A STUDY ON TREE BARK SAMPLES FOR ATMOSPHERIC POLLUTION MONITORING

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ABSTRACT

Tree barks are considered a promising indicator of air pollution monitoring, because of its accumulation of aerosol particles, simplicity of species identification and wide geographical distribution. However, there are no established protocols for its sampling as well as there are no detailed studies on its usability as an alternative or complementary indicator of atmospheric pollution. In this study, barks from very common tree species, Sibipiruna (*Poincianella pluviosa*) and Tipuana (*Tipuana tipu),* were analyzed to define experimental conditions for their use as biomonitor of air pollution. Bark samples collected at the São Paulo city were cleaned and ground for analysis. Instrumental neutron activation analysis (INAA) was applied for the determination of As, Br, Ca, Co, Cr, Fe, K, Sb, Sc and Zn and graphite furnace atomic absorption spectrometry (GF AAS) for Cd and Pb. Results obtained in these analyses indicated that species of trees, bark surface layers taken for analysis as well as tree trunk diameter or tree age should be considered for use tree bark as a biomonitor. Analytical control of results carried out by analyzing certified reference materials demonstrated that INAA and GF AAS techniques can provide reliable data for element concentrations with standardized differences, $|En_{score}| < 1$.

1. INTRODUCTION

Investigations on air pollution and its effects on public health have become important in programs related to the reduction of pollutant levels in many cities of the world and, São Paulo city is no exception.

The use of a biomonitor to evaluate pollution levels should be considered as an additional support to conventional instrumentation currently in use by the governmental agency, the Environmental Company of São Paulo State (CETESB) due to the extension of the São Paulo city, as well as, to serious pollution problems. Thus in order to develop a biomonitoring program it is very relevant to choose a suitable monitor.

With the needs to monitor environmental pollution, the applicability of tree barks for air monitoring purposes is increasing due to its simplicity of sampling without causing damage to the tree, easier sample treatment and tree species identification when compared with other species such as lichens or mosses that often require a specialist in taxonomy

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Tree barks have been employed to evaluate element concentrations in the atmosphere in several publications[1-3] as well as organic compound concentrations[4-6] and radionuclides[7-9].

Furthermore barks from several tree species such as *Jacaranda mimosifolia*[10], pine[6,11], black poplar[12], olive[13], oak[14,15], sargent cherry and sugar maple[16] and *F. Pennsylvanica*[17] have been analyzed to evaluate atmospheric pollutants

Surface layers of tree barks have been used as a potential indicator of air pollution since they retain pollutants directly from the air or from the rainwater running down the stems. And the retention of particulate matter in the bark occurs on a humid, rough or electrically charged surface[18]. According to Schulz et al.[6] the bark surface is considered inert porous and the absence of metabolic processes makes it almost inert in the presence of inorganic and organic substances.

As such, the retention of particulate matter on tree barks may depend on their surface state. Consequently, their element concentrations are dependent on the specific tree species due mainly to differences in bark porosity.

Within this context the present study focused on the evaluation of element pollutants in two arboreal species, Sibipiruna (*Poicianella pluviosa,* DC) and Tipuana (*Tipuana tipu,* Kuntze), for further validation and its use as biomonitors of atmospheric pollution. These two species were chosen since they are most abundant and dominant in urban areas of São Paulo city. However, a deeper insight into properties and capabilities of their barks as indicators of atmospheric pollution has not been published.

This study presents element concentrations obtained in tree barks in order to establish a protocol for sampling suitable species of trees and an adequate bark treatment for analyses. Parameters evaluated were arboreal species, trunk diameters and bark surface layers. Quality control of analytical results and detection limits were also assessed to examine the performance of the instrumental neutron activation analysis (INAA) and graphite furnace atomic absorption spectrometry (GF AAS) methods.

