http://dx.doi.org/10.5935/0103-5053.20160123

J. Braz. Chem. Soc., Vol. 27, No. 12, 2273-2289, 2016.
Printed in Brazil - ©2016 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Evaluation of Major and Trace Elements in Medicinal Plants

Paulo S. C. Silva,* Lucilaine S. Francisconi and Rodolfo D. M. R. Gonçalves

Instituto de Pesquisas Energéticas e Nucleares, CNEN/IPEN, Av Prof. Lineu Prestes, 2242, Cidade Universitária, CP 11049, 05508-000 São Paulo-SP, Brazil

This study presents the elemental concentration results obtained from 59 medicinal plants used in Brazil, determined by instrumental neutron activation analysis (INAA), inductively coupled plasma-optical emission spectrometry (ICP OES) and cold vapor atomic absorption spectrometry (CV AAS). The selected plant species were chosen from the Brazilian National Agency for Sanitary Vigilance (ANVISA) list of herbs recommended for utilization by the Public System of Health in Brazil (SUS). The results showed that high levels of foreign matter were found in almost 50% of the analyzed samples. The concentration of the elements varied in a wide range, although, generally in accordance with values found in literature. High concentrations of Ba, Cr, Fe, Hg, Se and Ni were found in some samples. The enrichment factor indicated that potentially hazardous elements can be accumulated mainly in the bark of the plants, possibly indicating an anthropogenic contribution.

Keywords: medicinal plant, major element, trace element, NAA, ICP OES, CV AAS

Introduction

Medicinal plants are widely used all over the world and, according to the World Health Organization (WHO), for many millions of people, traditional medicines, including herbal medicines, are the main source of health care and, sometimes, the only source of care.[1] Their demand is growing worldwide both in developing and industrialized countries, as a complementary way to treat and to prevent diseases.[2-5] The growing interest in this type of health care has also been accompanied by effectiveness, availability, preservation, quality, safety and regulation concerns. Therefore, the World Health Organization has also set out the need for quality control standards of medicinal plants including classification, botanical identification, active compounds determination and contaminant identification, following the recommendation of the World Health Assembly.[6] As a global strategy for traditional and complementary medicine, the WHO has stimulated the State Members to develop public policies in order to include herbal medicines and phytotherapics in their public health system.[1]

Besides being used for the treatment of diseases, the medicinal plants are also used as dietary supplements once they are found to be rich in one or more elements. Elemental content in medicinal plants can vary in a wide range, depending on factors such as soil geochemical characteristics, atmospheric deposition and the ability of each plant species to selectively accumulate some of them.[7,8] Nevertheless, medicinal herbs can be easily contaminated during growth, development and processing.

The determination of major, minor and trace elements in medicinal plants and their impacts on human health are also of great importance due to the growth of environmental pollution that directly affects the plants and, therefore, their phytotherapics. Besides, being essential in the living system, the elements can be at the same time toxic, when at concentrations beyond those necessary for metabolic functions.[9-11]

Brazil possesses one of the greatest vegetal genetic diversity of the world, accounting for approximately 20% of all known living species globally;[12] over one thousand species of plants are estimated to be used as medicine by the population. However, to be used by the Public System of Health, the National Agency for Sanitary Vigilance establishes that toxicological risks and the absence of toxic chemical substances must be within safe proven limits.

Despite the richness of the Brazilian flora, the extensive use of medicinal plants by the population and the importance exerted by trace elements in the human metabolism[13] lead to a consensus that scientific studies on elemental concentrations in medicinal plants are

*e-mail: pscsilva@ipen.br

insufficient in view of the importance of these results, considering individual and social consequences.

Therefore, the objective of this paper was to determine the content of inorganic constituents in herbal medicines: moisture, ash, insoluble acid ash and the element concentrations of As, Ba, Br, Ca, Cl, Co, Cr, Cs, Fe, Hf, K, Na, Mg, Mn, Rb, Sb, Sc, Se, Ti, V and Zn, by instrumental neutron activation analysis (INAA); Cd, Cu, Ni and Pb by inductively coupled plasma-optical emission spectrometry (ICP OES) and Hg by cold vapor atomic absorption spectrometry (CV AAS). The results were used to verify the quality of the products, the range of concentrations found in plants commonly used in folk medicine and whether these concentrations are within the safe limits stated by reference standards of intake, when existent. To verify the distribution pattern of the elemental concentrations, statistical analysis (correlation coefficient, cluster analysis and principal component analysis) was also applied to the results. As far as we know, the concentration of the elements proposed to be determined in this study has not been determined before, for the majority of the plants.

Experimental

Plant species were chosen from a list of 66 herbs recommended by the Brazilian National Agency for Sanitary Vigilance (ANVISA) to be used in the Public Health System. From this list, 59 species, in the form of dried material, were found in specialized pharmacies and drugstores. The plant names, used parts and medicinal applications are listed on Table 1.

Search for foreign matter

Foreign matter, as defined by WHO, is any part of the medicinal plant material or materials other than those named with the limits specified for the plant material concerned; any organism, part or product of an organism, other than that named in the specification and description of the plant material concerned or; any mineral admixtures not adhering to the medicinal plant materials, such as soil, stones, sand, and dust.[14]

For foreign matter determination, the whole sample

Table 1. Plants, scientific name (Brazilian popular name), used part to extract preparation, medicinal indication, dosage and mode of preparation according to ANVISA

Scientific name	Used part	Indication	Dosage / (tea-cups *per* day)	Preparation	
				Type of preparation (mass used) / g	Volume of water / mL
Achillea millefolium L. ("aquiléia")	shoots	lack of appetite, fever, inflammation and cramping	3-4	infusion (1-2)	150
Achyrocline satureioides Lam. DC. ("macela")	inflorescence	poor digestion and intestinal cramps, mild sedative, and anti-inflammatory	4	infusion (1.5)	150
Aesculus hippocastanum L. ("castanheiro-da-índia")	seeds in shell	capillary fragility, venous insufficiency (varicose veins and hemorrhoids)	2, after meals	decoction (1.5)	150
Ageratum conyzoides L. ("mentrasto")	shoots without flowers	joint pain (arthritis, arthrosis) and rheumatism	2-3	infusion (2-3)	150
Allium sativum L. ("cebola")	bulb	high cholesterol, as expectorant	2, before meals	maceration (0.5)	30
Anacardium occidentale L. ("cajueiro")	under bark	noninfectious diarrhea	3-4	decoction (4.5)	150
Arctium lappa L. ("bardana")	roots	dyspepsia, diuretic and anti-inflammatory such as the joint pain	2-3	decoction (2)	150
Arnica montana L. ("arnica Montana")	flowers	trauma, bruises, sprains, swelling due to fractures and sprains	compress (2 to 3 times daily)	infusion (3)	150
Baccharis trimera (Less.) DC. ("carqueja")	shoots	dyspepsia	2-3	infusion (2.5)	150
Bidens pilosa L. ("picão preto")	leaves	jaundice	4	infusion (2)	150
Calendula officinalis L. ("calendula")	flowers	inflammations and injuries, bruises and burns	compress (3 times daily)	infusion (1-2)	150
Caesalpinia ferrea Mart. ex Tul. ("pau-ferro")	beans	injuries as hemostatic astringent and antiseptic healing	compress (2-3 times daily)	decoction (7.5)	150
Casearia sylvestris Sw. ("guaçatonga")	leaves	pain and injuries, as an antiseptic and healing topic	3-4	infusion (2-4)	150

Table 1. Plants, scientific name (popular name), used part to extract preparation, medicinal indication, dosage and mode of preparation according to ANVISA (cont.)

Scientific name	Used part	Indication	Dosage / (tea-cups *per* day)	Preparation	
				Type of preparation (mass used) / g	Volume of water / mL
Cinnamomum verum J. Presl. ("canela")	bark	lack of appetite, mild cramping, flatulence and feeling of fullness	2-6	decoction (0.5-2)	150
Citrus aurantium L. ("laranja amarga")	flowers	mild cases of anxiety and insomnia, sedative	1-2, before bedtime	maceration, (1-2) (3-4 h)	150
Cordia verbenacea DC. ("erva-baleeira")	leaves	inflammation in bruises and pain	3	infusion (3)	150
Curcuma longa L. ("açafrão-da-terra")	rhizomes	dyspepsia, anti-inflammatory	1-2	decoction (1.5)	150
Cymbopogon citratus (DC.) Stapf. ("capim-limão")	leaves	intestinal and uterine cramping, mild anxiety cases, insomnia, sedative	2-3	infusion (1-3)	150
Echinodorus macrophyllus (Kunth) Micheli ("chapéu-de-couro")	leaves	edema by fluid retention and inflammation	3	infusion (1)	150
Equisetum arvense L. ("cavalinha")	shoots	edema by fluid retention and inflammation	2-4	infusion (3)	150
Erythrina verna Vell. (mulungu)	bark	mild cases of anxiety and insomnia, sedative	2-3	decoction (4-6)	150
Eucalyptus globulus Labill. ("eucalipto")	leaves	colds and flus to clear airway as an adjunct in the treatment of bronchitis and asthma	inhalation 2 times *per* day	infusion (2)	150
Eugenia uniflora L. ("pitanga")	leaves	noninfectious diarrhea	1 cup after making the feces (maximum 10 times *per* day)	infusion (3)	150
Glycyrrhiza glabra L. ("alcaçuz")	root	coughs, colds and flus	3-4	infusion (4.5)	150
Hamamelis virginiana L. ("amamélis")	bark	skin inflammations and mucous membranes, hemorrhoids	compress (2-3 times daily)	decoction (3-6)	150
Harpagophytum procumbens (Burch.) DC. ex Meisn ("garra-do-diabo")	root	joint pain (arthritis, arthrosis, arthralgia)	2-3	infusion (1)	150
Illicium verum Hook F. ("anis estrelado")	fruit	bronchitis, expectorant	3-4	infusion (1.5)	150
Lippia sidoides Cham. ("alecrim-pimenta")	leaves	gargles, mouthwashes and rinses	apply 2-3 daily	infusion (2-3)	150
Malva sylvestris L. ("malva")	leaves and flowers	respiratory expectorants	4	infusion (2)	150
Matricaria recutita L. ("camomila")	flowers	intestinal cramps, mild anxiety cases, mild tranquilizer	3-4	infusion (3)	150
Maytenus ilicifolia Mart. ex Reissek ("espinheira-santa")	leaves	dyspepsia, heartburn and gastritis, adjuvant ulcer prevention treatment	3-4	infusion (1-2)	150
Melissa officinalis L. ("melissa")	inflorescence	abdominal cramps, mild anxiety and insomnia cases, mild tranquilizer	2-3	infusion (2-4)	150
Mentha × piperita L. ("hortelã-pimenta")	leaves and inflorescence	colic, flatulence, liver problems	2-4	infusion (1.5)	150
Mentha pulegium L. ("poejo")	shoots	respiratory expectorant, appetite stimulant, digestive disturbances, gastrointestinal spasms	2-3, during the meals	infusion (1)	150
Mikania glomerata Spreng. ("guaco")	leaves	colds and flus, allergic and infectious bronchitis, expectorant	3	infusion (3)	150

Table 1. Plants, scientific name (popular name), used part to extract preparation, medicinal indication, dosage and mode of preparation according to ANVISA (cont.)

