

RARE EARTH ELEMENTS DETERMINATION IN MEDICINAL PLANTS BY NEUTRON ACTIVATION ANALISYS

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

Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN
Av. Prof. Lineu Prestes, 2242
05508-000 Cidade Universitária, São Paulo, SP
rdmrg89@usp.br

ABSTRACT

Rare Earth Elements (REEs) have been considered nontoxic for human health and for the environment; however, the use of REEs in the development of recent technologies has increased the interest in their biological effects. Some studies related to their concentration in foodstuffs were published but REEs levels in medicinal plants are still unknown. The objective of this study was to determine the REEs concentration in the set of 59 medicinal herbs commonly used by Brazilian folk. Results showed that plants can concentrate REEs in their aerial parts, but the amount transferred to the extract of these plants is relatively low, resulting in little ingestion of these elements by the population during the extract consumption.

1. INTRODUCTION

Investigations of Rare Earth Elements (REEs) in the environmental context have been limited due to the lack of a sensitive analytical technique to estimate the trace levels of these elements in the air, water, soil, sediment and various biological samples. In addition, the lack of interest on the ecotoxicological aspect of REEs is another reason. In the past, there was little knowledge of REEs concentration levels, their behavior and their uptake by plants from soils. However, the use of REEs in the development of recent technologies, such as magnetic bubble memory, superconducting materials, permanent magnet, and others, will make the demand for industrial usage of these elements increase rapidly so that environmental contamination and health problems can become a concern. Some studies related to their concentration in foodstuffs were published, but REEs levels in medicinal plants are still unknown [1].

It has been shown that REEs have interesting biological effects on plants. They can exert positive or negative physiological effects on plants, depending on the dosage and other conditions. The REEs had never received much attention, since they were characterized as non-essential elements for life and did not present a strong toxicity in the environment. More recently, new information was released about the occurrence, behavior and biological role of REEs in soil and plants, leading to an increasing interest in REEs application, including medicinal plants, since they affect directly or indirectly the growth and development of such plants [2,3]. Applications of the rare-earths in agriculture have been reported to increase crop yield by 10-20% over controls. The contents of REEs in plants depend on their type and on the relative amounts of rare-earths in the soil in which the plants grow [4], as well as the part of plant considered [5].

The objective of this study was to determine the REEs concentration in the set of 59 medicinal herbs commonly used by Brazilian people.

2. METHODOLOGY

The samples were obtained in pharmacies in São Paulo State, Brazil and were dried in a ventilated oven, at 60° C, until constant weight after separation of any strange matter. As strange matter, it was considered: any part of the plant different from that indicated for use by National Agency for Sanitary Vigilance (ANVISA), insects or part of insects, soil and rock particles. After that, the samples were transferred to a mortar, previously decontaminated with HNO₃, and crushed to 100 mesh size particles and homogenized: then, approximately 200 mg were packed in polyethylene bags for irradiation, together with Standards Reference Materials (SRM) from United States Geological Survey (USGS): Rhyolite, Glass Mountain (RGM) and Syenite, Table Mountain (STM). Also synthetic standards prepared by pipetting convenient aliquots of standard solutions onto small filter paper sheets. Samples, SRM and synthetic standards were irradiated for 8 h under a $1 \text{ to } 5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ thermal neutron flux, in the IEA-R1 nuclear reactor at IPEN and counted after 7 to 20 days, depending on the radionuclide half-live of interest to be determined.

Aqueous extracts of the plants considered for this study were obtained by infusion, decoction and maceration, as defined in ANVISA resolution for each type of plants. The extract solutions were dried, transferred to filter paper sheets, and so was the subsequent water used in the beakers washing. Paper sheets were dried under an infrared lamp, packed in polyethylene bags and sent to irradiation in the same way and conditions the plants had been.

Gamma spectrometry was performed using a Canberra gamma Hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV for the 122 keV line of ⁵⁷Co and 2.00 keV for the 1332 keV line of ⁶⁰Co.

3. RESULTS AND DISCUSSION

Quality control of the analysis was done by analyzing Standard Reference Materials (SRM) Apple Leaves (NIST SRM 1515) and Tomato Leaves (NIST SRM 1573a). The results are shown in table 1, together with relative standard deviation and relative error, which were calculated despite the fact that REEs are only information values in the certificates of the SRM to evaluate the measurements quality. It was observed good precision and accuracy, since the RSD and RE are generally low, less than 20%, except in the case of Eu (apple leaves), with a high value of relative error and Yb (tomato leaves), with a high value of relative standard deviation.

