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ORIGINAL PAPER

DETERMINATION OF 13 TOXIC AND PHYSIOLOGICAL ELEMENTS IN HERBS ORIGINATING FROM CHINA BY ICPMS*

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Abstract

The aim of the study was to develop an analytical procedure for determining 13 elements in 40 herbs and mixtures of herbs of Chinese origin by the ICPMS method after acidic digestion of samples. The correctness of the analytical procedure was verified by estimating the validation parameters. The traceability of a measurement result was established by the certified reference materials: Mixed Polish Herbs (INCT-MPH-2) Apple Leaves (1515 NIST) and Spinach Leaves (1570a NIST). Appropriate optimization has determined the sensitivity of determinations, precision, detection limits. The limits of detection were in the range 0.015-15 mg kg^{-1} for Co and Mg respectively, the precision was in the range 1% - 48% for Ba and Se, respectively, and the recoveries were in the range 69% - 101% for Ni and Mn, respectively. The determined content (mg kg^{-1}) of elements in all samples was in the ranges: Mg (288-5755), V (<0.031-2.4), Mn (8.1-2095), Co (0.020-1.36), Ni (<1.1-6.9), Cu (<0.55-24), Zn (3.2-232), As (<0.096-1.4), Se (<0.15-0.85), Sr (1.1-277), Cd (<0.048-1.5), Ba (2.1-117) and Pb (<0.15-2.94). The content of As was higher than 0.25 mg kg^{-1} in 30% of the samples, the content of Cd was above the 0.2 mg kg^{-1} in 42.5% of the samples, and the content of Pb was above the value 0.3 mg kg^{-1} in 72.5% of the herbs. This means that the toxic elements were present in significant amounts able to cause toxic effects in the human body. Principal component analysis allowed us to distinguish 3 groups in which elements are well correlated: (i) V, As and Mg , (ii) Mn, Zn and Pb and (iii) Ni, Co and Cu.

Keywords: herbs, Chinese plants, toxic elements, metrology, ICPMS, procedure development, validation, PCA.

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INTRODUCTION

Traditional Chinese medicine is a very broad field that combines various types of treatments, therapies and practices used in China for centuries, and herbal medicine is one of its branches known as CAM (complementary and/or alternative medicine). Nowadays, over 400 species of plants are selected and used for medicinal purposes, either as heterogeneous mixtures or herbal preparations from a single plant species. The commonly used parts of plants are roots, rhizomes, stems, flowers, seeds, fruits and leaves. Current regulations do not treat herbs as medicines but as food, therefore the pharmaceutical law cannot be applied to them. According to surveys in the United States and Europe, about 20% of adults use herbs for medicinal purposes (NAVARRO 1995). Incompetent use or combination with other herbs or medical supplies can cause adverse side effects. Herbal infusions used in large quantities for a long period can cause liver damage (BOULLATA, NACE, 2000) and poisoning with an element such as lead, which can result in anemia, lead deposition in soft tissues and bones (GERALDINE et al. 2007, GUANGMIN et al. 2017).

The plant composition is variable and depends on many factors, such as the geographical area of the crop, soil type, fertilization, harvesting season, parts of the plant, drying and processing methods (EGAN et al. 2011). Soil pollution in China is one of the most serious ecological problems. Most soils contaminated with toxic elements by industry and mining are found in the Yangtze River Delta, the Eastern Pearl River Delta, as well as in the northeastern and southern regions of China (ZHAO et al. 2015). Thus, plants used as medicinal herbs are grown on huge farms, the soil is strengthened with fertilizers, the vegetation of the plant depends on the production cycle, and all production is based on chemical plant protection products. The content of elements in herbs is comparable to the content of these elements in vegetables and fruits, but they can be additionally contaminated during drying and preserving (LAM et al. 2010). The availability of elements depends on geological fertilization, water, soil pH and cation exchange capacity (HE et al. 2016).

Nowadays, inductively coupled plasma mass spectrometry (ICPMS) is one of the most important technique of elemental analysis. It has many advantages: high sensitivity, low limits of detection and quantification, wide linearity range, ability to analyze small or complex samples. The main disadvantage is the occurrence of spectral and non-spectral interferences from plasma gas, solutions, sample matrix and atmospheric gases. Mathematical correction, cold plasma, reaction or collision chamber or high resolution instruments are applied to reduce interferences (DAMS et al. 1995, Feldmann et al. 1999). In order to obtain information on the total content of elements, plant material should be processed to a solution by acidic digestion, by which the organic matrix is decomposed to water and gaseous products, leaving inorganic components that are the subject of analysis (BADRAN et al. 2017).

