0 | 385 | 475 | 26 |
| 8 | 60 | 80 | 10.0 | 110 | 90 | 12 | 180 | 280 | 48.0 | 195 | 210 | 59 | 345 | 425 | 37.0 | 230 | 410 | 25 |
| 9 | 40 | 75 | 8.5 | 75 | 80 | 13 | 175 | 290 | 56.5 | 265 | 200 | 68 | 360 | 480 | 29.0 | 195 | 435 | 23 |
| 10 | 50 | 85 | 8.0 | 80 | 85 | 11 | 170 | 305 | 56.0 | 210 | 270 | 70 | 340 | 485 | 35.0 | 245 | 465 | 20 |
| 11 | 50 | 80 | 8.0 | 80 | 80 | 11 | 175 | 325 | 60.0 | 245 | 195 | 62 | 360 | 485 | 31.0 | 190 | 485 | 23 |
| 12 | 50 | 75 | 8.0 | 70 | 70 | 9 | 175 | 300 | 60.5 | 235 | 260 | 70 | 420 | 480 | 30.0 | 205 | 480 | 21 |
| 13 | 40 | 65 | 10.0 | 95 | 65 | 14 | 185 | 300 | 40.0 | 205 | 270 | 54 | 330 | 435 | 48.0 | 250 | 420 | 25 |

There are the onset ($T_i$) and peak ($T_p$) temperatures from the DTA peaks, the mass loss ($\Delta m$) from the TG curves, and the temperature range ($\Delta T$), peak temperature ($T_p$) and height ($h$) from the DTG peaks for three consecutive stages of decomposition of plant samples.

Table 2
Results of the thermal decomposition of bark

| Sample number | I stage | | | | | | II stage | | | | | | III stage | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | DTA | | TG and DTG | | | | DTA | | TG and DTG | | | | DTA | | TG and DTG | | | |
| | $T_i$ (°C) | $T_p$ (°C) | $\Delta m$ (%) | $\Delta T$ (°C) | $T_p$ (°C) | $h$ (mm) | $T_i$ (°C) | $T_p$ (°C) | $\Delta m$ (%) | $\Delta T$ (°C) | $T_p$ (°C) | $h$ (mm) | $T_i$ (°C) | $T_p$ (°C) | $\Delta m$ (%) | $\Delta T$ (°C) | $T_p$ (°C) | $h$ (mm) |
| 1 | 40 | 55 | 8.5 | 105 | 65 | 8 | 125 | 320 | 87.0 | 420 | 290 | 49 | 610 | 685 | 2.5 | 105 | 685 | 3 |
| 2 | 40 | 50 | 7.0 | 90 | 65 | 7 | 120 | 325 | 88.0 | 430 | 285 | 46 | 625 | 700 | 2.0 | 100 | 690 | 3 |
| 3 | 35 | 65 | 8.0 | 100 | 65 | 8 | 130 | 310 | 87.0 | 410 | 285 | 43 | 605 | 705 | 3.0 | 135 | 705 | 4 |
| 4 | 40 | 75 | 8.5 | 105 | 75 | 10 | 130 | 360 | 87.5 | 420 | 300 | 44 | 600 | 720 | 3.0 | 100 | 710 | 4 |
| 5 | 45 | 65 | 7.5 | 95 | 60 | 9 | 130 | 325 | 87.5 | 410 | 285 | 48 | 615 | 710 | 3.0 | 115 | 710 | 4 |
| 6 | 40 | 65 | 7.0 | 95 | 60 | 9 | 125 | 320 | 88.0 | 415 | 280 | 49 | 625 | 705 | 2.0 | 100 | 705 | 4 |
| 7 | 45 | 80 | 8.0 | 110 | 80 | 10 | 130 | 360 | 86.5 | 390 | 295 | 49 | 620 | 720 | 3.5 | 130 | 720 | 5 |
| 8 | 40 | 75 | 7.5 | 100 | 75 | 9 | 120 | 355 | 86.5 | 410 | 295 | 49 | 615 | 705 | 3.0 | 130 | 705 | 5 |
| 9 | 45 | 75 | 9.5 | 105 | 70 | 10 | 130 | 350 | 87.0 | 395 | 295 | 48 | 615 | 715 | 1.5 | 125 | 715 | 5 |

There are the onset ($T_i$) and peak ($T_p$) temperatures from the DTA peaks, the mass loss ($\Delta m$) from the TG curves, and the temperature range ($\Delta T$), peak temperature ($T_p$) and height ($h$) from the DTG peaks for three consecutive stages of decomposition of plant samples.