In table 2, the plants and plant parts that were analyzed are presented together with the concentration measurements for the REEs, in the samples. Blanks in the table mean values not measured. It can be observed that the concentrations varied in a wide range: Nd and Tb were the elements which were not measured in most samples. The highest concentrations were found in *Caesalpinia ferrea*, *Vernonia polyanthes*, *Plantago major*, *Malva sylvestris*,

Mentha pulegium, *Agerantum conyzoides*, *Momordica charantia*, *Solanum paniculatum*, *Salvia officinalis*, and *Taraxacum officinalles*.

The parts of the plant with the highest concentrations include, mainly, leaves, flowers and shoots. Among the plants with the lowest concentrations are included rhizomes, fruits, roots, beans, bark and also leaves and flowers. The highest concentrations found in bark were in the sample of *Schinus terebinthifolia* and the highest concentrations found in roots were in the sample of *Eugenia uniflora*. These results indicate that, once the REEs are absorbed by the plants from the soil, they are redistributed and, then, concentrate in the aerial parts of the plants or the aerial parts of the plants can absorb REEs from atmospheric particles, deposited on them.

Table 1: Results obtained for the reference materials, Apple Leaves (NIST SRM 1515) and Tomato Leaves (NIST SRM 1573a), relative standard deviation and relative error; MV means measured values, CV means certified values, RSD means relative standard deviation and RE means relative error.

	Apple Leaves					Tomato Leaves					
	MV	CV	RSD	RE		MV	CV	RSD	RE		
La	18.8	0.9	20	4.77	5.89	La	7.7	0.4	9	4.90	14.35
Ce	3.0	0.2	3	7.11	-0.65	Ce	8.5	0.5	10	5.87	14.82
Nd	17.2	2.7	17	15.94	-1.06	Nd	6.0	0.7	7	12.59	14.94
Sm	3.0	0.1	3	4.62	0.55	Sm	NM	NM	1		
Eu	0.25	0.02	0.2	8.60	-25.83	Eu	0.14	0.01	0.17	7.61	19.68
Tb	0.35	0.03	0.4	9.62	12.67	Tb	0.09	0.01	0.1	11.81	7.06
Yb	0.33	0.06	0.3	18.91	-11.34	Yb	0.19	0.05	0.2	25.44	4.45
Lu	0.025	0.003		10.79		Lu	0.015	0.002		10.79	

In figure 1, the distribution pattern of REEs normalized by the chondrite in order to evaluate the variation in REE abundance, is presented. The REE abundance is normalized to that in chondrite and ratios are plotted on a logarithmic scale against the rare earth elements, in crescent order of atomic number [6]. This plot is called an 'REE pattern'. The chondrite values from Anders and Ebihara [7] were used to normalize the abundance of REEs in the sample. It can be observed that the patterns of all plants resemble each other but, with a very large variation in the slope of all the curves. Normalized values of REEs have a tendency to be high in light REEs and low in heavy REEs. Such a tendency plus cerium and europium anomalies resemble the typical distribution pattern of the continental crusts [8,9]. The shape of the curves for the samples is the same to that obtained for the reference materials (apple leaves and tomato leaves) if the normalization process were applied to them.

In figure 3, it is shown the enrichment factor obtained for the analyzed plants, considering Sc as the conservative element and the Upper Continental Crust (UCC) values for REEs, as normalizer values, according to the formula $EF = (REE_{sample}/Sc_{sample})/(REE_{UCC}/Sc_{UCC})$. The values for Sc were presented elsewhere. It can be seen from the EF that the REEs are enriched in almost all the samples, indicating that the plants here analyzed absorb them, preferentially related to the conservative element. It can, also, be observed that little or no fractionation occurs between light REEs and heavy REEs during its absorption and/or redistribution by the plant, in the parts of the plants considered in this study.

Table 2: Analyzed plants, part of the plant used for extract preparation and rare earth elements concentrations.

