Determination of metal content in some herbal drugs—Empirical and chemometric approach ☆

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Abstract

The concentrations of Cu, Zn, Mn, Fe, K, Ca, Mg, Al, Ba and B in 26 herbal drugs of special importance in phytopharmacy were studied. Flame atomic absorption and emission spectrometry (FAAS, FAES), as well as inductively coupled plasma atomic emission spectrometry (ICP-AES), were applied in this work. The whole procedure, from sample preparation, via dissolution, to measurements, was validated by using CRM (NIST 1573a—tomato leaves), and the obtained recovery values are in the range from 91 to 102%. Drug samples originated from medicinal plants cultivated in Serbia contained Cu (4.47–14.08 mg kg^{-1}), Zn (8.4–54.5 mg kg^{-1}), Mn (9–155 mg kg^{-1}), Fe (47–546 mg kg^{-1}), K (0.20–6.24%), Ca (0.18–1.84%), Mg (0.13–1.09%), Al (16–416 mg kg^{-1}), Ba (11.70–84.83 mg kg^{-1}) and B (5.1–118.7 mg kg^{-1}). In order to get a better insight into the elemental patterns, a common chemometric approach to data evaluation was used. Four significant factors identified by principal component analysis (PCA) were attributed partly to the significant influential sources and high mobility of some elements thus referring to potential anthropogenic contamination as well.
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1. Introduction

Plants have always attracted the attention of scientists, especially nowadays, as our green planet is becoming less green everyday. In order to protect the environment and as a final goal, human health searching for answers and new solutions should provide a better insight into fundamental processes of plant physiology. Numerous processes are affected or regulated by minerals (also referred to as essential elements). Although the required levels of micronutrients are usually permanently fixed, they can vary depending on many factors, such as plant species, genotype and growth conditions, different organs and tissues of the same plant [1–3]. Medicinal plants are of special importance taking into account their role in health protection as preventive or supportive therapy for numerous diseases and disorders [1,4].

It is well known that some elements depending on their concentrations can play different roles in plant life [5–7]. Zinc, Mn and Fe are important co-enzymes; Cu is bound to amino acids [2] while Mn, Nd and Ce to some biomacromolecules forming coordination compounds [8]. Generally, the main characteristics of essential elements depend on the regulatory mechanisms, which are able to keep the elements at the nutrition level. Macro- and microelements, measured in this work, are critical components of many antioxidant processes; deficiency of any of these essential elements may impair the function of overall oxidant system [9]. Hence, better understanding of the uptake mechanism of elements, their functions in plant metabolism and their possible toxic effect [10] are of great importance in both basic and

applied plant studies. In that course/order, an accurate quantitative analysis at sensitivities down to trace and ultra-trace levels should always be made.

As a contribution in that sense, this work is dedicated to the determination of the total analyte content of major, minor and trace elements (Cu, Zn, Mn, Fe, K, Ca, Mg, Al, Ba and B) in 26 herbal drugs (commercially available at the Serbian market), originated from medicinal plants cultivated in Serbia. Flame atomic absorption and emission spectrometry (FAAS, FAES), as well as inductively coupled plasma atomic emission spectrometry (ICP-AES), were applied in this work.

2. Experimental

2.1. Solutions and reagents

All reagents used were of analytical grade. Calibration was performed using single and multi-element calibration solutions (2.5% HNO_3) prepared from 1 g/l Merck p.a. stock solutions.

Ionization in FAAS was controlled by adding a 5 ml (10 g/l CsCl + 100 g/l La, Merck, p.a.) buffer solution to all samples and standards and made up to final volume of 25 ml. All solutions and dilutions were made with deionized water.

2.2. Samples and analytes

Herbal drugs analyzed in this work are listed in Table 1.

2.3. Sample preparation procedure

Roots (carefully washed in situ and again in the laboratory with deionized water to remove soil) and the upper plant parts were dried at 105 °C until a constant weight was obtained and then ground.