2. MATERIALS AND METHODS

2.1. Sample Collection and Treatment

The two tree species chosen for this study were Sibipiruna (*Poicianella pluviosa*) and Tipuana (*Tipuana tipu*). Their tree barks were collected at the São Paulo University Campus, in São Paulo City, SP, Brazil. Both are the most abundant species in São Paulo city and belong to the Fabaceae family. They are ornamental trees widely found in city´s urban areas along streets, avenues and in parks. The Sibipiruna is a large tree with a height usually between 16-18 m and diameter of the crown up to 6 m. The Tipuana can reach a height of 9 - 12 m and its stem has dark gray bark, roughened surface and fissured.

The bark samples were removed from the trees at chest height of about 1.5 m above ground level and put into paper bags. They were collected from the four faces of the lichen free trunk. If the samples were wet, they were dried in an oven with air circulation at 40 ° C. The bark

layer surface was cleaned using a nylon brush and then 2 mm was removed using a Ti grater. This sample was pulverized for homogenization using an agate-type ball mill (Fritsch, Pulverisette 0) and finally preserved in a desiccator.

2.2. Instrumental Neutron Activation Analysis (INAA) Procedure

To use the comparative method of INAA[19], synthetic element standards were prepared. For this, 50 µL of the element standard solutions were pipetted onto sheets of Whatman No. 40 filter paper. These solutions containing one or more elements were obtained using certified standard solutions provided by Spex Certiprep Chemical, USA. The calibration of all pipettes and volumetric flasks were verified before use. These filter sheets were dried at room temperature inside a desiccator and then placed into clean polyethylene bags and sealed. In these standards, the quantities of each element, in µg (in parentheses) were the following:As(1.5), Br(5.0), Ca(1000.0), Co(0.150), Cr (2.0), Cs(0.60), Fe(360), K (500.0), La(1.0); Rb (10.0), Sb(0.6), Sc(0.10) and Zn(36.0).

The INAA procedure consisted of irradiating about 180 mg of the sample weighed in clean polyethylene bags at the IEA-R1 nuclear research reactor with synthetic standards of elements. Sixteen-hour irradiations under a thermal neutron flux of about 5×10^{12} n cm^{-2} s^{-1} were performed for As, Br, Ca, Co, Cr, Cs, Fe, K, La, Rb, Sb, Sc and Zn determinations. After adequate decay times, the irradiated samples and standards were measured by a hyperpure Ge detector Model GX2020 coupled to a Digital Spectrum Processor DSA 1000, both from Canberra. The resolution (FWHM) of the system was 0.90 keV for 122 keV gamma-ray peak of ^{57}Co and 1.87 keV for 1332 keV gamma ray of ^{60}Co. Counting times from 5,400 to 50,000 seconds were used, based on the half-lives or activities of the radioisotopes considered. Spectra were collected and processed using Canberra Genie 2000 Version 3.1 software. All samples and standards were measured at least twice for different decay times. The radionuclides measured were identified according to their half-lives and gamma-ray energies. The concentrations of elements were calculated by a comparative method. The radionuclides used were: ^{76}As, ^{82}Br, ^{47}Ca, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{59}Fe, ^{42}K, ^{140}La, ^{86}Rb, ^{122}Sb, ^{46}Sc and ^{65}Zn.

2.3.Graphite Furnace Atomic Absorption Spectrometry (GF AAS) Procedure

The GF AAS method[20]was used in the determination of Cd and Pb. Approximately 200 mg of the sample were digested in 4 mL of concentrated HNO_3 and 1 mL of 30 % H_2O_2 in closed perfluoroalcoxi PFA vessels in a digestion block for 3 h at 90 ^{0}C. The digested samples were allowed to cool to room temperature and then diluted with Milli-Q water up to a volume of 25 mL. The blanks were analyzed in the same manner as the samples. A Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer with Zeeman background correction at wavelength of 228.8 nm for Cd and 283.3 nm for Pb were used. EDL Cd and Pb lamps were used in the experiments. The optimized heating programs used for measurements of Cd and Pb are shown in Table 1.

