Journal of Trace Elements in Medicine and Biology 30 (2015) 54–58

Contents lists available at ScienceDirect

Journal of Trace Elements in Medicine and Biology

journal homepage: www.elsevier.com/locate/jtemb

Toxicology

Determination of toxic metals by ICP-MS in Asiatic and European medicinal plants and dietary supplements

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ARTICLE INFO

Article history:
Received 15 April 2014
Accepted 22 October 2014

Keywords:
Toxic metals
Asiatic herbs
Dietary supplements
ICP-MS

ABSTRACT

The potentially toxic metals content was determined in selected plants, used in Traditional Chinese Medicine (*Angelica sinensis*, *Bacopa monnieri*, *Bupleurum sinensis*, *Curcuma longa*, *Cola accuminata*, *Emblica officinalis*, *Garcinia cambogia*, *Mucuna pruriens*, *Ocimum sanctum*, *Panax ginseng*, *Pueraria lobata*, *Salvia miltiorrhiza*, *Schisandra sinensis*, *Scutellaria baicalensis*, *Siraitia grosvenorii*, *Terminalia arjuna* and *Terminalia chebula*), and some European herbs (*Echinacea purpurea*, *Hypericum perforatum*, *Vitis vinifera*). Samples were mineralized in a closed microwave system using HNO_3 and the concentrations of Cd, Pb, Al, As, Ba, Ni and Sb were determined by ICP-MS method. Some relevant aspects of potential toxicity of metallic elements and their compounds were also discussed. Results of metal content analysis in dietary supplements available on Polish market, containing studied plants, are presented as well. The results were analyzed by principal component analysis (PCA) and cluster analysis.

Introduction

Pollution of food and dietary supplements by different metals may be caused by contaminated environment, fertilizers used in agriculture, various anthropogenic pollutants or inappropriate storage techniques. The level of toxic elements in plants can be affected by the geochemical parameters of soil, pollution of water, air and by the ability of plants to selectively accumulate some elements. Furthermore, metals may also be related to the geographical origin, harvesting or collection of these plant materials. Some metals (such as Cr, Mn, Mo, Zn, Fe, Co, Cu, Al, Ni) are essentials plant nutrients, however, they are phytotoxic at higher concentrations.

Long term consumption of Cd, Pb, Hg, Ba, Sb, As is hazardous for human health and life. The hazardous effect of metals on animals and human beings decreases approximately in the following order: Hg > Cu > Zn > Ni > Pb > Cd > Cr > Sn > Fe > Mn > Al [1]. Hence, with increasing industrialization and environmental pollution, it is necessary to monitor the content of some toxic elements in medicinal herbs.

In the recent years, consumption of healthy food, nutraceuticals and herbal dietary supplements in Europe has increased significantly. These products are produced from plants or other natural sources. It is easier for people to believe that phytotherapy, medicinal herbs and plants are not aggressive and do not have side effects on health. However, the Act or Regulation of Food Safety do not define the quality requirements and control methods of dietary supplements. Producers are only obliged to carry out the analysis of microbiological purity and contamination by the most popular hazardous metals (Pb and Cd) in raw plant extracts. In consequence, herbal medicines and dietary supplements are marketed without certificates confirming their quality and content of toxic metals. Change in the regulation on medicinal plants and dietary supplements contamination by toxic metals could, therefore, help the quality assessment of these products and can reduce health risk by potentially contaminated supplements. Thus, it is necessary to monitor the content of potentially toxic elements.

In addition to different metals, the plant material can be contaminated with pesticides, microbial contaminants and other chemical toxins. They can also be contaminated during chemical treatment or storage [2,3].

The main aim of this work is evaluation of selected metals content in raw plant material and dietary supplements. The development of methods for detecting toxic, hazardous metals in traditional Chinese medicines and the investigation of the level of contamination of traditional Chinese medicines is our goal.