The plant samples were prepared according to AOAC 975.03 and 985.01 methods [11]. Accurately weighed samples (~1 g each) were slightly heated on a hot plate at 100–120 °C for 15 min, then placed into a furnace and further heated at 500 °C for 2 h (temperature thermostatically controlled). After cooling, 10 drops of deionized water and then 4.0 ml of 8 M HNO_3 was added into each sample, slightly heated on the hot plate to dryness and then placed in the furnace at 500 °C for 1 h. After cooling, 10 ml of 6 M HCl was added into each sample and the contents were transferred into 25 ml normal flasks.

2.4. Instrumental and operating conditions in FAAS/FAES and ICP-AES

The determination of Cu, Zn, Mn, Fe, K, Ca and Mg was performed on a Perkin-Elmer 5000 atomic absorption spectrophotometer under optimized measurement conditions us-

Table 1
The list of herbal drugs samples

	Herbal drug	Plant
	Family	Lamiacae
1	*Salviae folium*	*Salvia officinalis* L.
2	*Menthae piperitae folium*	*Mentha piperita* L.
3	*Melissae folium*	*Melissa officinalis* L.
4	*Rosmarini folium*	*Rosmarinus officinalis* L.
5	*Lavandulae flos*	*Lavandula officinalis*
6	*Basilici herba*	*Ocimum basilicum* L.
7	*Marubii herba*	*Marrubium vulgare*
8	*Origani herba*	*Origanum vulgare* L.
	Family	Asteracae
9	*Cynarae folium*	*Cynara scolymus*
10	*Chamomillae flos*	*Matricaria chamomilla*
11	*Absinthii herba*	*Artemisia absinthium* L.
12	*Cichorii herba*	*Cichorium intybus*
13	*Millefolii herba*	*Achilea millefolium*
14	*Inulae radix*	*Inula Britannica*
	Family	Apiacae
15	*Petroselini folium*	*Petroselinum apium* L.
16	*Anethi fructus*	*Anethum graveolens* L.
17	*Foeniculi fructus*	*Foeniculum vulgare* Mill.
18	*Petroselini fructus*	*Apium petroselinum* L.
	Family	Urticacae
19	*Urticae folium*	*Urtica dioica* L.
20	*Uritacae radix*	*Urtica dioica* L.
	Family	Fabacae
21	*Phaseoli legumen*	*Phaseolus vulgaris*
22	*Liquiritiae radix*	*Glycyrrhiza glabra*
	Family	Ericacae
23	*Uvae ursi folium*	*Artostaphylos uva-ursi* L.
	Family	Plantaginacae
24	*Plantaginis folium*	*Plantago lanceolata*
	Family	Hypericacae
25	*Hyperici herba*	*Hypericum perforatum* L.
	Family	Malvacae
26	*Althaeae radix*	*Althea officinalis* L.

ing hollow cathode lamps. The signals with background correction (deuterium lamp) were measured at optimal flame heights. ICP-AES operating conditions for the determination of B, Al and Ba are summed up in Table 2.

Characteristic elemental lines used in FAAS/FAES and ICP-AES are given in Table 3.

Table 2
Instrumental and operating conditions in ICP-AES

Spectrometer	Perkin-Elmer ICP/6500
Input RF power	1.2 kW
Frequency	27 MHz
Argon outer gas flow rate	15 l/min
Argon intermediate flow rate	0.5 l/min
Aerosol carrier argon flow rate	1.0 l/min
Nebulizer	Perkin-Elmer cross-flow
Sample uptake rate[a]	0.6–1.5 ml/min
Observation height above load coil	2.5–25 mm

[a] Controlled by peristaltic pump.

Table 3
Characteristics of elemental spectral lines

Element line	E_i/E_{exc} (eV)	λ (nm)
Cu	7.72/3.82	324.754[a]
Zn	9.39/5.80	213.86[a]
Mn	7.43/4.44	279.48[a]
Fe	7.87/4.99	248.327[a]
K	4.39/1.61	769.898[a]
Ca	6.11/2.93	422.673[a]
Mg	7.64/4.34	285.213[a]
Al	5.98/4.02	309.284[b]
Ba	5.21/2.72	455.403[b]
B	8.30/4.96	249.773[b]

[a] FAAS, FAES.
[b] ICP-AES.