Scientific name	Used part	Indication	Dosage / (tea-cups *per* day)	Preparation	
				Type of preparation (mass used) / g	Volume of water / mL
Momordica charantia L. (melão-de-São-Caetano)	fruit, and seeds	dermatitis and scabies	apply to affected areas 2 times *per* day	decoction (5)	1000
Passiflora alata Curtis ("maracujá-doce")	leaves	mild anxiety and insomnia, mild tranquilizer	1-2	infusion (3)	150
Passiflora incarnata L. ("maracujá")	shoots	mild anxiety and insomnia cases, mild tranquilizer	3-4	infusion (3)	150
Paullinia cupana Kunth (guarana)	seeds	fatigue, stimulant	used pure or diluted in water	0.5-2 g of the powder	
Peumus boldus Molina ("boldo do Chile")	leaves	dyspepsia, choleretic and cholagogue	2	infusion (1-2)	150
Phyllanthus niruri L. ("quebra-pedra")	shoots	elimination of small kidney stones	2-3	infusion (3)	150
Pimpinela anisum L. ("erva-doce")	fruit	dyspepsia, gastrointestinal cramps	3	decoction (1.5)	150
Plantago major L. ("tanchagem")	leaves	inflammations of the mouth and pharynx	mouthwashes and gargles 3 times *per* day	infusion (6-9)	150
Polygonum punctatum Elliot ("erva-de-bicho")	shoots	varicose veins and varicose ulcers	apply on the affected site 3 times a day	infusion (3)	150
Psidium guajava L. (guava)	young leaves	noninfectious diarrhea	1 cup after making the feces (maximum 10 times *per* day)	infusion (2)	150
Punica granatum L. ("romã")	fruit peel	inflammation and infection of the mouth and pharynx anti-inflammatory	mouthwashes and gargles 3 times *per* day	decoction (6)	150
Rhamnus purshiana DC. (cáscara sagrada)	bark	eventual intestinal constipation	½ tea-cup per day before bedtime	decoction, (0.5)	150
Rosmarinus officinalis L. ("alecrim")	leaves	circulatory disorders, antiseptic and healing	apply to the affected area 2 *per* day	infusion (3-6)	150
Salvia officinalis L. ("sálvia")	leaves	dyspepsia and excessive sweating	2-3	infusion (1.5-2)	150
Sambucus nigra L. ("sabugueiro")	flowers	colds and flus	2-3	infusion (3)	150
Schinus terebinthifolius Raddi ("aroeira")	bark	vaginal inflammation, leukorrhea, hemostatic, astringent and healing	compress, baths (2 times daily)	decoction (1)	1000
Senna alexandrina Mill. (sene)	fruit and folioles	eventual intestinal constipation	1, before bedtime	decoction (1)	150
Solanum paniculatum L. ("jurubeba")	whole plant	dyspepsia	3-4	infusion (1)	150
Stryphnodendron adstrigens (Mart.) Coville. ("barbatimão")	bark	injuries, healing and topical antiseptic on the skin, oral mucosa and genital	compress, baths (2-3 times daily)	decoction (3)	1000
Taraxacum officinale F. H. Wigg ("dente-de-leão")	whole plant	dyspepsia, appetite stimulant and as a diuretic	3	decoction (3-4)	150
Uncaria tomentosa (*Willd. ex Roem. & Schult.*) DC. ("unha-de-gato")	bark	joint pain (arthritis and osteoarthritis) and acute muscle anti-inflammatory	2-3	decoction (0.5)	150
Vernonia polyanthes Less. ("assa-peixe")	leaves	pain and dyspepsia	3, before meals	infusion (3)	150
Zingiber officinale Roscoe ("gengibre")	rhizome	sickness, nausea and vomiting of pregnancy, postoperative motion, dyspepsia	2-4	decoction (0.5-1)	150

pack, after being precisely weighed, was spread above a white and clean surface and any strange material was removed. Particles of soil, stone, sand, insects or parts of insects, as well as any part of the plant other than that indicated for use was considered foreign matter. Signs of mould, abnormal odor, discoloration, slime and deterioration were, also, searched.[14]

Moisture determination

For moisture determination, approximately 10 g of each sample was weighed in analytical balance and let to stand in an oven at temperature varying from 100 to 105 ºC, until constant weight, being weighed after cooling in a desiccator.[14]

Ash

The inorganic ash determination was done by calcinating the sample used in the moisture determination in a muffle, at 900 ºC, for 2 hours. The residue was allowed to cool in a desiccator and weighed.

Insoluble acid ash

The residue obtained in the inorganic ash determination was then treated with 25 mL of ultrapure concentrated HNO_3, filtered in paper filter. The paper was washed with 5 mL of ultra-pure water and let to dry in a ventilated furnace oven. The insoluble acid ash amount was determined by the difference in the filter paper weigh before and after the filtration.

INAA measurement

Instrumental neutron activation analysis (INAA) is a sensitive and multielemental technique, which has been frequently used to evaluate inorganic elemental content in medicinal plants.[15-17]

For the INAA determinations, the raw plant samples were dried in a ventilated furnace oven at 40 to 45 ºC and then powdered to a grain size lower than 0.150 mm. Approximately 150 mg of the powdered samples and 100 mg of powdered reference materials (United States Geological Survey-USGS-Rhyolite, Glass Mountain, RGM-2 and Syenite, Table Mountain, STM-2) were sealed in pre-cleaned polyethylene bags. Synthetic standards were also prepared by pipetting convenient aliquots of standard solutions (SPEX Certiprep Inc., USA) using Milli-Q water 18.2 MΩ cm at 25 °C (Millipore Corporation, USA), onto small filter paper sheets. The plant samples, reference materials and synthetic standards were irradiated for 8 h, in the IEA-R1 nuclear reactor at IPEN (Instituto de Pesquisas Energéticas e Nucleares, Brazil), for As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, K, Na, Rb, Sb, Sc, Se, and Zn determination and for 20 s for Cl, Mg, Mn, Ti and V determination under a thermal neutron flux of $1\text{-}5 \times 10^{12}$ cm^{-2} s^{-1}. The counting was done at different time frames, depending on the radionuclide half-live produced during the irradiation: this process was performed by Gamma Spectrometry, using an EG&G Ortec Ge Highpure Gamma Spectrometer detector (AMETEK Inc., USA) and associated electronics, with a resolution of 0.88 and 1.90 keV for ^{57}Co and ^{60}Co, respectively. The analysis of the data was done by using an in-house gamma ray software, VISPECT program, to identify the gamma-ray peaks. The methodology precision and accuracy were verified by using, as Standard Reference Materials (SRM) from the National Institute of Standards and Technology (NIST), apple leaves (NIST SRM 1515), peach leaves (NIST SRM1547) and tomato leaves (NIST SRM1573a).

ICP OES and CV AAS measurement

For the determination of Cd, Cu, Ni and Pb, approximately, 300 mg of each dried and powdered sample were dissolved with a mixture of concentrated acids (HNO_3, HCl, $HClO_4$) and H_2O_2; all reagents were of analytical grade, and digested in a MARS 5 (CEM Corporation, USA) microwave closed system. After the digestion process, the samples were allowed to cool and filtered. The concentrations were determined by using a Spectro Flame M120E ICP OES (AMETEK Inc., USA). For the determination of Hg by CV AAS, the same digested samples were measured by using a PerkinElmer AANALYST 800 instrument. The methodology precision and accuracy were verified by using the reference materials apple leave (NIST SRM 1515) and peach leave (NIST SRM1547). The detailed methodology for ICP OES and CV AAS measurements, as well as the calibration curves used for the concentrations in all the samples are presented in the literature.[18]

Results

Table 2 shows the percentages of foreign matter, moisture, ash, insoluble acid ash and the permitted amounts of these parameters, according to the Brazilian Pharmacopeia.[19]

Unless specified elsewhere, the total permitted foreign matter is 2% in the dried raw material. Among the analyzed samples, 47% showed foreign matter content above the recommended levels, with the highest values over 60%

Table 2. Foreign matter quantities (FM), permitted foreign matter (PFM), moisture (M), permitted moisture, permitted moisture (PM) total ash (TA), permitted total ash (PTA) insoluble acid ash (IAA) and permitted insoluble acid ash (PIAA)

Scientific name	FM / %	PFM / %	M / %	PM / %	TA / %	PTA / %	IAA / %	PIAA / %
Achillea millefolium	0.04	2	8.2	8-14	5.4	–	1.6	–
Achyrocline satureioides	7.3	2	5.7	10	3.5	8	0.5	–
Aesculus hippocastanum	0.1	2	8.6	10	2.2	4	0.4	–
Agerantum conyzoides	6.5	2	7.5	8-14	9.1	–	6.6	–
Allium sativum	0.1	5	9.2	7	3.2	5	0.1	–
Anacardium occidentales	–	2	8.2	8-14	0.7	2.6	1.1	–
Arctium lappa	2.6	2	7.5	8-14	11.0	6	1.6	–
Arnica montana	4.2	5	8.5	8-14	6.7	10	1.3	–
Baccharis trimera	2.3	2	7.9	12	2.6	8	0.8	–
Bidens pilosa	5.4	2	9.9	8-14	6.6	–	0.4	–
Caesalpinia ferrea	–	2	6.9	8-14	3.7	–	0.8	–
Calendula officinalis	0.4	3	8.0	12	6.4	10	0.8	–
Casearia sylvestris	10.1	3	7.4	12	5.4	8	0.6	2
Cinnamomum verum	0.03	2	6.1	8-14	24.9	5	1.7	–
Citrus auranrium	–	2	12.2	10	2.2	7	0.5	–
Cordia verbanacea	15.3	2	6.4	8-14	3.3	–	1.8	–
Curcuma longa	–	2	8.8	12	4.3	8	0.9	–
Cymbopogon citratus	3.6	1	8.2	11	6.3	9	1.0	–
Cynara scolymus	6.6	2	8.5	12	7.4	20	2.3	–
Echinodorus macrophyllus	1.9	2	8.1	9	7.1	12	2.3	–
Equisetum arvense	0.3	2	8.7	8-14	5.3	–	3.5	–
Eryhrina verna	–	5	7.2	12	4.9	5	1.5	–
Eucalyptus globulus	30.4	3	4.0	8-14	3.1	5	0.1	–
Eugenia uniflora	60.2	2	5.3	10	3.5	11	0.8	–
Glycyrrhiza glaba	–	2	8.0	10	1.0	6.5	1.2	2.5
Hamamelis virginiana	7.6	2	6.5	5	4.2	7	0.7	2
Harpagophytum procumbens	0.04	2	9.8	8-14	8.8	–	4.7	–
Illicium verum	1.4	2	11.6	7	36.1	6	0.2	–
Lippia sidoides	–	2	4.5	8-14	4.6	–	1.8	–
Malva sylvestris	5.3	2	6.7	8-14	6.8	16	0.6	–
Matricaria recutita	1.9	5	7.9	8-14	5.9	14	0.1	–
Maytenus ilicifolia	60.8	2	6.8	12	7.2	8	1.7	–
Melissa officinalis	0.3	10	6.8	10	5.6	12	1.7	–
Mentha piperita	–	10	7.5	12	10.1	15	0.5	–
Mentha pulegium	15.2	2	7.5	8-14	9.0	–	3.6	–
Mikania glomerata	52.8	2	6.2	8-14	8.5	–	3.7	–
Momordica charantia	8.4	2	6.4	8-14	5.1	–	3.6	–
Passiflora alata	5.0	2	7.3	11	5.8	10	4.8	0.4
Passiflora incarnata	9.1	2	8.2	8-14	5.1	–	1.1	–
Paulinia cupana	0.8	3	7.8	9.5	2.1	3	1.4	–
Peumus boldus	5.7	3	10.3	10	8.7	10	6.5	6
Phyllanihus niruri	0.6	2	5.6	10	3.9	6	0.7	–
Pimpinella anisum	0.7	2	7.6	8-14	4.6	11	1.1	–
Plantago major	7.9	2	9.0	8-14	9.2	–	3.2	–
Polygonum punctatum	0.05	2	6.8	8-14	7.1	–	4.6	–
Psidium guajava	45.2	2	7.4	12	4.0	9	0.6	–
Punica granatum	1.2	2	9.1	8-14	2.5	–	1.1	–
Rhamnus purshiana	0.9	1	7.8	12	3.5	6	1.6	2
Rosmarinus officinales	15.6	2	4.9	8-14	3.9	–	0.5	–
Sálvia officinalis	5.6	2	6.4	8-14	12.1	–	6.4	–
Sambucus nigra	26.5	8	7.0	11	6.8	9	1.6	–
Schinus terebinthifolia	0.2	2	8.1	8-14	5.9	–	0.1	–

Table 2. Foreign matter quantities (FM), permitted foreign matter (PFM), moisture (M), permitted moisture, permitted moisture (PM) total ash (TA), permitted total ash (PTA) insoluble acid ash (IAA) and permitted insoluble acid ash (PIAA) (cont.)