Scientific name	Used part	La	$\pm 1\sigma$	Ce	$\pm 1\sigma$	Nd	$\pm 1\sigma$	Sm	$\pm 1\sigma$	Eu	$\pm 1\sigma$	Tb	$\pm 1\sigma$	Yb	$\pm 1\sigma$	Lu	$\pm 1\sigma$
<i>Achillea Millefolium</i>	Shoots	0.15	0.02	0.23	0.03			0.020	0.002	0.0058	0.0006						
<i>Achyrocline satureioides</i>	Inflorescence	0.97	0.03	1.85	0.08			0.134	0.003	0.040	0.002	0.036	0.003	0.13	0.02	0.013	0.001
<i>Aesculus hippocastanum</i>	Seeds in shell	0.10	0.01					0.019	0.002							0.011	0.002
<i>Agerantum conyzoides</i>	Shoots without flowers	7.4	0.3	10.9	0.4	3.4	0.6	1.08	0.04	0.22	0.01	0.16	0.01	0.43	0.03	0.078	0.003
<i>Allium sativum</i>	Bulb																
<i>Anacardium occidentales</i>	Under bark	0.86	0.03	0.97	0.04	0.53	0.08	0.124	0.004	0.0180	0.0008	0.015	0.001			0.0069	0.0004
<i>Arctium lappa</i>	Roots	0.21	0.01	0.31	0.03			0.018	0.001							0.0013	0.0003
<i>Arnica montana</i>	flowers	0.36	0.03	0.58	0.09			0.035	0.004								
<i>Baccharis trimera</i>	Shoots	0.74	0.03	1.62	0.07			0.074	0.003	0.034	0.002					0.0023	0.0006
<i>Bidens pilosa</i>	Leaves	1.33	0.04	1.11	0.05			0.068	0.002	0.019	0.001			0.012	0.004	0.0030	0.0006
<i>Caesalpinia ferrea</i>	Flowers	21.7	0.8	3.8	0.2			1.14	0.04	0.24	0.01	0.086	0.008	0.06	0.02	0.010	0.002
<i>Calendula officinalis</i>	Beans	0.19	0.01	0.33	0.07			0.018	0.001	0.004	0.002						
<i>Casearia sylvestris</i>	Leaves	0.29	0.02	0.44	0.04			0.049	0.003	0.009	0.002						
<i>Cinnamomum verum</i>	Bark	0.05	0.02									0.006	0.002			0.0020	0.0005
<i>Citrus aurantium</i>	Flowers	0.154	0.006	0.11	0.03			0.0107	0.0006								
<i>Cordia verbanacea</i>	Leaves	3.11	0.10	2.42	0.09			0.30	0.01	0.083	0.003	0.031	0.002	0.075	0.007	0.0115	0.0006
<i>Curcuma longa</i>	Rhizomes	0.21	0.01	0.40	0.04			0.041	0.002	0.019	0.002						
<i>Cymbopogon citratus</i>	Leaves	0.49	0.02	0.71	0.03			0.061	0.002	0.006	0.002					0.0018	0.0004
<i>Cynara scolymus</i>	Leaves	1.13	0.03	1.57	0.06			0.105	0.005	0.018	0.003	0.009	0.003			0.0026	0.0008
<i>Echinodorus macrophyllus</i>	Shoots	0.34	0.01	0.90	0.07			0.059	0.002							0.002	0.001
<i>Equisetum arvense</i>	Bark	0.30	0.02	1.45	0.08			0.0139	0.0009								
<i>Erythrina verna</i>	Leaves	0.46	0.02	0.65	0.04			0.040	0.001	0.010	0.001					0.0049	0.0007
<i>Eucalyptus globulus</i>	Leaves	1.7	0.2	2.10	0.08			0.26	0.02	0.060	0.004	0.011	0.004	0.05	0.01		
<i>Eugenia uniflora</i>	Root	1.03	0.05	1.42	0.03	0.46	0.07	0.09	0.01	0.0195	0.0009	0.007	0.002	0.010	0.003	0.006	0.001
<i>Glycyrrhiza glaba</i>	Bark	0.48	0.02	0.46	0.02			0.024	0.001	0.0092	0.0006					0.0016	0.0002
<i>Hamamelis virginiana</i>	Root	0.41	0.03	0.69	0.09			0.035	0.003								
<i>Harpagophytum procumbens</i>	Fruit	0.82	0.03	1.32	0.06			0.135	0.004	0.026	0.002			0.069	0.009	0.022	0.001
<i>Illicium verum</i>	Leaves	0.166	0.008	0.40	0.02			0.029	0.001	0.0068	0.0005	0.0026	0.0007	0.024	0.004	0.0036	0.0003