In this study, the content of toxic metals (Pb, Cd, As, Al, Ni, Ba, Sb) in Asiatic medicinal plants, using in Ayurveda or Traditional Chinese Medicine (such as *Angelica sinensis*, *Bacopa monnieri*, *Bupleurum sinensis*, *Curcuma longa*, *Cola accuminata*, *Emblica officinalis*, *Garcinia cambogia*, *Mucuna pruriens*, *Ocimum sanctum*, *Panax ginseng*, *Pueraria lobata*, *Salvia miltiorrhiza*, *Schisandra sinensis*, *Scutellaria baicalensis*, *Siraitia grosvenorii*, *Terminalia arjuna* and

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http://dx.doi.org/10.1016/j.jtemb.2014.10.008
0946-672X/

Terminalia chebula), and some European herbs (*Echinacea purpurea*, *Hypericum perforatum*, *Vitis vinifera*) were determined by inductively coupled plasma with mass spectrometry (ICP-MS). The content of toxic metals in plants was compared with dietary supplements available on the Polish market, which contain studied plants and herbs from Asia and Europe.

Materials and methods

Materials

Angelica sinensis (AS), *Bacopa monnieri* (BM), *Bupleurum sinensis* (BS), *Cola accuminata* (CA), *Curcuma longa* (CL), *Garcinia cambogia* (GC), *Mucuna pruriens* (MP), *Ocimum sanctum* (OS), *Panax ginseng* (PG), *Pueraria lobata* (PL), *Scutellaria baicalensis* (SB), *Siraitia grosvenorii* (SG), *Salvia miltiorrhiza* (SM), *Schisandra sinensis* (SS), *Terminalia arjuna* (TA), *Terminalia chebula* (TCh), were purchased from STANLAB (Lublin, Poland). *Curcuma longa* (CL) was purchased from two different producers so we coded CL: CL-H and CL-P. Plant materials and herbs, such as: Emblica officinalis (Amla) and *Vitis vinifera* (VV) from Biofaktor (Gorzów Wlkp., Poland), *Echinacea purpurea* (EP) from FLOS (Mokrsko, Poland), while *Hypericum perforatum* (HP) from Herbapol (Lublin, Poland). Dietary supplements (coded as DS-AMLA, DS-AS1, DS-AS2, DS-BM, DS-CA, DS-CL, DS-GC1, DS-GC2, DS-PG1, DS-PG2, DS-PL1, DS-PL2, DS-PL3, DS-EP1, DS-EP2, DS-VV1, DS-VV2, and mixed DS-AMLA,VV; DS-PG,VV) were bought in local pharmacy. Ultrapure nitric acid (65%) was supplied from POCH (Poland). Multi-elemental mixture of metal standards was purchased from Agilent Technologies, Japan. Deionized water (conductivity $\leq 0.5\ \mu S$) was used for analysis

Sample preparation

For ICP-MS method – the grounded, dried samples (0.20–0.40 g ($\pm$0.0001 g)) of plants and dietary supplement were transferred to a Teflon dish, quenched with 5 mL of concentrated ultrapure nitric acid (65%), provided in the kit and were subjected to mineralization by microwave digestion (30 min). Then clear solutions were transferred quantitatively into the volumetric flasks (50 mL) and made up with deionized water (3 repetitions).

Apparatus and method

ICP-MS spectrometer with quadrupole analyzer 7500CX and collision chamber (Agilent Technologies, Japan) were used in analysis of Asiatic, European plants and dietary supplements after acidic digestion (65% ultrapure nitric acid).

The analysis was carried out according to the scheme, which can be described briefly as follows: the introduction of the sample, nebulization, the fragmentation of compounds having a characteristic ion charge, the ionization of elements in the high temperature argon plasma, mass discrimination in the quadrupole analyzer, detection based on ratio m/z and data analysis.