Scientific name	FM / %	PFM / %	M / %	PM / %	TA / %	PTA / %	IAA / %	PIAA / %
Senna alexandrina	–	2	6.2	10	10.8	12	2.6	3
Solanum paniculatum	1.1	2	7.6	8-14	6.8	14	2.0	–
Stryphnodendron adstringens	0.06	2	6.8	14	0.5	2	0.2	–
Taraxacum officinale	9.9	2	5.7	8-14	13.1	10	7.2	–
Uncaria tomentosa	2.4	2	8.2	8-14	2.1	–	1.4	–
Vernonia polyanthes	10.1	2	6.7	8-14	6.0	–	3.1	–
Zingirber officinale	–	2	7.5	10	2.9	6	2.3	–

and the main foreign matter found was represented by parts of the plant other than what was indicated for use. Soil particles were, also, detected, but in small amounts. Moisture was found varying from 4 to 12% and only three samples showed values above the permitted levels: *Allium sativum*, *Citrus auranrium* and *Illicium verum*. However, it was noted that the majority of the samples had moisture contents close to the recommended. High moisture percentage may favor the appearance of mould, slime and plant deterioration. The amount limit of permitted ash was not found in the Brazilian Pharmacopeia, for all of the analyzed plants and among those which presented it, only four possess ash content higher than the limits: *Arctium lappa*, *Cinnamomum verum*, *Illicium verum* and *Taraxacum officinalles*. Just a few plants showed the permitted values for insoluble acid ash and only in *Passiflora alata* and *Peumus boldus* the measured values were higher.

The amount of ash is related to the physiological and non-physiological inorganic material content. The obtained inorganic ash indicates the presence of non-physiological inorganic material that can be related to inorganic waste contaminants.

The precision and accuracy of the method evaluated by analyzing certified reference material are shown in Table 3, for the results obtained by INAA, and in Table 4, for the results obtained by ICP OES and CV AAS for quality measurement and control purposes. It can be seen that the relative errors are generally less than 20%, for most of the elements. Exceptions are K in peach leaves and Co in tomato leaves. Nevertheless, the general results were considered satisfactory regarding the low levels of concentrations normally observed in plant material. Cadmium concentrations in these reference materials was below the detection limit for ICP OES applied methodology (0.06 mg kg^{-1}).

Table 3. Results obtained for the certificate reference materials apple, peach and tomato leaves, in mg kg^{-1}, excepted where indicated with %, mean value (n = 5), standard deviation and relative error

	Apple leaves			Peach leaves			Tomato leaves		
	MV / (mg kg^{-1})	TV / (mg kg^{-1})	RE / (mg kg^{-1})	MV / (mg kg^{-1})	TE / (mg kg^{-1})	RE / (mg kg^{-1})	MV / (mg kg^{-1})	TV / (mg kg^{-1})	RE / (mg kg^{-1})
Ba	51 ± 11	49 ± 2	4.8	118 ± 26	124 ± 4	4.6	49 ± 10	63	21.9
Br							1489 ± 193	1300	14.6
Ca / %	1.20 ± 0.40	1.5 ± 0.005	20.0	1.2 ± 0.2	1.5 ± 0.02	20.0			
Co							0.8 ± 0.1	0.57 ± 0.02	42.1
Cr							1.9 ± 0.3	1.99 ± 0.06	2.8
Fe	86 ± 28	83 ± 5	3.2	236 ± 54	218 ± 14	8.2	316 ± 35	368 ± 7	14.2
Hf							0.16 ± 0.04	0.14	12.8
K / %	1.30 ± 0.30	1.61 ± 0.02	19.3	1.5 ± 0.3	2.43 ± 0.03	38.3	2.5 ± 0.2	2.7 ± 0.05	8.9
Mg	2710 ± 80	2674 ± 112	1.3	1.3					
Mn	54 ± 3	50 ± 2	6.5	7.4					
Na	29 ± 7	24.4 ± 1.2	18.8	26 ± 1	24 ± 2	10.3	112 ± 21	136 ± 4	17.9
Rb	10 ± 3	10.2 ± 1.5	0.3	19 ± 7	19.7 ± 1.2	6.0	12 ± 2	14.89 ± 0.27	18.6
Sb				0.024 ± 0.002	0.02	22.0			
Sc	0.03 ± 0.01	0.03	11.2	0.05 ± 0.01	0.04	20.3	0.09 ± 0.01	0.1	5.8
V	0.26 ± 0.03	0.23 ± 0.06	12	13					
Zn	15 ± 2	12.5 ± 0.3	18.9	21 ± 4	17.9 ± 0.4	15.8	28 ± 3	30.9 ± 0.7	9.6

MV: measured value; TV: true value; RE: relative error.

Table 4. Results of the Certificate Reference Materials apple and peach leaves obtained by ICP OES and CV AAS, in mg kg^{-1}, mean value (n = 5), standard deviation and relative error

	Apple leaves			Peach leaves		
	MV / (mg kg^{-1})	TV / (mg kg^{-1})	RE / (mg kg^{-1})	MV / (mg kg^{-1})	TV / (mg kg^{-1})	RE / (mg kg^{-1})
Cd	–	0.013 ± 2	–	–	0.026 ± 0.003	–
Cu	5 ± 1	5.64 ± 0.24	11.3	3.77 ± 0.07	3.7 ± 0.4	1.9
Ni	0.9 ± 0.2	0.91 ± 0.12	1.1	0.56 ± 0.02	0.69 ± 0.09	18.8
Pb	0.55 ± 0.08	0.47 ± 0.024	17	0.7 ± 0.3	0.87 ± 0.03	19.5
Hg	39 ± 4	44 ± 4	11.4	36 ± 9	36 ± 9	16

MV: measured value; TV: true value; RE: relative error.

The results obtained for the element concentrations in the samples, all in dry basis, are shown in Table 5. Blanks in Table 5 mean values below the limit of detection (LOD), presented by Francisconi.[18]

It can be noted, from the data in Table 5 that the concentration in the medicinal plant samples varies in a wide range for almost all the elements. The main reason for this variation certainly must be the fact that different species and different plant parts were analyzed. Furthermore, water sources, climatic conditions and environmental pollution must also contribute for the variation.[20]

Discussion

Good quality control of medicinal plants is important, since they are normally consumed without any limitation. It is almost a consensus that, being a natural product, they do not pose any harm to health. Concerning the element concentrations present in medicinal plants, besides the essential elements, they also may contain toxic and non-toxic elements, but, in concentrations above the permissible levels.

In fact, among the elements determined in this paper, only As, Cd and Pb has been limited by WHO[14] in plants

Table 5. Concentrations and expanded uncertainty (K = 2) obtained in the analyzed samples

Scientific name	As / (mg kg^{-1})	Cl / %	Cs / (mg kg^{-1})	Hf / (mg kg^{-1})	K / %	Mg / %
A. millefolium		0.56 ± 0.02	0.034 ± 0.004	0.048 ± 0.003	2.1 ± 0.6	0.19 ± 0.03
A. satureioides		0.52 ± 0.02	0.24 ± 0.01	0.63 ± 0.01	0.9 ± 0.2	0.25 ± 0.01
A. hippocastanum		0.56 ± 0.03	0.06 ± 0.01	0.72 ± 0.02	0.032 ± 0.002	0.069 ± 0.007
A. conyzoides		0.28 ± 0.01	0.20 ± 0.02	2.29 ± 0.07	1.9 ± 0.4	1.14 ± 0.04
A. sativum				0.034 ± 0.008		0.012 ± 0.008
A. occidentales		0.78 ± 0.06	0.026 ± 0.003	0.118 ± 0.004	0.30 ± 0.08	0.060 ± 0.005
A. lappa		0.5 ± 0.2	0.081 ± 0.006	0.062 ± 0.003	6.4 ± 0.7	0.034 ± 0.008
A. montana		0.08 ± 0.01	0.14 ± 0.02	0.056 ± 0.007	3.0 ± 0.5	0.11 ± 0.02
B. trimera			0.28 ± 0.02	0.11 ± 0.01	2.4 ± 0.6	0.17 ± 0.02
B. pilosa		0.24 ± 0.02	0.08 ± 0.01	0.141 ± 0.005	4.0 ± 0.3	0.28 ± 0.02
C. ferrea		0.32 ± 0.01			0.7 ± 0.2	0.073 ± 0.007
C. officinalis		0.59 ± 0.02	0.11 ± 0.01		3.2 ± 0.3	0.36 ± 0.02
C. sylvestris			2.0 ± 0.1	0.054 ± 0.006	1.3 ± 0.2	0.18 ± 0.02
C. verum		0.59 ± 0.02		0.014 ± 0.003	0.7 ± 0.1	0.024 ± 0.005
C. auranrium		0.62 ± 0.02	0.051 ± 0.006		0.7 ± 0.1	0.070 ± 0.004
C. verbanacea		0.70 ± 0.04	0.112 ± 0.007	0.056 ± 0.003	0.8 ± 0.1	0.22 ± 0.02
C. longa		0.32 ± 0.01	0.10 ± 0.01	0.042 ± 0.003	1.99 ± 0.04	0.12 ± 0.01
C. citratus		0.25 ± 0.02	0.183 ± 0.009	0.042 ± 0.003	3.3 ± 0.7	0.14 ± 0.01
C. scolymus				0.119 ± 0.008	8 ± 2	0.29 ± 0.01
E. macrophyllus		1.32 ± 0.04	0.15 ± 0.01	0.074 ± 0.008	4.9 ± 0.8	0.17 ± 0.02
E. arvense		1.9 ± 0.1	4.3 ± 0.2	0.04 ± 0.01	3 ± 1	
E. verna	0.06 ± 0.01	0.43 ± 0.02	0.15 ± 0.01	0.111 ± 0.005	2.7 ± 0.6	0.12 ± 0.01
E. globulus		0.17 ± 0.01		0.107 ± 0.008	0.29 ± 0.08	
E. uniflora		0.12 ± 0.02	0.065 ± 0.008	0.054 ± 0.005	1.5 ± 0.4	0.17 ± 0.03
G. glaba		0.14 ± 0.01	0.035 ± 0.003	0.025 ± 0.001	0.26 ± 0.05	0.10 ± 0.01
H. virginiana		1.3 ± 0.1	0.03 ± 0.01		1.0 ± 0.2	0.13 ± 0.01
H. procumbens		0.63 ± 0.03	0.12 ± 0.01	0.76 ± 0.02	1.4 ± 0.3	0.11 ± 0.03

Table 5. Concentrations and expanded uncertainty (K = 2) obtained in the analyzed samples (cont.)