Lippia sidoides	Leaves and flowers	0.246	0.007	0.45	0.06			0.045	0.002								
Malva sylvestris	Flowers	9.6	0.2	9.0	0.2	6.3	0.6	0.96	0.02	0.197	0.006	0.096	0.005	0.23	0.02	0.043	0.001
Matricaria recutita	Leaves	0.56	0.02	0.49	0.07	0.2	0.1	0.050	0.003	0.014	0.002						
Maytenus ilicifolia	Inflorescence	0.59	0.02	0.67	0.04			0.075	0.003					0.011	0.004	0.0014	0.0004
Melissa officinales	Leaves and inflorescence	1.45	0.03	0.72	0.05	1.3	0.3	0.060	0.002	0.018	0.002					0.0040	0.0009
Mentha piperita	Shoots	0.98	0.03	2.2	0.1			0.226	0.008	0.070	0.004			0.10	0.02	0.015	0.001
Mentha pulegium	Leaves	9.0	0.2	17.4	0.5	7.2	0.6	1.21	0.03	0.263	0.007	0.15	0.01	0.52	0.04	0.082	0.002
Mikania glomerata	Fruit, and seeds	0.170	0.008	0.38	0.02			0.027	0.001	0.0067	0.0006			0.018	0.003	0.0014	0.0002
Momordica charantia	Leaves	5.4	0.2	2.2	0.1	4.6	0.5	0.39	0.01			0.016	0.004	0.026	0.008	0.0057	0.0009
Passiflora alata	Shoots	3.18	0.07	3.46	0.10	2.4	0.2	0.232	0.006	0.053	0.002	0.039	0.005	0.033	0.004	0.0059	0.0005
Passiflora incarnata	Seeds	1.05	0.03	1.29	0.06			0.100	0.004	0.011	0.001			0.082	0.007	0.0099	0.0008
Paulinia cupana	Leaves	0.054	0.005	0.10	0.01			0.004	0.001								
Peumus boldus	Shoots	0.58	0.02	0.45	0.03			0.082	0.002	0.019	0.001			0.06	0.02	0.0042	0.0005
Phyllanthus niruri	Fruit	1.53	0.03	2.67	0.07	1.7	0.3	0.240	0.005	0.093	0.004	0.026	0.006	0.06	0.01	0.014	0.001
Pimpinella onisum	Leaves	0.14	0.01	0.30	0.02			0.016	0.002								
Plantago major	Leaves	10.6	0.3	3.0	0.1	5.7	0.5	0.99	0.03	0.238	0.009			0.35	0.03	0.049	0.002
Polygonum punctatum	Shoots	1.18	0.04	1.42	0.07			0.079	0.003							0.0016	0.0006
Psidium guajava	Young leaves	0.60	0.07	1.80	0.08			0.044	0.003	0.015	0.002						
Punica granatum	Fruit peel	0.23	0.05	0.22	0.04			0.0134	0.0008								
Rhamnus purshiana	Bark																
Rosmarinus officinales	Leaves	0.31	0.02	0.62	0.04			0.046	0.002	0.014	0.001			0.007	0.002	0.0011	0.0004
Sálvia officinalis	Leaves	4.6	0.2	11.4	0.5	2.7	0.9	0.40	0.01	0.108	0.006	0.09	0.01	0.15	0.02	0.025	0.002
Sambucus nigra	Flowers	0.28	0.01	0.34	0.05			0.040	0.003	0.008	0.001						
Schinus terebinthifolia	Bark	1.39	0.05	0.21	0.05			0.044	0.003								
Senna alexandrina	Fruit and folioles	0.65	0.02	1.49	0.08			0.096	0.003	0.019	0.002			0.047	0.009	0.009	0.001
Solanum paniculatum	Whole plant	4.90	0.09	4.6	0.1	3.3	0.3	0.652	0.009	0.161	0.007			0.106	0.010	0.021	0.002
Stryphnodendron adstringens	Bark	0.36	0.02	0.85	0.04			0.041	0.002	0.012	0.004			0.034	0.007	0.0050	0.0006
Taraxacum officinalles	Whole plant	3.5	0.1	4.6	0.2	2.2	0.8	0.271	0.008	0.059	0.004	0.020	0.007	0.07	0.02	0.025	0.002
Uncaria tomentosa	Bark	0.18	0.02	0.15	0.05			0.009	0.002							0.007	0.001
Vernonia polyanthes	Leaves	10.7	0.4	9.4	0.4	7	1	0.43	0.01	0.073	0.005			0.04	0.01	0.006	0.002
Zingiber officinale	Rhizome	0.29	0.02	0.75	0.04			0.043	0.002	0.012	0.001						

Table 3: Results obtained for rare earth elements concentrations in the extracts.