### 2.4. PCA calculations

Starting point for the PCA calculations was matrix of the data $X$ with dimensions $n \times p$, where $n$ is a number of objects (rows) and $p$ is a number of variables (columns) (Brereton, 1990; Wesołowski and Suchacz, 2001). In this study three matrices were constructed for roots and rhizomes, and three ones for bark. In each matrix medicinal plant samples were used as the rows. Columns were the results of thermal, non-metals and metals analyses of plant samples.

The first matrix contained data sets for the three stages of the thermal decomposition of roots, rhizomes and bark—$T_i$ and $T_p$ from DTA, $\Delta m$ from TG as well as $\Delta T$, $T_p$ and $h$ from DTG curves. The second one grouped data sets as the mean values of N, P, S, Cl, I and B content in the plant samples, and the third one consisted of the mean values of Ca, Mg, Fe, Mn, Cu and Zn content in the same plant samples.

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

## 3. Results and discussion

Thermal decomposition curves of exemplified samples of roots, rhizomes and bark are shown in Figs. 1 and 2. Because plant samples are multicomponent mixtures 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 peaks on the DTA curve result from the superposition of endo and exothermic effects due to 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 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. Consequently, the shape of the DTA, TG and DTG curves of particular raw plant materials are known to overlap with the effects of pyrolysis of all chemical substances contained in a sample. In this context, the thermal data may be

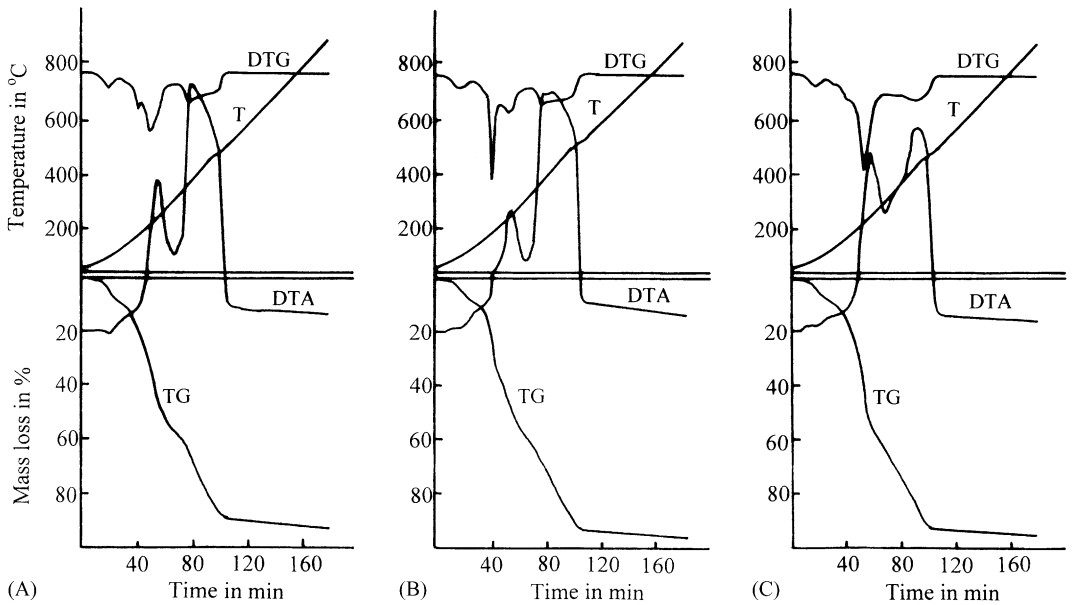


Fig. 1. DTA, TG and DTG curves of the thermal decomposition of roots and rhizomes: (A) Radix Bardanae (1), (B) Radix Inulae (5) and (C) Rhizoma Calami (12). Numbers in parentheses denote plant samples compiled in Table 1.