Scientific name	As / (mg kg^{-1})	Cl / %	Cs / (mg kg^{-1})	Hf / (mg kg^{-1})	K / %	Mg / %
I. verum		0.91 ± 0.08	1.15 ± 0.08	0.050 ± 0.008	1.6 ± 0.3	0.063 ± 0.007
L. sidoides	0.31 ± 0.02	0.11 ± 0.01			0.7 ± 0.1	0.301 ± 0.01
M. sylvestris		0.24 ± 0.01	0.17 ± 0.02	1.69 ± 0.04	3.3 ± 0.5	0.51 ± 0.03
M. recutita				0.093 ± 0.006	3.8 ± 0.6	0.21 ± 0.01
M. ilicifolia		0.04 ± 0.01	0.029 ± 0.008	0.042 ± 0.004	3.4 ± 0.5	0.68 ± 0.04
M. officinales		1.60 ± 0.06	0.12 ± 0.01	0.067 ± 0.006	2.1 ± 0.3	0.37 ± 0.01
M. piperita		0.32 ± 0.01		0.26 ± 0.01	0.63 ± 0.08	0.70 ± 0.05
M. pulegium			0.35 ± 0.04	2.34 ± 0.05	1.99 ± 0.04	0.22 ± 0.02
M. glomerata		0.072 ± 0.004	0.46 ± 0.02	0.055 ± 0.002	0.5 ± 0.2	0.11 ± 0.02
M. charantia		0.29 ± 0.01	0.21 ± 0.02	0.080 ± 0.006	6 ± 4	0.40 ± 0.02
P. alata		0.73 ± 0.05		0.065 ± 0.003	3.6 ± 0.9	0.32 ± 0.01
P. incarnata		0.87 ± 0.03	0.96 ± 0.06	0.38 ± 0.01	1.2 ± 0.3	0.20 ± 0.04
P. cupana	0.12 ± 0.01		0.13 ± 0.01	0.024 ± 0.002	0.62 ± 0.08	0.113 ± 0.005
P. boldus		0.029 ± 0.003	0.13 ± 0.01	0.058 ± 0.003	1.00 ± 0.02	0.18 ± 0.01
P. niruri	0.3 ± 0.05	1.06 ± 0.05		0.227 ± 0.007		0.29 ± 0.03
P. onisum		1.0 ± 0.2	0.039 ± 0.004	0.059 ± 0.003	2.6 ± 0.4	0.189 ± 0.008
P. major		0.025 ± 0.003	0.19 ± 0.03	0.18 ± 0.01	3.4 ± 0.9	0.75 ± 0.03
P. punctatum		0.48 ± 0.02	0.23 ± 0.02		2.0 ± 0.4	0.65 ± 0.02
P. guajava	0.05 ± 0.02	0.17 ± 0.01	0.047 ± 0.007	0.051 ± 0.005	0.011 ± 0.001	0.21 ± 0.02
P. granatum	0.17 ± 0.03	0.045 ± 0.002	0.071 ± 0.008	0.046 ± 0.004	4 ± 1	0.03 ± 0.01
R. purshiana		0.031 ± 0.003	0.036 ± 0.007	0.025 ± 0.003	0.7 ± 0.1	0.26 ± 0.02
R. officinales	0.25 ± 0.04	0.24 ± 0.04	0.08 ± 0.01	0.063 ± 0.006	2.1 ± 0.5	0.24 ± 0.01
S. officinalis		0.017 ± 0.002	0.32 ± 0.04	2.625 ± 0.081	1.9 ± 0.3	0.43 ± 0.02
S. nigra		0.18 ± 0.01	0.027 ± 0.008	0.042 ± 0.005	3.0 ± 0.2	0.32 ± 0.01
S. terebinthifolia		0.016 ± 0.003		0.069 ± 0.006	0.5 ± 0.1	0.26 ± 0.01
S. alexandrina	0.07 ± 0.02	0.39 ± 0.02	0.076 ± 0.01	0.228 ± 0.014	0.9 ± 0.2	0.46 ± 0.02
S. paniculatum		0.02 ± 0.002	0.22 ± 0.03	1.447 ± 0.045	1.7 ± 0.2	0.22 ± 0.02
St. adstringens		1.38 ± 0.06	0.022 ± 0.009	0.092 ± 0.004	0.8 ± 0.2	0.028 ± 0.006
T. officinalles	0.59 ± 0.08	0.48 ± 0.04	0.48 ± 0.06	0.792 ± 0.027	5 ± 3	0.29 ± 0.02
U. tomentosa				0.016 ± 0.006	0.09 ± 0.02	0.199 ± 0.008
V. polyanthes		0.58 ± 0.02	0.15 ± 0.03		1.8 ± 0.4	0.22 ± 0.02
Z. officinale	0.53 ± 0.05	0.12 ± 0.01	0.014 ± 0.007	0.027 ± 0.003	2 ± 1	0.14 ± 0.01

Scientific name	Sb / (mg kg^{-1})	Sc / (mg kg^{-1})	Cd / (mg kg^{-1})	Co / (mg kg^{-1})	Cr / (mg kg^{-1})	Cu / (mg kg^{-1})	Br / (mg kg^{-1})
A. millefolium	0.021 ± 0.004	0.018 ± 0.001	0.25 ± 0.04	0.18 ± 0.02	5.1 ± 0.4	12.71 ± 0.08	15.4 ± 0.2
A. satureioides	0.027 ± 0.005	0.132 ± 0.003	0.08 ± 0.05	0.40 ± 0.02	30 ± 2	9.67 ± 0.06	11.1 ± 0.1
A. hippocastanum		0.023 ± 0.001		1.76 ± 0.08	257 ± 20	9.2 ± 0.3	115.3 ± 0.6
A. conyzoides	0.05 ± 0.01	0.67 ± 0.02	0.12 ± 0.03	1.56 ± 0.09	23 ± 1	5.0 ± 0.2	109.3 ± 0.6
A. sativum		0.001 ± 0.001	0.07 ± 0.03	0.14 ± 0.01	0.7 ± 0.2	3.9 ± 0.1	1.16 ± 0.06
A. occidentales	0.013 ± 0.003	0.0021 ± 0.0001		0.22 ± 0.01	18 ± 1	3.5 ± 0.1	1.99 ± 0.03
A. lappa	0.049 ± 0.009	0.038 ± 0.001		0.44 ± 0.03	34 ± 2	10.7 ± 0.2	29.7 ± 0.2
A. montana		0.062 ± 0.002	0.51 ± 0.07	0.40 ± 0.04	13.9 ± 0.9	8.8 ± 0.2	45.6 ± 0.4
B. trimera	0.037 ± 0.007	0.066 ± 0.002	0.20 ± 0.03	0.60 ± 0.04	7.8 ± 0.4	10.09 ± 0.5	8.97 ± 0.1
B. pilosa		0.074 ± 0.002	0.24 ± 0.03	0.38 ± 0.02	6.3 ± 0.5	13.4 ± 0.2	41.6 ± 0.2
C. ferrea				0.19 ± 0.02	1.1 ± 0.1	2.65 ± 0.04	18.9 ± 0.3
C. officinalis	0.005 ± 0.002	0.024 ± 0.001	0.16 ± 0.05	0.25 ± 0.01	4.6 ± 0.2	8.30 ± 0.06	21.1 ± 0.1
C. sylvestris	0.081± 0.008	0.048 ± 0.001	0.10 ± 0.04	0.24 ± 0.01	4.6 ± 0.2	8.3 ± 0.2	40.2 ± 1.3
C. verum		0.0031 ± 0.0003	0.22 ± 0.01	0.14 ± 0.01	6.7 ± 0.4	3.11 ± 0.09	40.5 ± 0.2
C. auranrium	0.005 ± 0.001	0.0076 ± 0.0005		0.19 ± 0.01	13.4 ± 0.8	3.5 ± 0.1	1.66 ± 0.02
C. verbanacea		0.067 ± 0.002		0.95 ± 0.06	20.5 ± 0.9	13.8 ± 0.1	27.6 ± 0.2
C. longa		0.105 ± 0.003	0.04 ± 0.02	0.19 ± 0.01	1.00 ± 0.07	7.14 ± 0.08	26.1 ± 0.2
C. citratus		0.0145 ± 0.0004	0.07 ± 0.05	0.35 ± 0.02	14.4 ± 0.9	6.4 ± 0.2	74 ± 0.4
C. scolymus		0.126 ± 0.002		0.58 ± 0.02	31 ± 1	5.52 ± 0.01	33 ± 1
E. macrophyllus		0.101 ± 0.003	0.07 ± 0.03	0.98 ± 0.06	32 ± 2	7.4 ± 0.2	168 ± 1

Table 5. Concentrations and expanded uncertainty (K = 2) obtained in the analyzed samples (cont.)

Scientific name	Sb / (mg kg^{-1})	Sc / (mg kg^{-1})	Cd / (mg kg^{-1})	Co / (mg kg^{-1})	Cr / (mg kg^{-1})	Cu / (mg kg^{-1})	Br / (mg kg^{-1})
E. arvense	0.090 ± 0.006	0.007 ± 0.001		0.62 ± 0.04	6.2 ± 0.4	7.71 ± 0.01	142 ±1
E. verna	0.039 ± 0.004	0.063 ± 0.002		0.41 ± 0.03	14.8 ± 0.9	2.70 ± 0.04	8.74 ± 0.05
E. globulus	0.040 ± 0.007	0.16 ± 0.003	0.04 ± 0.03	0.38 ± 0.02	2.9 ± 0.1	9.1 ± 0.1	15.2 ± 0.2
E. uniflora	0.037 ± 0.006	0.04 ± 0.001	0.03 ± 0.01	3.7 ± 0.1	2.3 ± 0.1	8.9 ± 0.1	3.22 ± 0.09
G. glaba	0.010 ± 0.004	0.019 ± 0.001		0.29 ± 0.02	24 ± 1	3.39 ± 0.05	4.79 ± 0.06
H. virginiana		0.017 ± 0.001		0.24 ± 0.02	16 ± 2	4.23 ± 0.07	11.9 ± 0.2
H. procumbens	0.034 ± 0.008	0.26 ± 0.009		0.51 ± 0.03	11.7 ± 0.9	6.11 ± 0.07	45.4 ± 0.2
I. verum		0.045 ± 0.002	0.04 ± 0.02	0.27 ± 0.03	12.4 ± 0.9	8.6 ± 0.1	0.72 ± 0.01
L. sidoides		0.0081 ± 0.0002		0.21 ± 0.02	4.5 ± 0.4	6.82 ± 0.03	11.94 ± 0.06
M. sylvestris	0.02 ± 0.01	0.343 ± 0.008	0.05 ± 0.04	0.91 ± 0.04	52 ± 3	8.16 ± 0.08	67.2 ± 0.2
M. recutita		0.047 ± 0.001	0.04 ± 0.02	0.79 ± 0.04	68 ± 5	9.1 ± 0.2	34.1 ± 0.2
M. ilicifolia		0.026 ± 0.001	0.06 ± 0.04	0.16 ± 0.01	1.01 ± 0.09	5.89 ± 0.09	6.10 ± 0.07
M. officinales	0.025 ± 0.005	0.041 ± 0.001	0.06 ± 0.05	0.30 ± 0.02	8.1 ± 0.5	14.8 ± 0.3	7.69 ± 0.05
M. piperita	0.020 ± 0.009	0.59 ± 0.02	0.04 ± 0.02	0.94 ± 0.06	4.5 ± 0.2	11.9 ± 0.2	26.0 ± 0.2
M. pulegium	0.052 ± 0.006	3.66 ± 0.09	0.07 ± 0.01	9.12 ± 0.47	69 ± 3	10.7 ± 0.1	43.2 ± 0.2
M. glomerata	0.023 ± 0.004	0.029 ± 0.001	0.20 ± 0.08	0.21 ± 0.01	10.7 ± 0.5	10.9 ± 0.2	9.7 ± 0.1
M. charantia	0.034 ± 0.007	0.064 ± 0.002		2.49 ± 0.21	133 ± 7	9.3 ± 0.2	17.8 ± 0.2
P. alata	0.010 ± 0.002	0.039 ± 0.001		0.07 ± 0.01	2.6 ± 0.1	7.3 ± 0.2	6.59 ± 0.05
P. incarnata	0.077 ± 0.014	0.220 ± 0.004		0.66 ± 0.03	47.8 ± 1	7.0 ± 0.1	89 ± 3
P. cupana	0.009 ± 0.002	0.0139 ± 0.0004		0.38 ± 0.02	0.5 ± 0.03	16.5 ± 0.2	6.01 ± 0.05
P. boldus		0.080 ± 0.002		0.29 ± 0.01	18.1 ± 0.8	2.0 ± 0.1	18.6 ± 0.1
P. niruri	0.022 ± 0.004	0.59 ± 0.01	0.46 ± 0.05	0.65 ± 0.02	6.1 ± 0.2	7.9 ± 0.2	10.4 ± 0.3
P. onisum	0.013 ± 0.005	0.032 ± 0.001		0.45 ± 0.03	34 ± 2	11.66 ± 0.03	24.1 ± 0.2
P. major	0.011 ± 0.005	2.03 ± 0.06		3.81 ± 0.23	12.2 ± 0.7	15.9 ± 0.2	36.7 ± 0.2
P. punctatum	0.020 ± 0.008	0.065± 0.002	0.04 ± 0.01	0.57 ± 0.04	36 ± 2	11.7 ± 0.1	17.5 ± 0.2
P. guajava	0.024 ± 0.004	0.030 ± 0.001		0.25 ± 0.01	1.7 ± 0.1	13.88 ± 0.04	4.78 ± 0.07
P. granatum		0.017 ± 0.001		0.11 ± 0.02	1.08 ± 0.09	4.75 ± 0.05	63.5 ± 0.4
R. purshiana		0.013 ± 0.001		0.09 ± 0.01	1.3 ± 0.1	1.88 ± 0.07	66.9 ± 0.4
R. officinales		0.097 ± 0.002		0.31 ± 0.01	4.6 ± 0.2	4.57 ± 0.01	13.6 ± 0.1
S. officinalis	0.04 ± 0.01	0.91 ± 0.03	0.10 ± 0.04	0.91 ± 0.06	52 ± 3	24.5 ± 0.2	17.7 ± 0.3
S. nigra	0.040 ± 0.006	0.059 ± 0.001	0.06 ± 0.03	0.25 ± 0.01	11.2 ± 0.5	11.2 ± 0.1	7.1 ± 0.1
S. terebinthifolia		0.007 ± 0.001		0.15 ± 0.01	3.2 ± 0.2	3.57 ± 0.08	5.5 ± 0.1
S. alexandrina	0.006 ± 0.003	0.147 ± 0.005		0.38 ± 0.02	30 ± 1	4.92 ± 0.04	30.5 ± 0.1
S. paniculatum	0.023 ± 0.004	0.105 ± 0.002		0.76 ± 0.02	36 ± 1	14.68 ± 0.07	80 ± 3
St. adstringens	0.030 ± 0.005	0.003 ± 0.0003		0.19 ± 0.02	6.5 ± 0.3	5.9 ± 0.2	7.75 ± 0.1
T. officinalles	0.035 ± 0.007	0.58 ± 0.02	0.06 ± 0.03	1.22 ± 0.08	9.6 ± 0.7	7.04 ± 0.06	128 ± 1
U. tomentosa		0.049 ± 0.002		0.12 ± 0.01	0.8 ± 0.1	7.1 ± 0.1	1.66 ± 0.09
V. polyanthes	0.030 ± 0.009	0.101 ± 0.004	0.55 ± 0.08	0.31 ± 0.02	11.0 ± 0.8	11.0 ± 0.2	2.6 ± 0.1
Z. officinale	0.010 ± 0.002	0.016 ± 0.001	0.26 ± 0.01	0.60 ± 0.03	16.0 ± 0.8	3.93 ± 0.02	2.82 ± 0.04