Optimal operating conditions for ICP-MS analysis are given in Table 1. The high radio frequency power (500–1600 W) helped maintain a stable plasma in the presence of studied samples after acidic digestion, and the plasma gas (argon) flow rate was increased to 17 L/min because of the higher power used. ICP-MS spectrometer was equipped with concentric nebulizer, quadrupole mass analyzer and collision chamber ORS. Argon was used as a plasma gas, and helium as gas in collision chamber. The purity of He was 5.5, because of reduction on molecular interferences.

Before the measurement, calibration of ICP-MS spectrometer using multielemental mixture of metal standards (Agilent Technologies, Japan) was carried out. Five multielement calibration solutions were prepared at different concentration levels ($0.10 - 5.0\ \mu g\ mL^{-1}$) using ultra purity nitric acid matched to the samples matrix. The calibration curve for all the elements reveal a good linearity over the whole range of concentrations, with determination coefficients higher than 0.999. A five sample blank replicate analysis was used to calculate the limit of quantitation (LOQ = standard deviation (SD) 10) and limit of detection (LOD = standard deviation (SD) 3). The blank consisted of deionized water with 2% HNO_3. The detection limits of the studied isotopes lie between $0.8 \times 10^{-6}\ \mu g\ mL^{-1}$ for Sb and $11.5 \times 10^{-6}\ \mu g\ mL^{-1}$ for Al (Table 1). On the other hand, the instrument detection limit was <1.5 ^{9}Be, <0.5 ^{115}In, <4 ^{78}Se, <0.5 ^{209}Bi [ppt] (Table 1). The accuracy of the method was assessed using replicate analysis of 3 different samples of standard reference materials (SRM 1570a). Recovery for studied elements in SRM 1570a was higher than 95.0% (95.04% for Cd, 95.66% for Pb, 98.23% for Al, 97.83% for Ni and 95.15% for As).

Quantitative analysis was also performed using addition of an external standard (ISTD). Moreover, analyzes were made using the controls analysis of rare elements (indium, beryllium).

Table 1
Optimal ICP-MS operating conditions for analysis of studied samples.

Instrument parameter	Condition
RF power	1500 W
RF frequency	27.12 MHz
RF Matching	1.72 V
Carrier gas (inner)	0.9 L/min
Makeup Gas	0.17 L/min
Plasma gas	Ar X50S 5.0
Plasma gas flow (Ar)	17 L/min
Nebulizer pump	0.1 rps
Sample untake	0.5 mL/min
Spray chamber temperature	2 °C
Extract 1	3.3 V
Extract 2	−110 V
Cell entrance	−30 V
QP focus	−10 V
Cell exit	−40 V
Resolution m/z	238 amu
Background	<5 cps (9 amu)
Isotope ratio precision CeO/Ce	<3%
Short-term stability	<3% RSD
Long-term stability	<4% RSD/2 h
Sensitivity [cps/ppm]	80.10^{689}Y
Instrument limit of detection (ppt)	<1.5 ^{9}Be, <0.5 ^{115}In, <4 ^{78}Se, <0.5 ^{209}Bi
Isotopes measured	^{114}Cd, ^{208}Pb, ^{121}Sb, ^{27}Al, ^{75}As, ^{60}Ni, ^{135}Ba
Limit of detection [$\mu g\ mL^{-1}$]	
Cd	0.9×10^{-6}
Pb	1.3×10^{-6}
Sb	0.8×10^{-6}
Ni	5.1×10^{-6}
Ba	3.5×10^{-6}
Al	11.5×10^{-6}
As	9.4×10^{-6}

Statistical analysis

The results of toxic metals in the studied medicinal plants and dietary supplements were presented as mean (c) $\pm$ confidence interval (μ) and listed in Tables 2 and 3. Principal component analysis (PCA) and cluster analysis were performed for the results of bioelements and toxic metals content in the studied samples using Statistica (Windows software package, version 10PL). PCA score plot was used to determine whether Asiatic plants, European herbs and dietary supplements could be grouped into different classes.

Results and discussion

The notion that some metals have positive health effects is based on ancient concepts which are not sustainable in the light of modern science. Therefore, potentially toxic metals have no place in