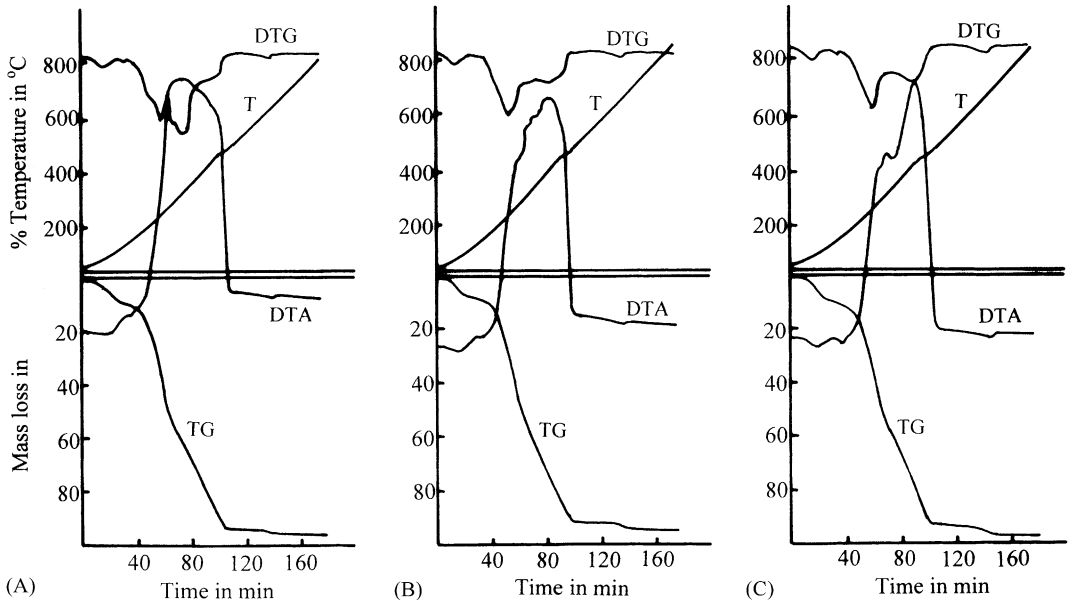


Fig. 2. DTA, TG and DTG curves of the thermal decomposition of bark: (A) Cortex Frangulae (1), (B) Cortex Quercus (5) and (C) Cortex Salicis (9). Numbers in parentheses denote plant samples compiled in Table 2.

potentially useful as the "fingerprint region" for identifying the plant samples of unknown origin and for evaluation of some quality features.

As it has been shown in Figs. 1 and 2 and Tables 1 and 2, bark are characterized by different course of thermal decomposition from other plant materials. Regardless of these differences, which are the result of the distinct chemical composition, especially the higher contents of mineral constituents in bark than that of roots and rhizomes, the thermal decomposition of plant materials can be in general treated according to the three-stage model. 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 plant material together with the evaporation of volatile components. Next, the second stage of decomposition is accompanied with strong exothermic effect on the DTA curve and high mass loss as reflected by the TG and DTG curves. These are due to the destruction and combustion of compounds contained in the plant samples. Charred residue after the destruction of low-molecular compounds is decomposed finally in the third stage. In the case of bark this stage is connected with the thermal decomposition of inorganic compounds, probably carbonates, and is shifted to the higher temperatures. Mineral residue is the final decomposition product of all the samples.

The analysis of non-metals content in studied plant samples led to conclusion that the total concentration of N, P, S, Cl, I and B represent different levels depending on plant species and geographic region of Poland, from which roots, rhizomes and bark originated. All plant samples are characterized by high N concentrations and relatively high amounts of Cl, too. On the contrary, total P, S and especially I and B levels are significantly lower, and these elements are in a narrow range of concentrations.