Scientific name	Ca / %	Fe / (mg kg^{-1})	Hg / (μg kg^{-1})	Ni / (mg kg^{-1})	Mn / (mg kg^{-1})	Na / (mg kg^{-1})	Ba / (mg kg^{-1})
A. millefolium	1.1 ± 0.2	93 ± 1	101 ± 3	10.7 ± 0.6	128 ± 7	104 ± 3	19.9 ± 0.9
A. satureioides	0.33 ± 0.04	429 ± 5	40 ± 3	6.7 ± 0.2	73 ± 2	270 ± 7	68 ± 3
A. hippocastanum	0.22 ± 0.04	1215 ± 13	2.5 ± 0.5	27.0 ± 0.4	126 ± 3	113 ± 5	
A. conyzoides	2.2 ± 0.3	2189 ± 23	24 ± 2	0.8 ± 0.1	239 ± 6	1633 ± 38	121 ± 7
A. sativum	0.03 ± 0.01	26 ± 4	13 ± 5	0.4 ± 0.2	6.9 ± 0.5	489 ± 17	
A. occidentales	1.8 ± 0.7	236 ± 3	8 ± 2	6.1 ± 0.1	94 ± 4	87 ± 2	96 ± 5
A. lappa	1.3 ± 0.2	177 ± 2	42 ± 1	9.2 ± 0.5	17.1 ± 0.7	82 ± 2	33 ± 2
A. montana	1.0 ± 0.1	285 ± 6	52 ± 4	2.9 ± 0.1	733 ± 274	162 ± 5	48 ± 3
B. trimera	0.61 ± 0.06	283 ± 4	52 ± 1	4.3 ± 0.3	424 ± 10	738 ± 17	81 ± 5
B. pilosa	0.87 ± 0.13	317 ± 4	32 ± 6	2.4 ± 0.2	102 ± 2	76 ± 3	141 ± 6
C. ferrea	2.4 ± 0.3		20 ± 9	0.7 ± 0.3	67 ± 2		101 ± 5
C. officinalis	0.47 ± 0.06	175 ± 4	3 ± 2	1.2 ± 0.2	150 ± 4	793 ± 19	20 ± 2
C. sylvestris	0.43 ± 0.05	134 ± 4	63 ± 3	3.9 ± 0.2	716 ± 15	8 ± 1	47 ± 2
C. verum	1.4 ± 0.1	55 ± 3	104 ± 6	2.4 ± 0.3	565 ± 213	9 ± 1	2 ± 1

Table 5. Concentrations and expanded uncertainty (K = 2) obtained in the analyzed samples (cont.)

Scientific name	Ca / %	Fe / (mg kg^{-1})	Hg / (µg kg^{-1})	Ni / (mg kg^{-1})	Mn / (mg kg^{-1})	Na / (mg kg^{-1})	Ba / (mg kg^{-1})
C. auranrium	0.48 ± 0.05	88 ± 3	44 ± 3	5.1 ± 0.3	6.1 ± 0.3	374 ± 9	53 ± 3
C. verbanacea	1.2 ± 0.1	357 ± 4	37 ±7	9.5 ± 0.3	142 ± 3	63 ± 2	107 ± 6
C. longa	0.12 ± 0.01	327 ± 5	90 ± 12	0.7 ± .2	193 ± 5	76 ± 3	20 ± 2
C. citratus	0.52 ± 0.08	161 ± 2	116 ± 7	6.2 ± 0.3	163 ± 4	28 ± 3	18 ± 1
C. scolymus	1.5 ± 0.1	720 ± 9	32 ± 3	1.9 ± 0.3	47 ± 2	2255 ± 75	47 ± 3
E. macrophyllus	1.4 ± 0.6	499 ± 7	27 ± 6	8.9 ± 0.1	370 ± 9	51 ± 1	102 ± 6
E. arvense	1.2 ± 0.1	360 ± 5	48 ± 5	5.0 ± 0.1	147 ± 5	343 ± 11	23 ± 3
E. verna	1.5 ± 0.2	364 ± 5		5.2 ± 0.3	79 ± 3	44 ± 1	176 ± 9
E. globulus	1.2 ± 0.2	490 ± 8	434 ± 11	6.5 ± 0.2	809 ± 16		99 ± 6
E. uniflora	0.71 ± 0.09	179 ± 3	82.82 ± 0.07	4.0 ± 0.2	117 ± 7	51 ± 5	234 ± 9
G. glaba	0.21 ± 0.03	151 ± 2	77.5 ± 0.3	9.4 ± 0.3	46 ± 1	56 ± 1	20 ± 1
H. virginiana	0.8 ± 0.1	209 ± 8	27 ± 1	5.6 ± 0.3	396 ± 10	88 ± 8	37 ± 4
H. procumbens	0.7 ± 0.2	849 ± 10	40 ± 1	5.0 ± 0.2	23.5 ± 0.8	112 ± 3	98 ± 4
I. verum	0.20 ± 0.03	187 ± 7	116 ± 4	10.8 ± 0.5	336 ± 8	100 ± 3	6 ± 3
L. sidoides	1.1 ± 0.1	299 ± 8	70 ± 1	1.47 ± 0.07	20.7 ± 0.6	52 ± 2	
M. sylvestris	1.30 ± 0.09	1370 ± 11	81 ± 2	4.3 ± 0.2	309 ± 9	144 ± 3	187 ± 6
M. recutita	0.49 ± 0.05	482 ± 7		0.9 ± 0.2	73 ± 2	140 ± 5	4 ± 2
M. ilicifolia	2.3 ± 0.2	103 ± 2	145 ± 3	0.7 ± 0.3	38 ± 1	19 ± 2	136 ± 5
M. officinales	2.0 ± 0.2	174 ± 4	47 ± 3	2.7 ± 0.2	123 ± 3	54 ± 1	56 ± 3
M. piperita	2.0 ± 0.2	1972 ± 19	98 ± 5	2.8 ± 0.3	164 ± 6	4702 ± 141	33 ± 3
M. pulegium	1.1 ± 0.4	12259 ± 84	34 ± 2	8.21 ± 0.06	297 ± 7	459 ± 8	116 ± 5
M. glomerata	1.51 ± 0.09	189 ± 2	75 ± 5	2.7 ± 0.1	1046 ± 68	1591 ± 29	13 ± 1
M. charantia	0.76 ± 0.07	860 ± 10	94 ± 5	53.1 ± 0.4	188 ± 5	156 ± 6	
P. alata	1.7 ± 0.1	202 ± 2	54.8 ± 0.1	12.8 ± 0.2	27.2 ± 0.8	22 ± 1	156 ± 6
P. incarnata	0.81 ± 0.08	898 ± 10	117 ± 2	4.0 ± 0.4	1022 ± 29	88 ± 2	8 ± 2
P. cupana	0.10 ± 0.01	111 ± 1	69 ± 2	2.7 ± 0.2	16.6 ± 0.5	48 ± 1	
P. boldus	1.15 ± 0.07	308 ± 3	119 ± 6	1.2 ± 0.2	103 ± 3	239 ± 4	25 ± 2
P. niruri	0.78 ± 0.05	1882 ± 16	74 ± 1	2.0 ± 0.1	204 ± 5	103 ± 4	54 ± 3
P. onisum	0.88 ± 0.05	334 ± 4	13.9 ± 0.2	13.2 ± 0.2	39 ± 1	91 ± 3	20 ± 1
P. major	1.23 ± 0.08	3021 ± 31	62 ± 10	14.6 ± 0.3	103 ± 3	100 ± 4	63 ± 5
P. punctatum	1.2 ± 0.2	421 ± 5	85 ± 2	7.5 ± 0.3	132 ± 3	7718 ± 167	39 ± 3
P. guajava	2.0 ± 0.3	154 ± 5	214 ± 7	1.5 ± 0.2	183 ± 5	85 ± 3	83 ± 4
P. granatum	0.36 ± 0.06	68 ± 2	294 ± 11	0.45 ± 0.1	2.4 ± 0.3	21 ± 1	33 ± 2
R. purshiana	1.10 ± 0.07	43 ± 2	10.70 ± 0.04	1.5 ± 0.3	295 ± 7	78 ± 4	113 ± 7
R. officinales	0.80 ± 0.05	313 ± 6	36.42 ± 0.01	3.2 ± 0.2	20 ± 1	84 ± 2	15 ± 2
S. officinalis	1.6 ± 0.2	3370 ± 39	70 ± 4	15.9 ± 0.3	87 ± 2	219 ± 13	44 ± 5
S. nigra	0.49 ± 0.04	381 ± 4	56 ± 2	1.2 ± 0.2	52 ± 2	144 ± 4	26 ± 2
S. terebinthifolia	2.1 ± 0.2	43 ± 4	10 ± 5	2.72 ± 0.08	13.5 ± 0.5	20 ± 3	390 ± 15
S. alexandrina	1.3 ± 0.1	520 ± 6	222 ± 11	1.7 ± 0.1	24.3 ± 0.8	279 ± 8	10 ± 1
S. paniculatum	0.53 ± 0.06	618 ± 7	204 ± 1	0.4 ± 0.3	129 ± 4	43 ± 2	116 ± 4
St. adstringens	0.14 ± 0.02	59 ± 3	194 ± 2	0.7 ± 0.1	6.6 ± 0.3	12 ± 2	33 ± 2
T. officinalles	1.1 ± 0.1	1979 ± 25	187 ± 47	2.6 ± 0.2	128 ± 4	229 ± 6	124 ± 7
U. tomentosa	0.28 ± 0.04	123 ± 6	73 ± 15	0.7 ± 0.1	22 ± 1	59 ± 5	17 ± 3
V. polyanthes	1.2 ± 0.2	490 ± 11	254 ± 38	1.0 ± 0.2	389 ± 9	22 ± 5	242 ± 10
Z. officinale	0.18 ± 0.02	109 ± 2	59 ± 11	1.2 ± 0.2	484 ± 12	64 ± 2	6.4 ± 0.8

Scientific name	Pb / (mg kg^{-1})	Rb / (mg kg^{-1})	Se / (mg kg^{-1})	Ti / (mg kg^{-1})	V / (mg kg^{-1})	Zn / (mg kg^{-1})
A. millefolium	0.9 ± 0.2	12.5 ± 0.4	0.10 ± 0.04			32 ± 2
A. satureioides	2.8 ± 0.6	25.3 ± 0.7	0.17 ± 0.09	92 ± 18	0.08 ± 0.06	
A. hippocastanum	38.2 ± 0.8	2.9 ± 0.3		45 ± 14	1.0 ± 0.1	17.5 ± 0.8
A. conyzoides	6.6 ± 0.3	32 ± 1	0.6 ± 0.2	417 ± 51	4.9 ± 0.9	36 ± 1
A. sativum		6.0 ± 0.5				23 ± 1
A. occidentales	3.9 ± 0.4	6.8 ± 0.3	0.19 ± 0.03	76 ± 14		9.8 ± 0.4
A. lappa	1.8 ± 0.3	46 ± 2				23.7 ± 0.9

Table 5. Concentrations and expanded uncertainty (K = 2) obtained in the analyzed samples (cont.)