Table 4
Results ($mg\,kg^{-1}$) for certified reference material (NIST 1573a—tomato leaves)

Element	Found[a]	Certified value[a]	Recovery (%)
Cu	4.26 ± 0.29	4.70 ± 0.14	90.64
Zn	29.4 ± 0.6	30.9 ± 0.7	95.15
Mn	246 ± 2	246 ± 8	100
Fe	339 ± 1	368 ± 7	92.12
Al	577 ± 11	598 ± 12	96.49
B	30.4 ± 1.9	33.3 ± 0.7	91.29
Ba	51.60 ± 2.12	Not specified	–
K	2.63 ± 0.17	2.70 ± 0.05	97.41
Mg	1.82 ± 0.10	Not specified	–
Ca	5.13 ± 0.11	5.05 ± 0.09	101.58

Data corresponding to Ca, K and Mg are percentages.

2.5. Data analysis

The statistical data analysis was made using the SPSS for Windows Release 10.0 software package (SPSS Inc., Chicago, USA). The PCA was applied to analyze the trace element patterns in 26 herbal drugs. The details about the computational aspects of PCA can be readily found elsewhere [12].

3. Results and discussion

An extensive study of elemental composition of 26 herbal drugs widely used in phytopharmacy was carried out. Each plant sample analyzed in this work was more or less different due to complex matrices (inorganic + organic components); thus, sample preparation was the most critical part of the analysis. Many traps are often responsible for the largest and often hidden sources of error. It is not enough to intuitively apply a standard procedure (mineralization, dissolution, measurement technique . . .) to a sample with an unknown composition. Reliable results in terms of accuracy and precision as a final goal are mandatory as well.

A large number of procedures that can be found in literature [2,4,13–15] illustrate a lack of consensus, even inside a sample family. However, basic principles were established. The use of wet decomposition in trace element determination is rather limited due to high blank values introduced from the reagents and vessels. Analyte losses may be provoked by volatilization, absorption, transformation, precipitation or coprecipitation utilized during sample preparation steps. On the other hand, the biggest advantage of dry ashing procedure, applied in this work, is the possibility of treating large sample amounts and dissolving the resulting ash in a small volume of acid. Besides, the resulting ash was completely free of organic matter [15]. The choice of acids (nitric + hydrochloric) in dissolution step shows that no severe analytical problems exist with nitric acid at concentrations up to 10%. Also, hydrochloric acid was not troublesome in applied techniques [13]. The sample matrix was largely simplified and the resulting solutions were clear, colorless and odorless. No retention of residue was observed. The organic matter decomposed into carbon dioxide, nitrogen oxide and water released elements initially associated with it into solution. Thus, dissolution was completed in most cases.

Taking into account basic knowledge of inorganic compositions of plants [3,13–15] and preliminary investigation [16], the analysis was conducted applying FAAS/FAES and ICP-AES. Measurements were performed under optimal flame/plasma conditions. As for atomic spectroscopic analysis, no particular precaution will have to be taken if measured concentrations satisfy the principal criteria (sensitivity, detection limits, working range) and/or if possible interferences are under control [17,18]. Plant samples have variable content of insoluble silicate compounds (0.02–5%) [14]. High content of silicates, as a well-known problem, may result (= incomplete dissolution) in poor recoveries of many elements, especially Al, Fe and B [14]. The best indication of this phenomenon is the determination of aluminium, relatively abundant in plant media and partly associated with silicates [15], thus resulting in poor recoveries. The use of certified reference materials (CRM), therefore, is of crucial importance. For that reason, the whole procedure (from mineralization, via dissolution, to measurements) applied in this work was validated with CRM (NIST 1573a—tomato leaves). The recovery values obtained (Table 4) are in very good agreement with the certified values. Both FAAS/FAES and ICP-AES analysis gave the concentration values close to the certified ones for Al, Fe and B as critical.

According to the literature data, referring to the plant samples generally, the main matrix elements (Ca, K, Mg . . .) are present in concentrations superior to 0.1%, minor elements (Fe, Al . . .) lower than 0.1%, trace elements in mg/kg and ultra-trace elements below µg/kg or lower [13,14]. The results of elemental contents in investigated herbal drugs are presented in Table 5. There is a significant difference ($P < 0.05$), in elemental profiles among herbal drugs, attributed to the differences in their botanical structures; their element mobility within the plant, absorption from soil, as well as from other anthropogenic emission sources. A descriptive statistic of all data is also presented in Table 5.