The aim of this study was to assess the content of 13 chemical elements, both physiological and toxic ones, in herbs originating from China and used in alternative medicine practices. In order to obtain the data, plant material was digested and resulting solutions were analyzed by the ICPMS. The analytical procedure was validated using the certified reference materials (CRM), Mixed Polish Herbs (INCT- MPH-2), Apple Leaves (1515 NIST) and Spinach Leaves (1570a NIST), and by applying the metrological rules.

MATERIAL AND METHOD

Research material

The material for research were 40 samples of mixed herbs and parts of herbal plants of Chinese origin. In the case of herbs, they were dried parts of plants such as roots, rhizomes, stems, fruits and leaves. Material was acquired in online stores specializing in the sale of herbal products imported from China. The initial preparation consisted of finely ground material to facilitate the further stage of sample preparation.

Sample preparation

The basic stage of the analytical procedure was wet digestion in a closed system. About 0.3 g of a dried sample was used for digestion in 65% nitric acid (Suprapur, Merck, Germany) and 30% hydrogen peroxide (Suprapur, Merck, Germany) added in a 3:1 ratio in quartz vessels. The entire process was carried out in the microwave assisted digestion system Ethos One (Milestone Srl, Italy) in 3 stages: ramp time – 20 min to reach 200°C, hold time – 30 min at 200°C and cooling – 30 min. The final part of sample preparation for analysis was the quantitative transfer of digested samples into polypropylene Falcon tubes and 80-fold dilution with demineralized water (Direct-Q 3 UV, Merck, Germany).

Analytical procedure

Calibration solutions were prepared by appropriate dilution of 10 mg L^{-1} multielemental stock solution in 5% HNO_3 (Multi-Element Calibration Standard 3, PerkinElmer, MA, USA). The calibration curves were constructed in the concentration ranges: 0.05-10 μg L^{-1} for V, Co, As, Se, Cd, Pb, 0.05-50 μg L^{-1} for Ni, 0.05-200.0 μg L^{-1} for Cu, Sr, 0.05-1000 μg L^{-1} for Ba, 0.05-2000 μg L^{-1} for Mn, Zn, Mg. In order to determine the 13 elements, two modes of analysis by ICPMS were performed: with helium (Pb, Ba, Sr, As, Cu, Zn, Ni, Co, Mn, V, Mg) and in the standard mode (Se, Cd). The non-spectral interferences were reduced by diluting the sample and using an internal standard (solution containing the 10 μg L^{-1} of Rh), introduced in parallel with all analyzed solutions by a T-piece (Markiewicz et al. 2017). Analyses were performed using ICPMS (Agilent 7700x, USA) with Octopole Reaction System (ORS).

To assess the precision and trueness of the analytical procedure, three CRMs were used: Mixed Polish Herbs (INCT-MPH-2, Institute of Nuclear Chemistry and Technology, Warsaw, Poland), Trace Elements in Spinach Leaves (1515, NIST,USA), Apple Leaves (1570a, NIST, USA). Elemental correlations in Chinese herbs were determined by statistical tools such as ANOVA and Microsoft Excel. The principal components analysis was performed with the statistical software Statistica (Statsoft).

Quality assurance

The procedure used to determine analytes in samples has to be validated to provide high quality results. This is especially important in the case of components that may have toxic effects on people who consume the food. Calibration was carried out using multielemental standard solutions and calibration curves were determined by the interpolation method. For all analytes the calibration curves demonstrated very good linearity, and the correlation coefficients were >0.999. The limit of detection (LOD) and limit of quantification (LOQ) were based on consideration of the blank prepared with the same procedure as samples. The method recommended by the International Union of Pure and Applied Chemistry (IUPAC) is determining LOD as three times the standard deviation (SD) for the blank, and LOQ as ten times the SD of the blank (Sajnóg et al. 2018). The measure of precision is the relative standard deviation (RSD), expressed as a coefficient of variation, CV (Markiewicz et al., 2017). The analytical procedure parameters are presented in Table 1.