Scientific name	Used part	La	$\pm 1\sigma$	Ce	$\pm 1\sigma$	Nd	$\pm 1\sigma$	Sm	$\pm 1\sigma$	Eu	$\pm 1\sigma$	Tb	$\pm 1\sigma$	Yb	$\pm 1\sigma$	Lu	$\pm 1\sigma$
<i>Achillea Millefolium</i>	Shoots									0.00056	0.00008						
<i>Achyrocline satureioides</i>	Inflorescence																
<i>Aesculus hippocastanum</i>	Seeds in shell	0.0032	0.0004														
<i>Agerantum conyzoides</i>	Shoots without flowers	0.113	0.004	0.13	0.01			0.0173	0.0005	0.0037	0.0002	0.0024	0.0002	0.005	0.001	0.0010	0.0001
<i>Allium sativum</i>	Bulb	0.012	0.001							0.0049	0.0004						
<i>Anacardium occidentales</i>	Under bark	0.133	0.004	0.134	0.007	0.12	0.01	0.02753	0.0008	0.0047	0.0003	0.0025	0.0002	0.011	0.001	0.0023	0.0001
<i>Arctium lappa</i>	Roots	0.011	0.002														
<i>Arnica montana</i>	flowers	0.034	0.004	0.050	0.007			0.032	0.003	0.0019	0.0003						
<i>Baccharis trimera</i>	Shoots	0.011	0.001	0.04	0.01			0.0021	0.0002	0.0016	0.0003						
<i>Bidens pilosa</i>	Leaves	0.024	0.001					0.0021	0.0002	0.0012	0.0001						
<i>Caesalpinia ferrea</i>	Flowers	0.101	0.003	0.045	0.003	0.065	0.004	0.0064	0.0002	0.0014	0.0001	0.0006	0.0001				
<i>Calendula officinalis</i>	Beans	0.0143	0.0009					0.0022	0.0002	0.0008	0.0001						
<i>Casearia sylvestris</i>	Leaves	0.026	0.001	0.06	0.01			0.0046	0.0002							0.0003	0.0001
<i>Cinnamomum verum</i>	Bark	0.0087	0.0007	0.014	0.003			0.0034	0.0002	0.0100	0.0004					0.0012	0.0001
<i>Citrus aurantium</i>	Flowers	0.0121	0.0009					0.0007	0.0001								
<i>Cordia verbanacea</i>	Leaves	0.006	0.002	0.05	0.01												
<i>Curcuma longa</i>	Rhizomes	0.016	0.002	0.024	0.003			0.0022	0.0002	0.0008	0.0001						
<i>Cymbopogon citratus</i>	Leaves	0.015	0.001					0.0017	0.0002	0.0004	0.0001						
<i>Cynara scolymus</i>	Leaves	0.03	0.00	0.09	0.01			0.0041	0.0004	0.0007	0.0002						
<i>Echinodorus macrophyllus</i>	Shoots	0.031	0.003	0.06	0.02			0.0058	0.0006	0.0016	0.0003						
<i>Equisetum arvense</i>	Bark									0.0028	0.0003						
<i>Erythrina verna</i>	Leaves	0.0051	0.0004	0.008	0.003			0.0004	0.0001	0.0142	0.0007						
<i>Eucalyptus globulus</i>	Leaves	0.075	0.003	0.115	0.009			0.0094	0.0004	0.0038	0.0004					0.0006	0.0001
<i>Eugenia uniflora</i>	Root	0.057	0.002	0.085	0.008			0.006	0.000	0.0012	0.0002			0.003	0.001		
<i>Glycyrrhiza glaba</i>	Bark	0.029	0.001	0.019	0.001			0.0032	0.0002	0.0004	0.0001					0.00008	0.00002
<i>Hamamelis virginiana</i>	Root	0.021	0.001	0.032	0.002			0.0026	0.0001	0.00225	0.00008	0.00029	0.00004				
<i>Harpagophytum procumbens</i>	Fruit	0.036	0.001	0.06	0.01			0.0064	0.0002								
<i>Illicium verum</i>	Leaves	0.011	0.001	0.070	0.009			0.0021	0.0003	0.0010	0.0004						
<i>Lippia sidoides</i>	Leaves and flowers			0.017	0.004			0.0008	0.0001			0.0015	0.0004	0.003	0.001		