Table 5
Element content in herbal drugs (mg/kg) expressed on dry basis (mean ± S.D.)

Sample	Cu	Zn	Mn	Fe	K (%)	Ca (%)	Mg (%)	Al	Ba	B
1	6.48 ± 0.31	43.0 ± 0.7	35 ± 1	331 ± 3	2.16 ± 0.30	0.90 ± 0.13	0.28 ± 0.03	198 ± 21	26.7 ± 0.62	55.6 ± 4.1
2	10.94 ± 0.60	25.7 ± 0.6	111 ± 2	405 ± 3	1.80 ± 0.14	1.43 ± 0.14	0.53 ± 0.02	331 ± 13	15.53 ± 1.12	55.4 ± 1.4
3	10.37 ± 0.035	21.4 ± 0.5	38 ± 1	285 ± 3	1.88 ± 0.23	1.32 ± 0.21	0.67 ± 0.04	225 ± 8	44.62 ± 1.7	55.5 ± 18.1
4	5.92 ± 0.35	15.0 ± 0.8	29 ± 3	546 ± 10	2.11 ± 0.24	0.95 ± 0.02	0.23 ± 0.01	360 ± 7	47.16 ± 1.81	47.1 ± 2.2
5	9.14 ± 0.63	257 ± 0.6	25 ± 1	152 ± 13	2.45 ± 0.14	1.06 ± 0.04	0.34 ± 0.02	139 ± 4	67.37 ± 1.14	56.5 ± 0.8
6	14.79 ± 0.33	24.5 ± 1.1	68 ± 7	438 ± 9	3.48 ± 0.07	1.33 ± 0.01	1.09 ± 0.17	378 ± 14	61.05 ± 4.04	36.2 ± 13.4
7	8.37 ± 0.32	24.4 ± 1.0	52 ± 1	390 ± 3	6.24 ± 0.70	1.10 ± 0.22	0.23 ± 0.05	344 ± 8	69.84 ± 4.10	40.1 ± 5.5
8	7.27 ± 0.60	35.7 ± 0.8	32 ± 2	74 ± 4	2.38 ± 0.10	0.90 ± 0.17	0.17 ± 0.02	49 ± 1	16.96 ± 0.25	34.7 ± 1.4
9	9.28 ± 0.72	54.5 ± 5.8	80 ± 1	415 ± 15	2.98 ± 0.06	1.07 ± 0.25	0.24 ± 0.05	198 ± 14	11.70 ± 2.19	32.5 ± 0.5
10	10.89 ± 0.58	29.2 ± 0.6	49 ± 3	253 ± 1	5.89 ± 0.05	0.55 ± 0.07	0.41 ± 0.02	168 ± 10	19.46 ± 0.83	41.7 ± 15.1
11	12.25 ± 0.01	31.7 ± 1.0	37 ± 1	182 ± 16	3.32 ± 0.24	0.55 ± 0.06	0.21 ± 0.03	102 ± 2	23.26 ± 0.79	43.6 ± 8.6
12	9.13 ± 0.06	22.7 ± 0.9	28 ± 1	76 ± 13	2.39 ± 0.25	0.69 ± 0.09	0.23 ± 0.02	53 ± 4	32.18 ± 1.48	55.6 ± 4.7
13	7.53 ± 0.30	18.8 ± 0.3	63 ± 4	107 ± 6	2.91 ± 0.12	0.56 ± 0.02	0.19 ± 0.02	67 ± 10	67.50 ± 2.26	39.9 ± 2.8
14	14.08 ± 0.39	49.1 ± 0.2	36 ± 3	161 ± 39	2.72 ± 0.21	0.18 ± 0.01	0.14 ± 0.02	172 ± 27	51.44 ± 3.96	7.6 ± 2.2
15	9.33 ± 0.33	33.8 ± 1.5	117 ± 3	503 ± 48	5.59 ± 0.12	1.11 ± 0.13	0.34 ± 0.06	416 ± 24	37.18 ± 1.88	36.4 ± 2.5
16	8.52 ± 0.04	23.3 ± 1.2	41 ± 2	319 ± 16	1.48 ± 0.09	0.93 ± 0.05	0.30 ± 0.01	175 ± 9	2074 ± 1.85	23.7 ± 1.6
17	10.11 ± 0.34	17.4 ± 0.5	50 ± 1	57 ± 5	1.22 ± 0.22	0.76 ± 0.06	0.36 ± 0.03	16 ± 6	12.64 ± 1.28	32.2 ± 8.3
18	12.82 ± 0.09	28.2 ± 0.6	62 ± 2	70 ± 2	1.45 ± 0.14	0.91 ± 0.09	0.39 ± 0.03	25 ± 2	15.36 ± 0.19	27.8 ± 0.5
19	12.48 ± 0.37	31.0 ± 1.1	55 ± 3	288 ± 42	4.18 ± 0.14	1.68 ± 0.27	0.43 ± 0.06	189 ± 19	26.14 ± 1.89	51.2 ± 0.2
20	8.34 ± 0.32	17.7 ± 0.5	22 ± 1	317 ± 15	2.60 ± 0.20	0.52 ± 0.07	0.21 ± 0.01	247 ± 47	47.61 ± 0.91	27.0 ± 2.8
21	7.86 ± 0.25	12.7 ± 1.7	23 ± 1	47 ± 3	2.78 ± 0.28	0.99 ± 0.35	0.40 ± 0.08	31 ± 6	40.15 ± 0.49	32.0 ± 12.8
22	5.60 ± 0.33	8.4 ± 0.5	22 ± 2	458 ± 15	0.20 ± 0.03	0.61 ± 0.07	0.38 ± 0.02	413 ± 38	84.83 ± 3.25	24.6 ± 5.2
23	4.47 ± 0.38	36.1 ± 0.6	17 ± 1	131 ± 1	0.37 ± 0.03	0.88 ± 0.07	0.13 ± 0.01	196 ± 21	70.10 ± 2.67	118.7 ± 14.6
24	9.38 ± 0.40	37.5 ± 0.3	51 ± 1	369 ± 19	3.51 ± 0.06	1.84 ± 0.02	0.35 ± 0.023	278 ± 11	44.75 ± 7.11	66.7 ± 0.8
25	10.18 ± 0.58	30.0 ± 1.0	155 ± 1	56 ± 3	0.96 ± 0.14	0.29 ± 0.01	0.18 ± 0.01	29 ± 1	13.69 ± 2.40	25.3 ± 2.9
26	13.74 ± 0.64	17.5 ± 0.9	9 ± 1	63 ± 1	1.02 ± 0.20	0.59 ± 0.17	0.35 ± 0.06	28 ± 1	21.56 ± 5.67	5.1 ± 0.4
Mean	9.60	27.5	50	250	2.62	0.91	0.34	186	38.10	41.2
S.D.	2.70	10.9	34	159	1.55	0.40	0.20	130	21.70	21.8
Minimum	4.50	8.4	9	47	0.20	0.18	0.13	16	11.70	5.1
Maximum	14.80	54.5	155	546	6.24	1.84	1.09	416	84.80	118.7
Maximum/minimum	3.30	6.5	17	12	31.43	10.12	8.39	26	7.20	23.4