The results of the analysis for CRMs: Mixed Polish Herbs (INCT--MPH-2), Apple Leaves (1515 NIST) and Spinach Leaves (1570a NIST), presented in Table 1, are comparable to the certified element content provided by the manufacturer. The percentages of recoveries are in the range 69%-101%, for Mixed Polish Herbs, 73%-100% for Apple Leaves, 85%-99% for Spinach Leaves. Based on the data, it can be concluded that the prepared procedure gives reliable results. Lower recovery values for some elements may have been caused by the properties of the CRM, reactions occurring in the sample preparation process, or temporary changes in the apparatus operating parameters during the analysis.

RESULT AND DISCUSSION

The presented procedure was used to determine 13 elements in 40 samples of herbs and herbal mixtures of Chinese origin by the ICPMS method. The samples included plant parts: roots (n=18), stalks (n=6), rhizome (n=5), mix of herbs (n=4), teas (n=3), fruit (n=1), phloem (n=1), branch (n=1) and bark (n=1). The results of analysis for each group, distinguished by the plant part, are presented in Table 2 as the average and standard deviation

Table 1

Values of analytical procedure parameters

Analytical procedure parameters	Analyte												
	As	Cd	Pb	Mg	V	Mn	Co	Ni	Cu	Zn	Se	Sr	Ba
Linearity	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
LOD (mg kg^{-1})	0.096	0.048	0.146	14.82	0.031	0.694	0.015	1.098	0.551	2.836	0.146	0.299	0.339
LOQ (mg kg^{-1})	0.265	0.139	0.392	41.95	0.076	1.901	0.040	2.914	1.413	6.560	0.391	0.794	0.950
Recovery (%)													
Mixed Polish Herbs (INCT- MPH-2)	89	99	80		81	101	87	69	99	98			91
Apple Leaves (1515 NIST)		94	79	100	73	93		74	94	96			89
Spinach Leaves (1570a NIST)	99	93			97	98	90	85	97	96	86	98	
Traceability	Established by CRMs												
CV (%)													
Mixed Polish Herbs (INCT- MPH-2)	2	10	2	4	4	3	3	5	7	1	48	2	1
Apple Leaves (1515 NIST)	8	41	14	10	13	7	8	8	9	12	16	5	5
Spinach Leaves (1570a NIST)	16	4	7	3	3	2	2	2	3	3	31	3	4

Table 2

Average contents and standard deviations of analyzed elements (mg kg^{-1}) in groups of different type of samples, which included parts of plants, mixes of herbs and teas

Specification		As		Cd		Pb		Mg		V		Mn	
Sample type	*N*	average	SD	average	SD	average	SD	average	SD	average	SD	average	SD
Bark	1	<LOD*	-	0.872*	-	1.419*	-	599.7*	-	0.143*	-	372.4*	-
Branch	1	<LOD*	-	0.292*	-	0.495*	-	578.3*	-	0.032*	-	165.7*	-
Phloem	1	<LOD*	-	0.279*	-	1.796*	-	288.5*	-	<LOD*	-	255.3*	-
Fruit	1	0.149*	-	<LOD*	-	0.196*	-	871.5*	-	0.602*	-	8.489*	-
Tea	3	0.163	0.089	0.078	0.047	1.479	1.215	2441	191.1	0.336	0.101	1429	665.7
Mix of herbs	4	0.235	0.214	0.052	0.010	0.401	0.127	2791	1154	0.388	0.165	436.6	482.9
Rhizome	5	0.170	0.157	0.408	0.490	0.946	1.001	1918	1691	0.535	0.236	117.6	123.0
Stalk	6	0.096	0.116	0.183	0.194	0.675	0.342	1803	1126	0.274	0.239	64.35	47.33
Root	18	0.299	0.323	0.372	0.404	0.709	0.758	2119	1419	1.052	0.708	60.77	78.08