Scientific name	Pb / (mg kg^{-1})	Rb / (mg kg^{-1})	Se / (mg kg^{-1})	Ti / (mg kg^{-1})	V / (mg kg^{-1})	Zn / (mg kg^{-1})
A. montana	0.5 ± 0.4	97 ± 4				32 ± 1
B. trimera	10.7 ± 0.4	129 ± 5				43 ± 2
B. pilosa	8.5 ± 0.6	72 ± 2	0.37 ± 0.08	0.7 ± 0.3	0.15 ± 0.08	
C. ferrea	1.02 ± 0.5	4.8 ± 0.4				46 ± 4
C. officinalis	0.6 ± 0.4	83 ± 3				54 ± 1
C. sylvestris		34 ± 1	0.4 ± 0.1		0.9 ± 0.2	25.9 ± 0.7
C. verum	5.6 ± 0.7	7.1 ± 0.2	0.13 ± 0.05			10.6 ± 0.5
C. auranrium	7.0 ± 0.6	13.8 ± 0.6			0.10 ± 0.04	7.9 ± 0.4
C. verbanacea	5.26 ± 0.09	27 ± 1			0.6 ± 0.1	30 ± 1
C. longa	0.7 ± 0.5	30.5 ± 0.7		71 ± 18		15.8 ± 0.7
C. citratus	14.7 ± 0.7	46 ± 1			0.14 ± 0.05	21.9 ± 0.8
C. scolymus	1.0 ± 0.8	28.9 ± 0.7	0.20 ± 0.09	86 ± 28		23.1 ± 0.8
E. macrophyllus	5.3 ± 0.5	74 ± 3				24 ± 1
E. arvense		229 ± 5				169 ± 8
E. verna	11.8 ± 0.9	32 ± 1			0.7 ± 0.2	9.2 ± 0.6
E. globulus	1.6 ± 0.4	28 ± 1	0.18 ± 0.07		0.53 ± 0.09	19.7 ± 0.8
E. uniflora	76.9 ± 0.5	75 ± 4	0.03 ± 0.01			24.5 ± 0.6
G. glaba	1.5 ± 0.3	3.7 ± 0.1	0.04 ± 0.02			8.5 ± 0.5
H. virginiana	5.0 ± 0.5	3.6 ± 0.4				16.1 ± 0.9
H. procumbens		10.1 ± 0.5		227 ± 46	0.5 ± 0.3	17.3 ± 0.7
I. verum	0.80 ± 0.05	69 ± 4				16 ± 2
L. sidoides	2 ± 1			49 ± 10		18 ± 1
M. sylvestris	2.3 ± 0.3	29.0 ± 0.8	0.20 ± 0.08	186 ± 35	2.7 ± 0.2	67 ± 2
M. recutita		79 ± 2	0.8 ± 0.3		0.5 ± 0.2	29 ± 1
M. ilicifolia		68 ± 3	0.32 ± 0.07			20.5 ± 0.8
M. officinales		19.2 ± 0.7			0.31 ± 0.06	33 ± 2
M. piperita	4.3 ± 0.6	10.4 ± 0.5		178 ± 39	6 ± 1	19.4 ± 0.8
M. pulegium	4.6 ± 0.6	23.7 ± 0.7		644 ± 59	5.5 ± 0.4	48 ± 1
M. glomerata	0.7 ± 0.5	176 ± 5				30.5 ± 0.9
M. charantia	49.2 ± 0.6	19.3 ± 0.8		34 ± 14	0.6 ± 0.1	34 ± 1
P. alata	1.2 ± 0.7	73 ± 2	0.17 ± 0.05	22 ± 19	0.12 ± 0.06	40 ± 1
P. incarnata		49 ± 2	0.6 ± 0.1		1.4 ± 0.4	44 ± 1
P. cupana	1.2 ± 0.5	23.0 ± 0.6	0.15 ± 0.03		0.19 ± 0.03	20.9 ± 0.6
P. boldus		14.7 ± 0.4	0.23 ± 0.09		1.0 ± 0.2	15.1 ± 0.5
P. niruri	1.2 ± 0.4	8.8 ± 0.4		440 ± 63	7.1 ± 0.5	40.6 ± 0.9
P. onisum	13.4 ± 0.7		0.26 ± 0.05		0.12 ± 0.07	40 ± 2
P. major		41 ± 2		87 ± 30	5.3 ± 0.7	26 ± 1
P. punctatum	7.3 ± 0.2	24.8 ± 0.9			0.6 ± 0.1	35 ± 2
P. guajava	2.3 ± 0.1	13.2 ± 0.6				50 ± 2
P. granatum		37 ± 1	0.55 ± 0.09			8.0 ± 0.5
R. purshiana	0.9 ± 0.4	11.4 ± 0.5	0.18 ± 0.07			7.4 ± 0.3
R. officinales	3 ± 1	2.6 ± 0.2	0.15 ± 0.03			
S. officinalis	12.7 ± 0.5	3.7 ± 0.5		636 ± 48	8.2 ± 0.9	102 ± 9
S. nigra	2.9 ± 0.3	11.0 ± 0.4	0.5 ± 0.1	193 ± 66		42 ± 2
S. terebinthifolia	2.3 ± 0.3	6.0 ± 0.4				10 ± 1
S. alexandrina	1.6 ± 0.6	7.1 ± 0.3	1.1 ± 0.1	97 ± 16		10.7 ± 0.4
S. paniculatum	2.1 ± 0.3	28 ± 1				23.3 ± 0.7
St. adstringens	0.9 ± 0.3	7.9 ± 0.3	0.17 ± 0.06			18 ± 1
T. officinalles	1.5 ± 0.1	105 ± 4		338 ± 36	7 ± 2	63 ± 6
U. tomentosa		17.9 ± 0.8			0.34 ± 0.05	24 ± 2
V. polyanthes	20.3 ± 0.3	53 ± 2	0.6 ± 0.2	46 ± 23	0.7 ± 0.1	131 ± 11
Z. officinale	1.7 ± 0.9	3.9 ± 0.2	0.60 ± 0.06			23.1 ± 0.9

used as raw material, in concentrations of 1.0, 0.3 and 10 mg kg^{-1}. Observing the data in Table 5, it can be noted that this value exceeded by 15% of the samples for Pb, by 5% of the samples for Cd and in no sample for As.

Mentha pulegium showed the highest concentrations for the elements Co, Fe, Sc and Ti and relatively high concentrations for the elements Ba, Cr, Cs, Hf, Na, Sb, V, Zn; *Taraxacum officinale* showed the highest concentration for As and relatively high concentrations for Ba, Br, Co, Cs, Fe, Hf, Hg, Rb, Sc, Ti, V, Zn; *Salvia officinalis* showed the highest concentrations for the elements Cu, Hf and V and relatively high concentrations for Ca, Co, Cs, Fe, Hf, Mg, Ni, Sb, Sc, Ti, Zn; *Agerantum conyzoides* showed the highest concentrations for Mg and relatively high concentrations for Ba, Br, Co, Fe, Na, Sb, Sc, Ti, V; the highest concentration of Cd, Pb and Hg was observed in the samples of *Vernonia polyanthes*, *Eugenia uniflora* and *Eucalyptus globulus*, respectively. High concentrations were also observed in *Malva sylvestris* for Ba, Br, Cr, Fe, Hf, K, Mg, Sc, Ti, V and Zn and in *Passiflora incarnate*, for Br, Cr, Cs, Fe, Hf, Hg, Sb, Sc, Se, Mn and Zn.

Low concentrations for the majority of the determined elements were, generally, measured in the samples of *Allium sativum*, *Calendula officinalis*, *Casearia sylvestris*, *Cinnamomum verum*, *Citrus auranrium*, *Glycyrrhiza glaba*, *Illicium verum*, *Maytenus ilicifolia*, *Psidium guajava* and *Punica granatum*.

Major elements

Calcium is an essential element for plants and its content varied from 0.035 to 2.4% in the samples of *Allium sativum* and *Caesalpinia ferrea*, respectively. Low Ca concentrations were also found in the literature for *Allium sativum*[21] and high concentrations, varying from 1.5 to 2.0%,[7,22] have been found in *Glycyrrhiza glabra* and *Malva sylvestris*. Compared with our results, the highest values are in the same order of magnitude and the lowest are well below the reported figures. Potassium, an essential element that is generally supplied to plants by means of fertilization processes also showed a wide variation with a higher value found in *Echinodorus macrophyllus*. In the plants with this element, the concentrations determined ranged from 0.16 to 7.4%. Magnesium, besides being a chlorophyll component is also an enzyme co-factor.[23] Its concentration varied from below LOD up to 1.14% in the sample of *Agerantum conyzoides* and these values are in good agreement with the literature, registering concentrations which vary from 0.0004 to 2.3% in *Melissa officinales* and *Matricaria recutita* samples, respectively.[22,24] Another essential element for plants, Cl concentrations varied from below LOD up to 1.8% in the *Equisetum arvense* sample.

Minor elements

Iron and manganese are essential elements for plant protein synthesis.[25] *Allium sativum* was the sample with the lowest Fe value, while the highest was registered in the *Mentha pulegium* sample: the range of variation for this element was from 26 to 12259 mg kg^{-1}, respectively. The range of Fe concentrations, found in the literature,[26,27] vary from 6.7 to 1787 mg kg^{-1}, considering the same plant species included in this study. Manganese concentrations varied from 2.4 to 1046 mg kg^{-1} in *Punica granatum* and *Mikania glomerata*, respectively.

Copper is a micronutrient and an essential enzymatic element for normal plant growth and development, but it can be toxic at excessive levels and it is a harmful element for human health.[28] The concentrations here obtained varied from 1.88 to 24.5 mg kg^{-1} in samples of *Rhamnus purshiana* and *Salvia officinalis*, respectively. These values are in well agreement with those found in the literature, which vary from 0.1 mg kg^{-1} in *Zingirber officinale* up to 27.4 mg kg^{-1} in *Plantago major*,[29,30] although higher concentrations, up to 177 mg kg^{-1}, had been reported for *Aesculus hippocastanum* leaves.[31] Ni concentrations varied from 0.4 mg kg^{-1} in *Allium sativum* to 53 µg kg^{-1} in *Momordica charantia* samples. It was observed that the concentration of this element, for most of the species, were in agreement with values found in the literature,[32,33] varying from 0.32 to 6.7 µg kg^{-1} in samples of *Cinnamomum verum* and *Anacardium occidentales*, respectively, although approximately one quarter of the samples showed an enrichment for this metal. Zinc is an essential element for plants and animals whose biological functions can be catalytic, structural or regulatory. In this study, Zn concentrations varied from 7.4 mg kg^{-1} in *Rhamnus purshiana* to 169 mg kg^{-1} in *Equisetum arvense* samples. The literature[34,35] reported values showing variations ranging from 0.86 to 168 mg kg^{-1} in *Aesculus hippocastanum* and *Bidens pilosa*, respectively.