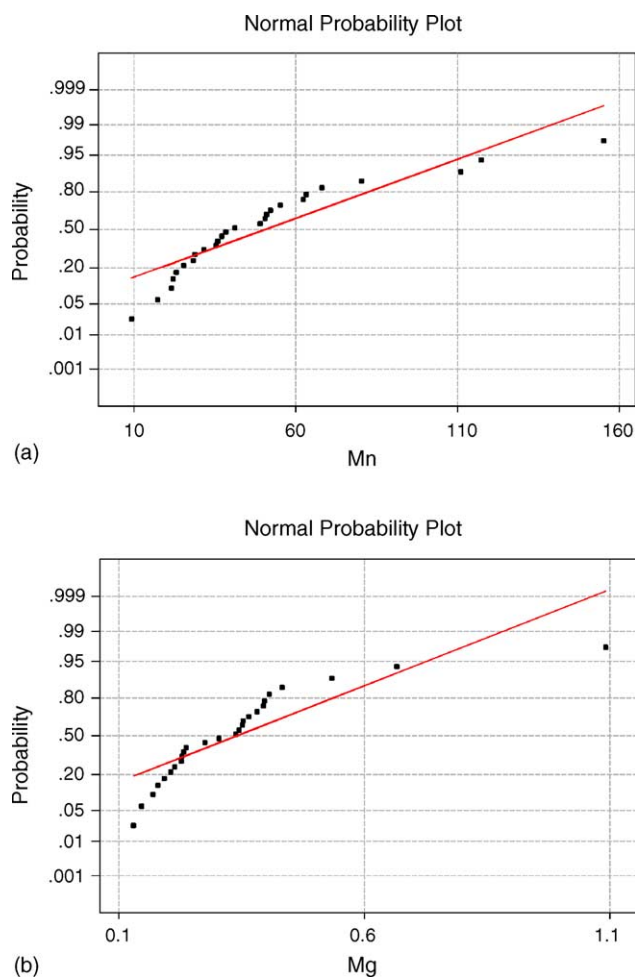Fig. 1. Normal probability plot for original data: (a) Mn and (b) Mg.