		Co		Ni		Cu		Zn		Se		Sr		Ba	
Sample type	*N*	average	SD	average	SD	average	SD	average	SD	average	SD	average	SD	average	SD
Bark	1	0.119*	-	<LOD*	-	4.809*	-	9.146*	-	<LOD*	-	37.30*	-	101.1*	-
Branch	1	0.036*	-	<LOD*	-	4.762*	-	44.24*	-	<LOD*	-	11.50*	-	14.17*	-
Phloem	1	0.032*	-	<LOD*	-	3.297*	-	19.32*	-	<LOD*	-	1.076*	-	3.606*	-
Fruit	1	0.158*	-	<LOD*	-	6.413*	-	11.64*	-	<LOD*	-	8.635*	-	7.527*	-
Tea	3	0.474	0.344	6.770	0.264	16.66	2.261	36.02	1.330	0.040	0.030	12.37	6.874	30.36	26.02
Mix of herbs	4	0.135	0.048	1.685	1.799	10.79	5.941	28.88	10.86	0.303	0.350	111.4	131.4	25.58	21.25
Rhizome	5	0.476	0.569	1.230	1.520	6.087	6.437	66.42	92.94	0.202	0.367	21.12	15.77	32.57	18.89
Stalk	6	0.189	0.116	0.446	0.583	7.058	5.293	15.93	15.36	0.010	0.036	55.16	24.65	37.36	19.01
Root	18	0.361	0.290	0.933	1.017	6.535	5.185	21.47	9.575	0.079	0.178	48.59	56.79	37.67	28.02

* Value of concentration for a single sample in a given group.

Table 3

Basic statistics of determined contents (mg kg^{-1}) of 13 elements in 40 samples of herbs used in traditional Chinese medicine

Analyte	Average	Median	Minimum	Maximum	5th percentile	95th percentile
Elements causing toxic effects						
As	0.212	0.156	<0.096*	1.393	0.019	0.550
Cd	0.271	0.095	<0.048*	1.455	<0.048*	1.263
Pb	0.787	0.485	<0.15*	2.865	<0.15*	2.436
Ni	1.353	0.797	<1.1*	6.937	<1.1*	6.487
Physiological elements						
Mg	1984	1634	288.5	5755	499.0	4893
V	0.665	0.461	<0.031*	2.365	0.031	2.018
Mn	222.6	48.20	8.055	2095	12.86	1101
Co	0.308	0.223	0.020	1.355	0.035	0.946
Cu	7.571	6.056	<0.55*	23.71	1.314	18.76
Zn	28.05	19.77	3.190	232.0	5.006	44.56
Se	0.094	0.028	<0.15*	0.852	<0.15*	0.695
Non-essential elements						
Sr	46.30	20.72	1.076	277.3	4.330	159.1
Ba	34.62	29.50	2.055	117.4	3.566	77.29

* value indicates LOD

of measurements in a given group. In groups where only one sample was available, the measured value for this sample is stated. The statistical parameters of all the results are presented in the Table 3.

The studied elements affect living organisms in three ways. Elements like As, Cd and Pb exhibit toxic effects even in very low doses in almost all living organisms. Nickel is an essential element in some plants, but it is considered toxic to humans. The physiological elements, Mg, V, Mn, Co, Cu, Zn and Se, exhibit stimulating effects necessary for metabolic processes, but they are harmful to plants and humans in excessive amounts. There are also non-essential elements, like Sr and Ba, which are considered not harmful or low toxic to plants and humans if present in naturally occurring contents.

Elements causing toxic effects

The inorganic compounds of As have much higher toxicity than organic ones. Soils in most Chinese provinces specializing in the cultivation of plants are contaminated by arsenic (5.7-31 mg kg^{-1}) (Chen et al. 2015). The degree of accumulation depends on the acidity of soil, and plant roots contain more arsenic than other parts. Furthermore, arsenic from pesticide residues found in foodstuffs should not exceed 0.01 mg kg^{-1} (Mania et al. 2014). In 68% of the tested samples, the arsenic content above LOD was shown. In the remaining samples, the average level of this element was 0.29 mg kg^{-1} (range 0.09-1.4 mg kg^{-1}).

Cadmium is an element very similar to zinc. Similarly, it is taken up by plants and can replace it in metabolic functions. However, it is a toxic element, both to plants and to animals. This is due to the high affinity of cadmium for whole enzyme and protein groups. Cadmium was determined in the tested samples at an average level of 0.41 mg kg^{-1}. In 11 samples, the content of this element was below the LOD, while in 18 samples, that is 45% of all samples, the content exceeded the threshold amount specified in the Commission Regulation (WE) No 1881/2006 of 19 December 2006 for cadmium content in plant foods, which is 0.2 mg kg^{-1}.