Perkin Elmer pure certified solutions of Cd (1000 ± 3 mg L^{-1}) and Pb (1003 ± 3 mg L^{-1}) were diluted accordingly to obtain a 7.0 ng mL^{-1} and 118.75 ng mL^{-1} stock solutions for Cd and Pb, respectively. These solutions were further diluted by an AS-800 autosampler for construction of Cd and Pb calibration curves. Twenty microliters of the sample solution and ten microliters of matrix modifier ($NH_4H_2PO_4$ 0.5 %) and $Mg(NO_3)_2$ 0.03 % were introduced to the furnace

tube by the autosampler. After the atomization step, Cd and Pb concentrations were obtained and the arithmetic mean of two measurements was used.

Table 1:Graphite furnace program for Cd and Pb determinations

Steps	Temperature (^{o}C)		Time (s) (ramp, hold)		Argon flow (mL/minute)	
	Cd	Pb	Cd	Pb	Cd	Pb
Drying	110	110	1, 30	1, 30	250	250
Ashing	130	130	15, 30	15, 30	250	250
Pyrolis	500	800	10, 20	10, 20	250	250
Atomization	1500	1600	0, 5	0, 5	0	0
Cleaning	2450	2450	1, 3	1, 3	250	250

2.4.Quality Control of the Results

The quality control of the analytical results was evaluated by analyzing certified reference materials CTA-VTL-2 Virginia Tobacco Leaves and INCT-MPH-2 Mixed Polish Herbs both provided by the Institute of Nuclear Chemistry and Technology, Poland. These reference materials were analyzed by applying the same experimental conditions used for tree bark analyses and were evaluated on a dry weight basis, as recommended in their certificates.

3. RESULTS AND DISCUSSION

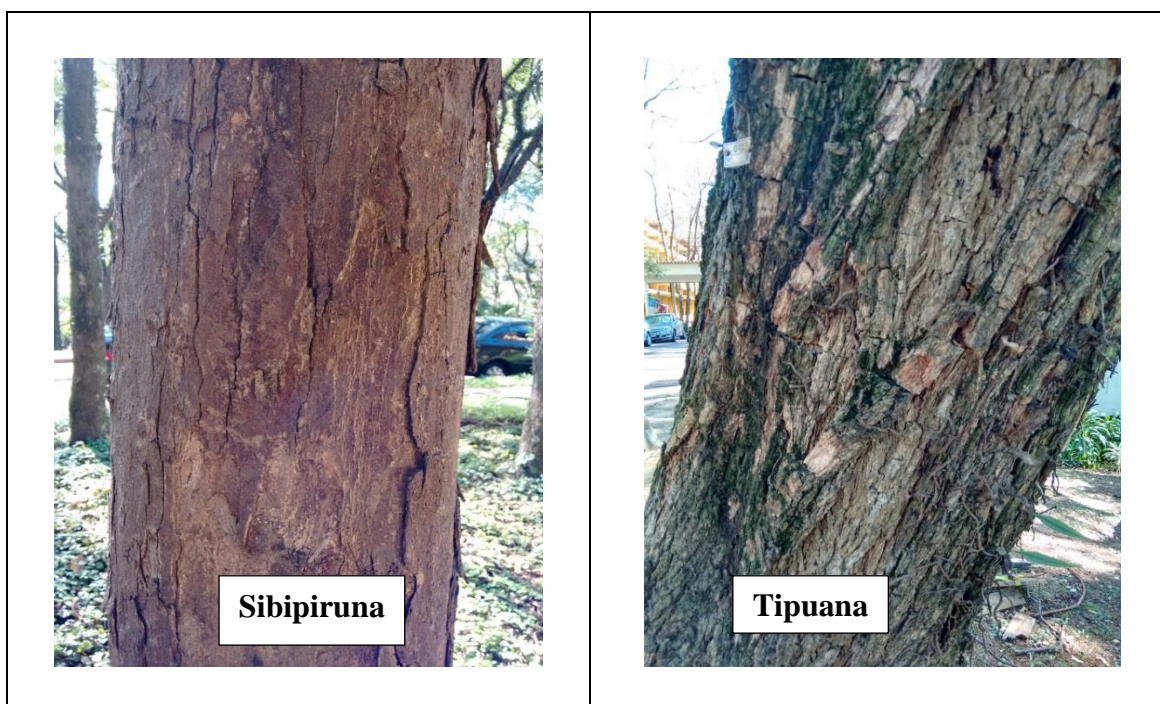### 3.1.Element Concentrations in Sibipiruna and Tipuana Tree Barks