When comparing the level of non-metals in roots and rhizomes, it can be said that only Cl concentration in rhizomes is on the same level like it was determined in roots. As for the other elements, their level in rhizomes is lower even in comparison to the concentration in roots generally poor in non-metals. In the group of roots, the most characteristic is Radix Bardanae (1). With the exception of I level, this root contains the other elements in high amounts. The plant samples with the lowest level of non-metals appeared to be Radix Hydrolapathi (3 and 4), Levistici (6) and Cichorii (2). In the case of bark, because of low (with the exception of B) level of non-metals and narrow range of their concentration, it is difficult to indicate

bark with higher than other contents of the analyzed elements. Characteristic materials can be two samples of Cortex Quercus (5 and 6), which contain very low level of N, P and S. In both samples non-metals were determined almost on the same level, only the content of Cl was higher than in other bark.

The results of metals determination in roots, rhizomes and bark revealed that analyzed material contained Ca in the highest concentration, ranging from several to tens of milligrams per gram of dry plant tissue. The concentration of Mg varied from several hundred micrograms per gram to several milligram per gram of dry plant material. The contents of other metals—Fe, Mn, Cu and Zn in studied plant samples were on the level varied form several to several hundred micrograms per gram of dry plant tissue.

Most of the roots and rhizomes contained high level of Fe in comparison to bark. The highest concentration of that element was determined in Radix Levistici (6) and the lowest in Radix Symphyti (8). The content of the other metals did not differ by a significant level from the concentration in the other organs of plants. Worth admitting is the sample of Rhizoma Tormentillae (13), in which very high level of Zn was determined, outstanding from the mean concentration of that metal in other samples. Since each of the analyzed roots and rhizomes originated from the plants of different plant species, it is difficult to compare the concentration of metals between the samples from the same plant species. The only exceptions are two samples of Radix Hydrolapathi (3 and 4), which differed twice, one from another, in their contents of metals. Only the level of Zn was the same in these two samples of roots. From the analyzed bark samples, two samples of Cortex Frangulae (1 and 2) are characteristic because of the higher Mg level. Also, especially high concentration of Zn was determined in the three samples of Cortex Salicis (7–9). On the other hand, sample of Cortex Fraxini (3) was outstanding from the others because of the low concentration of Mn.

The large number of the data which are the results of thermal, non-metals and metals analyses of plant samples makes serious interpretative problems in the case of the need to distinguish slight differences in a course of the thermal decomposition and elemental composition of the analyzed raw materials. PCA seems to be a particular useful tool, because one of its supreme advantages is a reduction of the number of variables describing studied group of the experimental data. According to such a plot, it is possible to classify plant samples by their species.

Thermoanalytical data for roots and rhizomes were set in matrix with dimension $13 \times 18$. As a result of PCA calculations, 18 new variables were obtained which were characterized by consecutive eigenvalues—5.56, 3.27, 2.46, 2.34 and 1.41, seven following variables with values less than 1.0, and last six ones with values less than $1 \times 10^{-7}$. Two first PC's account for more than 49% of the total variance. Taking into account eigenvalues that were more than 2, the distribution of plant samples is illustrated in two-dimensional plot of PC1 versus PC2. As illustrated in Fig. 3A, with the exception of Radix Bardanae (1), Radix Symphyti (8) and Rhizoma Tormentillae (13) all of the other plants are grouped in the narrow range of the PC1 values. They are differentiated according to PC2 values. The other rhizomes—Rhizoma Agropyri (11) and Calami (12) are located according to the same values of PC1 and PC2. The same is for two samples of Radix Hydrolapathi (3 and 4).

Application of PCA to the non-metals and metals data sets revealed, that according to the distribution of plant materials along PC1 and PC2 axis, it is possible to separate at least three main classes of samples. They are differentiated because of their contents of elements. Medicinal plants drugs with low concentration of the analyzed 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 plant samples belonging to the same plant species.