Other trace elements

Barium was found in the range of 2 to 390 mg kg^{-1} in *Cinnamomum verum* and *Schinus terebinthifolia*, respectively. Reported concentrations[32,36] vary from 2 to 100 mg kg^{-1}, indicating that some of the herbs here analyzed are enriched with this element. Enrichment in some herbs can also be observed for Br. For this reported concentrations[37,38] vary from 2 to 45 mg kg^{-1} and, in the samples analyzed in this study, varied from 0.7 to 168 mg kg^{-1}, for *Illicium verum* and *Echinodorus macrophyllus*, respectively. The values found for Se in the literature[33,37] range from 76 to 500 µg kg^{-1}, in samples of *Anacardium occidentale* and *Curcuma longa,* while the values obtained in this study ranged from 31 to 1100 µg kg^{-1} in *Eugenia uniflora* and *Senna alexandrina*, also, indicating a Se enrichment in the present samples.

Concentrations of Co varying from 69 to 9100 µg kg^{-1} were found in our samples, with the lowest values in *Passiflora alata* and the highest in *Mentha pulegium* while reported values ranges from 17 to 1200 µg kg^{-1} in *Allium sativum* and *Malva sylvestris*, respectively.[22,37] Chromium(VI), which is a by-product of numerous industrial processes, is recognized as a carcinogen when inhaled and Cr^{III} is the most stable oxidation state and, presumably, the form that is present in food supply, due to the presence of reducing substances.[39] The levels of Cr in our samples ranged from 0.5 to 256 mg kg^{-1} in the samples of *Paulinia cupana* and *Aesculus hippocastanum*, respectively: some samples showed higher values than those found in the literature,[33,40] which ranged from 0.012 to 115 mg kg^{-1} in samples of *Anacardium occidentale* and *Casearia sylvestris*, respectively.

Very few values have been reported in the literature for Cs, Hf, Rb, Sb, Sc, Ti and V in the same species here analyzed.

The elements Rb, Sc and Sb were found in the range of 2.6 to 229, 1.2 to 3660 and 5 to 90 µg kg^{-1}, respectively. The reported values in the literature are 2 to 80,[41,40] 0.14 to 10.3[25,40] and 0.4 to 20000 µg kg^{-1},[33,34] respectively. The plants with higher concentrations for these elements, observed in this study, were *Equisetum arvense* for Rb and Sb and *Mentha pulegium* for Sc. As to the values found in the literature, *Casearia sylvestris* showed the highest concentration of Rb and Sc[40] and *Equisetum arvense* of Sb.[35] Vanadium concentrations were found varying between below LOD up to 8.2 µg kg^{-1} in the sample of *Salvia officinalis*, what was consistent with those values found in the literature. The results obtained for Ti showed enrichment in some of the medicinal plants here analyzed with concentrations reaching values up to 644 µg kg^{1}, once a range varying from 1.4 to 57 µg kg^{-1} was verified for plants of the same species.[22,25]

Cesium was found in values up to 1.19 mg kg^{-1} in *Curcuma longa*[37] and compared to our samples about half of the plants, in which this element was measured, contain higher levels of this element. A concentration of 53 µg kg^{-1} is registered for Hf in *Anacardium occidentale* and this value is much lower than that encountered in almost all the herbs here analyzed.

Potentially hazardous elements

Arsenic was measured only in a small number of samples with concentrations varying from 0.05 µg kg^{-1}, in *Psidium guajava*, to 0.59 µg kg^{-1} in *Taraxacum officinalles* species, respectively.

The chronic toxicity of Cd to humans has been documented with cases of poisoning from herbal products in India, China, Brazil, Argentina and Mexico.[42] Short term effects include nausea, vomiting, diarrhea and cramps.[43] In the present samples, Cd concentrations varied from below LOD up to 0.55 µg g^{-1}, in the sample of *Vernonia polyanthes*. Low level of this element was found[44] in *Curcuma longa*, 0.004 µg g^{-1}, and the highest amount was found[45] in *Taraxacum officinalles*, 7.24 µg g^{-1}, considering the plants included in this paper.

Very few data about Hg are found in medicinal plants and values from 0.065 up to 54 µg kg^{-1} were reported[29,46] for *Salvia officinalis* and *Momordica charantia*, respectively. Among the samples analyzed in this work, almost all of them showed measurable amounts of this element and the concentrations varied from 2.5 to 434 µg kg^{-1}, in *Aesculus hippocastanum* and *Eucalyptus globulus* samples, respectively, indicating an one order of magnitude enrichment for this element, when compared to that found in foods other than fish products that, generally, varies between 1 and 50 µg kg^{-1}.

Lead is a non-essential element, but it is found widespread in the environment. In the present samples, its concentration varied from below LOD to 76.9 mg kg^{-1} in the *Eugenia uniflora* sample. The literature registers values up to 1544 mg kg^{-1} for this element in plants belonging to the same set of those here analyzed.[42] It is worth noting that nine of our samples showed values higher than the permitted by WHO for this element.

Elemental distribution pattern

In Figure 1, the mean concentration distribution, according to the part of the plant used as medicine, is shown. The elements were distributed in the figure according to their magnitude. It can be seen that shoots showed high concentrations for the elements Br, Cl, Co, Cr, Cs, Fe, Hf, Mg, Mn, Na, Rb, Sb, Sc, Ti, V, Zn and for the potentially toxic Cd. When the whole plant was analyzed high concentrations was verified for the elements Ba, Br, Fe, Hf, K, Rb, Sc, Ti, V, Zn and Cu and for the potentially toxic As and Hg. It can also be verified that seeds showed high concentrations for the elements Ba, Co, Cr, Cu, Ni and Pb; rhizome samples showed high concentrations for the elements As, Mn and Se and inflorescence, for the elements Ca, Cl, Mg, Na and Cu; fruits showed high values of mean concentrations for Se, Hg and Ni; leaves showed high concentrations for Hg and Pb; flowers, for Cr and Cd; beans, for Ca and Zn and, finally, barks showed higher Cd concentrations.

The role of essential and non elements in the plant parts analyzed in this study is beyond the scope of this paper but the distribution pattern observed must be related to the plant metabolism and the availability of these elements for transfer from soil to plant.[47] Also, it is increasingly recognized that the availability of a given micronutrient or contaminant varies substantially in relation to the different chemical species present,[48,49] being this elemental speciation, among other factors, a function of soil mineralogy, pH and redox potential.[50] Another possible contribution source is the pollution of air, soil, and water that arose from the industrial growth and from the agricultural practices that have caused the environmental dispersion of these elements, including the potentially toxic ones, resulting in their entry into food chains, including the medicinal plants.[51] A remarkable challenge in this field is, therefore, to estimate the anthropogenic contribution for the observed concentrations.

Since the concentration of all the elements varies widely in the analyzed parts of the plants, the main implication of this variation must be that their bioavailability will also vary for consumption depending on the solvent and preparation mode.

Enrichment factor

Enrichment factor (EF) analysis is generally used to assess anthropogenic contribution to the environment.[52,53] EF represents the ratio between a given element (E_i) and a conservative element (E_r) in the sample normalized by the same ration, in a geological reference. Generally, the upper continental crust (UCC) is used as the geological reference and the formula is given as EF = (E_i/E_r) sample/$(E_i/E_r)_{UCC}$. Magnesium was chosen as the conservative element, since it is both ubiquitous and an essential element for plants.

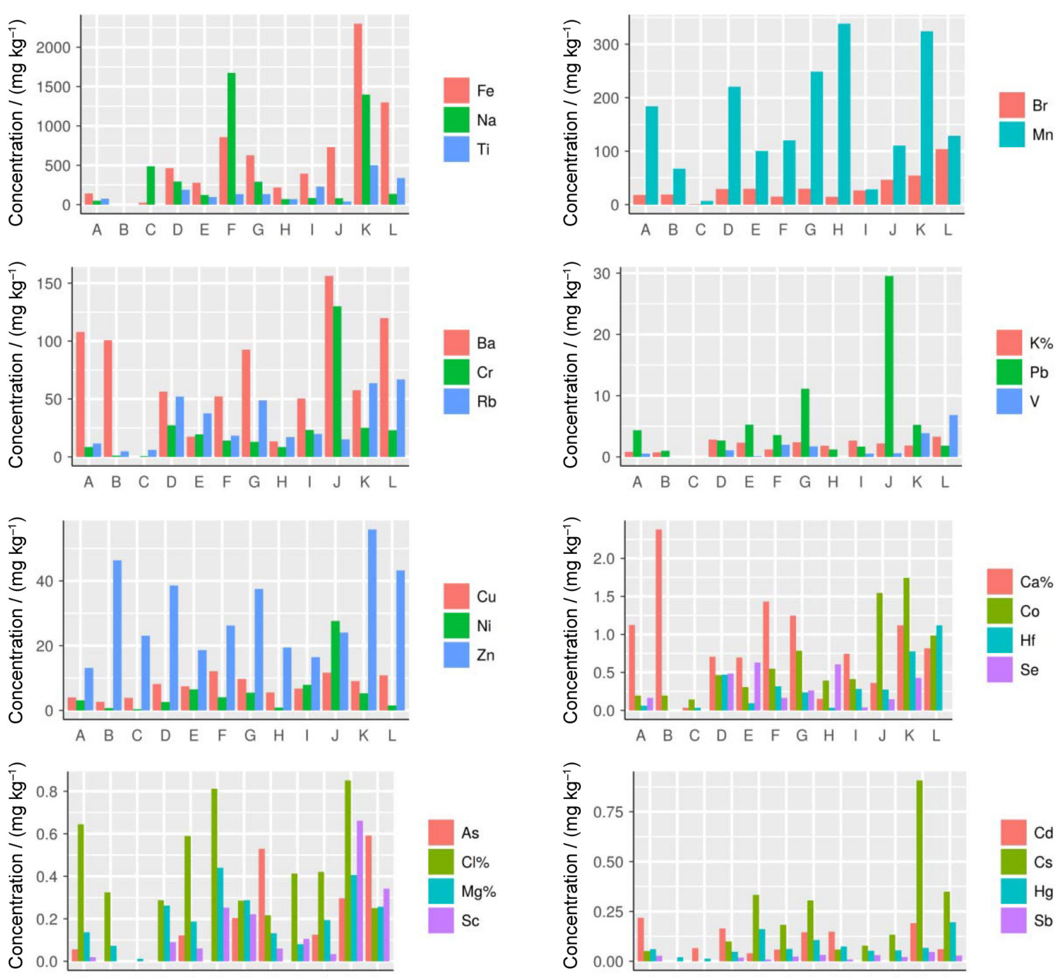

Figure 1. Mean concentration, in mg kg^{-1}, except were indicated %, according to the part of the plant, A (bark), B (bean), C (bulb), D (flower), E (fruit), F (inflorescence), G (leaves), H (rizome), I (roots), J (seeds), K (shots), and L (whole plant).

The calculated EF values for the present samples showed a large variation, ranging from 0.01 up to 500 and were categorized in three groups: (*i*) EF < 1: As, Ba, Co, Cs, Fe, Hf, Na, Sb, Sc, Ti, V and Ni; (*ii*) 1 < EF < 10: Ca, Cr, K, Mn, Rb, Zn, Cu and Pb; (*iii*) EF > 10: Br, Cl, Se, Hg, and Cd.

The first group is composed, mainly, by non-essential trace elements, that are generally transferred to plants in amounts smaller than the essential ones. The presence of Fe, as well as of V, in this group can be explained because they are major components of the soil.[54] Most of the essential elements for plants were categorized in the second group, that also include the potentially toxic, Pb. These elements tend to be enriched in the plants up to two orders of magnitude related to the non-essential elements.[55,56] Although being a non-essential element Rb was included in this group possibly due to its ionic radius close to the K radius.[54] The third group contains, besides the halogens, the potentially hazardous elements Se, Hg and Cd.