Lead accumulates mainly in roots (93%-95%), in cell walls and cell membranes. The daily acceptable intake (ADI) for lead according to WHO is 0.428 mg. Meanwhile, Commission Regulation (WE) No 1881/2006 of 19 December 2006 states the maximum level at 0.3 mg kg^{-1} (Staniak 2014). The highest content of lead was found in green and red tea (1.7-2.6 mg kg^{-1}), in rhizomes (0.2-2.4 mg kg^{-1}) and roots (0.15-2.9 mg kg^{-1}). Lead is the element that exceeds the maximum permissible level in most analyzed samples. In 72.5% of the analyzed herbs, the content of lead was above the value 0.3 mg kg^{-1}.

Heavy elements include nickel, whose source in soil are soil-forming processes, the use of agricultural waste containing this element as well as gases and dusts from heavy industry. The toxic effect of this metal on plants is manifested in the limited uptake and transport of nutrients to the aerial parts of plants and in the inhibition of photosynthesis and transpiration (Kuziemska et al. 2014). Nickel accumulates in plant roots in most cases. The nickel content in plants usually ranges from 0.1 to 5 mg kg^{-1} dry weight (Szatanik-Kloc 2004). In 54% of the samples of the tested herbs, the nickel level was below the detection limit, while its content in green and red tea was high (6.5-6.9 mg kg^{-1}).

Physiological elements

Magnesium is a macroelement involved in many chemical reactions in the plant. This is the main component of chlorophyll. It is an essential ingredient for the synthesis, transport and storage of important plant components (carbohydrates, proteins and fats) and it acts as an activator of numerous enzymes. Magnesium is taken up by plants in the form of Mg^{2+} through both roots and leaves. A positive correlation between the magnesium content in plants and cadmium present in contaminated soil was found in studies carried out by Ciećko et al. (2005). The content of this macroelement was high in all samples (289-5755 mg kg^{-1}).

Anthropogenic sources of vanadium in soils include mining, burning fossil fuels and using phosphate fertilizers. It is essential in trace amounts and toxic when it occurs in excess. Its positive effect is observed as improved synthesis of chlorophyll or nitrogen assimilation. Vanadium can be accumulated in roots and shoots, depending on its content in soil and bioavailability. In plants growing on soils contaminated with vanadium, the level of vanadium is in the range of 6.1-157 mg kg^{-1} (Aihemaiti et al. 2018). Analyses of the herbal samples showed an average content of 0.71 mg kg^{-1} in the range of 0.03-2.4 mg kg^{-1}. The highest content was found in plant roots.

Manganese is an activator of many enzymatic processes, and it is involved in the process of photosynthesis and chlorophyll formation, nitrogen absorption and protein synthesis. Unlike other microelements, manganese is found in large quantities in plants. According to literature data, its content can vary widely (6-800 mg kg^{-1} of dry weight). As the acidification of soil increases, the amount of manganese in the plant increases (Koter et al. 1968, Najmowicz et al. 2012). In 90% of the samples, the manganese content was in the range of 30-50 mg kg^{-1}. The highest levels of manganese were found in herbal mixtures and teas (524-2095 mg kg^{-1}).

The presence of cobalt in the soil is associated with the presence of manganese and iron, as well as with organic fertilization. It is not a mobile element, but its mobility increases in an acidic environment. Cobalt affects plant development. It is absorbed by the roots in the form of Co^{2+}. It is especially important for papilionaceous plants. Nutritional requirements for plants determine the content of cobalt in tissues, which is not lower than 0.08 mg kg^{-1} (Kosiorek 2019). Herbs and herb mixtures contained on average 0.31 mg kg^{-1} of cobalt, with the range of 0.02-1.4 mg kg^{-1}.

Zinc plays an important role in plants in the synthesis of growth hormones, it affects protein metabolism and regulates phosphorus metabolism. Plants absorb zinc mainly in the form of Zn^{2+} ions and hydroxide ions (at higher pH values). Copper is also available for plants only in the form of Cu^{2+} ions. It is an element that affects the development and structure of tissues, in addition to which it is involved in nitrogen transformations, protein synthesis and vitamin C. Excess phosphorus in the soil can also lead to zinc retardation because zinc, manganese and copper can compete at low pH. The Zn content of the herbal products ranged from 3.2 to 232 mg kg^{-1}, and the average of values of measurement was 28 mg kg^{-1}. The average copper content is reported to be 7.8 mg kg^{-1}, with the range <0.55-24 mg kg^{-1} (Deng et al. 2004).