Malva sylvestris	Flowers	0.151	0.006	0.26	0.02			0.0286	0.0009	0.0085	0.0006	0.006	0.001	0.016	0.004	0.0023	0.0003
Matricaria recutita	Leaves	0.028	0.002					0.0042	0.0005								
Maytenus ilicifolia	Inflorescence	0.021	0.001	0.043	0.007			0.0065	0.0002	0.0018	0.0002						
Melissa officinales	Leaves and inflorescence	0.012	0.001					0.0015	0.0001	0.0010	0.0002						
Mentha piperita	Shoots	0.0057	0.0004					0.00088	0.00007	0.0020	0.0002						
Mentha pulegium	Leaves	0.129	0.007	0.264	0.026			0.0207	0.0010	0.0077	0.0007	0.0043	0.0011				
Mikania glomerata	Fruit, and seeds	0.019	0.003	0.042	0.004			0.0032	0.0003	0.0012	0.0001	0.0015	0.0003				
Momordica charantia	Leaves	0.072	0.003	1.11	0.05			0.0058	0.0005	0.0068	0.0004						
Passiflora alata	Shoots	0.174	0.009	0.124	0.010	0.15	0.03	0.0205	0.0006	0.0059	0.0003					0.0007	0.0002
Passiflora incarnata	Seeds	0.126	0.005	0.168	0.010	0.13	0.02	0.0111	0.0004	0.0015	0.0002						
Paulinia cupana	Leaves																
Peumus boldus	Shoots	0.030	0.002	0.065	0.008			0.0045	0.0003	0.0009	0.0003						
Phyllanthus niruri	Fruit	0.064	0.002	0.14	0.01			0.0104	0.0004	0.00347658	0.00050001						
Pimpinella onisum	Leaves	0.0064	0.0008					0.0009	0.0002								
Plantago major	Leaves	0.43	0.01	0.090	0.005	0.31	0.03	0.053	0.002	0.015	0.001	0.012	0.001	0.030	0.002	0.0051	0.0002
Polygonum punctatum	Shoots	0.088	0.004	0.08	0.01			0.0097	0.0005	0.0040	0.0003	0.0024	0.0006	0.004	0.001		
Psidium guajava	Young leaves							0.0018	0.0003								
Punica granatum	Fruit peel	0.043	0.002	0.076	0.006			0.0051	0.0002								
Rhamnus purshiana	Bark															0.0017	0.0005
Rosmarinus officinales	Leaves	0.034	0.002	0.074	0.008			0.0089	0.0004	0.0021	0.0003	0.0019	0.0006			0.0006	0.0001
Sálvia officinalis	Leaves	0.040	0.001	0.18	0.01			0.0072	0.0003	0.0025	0.0002						
Sambucus nigra	Flowers	0.007	0.001					0.0012	0.0003	0.0006	0.0002						
Schinus terebinthifolia	Bark	0.056	0.003	0.124	0.009			0.0030	0.0002								
Senna alexandrina	Fruit and folioles	0.0024	0.0006					0.0015	0.0003	0.0028	0.0003						
Solanum paniculatum	Whole plant	0.330	0.012	0.375	0.016	0.30		0.0537	0.0019	0.0122	0.0005	0.0054	0.0007	0.010	0.001	0.0014	0.0001
Stryphnodendron adstringens	Bark	0.077	0.004	0.212	0.007	0.078	0.008	0.0202	0.0005	0.00171	0.00007	0.0023	0.0001	0.0040	0.0005	0.00108	0.00005
Taraxacum officinales	Whole plant	0.108	0.004	0.176	0.006			0.0129	0.0004	0.0038	0.0002	0.0011	0.0002	0.0027	0.0005	0.000627	0.0001
Uncaria tomentosa	Bark	0.019	0.002	0.047	0.012			0.0015	0.0003								
Vernonia polyanthes	Leaves	0.132	0.005	0.120	0.007			0.0086	0.0004	0.0017	0.0001						
Zingiber officinale	Rhizome	0.0040	0.0007														

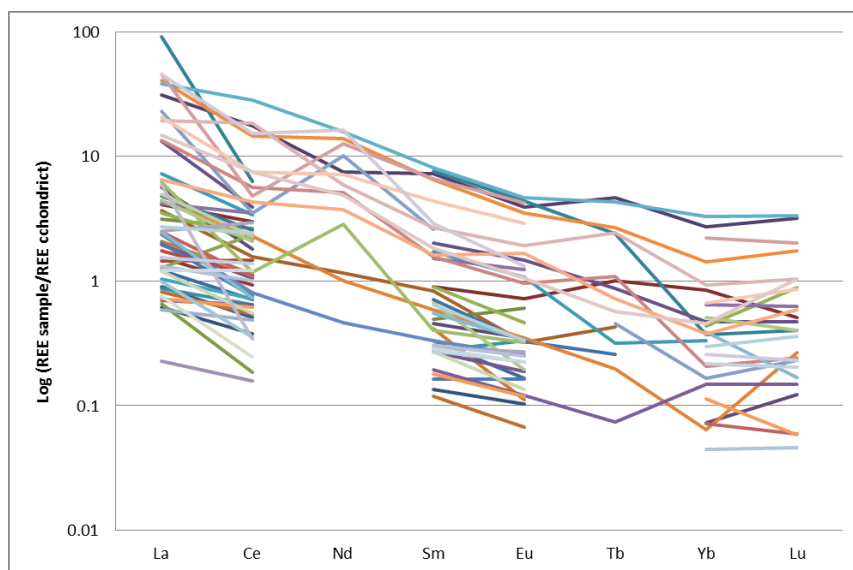


Figure 1: Rare earth elements normalization pattern by the chondrite.