In order to evaluate the differences between the element concentrations retained in barks from Sibipiruna and Tipuana, bark samples were collected in same sampling point, on the same day and from tree trunks of similar diameters. These results shown in Fig. 1 indicate that the Tipuana bark presented higher concentrations of As, Cd, Co, Cr, Fe, La, Pb, Sb, Sc and Zn than those for Sibipiruna. On the other hand, the elements Br, Cs, K and Rb resulted in slightly higher concentrations for Sibipiruna. Calcium concentrations obtained in the barks from these two species were of the same order of magnitude.

According to the results obtained for Sibipiruna and Tipuana bark analyses, the capacity of element retention in these two arboreal species showed differences. Higher element concentrations obtained for Tipuana than those for Sibipiruna can be attributed to the characteristics of the bark surface. The Tipuana bark surface is porous, roughened and fissured while Sibipiruna presents barks in squamous form. Fig. 2 shows trunk bark images of the Sibipiruna and Tipuana tree species. The entrapment and accumulation of elements in tree barks depends on structure porosity. This means that when doing passive or active

biomonitoring studies using tree barks, it is preferable to use only one species, mainly when an accurate comparison is required between the sampling sites.
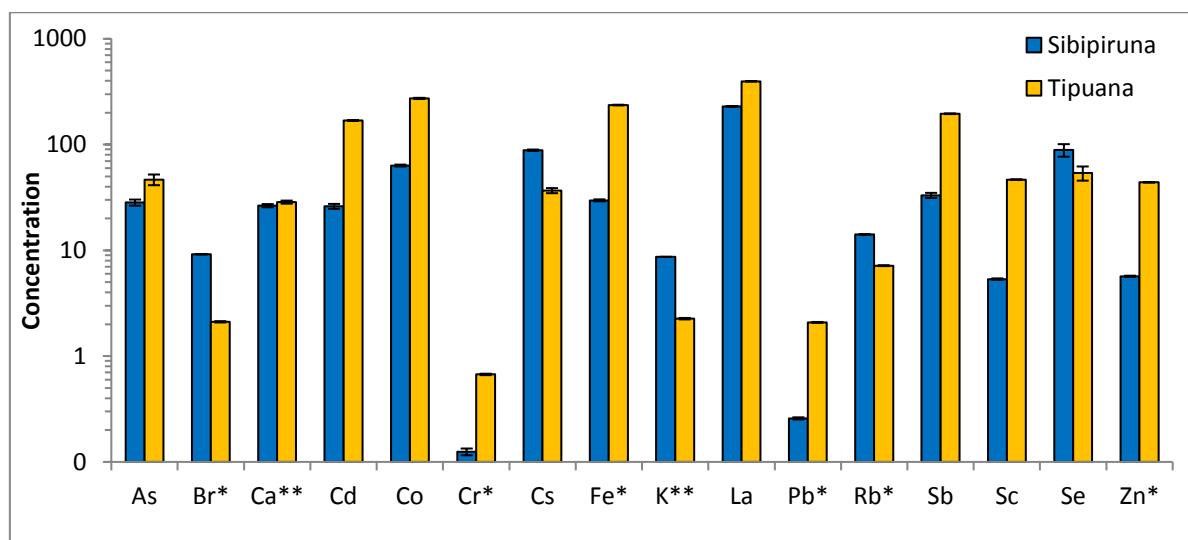
Figure 1: Element concentrations in Sibipiruna and Tipuana tree barks collected at the same sampling point. Concentrations are given in µg kg⁻¹ unless indicated with asterisks (* - indicates concentration in mg kg⁻¹ and ** - in g kg⁻¹).