Plants have different ability to accumulate selenium from soils. Vegetables and fruits have a low content of selenium, not exceeding 0.01 mg kg^{-1}, and other plants such as grass or weeds can accumulate it up to 50 mg kg^{-1} when grown on selenium rich soils (Ferri et al. 2007). Studies of Chinese herbs from the Dashan region characterized by selenium rich soils showed an average selenium content of 370 mg kg^{-1} in these plants, with the highest reaching up to 1500 mg kg^{-1} (Zhao et al. 2018). In our experiment, values above the detection limit (<0.15-0.85 mg kg^{-1}) were obtained only for four of the tested samples of herbs and teas. This suggests that the herbs come from regions that are rather poor in selenium or that the element had been lost as a result of plant processing.

Non-essential elements

Strontium is a trace element that accumulates in deciduous plants and legumes. The increased amount of strontium in soils results from the presence of rocks and minerals, carbonates, or the alkaline reaction of the soil. It has a high resemblance to calcium (Ermakov et al. 2019). The range of strontium content in the tested samples is large, from 1.1 to 277 mg kg^{-1}.

Barium in soils form soluble complexes with humic and fulvic material, thus it is not expected to be very mobile. Despite relatively high contents in soils, only a limited amount of barium is taken up in plants, hence in most food the barium content is relatively low, <0.1 mg kg^{-1} (Llugany et al. 2000). The average content of barium in the tested herbs was 35 mg kg^{-1}.

Statistical and chemometric analysis

Correlation analysis quantifies a relationship between two variables and is measured using a correlation coefficient of –1 (negative correlation) to +1 (positive correlation). Correlation analyses of the total content of elements are presented in Table 4. The strongest correlations between two elements are the ones with the highest absolute value, as shown in Table 4. Signifi-

Table 4

Correlation matrix for the element contents in Chinese herbs

Analyte	Mg	V	Mn	Co	Ni	Cu	Zn	As	Se	Sr	Cd	Ba	Pb
Mg	**1**												
V	**0.45**	**1**											
Mn	-0.22	**-0.33**	**1**										
Co	-0.01	**0.60**	0.22	**1**									
Ni	0.23	**0.43**	**0.40**	**0.66**	**1**								
Cu	**0.48**	0.27	0.24	0.27	**0.53**	**1**							
Zn	0.05	0.06	**0.33**	0.13	0.22	**0.46**	**1**						
As	**0.58**	**0.72**	-0.24	**0.35**	0.23	0.18	0.22	**1**					
Se	0.27	**0.42**	0.06	**0.36**	0.30	0.02	-0.04	**0.45**	**1**				
Sr	**0.44**	**0.35**	**-0.45**	-0.02	-0.07	0.08	**-0.34**	0.27	0.11	**1**			
Cd	-0.30	-0.01	0.15	0.04	-0.20	-0.16	0.05	-0.05	0.15	-0.20	**1**		
Ba	0.16	**0.35**	-0.14	**0.39**	0.09	0.11	-0.02	0.25	0.24	**0.54**	0.03	**1**	
Pb	-0.18	-0.11	**0.41**	0.14	-0.05	0.06	**0.32**	0.07	0.01	-0.18	**0.46**	0.10	**1**

Values in bold are different from 0 at the significance level α=0.05.

cant and strong positive correlations are observed between As and V, As and Mg, Ni and Co, V and Co, Ba and Sr. Ngative and significant correlations are less common, and include Sr and Mn, Sr and Zn, V and Mn.

Principal component analysis (PCA) enables the presentation of relationships between multidimensional data by reducing variables and limiting them to two most prominent principal components. The application of PCA to the discussed data allowed us to distinguish two main components, explaining 47.4% of variance in the data set (Table 5). The first main compo-

Table 5

Values of principal component analysis, eigenvalues, variability and cumulative

Factor loadings	PC1	PC2
Mg	**0.66**	-0.28
V	**0.86**	-0.11
Mn	-0.13	**0.82**
Co	**0.64**	0.42
Ni	**0.61**	0.49
Cu	**0.51**	0.37
Zn	0.17	**0.62**
As	**0.77**	-0.08
Se	**0.54**	0.07
Sr	0.44	**-0.64**
Cd	-0.17	0.31
Ba	**0.51**	-0.16
Pb	-0.06	**0.57**
Eigenvalue	3.63	2.58
Variability (%)	27.9	19.8
Cumulative (%)	27.9	47.7