The results of PCA calculations for non-metals are illustrated in Fig. 3B. It confirms the fact that rhizomes are plant materials relatively poor in non-metals; on the left side of the plot are grouped Rhizoma Agropyri (11) along with Rhizoma Tormentillae (13) and Radix Cichorii (2). On the other hand, Radix Bardanae (1) can be given as an example of a plant material with the highest content of non-metals, when compared to the other roots. Values of the two first PC's allow to identify Radix Inulae (5), Rhei (7) and Taraxaci (9) as materials with comparable levels of six analyzed elements. Two samples of Radix Hydrolapathi (3 and 4) are located in very similar values of PC1 and PC2 in the left side of the plot.

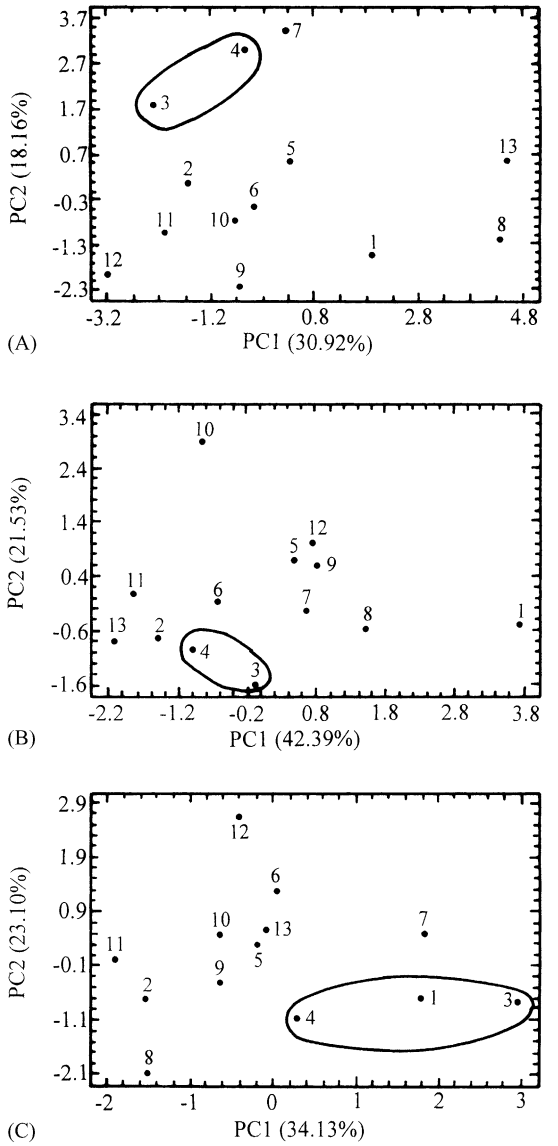


Fig. 3. Scatterplots of the first two principal component vectors (PC1 vs. PC2) for roots and rhizomes. Classification of 13 samples according to the (A) thermoanalytical, (B) non-metals and (C) metals data.

In Fig. 3C the distribution of roots and rhizomes according to the metals content is shown. In the middle of that plot there is Rhizoma Tormentillae (13) with the high content of Zn. Hence, one can indicate the two samples of Radix Hydrolapathi (3 and 4) because of their different PC1 values. It is caused by the different level of Fe and Mn in these samples. Analyzing roots and rhizomes it is possible to conclude, that these plant materials are differentiated mostly by the value of the first principal component.

Basing on the thermoanalytical results for bark, the matrix with dimension 9 × 18 was constructed. After PCA calculations 18 new variables were obtained. Their eigenvalues were as follows—8.90, 2.63, 1.87,