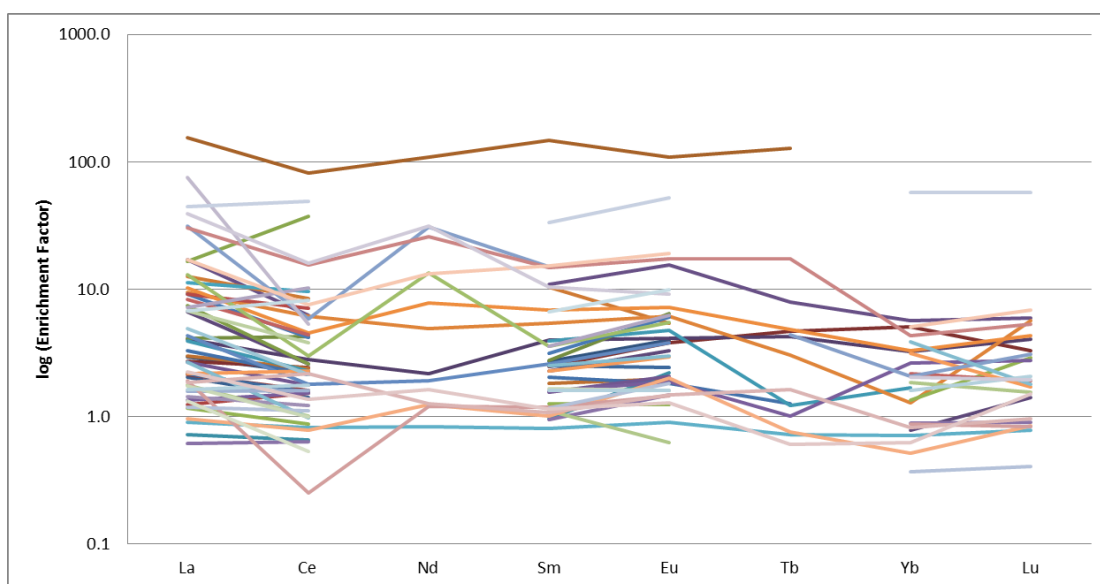


Figure 2: Enrichment factor obtained for the plant samples.

The values presented in table 3 were obtained in the extract analysis. The elements Lu, Nd, Tb and Yb were determined in a few numbers of samples. Higher concentrations were observed in samples of *Plantago major*, *Solanum paniculatum*, *Passiflora alata*, *Malva sylvestris*, *Anacardium occidentales*, *Vernonia polyanthes*, *Mentha pulegium*, *Passiflora incarnate*, *Agerantum conyzoides* and *Taraxacum officinalles*. No pattern could be observed in the plant part related to the concentrations observed in the extracts. Nevertheless, the extract concentrations obtained can be considered as a function of the concentration in the

plant, as it can be seen in Figure 3, where La concentration in the plant was plotted against the La concentration in the extract.

In Figure 4, the Transfer Factor (TF), the amount of the element transferred from the plant to the extract, it is shown. Generally, the TF for the REEs is lower than 10%, indicating a very low solubility for these elements, in the extract preparation conditions. Although it was also observed that heavy REEs tend to be more soluble than light REEs.

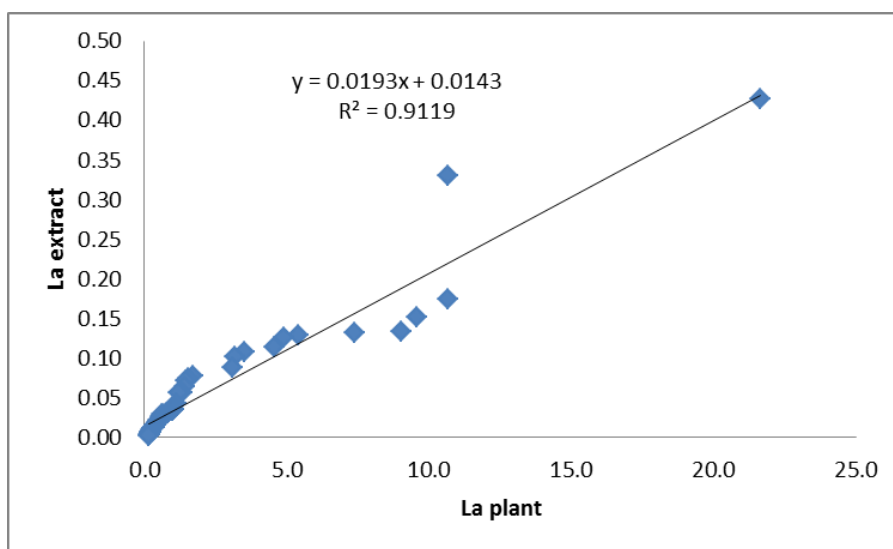


Figure 3: Linear regression curve obtained for La in the plant and in the extract.