Figure 2: Bark surfaces of the Sibipiruna and Tipuana trunks

3.2. Element Concentrations in Different Tree Bark Layers

The sample of the outer layer was obtained grating 1 mm thickness of the outer layer. The inner layer was obtained by grating (1mm) of the subsequent layer after removal of the outer layer. A caliper was used to measure the thickness of the layers. Results obtained in different layers of tree bark indicated that most of element concentrations in the outer layer are higher than those found in the inner layer (Fig. 3).

These results are consistent with the results presented by Berlizov et al. [12] and De Bruin and Hackenitz [21]. They found lower element concentrations in inner than those in outer bark layer. Harju et al.[22] also found great variations in element concentrations between different layers of the bark. These results show the importance of obtaining samples from same layer thickness by separating the outer and inner layers. The thickness of the bark can be measured in the laboratory using a caliper or using a bark sampling device with a special coated high speed cutter that allows a standardized removal of the outer bark layer [23].
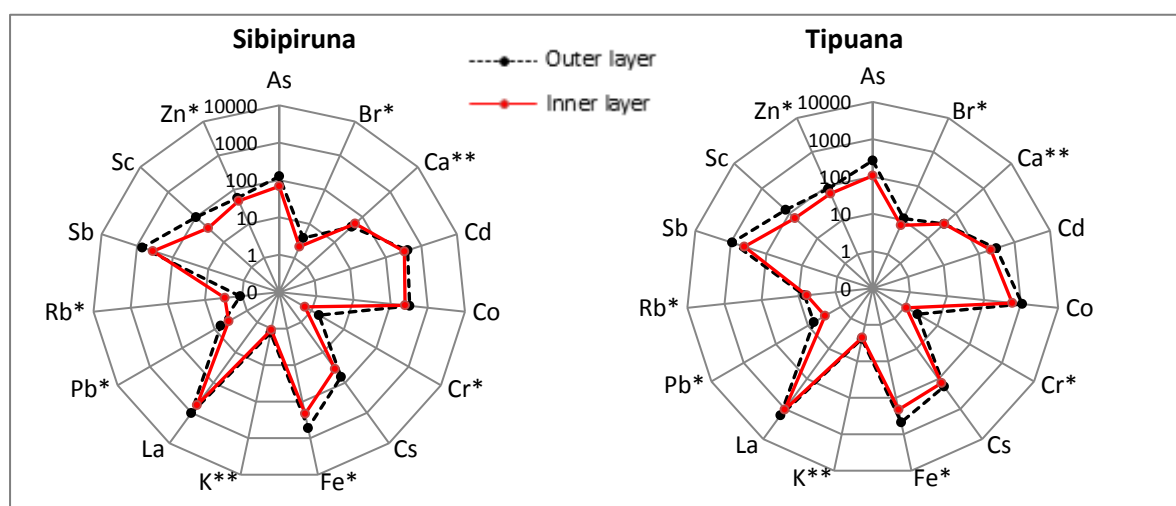
Figure 3: Radar chart of element concentrations in different bark layers of Sibipiruna and Tipuana trees. Concentrations are given in µg kg^{-1} unless indicated with asterisks (* - indicates concentration in mg kg^{-1} and ** - in g kg^{-1}).

3.3. Element Concentrations in Barks of Different Trunk Diameters

The results of the barks from Tipuana tree trunks presenting different diameters are shown in Table 2. These samples were collected at the same day and same site highly polluted by vehicular traffic emissions. The distances between the trees were less than 5 m. As shown in Table 2 when the diameters of the Tipuana tree trunks varied from 50 to 73 cm there was an increase of concentrations for most elements.