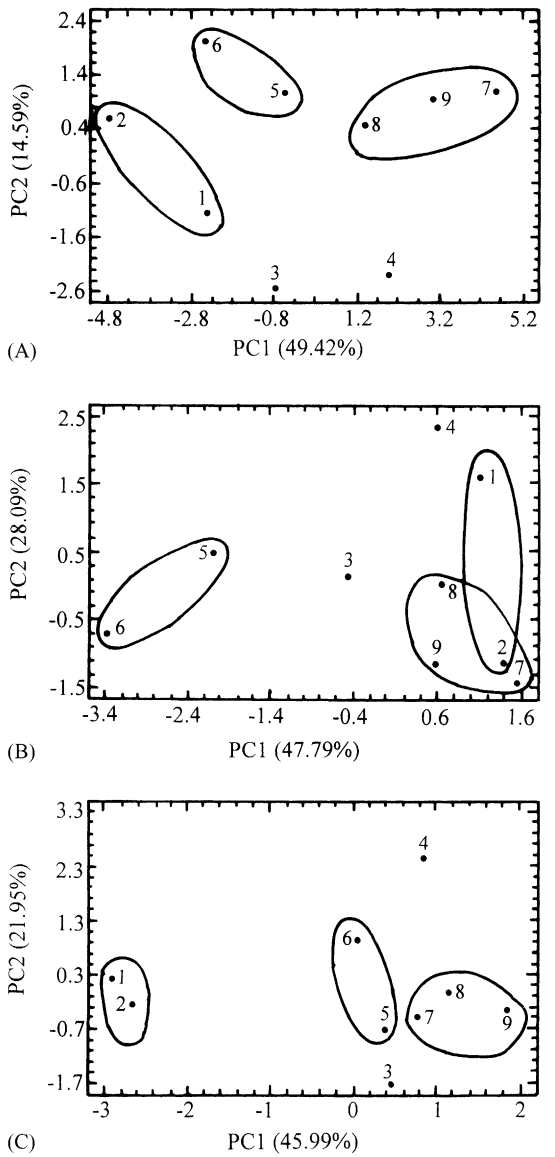


Fig. 4. Scatterplots of the first two principal component vectors (PC1 vs. PC2) for bark. Classification of 9 samples according to the (A) thermoanalytical, (B) non-metals and (C) metals data.

1.68 and 1.46, for next three values less than 1.0, and for the last ten values less than $1 \times 10^{-8}$. Taking into account eigenvalues that were more than 2, the distribution of plant samples was shown in two-dimensional plot of PC1 versus PC2, which explain together more than 64% of the total variance.

As it is illustrated in Fig. 4A, the bark samples are located in three different sectors. In the left side down corner of the plot there are two samples of Cortex Frangulae (1 and 2) originating from plants belonging to *Rhamnaceae* family. In the central part of the plot are located two samples of Cortex Quercus (5 and 6) from plants of *Fagaceae* family. They are described by very similar values of PC1 and PC2. Three samples of Cortex Salicis (7–9) can be found at the top of the plot, they come from *Salicaceae* family.

The results of PCA calculations for non-metals data set are illustrated in Fig. 4B. They have shown that samples of bark can also be described in a very similar way as in the case of thermoanalytical data. Raw plant materials originating from the same plant species are characterized by similar concentrations of non-metals, but not in such high degree, like it was in the case roots. It is confirmed by the location of Cortex Frangulae (1 and 2) and Salicis (7–9) in the right area of the plot, and Cortex Quercus (5 and 6) in its left side.

The spatial distribution of the bark according to the metal concentrations is presented in Fig. 4C. Characteristic is the location of the two samples of Cortex Frangulae (1 and 2) in the left side of the plot. Besides two samples of Cortex Quercus (5 and 6) are characteristic because of their similar PC1 values. Also all of the three samples of Cortex Salicis (7–9) are located in the right side of the plot. They are described by very similar content of six metals.

## 4. Conclusions

Results obtained in this study enable to gain some important knowledge about the thermal decomposition and the quantitative relationship between the levels of selected non-metals and metals in plant samples belonging to the same species.

PCA calculations for thermoanalytical, non-metals and metals data sets for plant drugs revealed that there are mutual relations between the results of thermal analysis and chemical composition of analyzed material. The distribution of plant samples in the two-dimensional space indicates, in some cases, similarity in the course of thermal decomposition of the particular plant belonging to the same plant species.

Because of high complexity of the chemical contents of plant material, one should not expect, that PCA and thermoanalytical methods would classify medicinal plants by the taxonomic groups, which they belong to. But these techniques can be treated as supporting methods in chemotaxonomy of medicinal plants and evaluation of their quality.

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