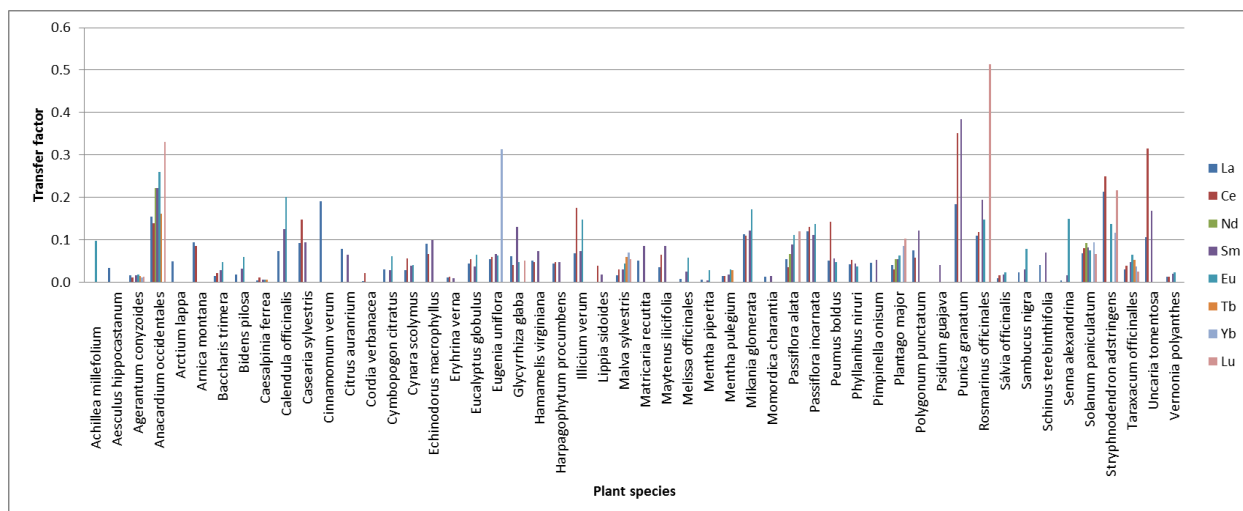


Figure 4: Transfer factor from the plant to the extract for the REEs.

3. CONCLUSIONS

In this paper, 59 samples of medicinal plants commonly used by Brazilian people were analyzed and the concentrations of rare earth element were determined. Although the concentrations varied in a wide range, it was observed that the distribution of REEs followed

the same distribution generally found in the earth crust. The results indicate that the aerial parts of the plants concentrate REEs, preferentially, either by redistribution from the elements absorbed from the soil or by absorbing REEs from atmospheric particles deposited on it. No pattern could be observed concerning the REEs amount in the extract and the part of the plant used in its preparation. A good correlation was found between the concentrations in the plant and in the extract, but the total amount of REEs transferred to the extract was generally less than 10% of the total amount of these elements found in the plants. It can be concluded that the consumption of the extracts, as in teas, does not result in a significant amount of REEs ingestion by the population. However, since the biological effects of rare earth are not well established, more studies are needed to effectively demonstrate that these elements are not a concern.

ACKNOWLEDGMENTS

This study is being supported by fundação de Amparo à Pesquisa do Estado de São Paulo, (2012/016642-9) to whom the authors are thankful.

REFERENCES

1. H. Ichihashi, H. Morita, R. Tatsukawa, Rare earth elements (REEs) in naturally grown plants in relation to their variation in soils, *Environ. Pollut.*, **Vol. 76**, pp. 157–162, (1992).
2. R. M. Welch, Micronutrient nutrition of plants, *Crit. Rev. Plant Sci.*, **Vol. 14**, pp. 49–82. (1995).
3. C. Zhang, Q. Li, M. Zhang, N. Zhang, M. Li., Effects of rare Earth elements on growth and metabolism of medicinal plants, *Acta Pharm. Sin. B*, **Vol. 3**, n. 1, pp. 20–24, (2013).
4. S. Li, S. Li, Y. Zhang, Spectrophotometric determination of the total amount of rare earth elements in agricultural samples with p-Chloro-chlorophosphonazo, *Talanta*, **Vol. 39**, pp. 987–991. (1992).
5. D. Shiming, L. Tao, C. Zhang, Y. Juncai, Z. Zhang, Accumulation and fractionation of rare earth elements (REESs) in wheat: controlled by phosphate precipitation, cell wall absorption and solution complexation, *J. Exp. Bot.*, **Vol. 56**, pp. 2765–2775, (2005).
6. F. F. Fu, T. Akagi, S. Yabuki, M. Iwaki, The variation of REE (rare earth elements) patterns in soil-grown plants: a new proxy for the source of rare earth elements and silicon in plants, *Plant and Soil*, **Vol. 235**, pp. 53–64, (2001).
7. E. Anders, M. Ebihara, Solar-system abundances of the elements, *Geochim. Cosmochim. Acta*, **Vol. 46**, pp. 2363–2380, (1982).
8. S. R. Taylor, S. M. McLennan, The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks, *Phil. Trans. R. Soc. Lond. A*, **Vol. 301**, pp. 381–399, (1981).

9. H. Ichihashi, H. Morita, R. Tatsukawa, Rare earth elements (REEs) in naturally grown plants in relation to their variation in soils, *Environ. Pollut.*, **Vol. 76**, pp. 157–162, (1992).