Fig. 2. Normal probability plot for log-transformed data: (a) Mn and (b) Mg.

The arithmetic mean and standard deviation of elemental concentrations for all samples were used to describe the central tendency and variations of the data. In order to get a better insight into the elemental patterns, a common chemometric approach to data analysis was used [12,19]. In the first step of statistic evaluation, using Shapiro–Wilk's test [20] (significance level α was 0.05), it was found that the original data set (Table 5) deviates from the normal distribution to a different extent. The highest deviation was observed for Mn and Mg (Fig. 1). In contrast, the log-transformed data were normally distributed for all metals and the normal probability plots for Mn and Mg, as representative examples, are presented in Fig. 2.

The data set of concentration measurements was subjected to the principal component analysis (PCA) in order to highlight the relations between the elements. With PCA, the data reduction is performed by transforming the data into orthogonal components that are a linear combination of the origin variables. Firstly, the data matrix was tested in order to remove outliers from the data set by applying Grubb's test [21]. The critical value for $\alpha = 0.05$ and $n = 26$ was 2.84. It resulted in det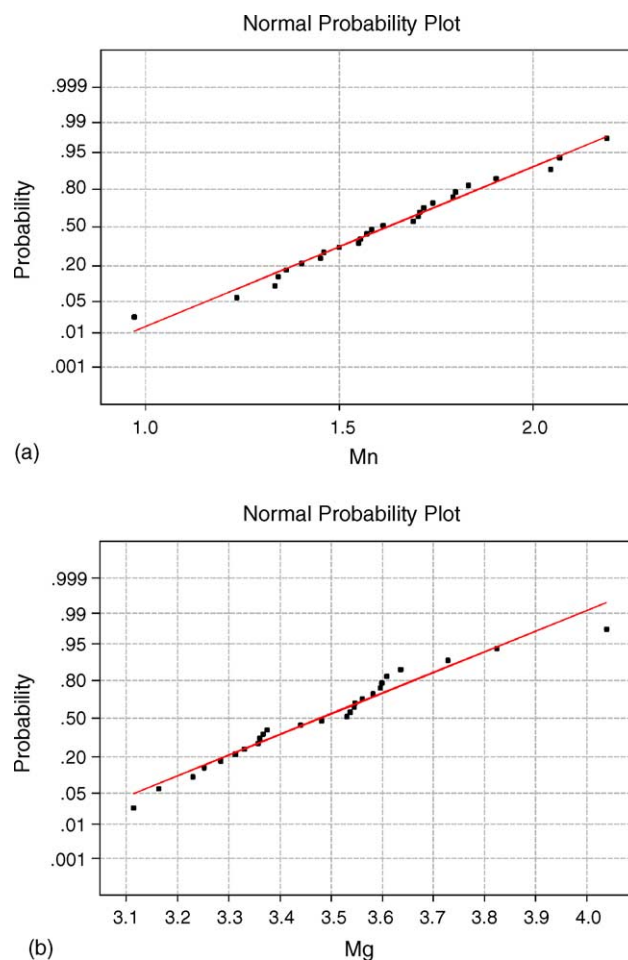ection of two outliers. Outliers detected in original data set were *Uvae ursi folium,* B = 118.73 (high) and *Hyperici herba,* Mn = 155.26 (high). Outliers in log-transformed data set were *Althaeae radix,* B = 0.71 (low) and *Inulae radix,* B = 0.88 (low). These values were discarded and not included in the PCA modeling. The correlation matrix of 10 elements obtained afterwards is presented in Table 6.