Table 2: Element concentrations in barks collected in a polluted sampling site from Tipuana trunks presenting different diameters

Elements	Diameter (D) of the tree trunks		
	D = 50 cm	D = 56 cm	D =73 cm
As, μ kg^{-1}	92.2± 2.1	105.2± 2.6	262.2 ± 5.4
Br, μg g^{-1}	5.87 ± 0.03	12.87 ± 0.05	9.65 ± 0.05
Ca, mg g^{-1}	49.9 ± 1.8	37.1 ± 1.4	34.1 ± 1.3
Cd, μg kg^{-1}	295.2 ± 3.1	355.6 ± 3.4	410.4 ± 1.0
Co, μg kg^{-1}	718.2 ± 7.6	1313± 13	1324 ± 14
Cr, μg g^{-1}	1.08± 0.01	1.75± 0.02	4.86 ± 0.03
Cs, μg kg^{-1}	52.9± 2.5	113.1± 3.0	378.1 ± 4.7
Fe, μg g^{-1}	346.3± 2.1	583.1± 3.1	1888.9 ± 8.6
K, mg g^{-1}	0.708± 0.003	1.330 ± 0.004	1.53 ± 0.01
La, μg kg^{-1}	1146.7± 3.3	1734.5± 4.6	3118.9 ± 8.2
Pb, μg g^{-1}	5.19± 0.04	12.01± 0.01	11.98 ± 0.04
Rb, μg g^{-1}	2.15± 0.05	5.00± 0.07	7.68 ± 0.09
Sb, μg kg^{-1}	549.1± 1.9	854.8± 2.7	1027.3 ±3.2
Sc, μg kg^{-1}	88.25± 0.34	124.87± 0.44	427.8 ± 1.3
Zn, μg g^{-1}	102.87± 0.39	113.26± 0.43	121.28 ± 0.46

Concerning the barks from trunks presenting different diameters, the results showed an increase of element concentrations with the diameter. These results are consistent if there is increase of the trunk diameter with the tree age or exposure time. There is possibility of using barks of similar trunk diameters instead of using trees of similar age or exposure time. Ideally, in a monitoring program it would be better to collect samples from trees with the same exposure time or of the same age. However, this is usually no easy task. Unfortunately, studies on diameter growth of Tipuana and Sibipiruna trees with age were not found

3.4. Quality Control of Analytical Results

Results obtained for certified reference materials Virginia Tobacco Leaves Mixed Polish Herbs are presented in Table 3 along with the values of the certificates and the standardized difference or En $_{score}$ values [26]. Since there is no certified reference material of tree barks, these materials were analyzed. The |En $_{score}$| values obtained were lower than 1 indicating that the results are satisfactory and in agreement with the certified values at the confidence level of 95 %. The only exceptions were for As in the reference material Mixed Polish Herbs due to low concentration of this element in the material that results in low statistical counting rate

Table 3: Element concentrations in the certified reference materials Mixed Polish Herbs and Virginia Tobacco Leaves. (Concentrations are given with respective expanded uncertainties corresponding to 95% confidence level)