It was, also, verified that high EF values, for the majority of the elements, were observed, mainly, in the roots and bark, while the potentially toxic elements are mainly enriched in barks. This enrichment for the elements of the third group may possibly reflect some anthropogenic contribution, since they are not essential elements and their mean EF values were up to three orders of magnitude greater than the values obtained for the elements of the other groups and also that its own values obtained in other parts of the plants.

Conclusions

This study presents the results obtained for 59 medicinal plants commonly used in Brazil. Impurities were found in 50% of the samples, most of them in parts of plants not used for medicinal purposes; moisture levels varied up to 12%. The elemental concentrations varied in a wide range for almost all the determined elements, with a variation coefficient ranging from 50 to 245%. The species in which relatively high concentrations were measured were *Mentha pulegium*, *Taraxacum officinale*, *Malva sylvestris*, *Salvia officinalis*, *Passiflora incarnateand*, *Agerantum conyzoides*, while low concentrations were found in the *Allium sativum*, *Calendula officinalis*, *Casearia sylvestris*, *Cinnamomum verum*, *Citrus auranrium*, *Glycyrrhiza glaba*, *Illicium verum*, *Maytenus ilicifolia*, *Psidium guajava* and *Punica granatum* samples.

Good agreement was found between the results obtained in this work and the level of elements reported in the literature, although higher values for some elements such as Ba, Cr, Fe, Hg, Se and Ni were found in some samples.

It was observed that the pattern of elemental distribution varies according to the part of the plant analyzed. Non-essential elements tend to show a low enrichment factor, generally, inferior to 1, while essential elements show EF between 1 and 10. Higher EF values include the potentially hazardous elements Hg and Cd, mainly, in the bark of the plants, possibly indicating anthropogenic contribution.

Acknowledgments

Research supported, under fellowship contracts 2011/06768-2 and 2011/06827-9, by the São Paulo State Research Support Foundation (Fundação de Amparo à Pesquisa do Estado de São Paulo-FAPESP), to whom the authors are grateful and to Prof Mario Olimpio Menezes for the help with the graphics.

References

1. World Health Organization (WHO); *Traditional Medicine Strategy*: 2014-2023. http://apps.who.int/iris/bitstream/10665/92455/1/9789241506090_eng.pdf, accessed in April 2016.
2. Thomson, G. E.; *J. Med. Plants Res.* **2010**, *4*, 125.
3. Kalaivanan, C.; Chandrasekaran, M.; Venkatesalu, V.; *J. Mycol. Med.* **2013**, *23*, 247.
4. Calvo, M. I.; Akerreta, S.; Cavero, R. Y.; *Eur. J. Integr. Med.* **2013**, *5*, 537.
5. Maslennikov, P. V.; Chupakhina, G. N.; Skrypnik, L. N.; *Biol. Bull.* **2014**, *41*, 133.
6. World Health Organization (WHO); WHA62.13, *Sixty-Second World Health Assembly, Geneva, 18-22 May 2009, Resolutions and Decisions, Annexes*; WHO Publications: Geneva, 2009. WHA62/2009/REC/1; http://apps.who.int/gb/ebwha/pdf_files/WHA62-REC1/WHA62_REC1-en.pdf, accessed in April 2016.
7. Łozak, A.; Sołtyk, K.; Ostapczuk, P.; Fijałek, Z.; *Sci. Total Environ.* **2002**, *289*, 33.
8. Sattar, S. A.; Reddy, B. S.; Rao, V. K.; Pradeep, A. S.; Raju, G. J. N.; Ramanarayana, K.; Rao, P. V. M.; Reddy, S. B.; *J. Radioanal. Nucl. Chem.* **2012**, *294*, 337.
9. Fei, T.; Dehong, L.; Fengqun, Z.; Junhua, L.; Hua, T.; Xiangzhong, K.; *J. Radioanal. Nucl. Chem.* **2010**, *284*, 507.
10. Ebrahim, A. M.; Eltayeb, M. H.; Khalid, H.; Mohamed, H.; Abdalla, W.; Grill, P.; Michalke, B.; *J. Nat. Med.* **2012**, *66*, 671.
11. Ranđelović, S. S.; Kostić, D. A.; Zarubica, A. R.; Mitić, S. S.; Mitić, M. N.; *Hem. Ind.* **2013**, *67*, 585.
12. Bolzani, V. S.; Castro-Gamboa, I.; Silva, D. H. S. In *Comprehensive Natural Products II Chemistry and Biology*, Vol. 3; Verpoorte, R., ed.; Elsevier: Oxford, UK, 2010, ch. 3.05, p. 95.

13. Ermidou-Pollet, S.; Pollet, S.; *Cell Biol. Toxicol*. **2008**, *24*, 341.
14. World Health Organization (WHO); *Quality Control Methods for Medicinal Plants Materials*; http://apps.who.int/iris/bitstream/10665/41986/1/9241545100.pdf, accessed in April 2016.
15. Oladipo, M. O. A.; Njinga, R. L.; Baba, A.; Muhammad, H. L.; *Appl. Radiat. Isot*. **2012**, *70*, 917.
16. Fatima, I.; Waheed, S.; Zaidi, J. H.; *Appl. Radiat. Isot.* **2013**, *71*, 57.
17. Nedjimi, B.; Beladel, B.; *J. Appl. Res. Med. Aromat. Plants* **2015**, *2*, 203.
18. Shirisha, K.; Sahrawat, K. L.; Devi, B. P.; Wani, S. P.; *Commun. Soil Sci. Plant Anal.* **2014**, *45*, 2201.
19. *Farmacopeia Brasileira*, Vol. 2; Agência Nacional de Vigilância Sanitária, ANVISA: Brasília, 2010.
20. Lagad, R. A.; Alamelu, D.; Acharya, R.; Aggarwal, S. K.; *J. Radioanal. Nucl. Chem*. **2011**, *288*, 613.
21. Méndez, C. M. V.; Rodriguez, E. M. R.; Romero, C. D.; Gonález, M. C. M.; Isasa, M. E. T.; *Int. J. Food Sci. Nutr*. **2008**, *59*, 660.
22. Hiçsönmez, Ü.; Ereeş, F. S.; Özdemir, C.; Özdemir, A.; Çam, S.; *Biol. Trace Elem. Res*. **2009**, *128*, 248.
23. Bybordi, A.; Shabanov, J. A.; *Not. Sci. Biol*. **2010**, *2*, 81.
24. Petenatti, M. E.; Petenatti, E. M.; del Vitto, L. A.; Téves, M. R.; Caffini, N. O.; Marchevsky, E. J.; Pellerano, R. G.; *Braz. J. Pharmacog*. **2011**, *21*, 1144.
25. Hänsch, R.; Mendel, R. R.; *Curr. Opin. Plant Biol*. **2009**, *12*, 259.
26. Lamari, Z.; Landsberger, S.; Braisted, J.; Neggache, H.; Larbi, R.; *J. Radioanal. Nucl. Chem*. **2008**, *276*, 95.
27. Sinha, S.; Gupta, A. K.; Bhatt, K.; Pandey, K.; Rai, U. N.; Singh, K. P.; *Environ. Monit. Assess*. **2006**, *115*, 1.
28. Yruela, I.; *Braz. J. Plant Physiol*. **2005**, *17*, 145.
29. Alwakeel, S. S.; *Res. J. Microbiol*. **2008**, *3*, 683.
30. Siromlya, T. I.; *Contemp. Probl. Ecol*. **2011**, *4*, 499.
31. Kim, N. D.; Fergusson, J. E.; *Environ. Pollut*. **1994**, *86*, 89.
32. Karadaş, C.; Kara, D.; *Food Chem*. **2012**, *130*, 196.
33. Rodushkin, I.; Engström, E.; Sörlin, D.; Baxter, D.; *Sci. Total Environ*. **2008**, *392*, 290.
34. Robinson, B. H.; Bischofberger, S.; Stoll, A.; Schroer, D.; Furrer, G.; Roulier, S.; Gruenwald, A.; Attinger, W.; Schulin, R.; *Environ. Pollut*. **2008**, *153*, 668.
35. Tomašević, M.; Vukmirović, Z.; Rajšić, S.; Tasić, M.; Stevanović, B.; *Chemosphere* **2005**, *61*, 753.
36. Oliva, S. R.; Valdés, B.; Mingorance, M. D.; *Food Chem. Toxicol*. **2008**, *46*, 65.
37. Singh, V.; Garg, A. N.; *Food Chem*. **2006**, *94*, 81.
38. Gowrishankar, R.; Kumar, M.; Menon, V.; Divi, S. M.; Saravanan, M.; Magudapathy, P.; Panigrahi, B. K.; Nair, K. G. M.; Venkataramaniah, K.; *Biol. Trace Elem. Res*. **2010**, *133*, 357.
39. World Health Organization (WHO); *Guidelines for Drinking-Water Quality*, Vol. 2, 2nd ed.; WHO Publications: Geneva, 1996. http://www.who.int/water_sanitation_health/dwq/chemicals/chromium.pdf, accessed in April 2016.
40. Yamashita, C. I.; Saiki, M.; Vasconcellos, M. B. A.; Serti, J. A. A.; *Appl. Radiat. Isot*. **2005**, *63*, 841.
41. Khuder, A.; Sawan, M. Kh.; Karjou, J.; Razouk, A. K; *Spectrochim. Acta, Part B* **2009**, *64*, 721.
42. Arpadjan, S.; Çelik, G.; Taşkesen, S.; Güçer, Ş.; *Food Chem. Toxicol*. **2008**, *46*, 2871.
43. Bedoui, K.; Abbes-Bekri, I.; Srasra, E.; *Desalination* **2008**, *223*, 269.
44. Meena, A. K.; Bansal, P.; Kumar, S.; Rao, M. M.; Garg, V. K.; *Environ. Monit. Assess*. **2010**, *170*, 657.
45. Gjorgieva, D.; Kadifkova-Panovska, T.; Bacĕva, K.; Stafilov, T.; *Arch. Environ. Contam. Toxicol*. **2011**, *60*, 233.
46. Choudhury, R. P.; Acharya, R.; Nair, A. G. C.; Reddy, A. V. R.; Garg, A. N.; *J. Radioanal. Nucl. Chem*. **2008**, *276*, 85.
47. Lombi, E.; Scheckel, K. G.; Kempson, I. M.; *Environ. Exp. Bot.* **2011**, *72*, 3.
48. Nolan, A. L.; Lombi, E.; McLaughlin, M. J.; *Aust. J. Chem.* **2003**, *56*, 77.
49. Scheckel, K. G.; Chaney, R. L.; Basta, N. T.; Ryan, J. A.; *Adv. Agron.* **2009**, *104*, 1.
50. Abedin, M. J.; Feldmann, J.; Meharg, A. A.; *Plant Physiol.* **2002**, *128*, 1120.
51. Awodele, O.; Popoola, T. D.; Amadi, K. C.; Coker, H. A. B.; Akintonwa, A.; *J. Ethnopharmacol.* **2013**, *150*, 614.
52. Szczepaniak, K.; Biziuk, M.; *Environ. Res*. **2003**, *93*, 221.
53. Aničić, M.; Spasić, T.; Tomašević, M.; Rajšić, S.; Tasić, M.; *Ecol. Indic*. **2011**, *11*, 824.
54. Uchida, S.; Tagami, K.; Hirai, I.; *J. Nucl. Sci. Technol.* **2007**, *44*, 628.
53. Bargagli, R.; *Trace Elements in Terrestrial Plants: an Ecophysiological Approach to Biomonitoring and Biorecovery*; Springer-Verlag: Berlin, Heidelberg, NY, 1998.
56. Markert, B.; *Instrumental Element and Multi-Element Analysis of Plant Samples*; John Wiley & Sons: Chichester, 1996.

Submitted: December 17, 2015
Published online: April 26, 2016

FAPESP has sponsored the publication of this article.