Uptake of various elements by plants through the root system from the soil depends on particular plant, botanical structure of specific tissue, soil type and element as well. Besides, microelements can enter the plant from the external environmental compartments. On the other hand, essential elements content in living organisms depends on physiological processes, being a part of regulatory mechanisms which are able to keep the elements below toxic level. This is consistent with data obtained for Cu in this work and literature data as well [22]. However, boron does not follow that rule as it is also essential for plants and probably for humans. However, there is a tendency of boron to accumulate in plant tissues [23]. It tends to be a potential hazard if there is high content in environmental compartments, the soil or water (as a possibility in this case) as higher boron concentrations was found in *Uvae ursi folium* than in root samples, *Althaeae radix* and *Inulae radix*, respectively.

Table 6
Correlation matrix of elements (Pearson correlation)

	Cu	Zn	Mn	Fe	K	Ca	Mg	Al	Ba
Zn	0.242								
Mn	0.306	0.385							
Fe	−0.123	0.108	0.220						
K	0.431*	0.397*	0.364	0.227					
Ca	−0.099	0.002	0.123	0.392	0.218				
Mg	0.437*	−0.287	0.181	0.275	0.132	0.562**			
Al	−0.215	0.119	0.118	0.950**	0.172	0.330	0.181		
Ba	−0.370	−0.324	−0.370	0.311	−0.068	0.035	−0.017	0.507**	
B	−0.266	0.325	−0.183	0.130	0.038	0.382	−0.073	0.278	0.301

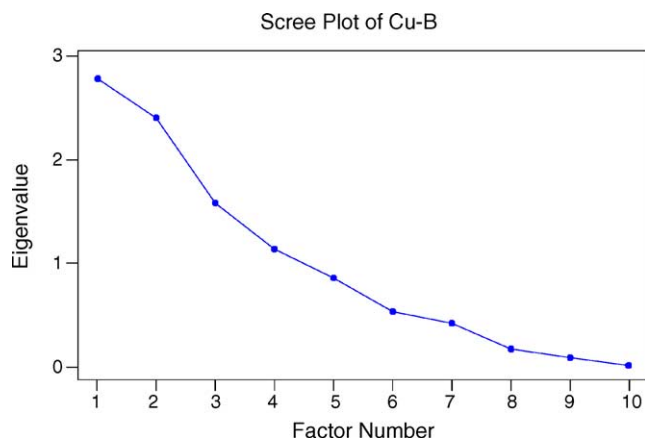Correlation is significant at the 0.05 level (*) and 0.01 level (**) (two-tailed). $N = 26$.

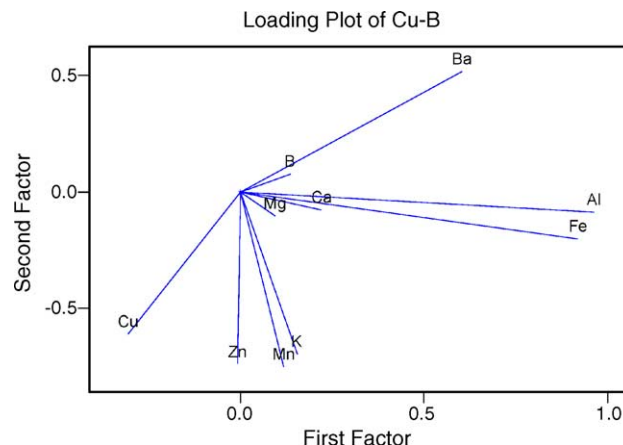Fig. 3. Eigen analysis of the correlation matrix.

Fig. 4. Loading plots of elements data in herbal drugs samples.