Values greater than |0.50| are in bold.

nent of PC1 explains 27.9% variability and the elements V, As and Mg, which are well correlated with each other, make up the largest share (Figure 1). The second main component of PC2 explains 19.8% variability, and the elements Mn, Zn and Pb have the largest share. There is also a group of elements, Ni, Co and Cu, which are well correlated with each other, while no significant correlations are observed with the other elements. Strontium is negatively correlated with the elements explained by the PC2 component (Mn, Zn and Pb), which may suggest antagonisms in the absorption of these elements. The least impact on the data variability is produced by the elements with the smallest eigenvectors: Cd, Se and Ba.

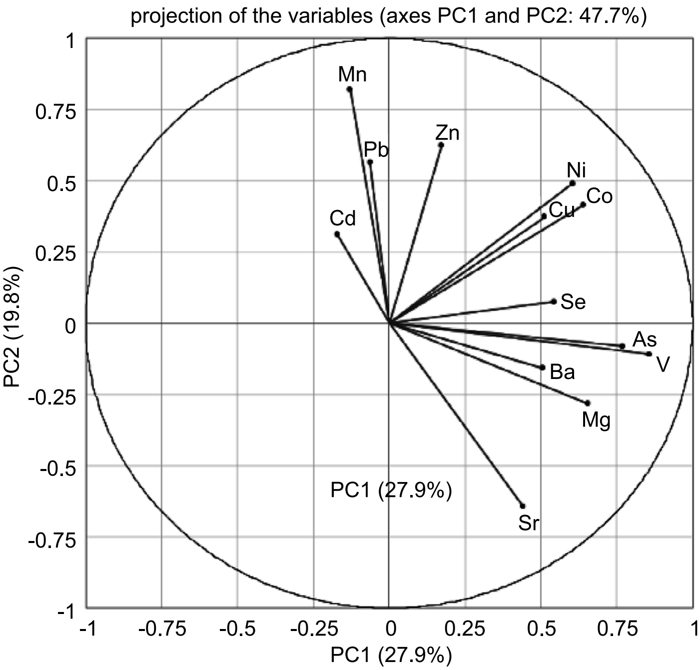

Fig. 1. Projection of variables PC1 and PC2 in PCA

CONCLUSIONS

The rapid and accurate ICPMS method enables the detection and quantification of 13 toxic and physiological elements in herbs of Chinese origin. ICPMS is an analytical technique that is an appropriate tool in the analysis of food and environmental samples owing to its sensitivity and effective interference removal options. The developed procedure was validated in order to estimate the parameters and the scope of application of the procedure. The LOD was determined by the modified blank determination method with the following estimated values: 0.020-0.10 mg kg^{-1} for V, Co, As and Cd, 0.15-0.69 mg kg^{-1} for Mn, Cu, Se, Sr, Ba and Pb, and 1.1-15 mg kg^{-1} for Mg, Ni and Zn, which allowed us to determine elements present in herbs at trace levels. The regression coefficient for all elements is >0.999, thus demonstrating the linearity and reproducibility of the method. Quantitative analysis of three matrix-matched CRMs, Mixed Polish Herbs (INCT- MPH-2), Apple Leaves (1515 NIST) and Spinach Leaves (1570a NIST), resulted in the recoveries for all elements between 69% and 101%. The toxic elements, such as As, Cd and Pb, reach high concentrations in many samples, exceeding the maximum levels allowed in the EU regulations. For example, the content of arsenic was higher than 0.25 mg kg^{-1} in 30% of samples, the content of cadmium was above the 0.2 g kg^{-1} in 42.5% of samples and the content of lead was above the value 0.3 mg kg^{-1} in 72.5% of herbs. Nickel was found in high content in green and red tea. The excessive consumption of herbs and herbal infusions, with such a high content of toxic elements, over a long time may lead to systemic toxicity or accumulation of toxic elements in organs, for example the accumulation of lead in bones. The physiological elements, such as Mg, V, Mn, Cu, Zn and Se, occur in the content that is found in plants naturally, and may be considered as not hazardous for humans. The statistical and chemometric analysis was performed in order to reveal correlations between pairs of the determined elements, and then the PCA showed correlations between 3 groups of elements: (i) V, As and Mg, (ii) Mn, Zn and Pb and (iii) Ni, Co and Cu.

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