According to the literature data, Mn is expected to concentrate mostly in leaves, decreasing in roots and stems [4,22], although its content may be very high in the soil. This can partly justify high Mn concentration in *Hyperici herba*. In order to highlight possible correlations of elements in the plants and soil samples, further investigation should be conducted.

It can be seen that Al is highly correlated with Fe as well with Ba. Not so high but good correlation exists between other elements (other marked figures).

Fig. 3 shows an initial statistics of eigen analysis of the correlation matrix. Loading plot of correlated elements is presented in Fig. 4. The loading plot indicates the similarities and correlations between elements. The elements with small loadings located near the origin have only little influence on data structure, whereas the elements with high loadings represent those elements with the greatest influence on the grouping and separation of plant samples. A close relation (covariation) was observed between the concentrations of: (a) Al and Fe; (b) Zn, Mn and K and (c) Ca, Mg and B. Thus,

Table 7
Varimax rotated factor loadings of elements data in herbal drugs samples

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Cu	−0.305	−0.612[a]	0.328	−0.315	0.674
Zn	−0.008	−0.742[a]	−0.366	0.451	0.888
Mn	0.118	−0.752[a]	0.075	−0.185	0.620
Fe	0.919[a]	−0.201	0.190	0.032	0.923
K	0.155	−0.700[a]	0.133	0.102	0.542
Ca	0.221	−0.079	0.732[a]	0.496	0.838
Mg	0.095	−0.103	0.940[a]	−0.153	0.926
Al	0.963[a]	−0.089	0.088	0.145	0.965
Ba	0.604[a]	0.517[a]	−0.032	0.131	0.650
B	0.137	0.075	0.020	0.926[a]	0.882
Variance	2.3462	2.3183	1.7294	1.5136	7.9075
% Variance	0.235	0.232	0.173	0.151	0.791

[a] Loadings >0.5 and <−0.5.

a high concentration of Al is expected to be associated with high concentrations of Fe. It can also be seen that there is a general connection between Zn and Mn, and K.

One of the main objectives of PCA is to identify factors that are substantially meaningful. According to the Kaiser criterion [24], only the first four PCs are retained because subsequent eigenvalues are all less than one. Hence, reduced dimensionality of the descriptor space is four. To get a better insight of the latent structure of the data, the principal component extracted correlation matrix was subjected to varimax orthogonal rotation (Table 7).

Table 7 shows four significant factors obtained. These factors are related to the sources of the elements in the studied herbal drug samples. The first factor with 23.5% of variance comprises Fe, Al and Ba with high loadings (see also Fig. 4) and Mn, K, Ca, Mg and B with relatively low loadings. All elements, except Cu and Zn, have positive loadings in this factor (see Fig. 4). No significant loading value, except for Ba, was obtained for any variable of the second factor, which is responsible for 23.2% of total variance. This factor, dominantly loaded by Ba, is attributed to the influence of its high mobility and refers to potential anthropogenic contaminant [22].

The other variables have relatively low loadings and are highly negative for Cu, Zn, Mn and K. This negative correlation strongly supports the fact that there is a strong influence between matrix elements and traces, which often causes difficulties and bad recoveries. The third factor with 17.3% of variance was composed of Ca and Mg with high loadings. In addition, Cu has positive, but medium-low loadings. The fourth factor with 15.10% of variance comprises only B. Boron is an essential element for plants and probably for humans. Excess boron is toxic for plants and animals as well [23]. It is obvious that some elements, such as Ba have high score in more than one factor indicating the existence of more than one significant source. In general, using more tracer elements for different sources that are expected to contribute is valuable for this approach.

4. Conclusion

Determination of 10 elements in 26 herbal drugs of special importance in phytopharmacy was performed. Complete procedures, sample preparation and measurements were validated by using certified reference material. Good recovery values for all elements in all samples were obtained thus confirming complete mineralization and dissolution, as well as the absence of any problem in measurements.

Chemometric approach was used in order to recognize the patterns and thus possible influences of outer or inner sources. Tracer elements are not unique to a certain source category. Moreover, markers and source profiles change with time; as the environment is a very dynamic and changeable system, it requires frequent monitoring.

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