Elements	INCT-MPH-2 Mixed Polish Herbs			CTA-VTL-2 Virginia Tobacco Leaves		
	This study[a]	Values of the Certificate [24]	En score	This study	Values of the Certificate [25]	En score
As, $\mu g\ kg^{-1}$	151± 44	191 ± 23	-1.23	887 ± 218	969 ± 72	-0.36
Br, $\mu g\ g^{-1}$	8.50 ± 1.62	7.71 ± 0.61	0.46	16.5 ± 3.0	14.3 ± 1.4	0.66
Ca, %	1.070 ± 0.086	1.08 ± 0.07	-0.09	3.58 ± 0.22	3.58 ± 0.01	-0.08
Cd, $\mu g\ kg^{-1}$	205 ± 17	199 ± 23	0.33	1525 ± 26	1520 ± 170	0.031
Co, $\mu g\ kg^{-1}$	216 ± 34	210 ± 25	0.14	426 ± 37	429 ± 26	-0.05
Cr, $\mu g\ g^{-1}$	1.85 ± 0.32	1.69 ± 0.13	0.46	2.09 ± 0.44	1.87 ± 0.16	0.47
Cs, $\mu g\ kg^{-1}$	73.9 ± 10.7	76.0 ± 7.0	-0.17	527 ± 50	515 ± 46	0.18
Fe, $\mu g\ g^{-1}$	523 ± 20	(460)[b]	-	1116 ± 80	1083 ± 33	0.38
K, %	1.95 ± 0.15	1.91 ± 0.12	0.23	1.07 ±0.14	1.03 ± 0.04	0.30
La, $\mu g\ kg^{-1}$	533 ± 116	571 ± 46	-0.30	1012 ± 134	1010 ± 100	0.01
Pb, $\mu g\ g^{-1}$	1.98 ± 0.30	2.16 ± 0.16	-0.64	22.4 ± 1.4	22.1 ± 1.2	0.24
Rb, $\mu g\ g^{-1}$	10.8 ± 0.7	10.7 ± 0.7	0.12	48.5 ± 2.0	48.6 ± 2.3	-0.03
Sb, $\mu g\ kg^{-1}$	63.2 ± 9.6	65.5 ± 9.1	-0.17	309 ± 42	312 ± 25	-0.06
Sc, $\mu g\ kg^{-1}$	119 ± 12	123 ± 9	-0.27	315 ± 15	(268)	-
Zn, $\mu g\ g^{-1}$	33.8 ±2.6	33.5 ± 2.1	0.09	44.2 ± 1.3	43.3 ± 2.1	0.36

a.Arithmetic mean and expanded uncertainty from 3 to 7 determinations; b. Numbers in parenthesis indicate informative values.

3.5 Sample Homogeneity and Limits of Detection and of Determination

Results of replicate analyses of a tree bark sample (Table 4) showed reproducibility with relative standard deviations varying from 0.7 to 4.5 %. Detection and determination limits for tree bark analyses were evaluated according to Currie [27, 28] for INAA and to Welz and Sperling[20] for GF AAS and these values shown in Table 6 indicate that both methods present high and enough sensitivity for tree bark sample analyses.

Table 4: Replicate analyses of a sample of Tijuana tree bark and detection and determination limit values

Elements	M ± SD[a] (RSD)[b]	Detection limit	Determination limit
Br, $\mu g\ g^{-1}$	4.05 ± 0.06 (1.5)	0.040	0.130
Ca, $mg\ g^{-1}$	23.6 ± 0.5 (2.1)	0.32	0.98
Cd, $\mu g\ kg^{-1}$	169.0 ±1.2 (0.7)	0.72	2.40
Co, $\mu g\ kg^{-1}$	299± 11 (3.8)	3.6	11.3
Cs, $\mu g\ kg^{-1}$	132.9 ± 5.9 (4.5)	6.3	20
Fe, $\mu g\ g^{-1}$	603 ± 17 (2.8)	2.2	6.8
K, $mg\ g^{-1}$	1.461 ± 0.042 (2.9)	0.0014	0.0042
La, $\mu g\ kg^{-1}$	1246 ± 53 (4.2)	2.0	5.5
Pb, $\mu g\ kg^{-1}$	2080 ± 20 (1.0)	19	63
Rb, $\mu g\ g^{-1}$	5.4 ± 0.1 (0.9)	0.12	0.36
Sb, $\mu g\ kg^{-1}$	679 ± 25 (3.6)	3.2	9.8
Sc, $\mu g\ kg^{-1}$	113.1 ± 1.9 (1.7)	0.36	1.1
Zn, $\mu g\ g^{-1}$	59.4 ± 1.6 (2.7)	0.18	0.56

a. Arithmetic mean and standard deviation; b. Relative standard deviation in %. For Cd and Pb the results are means of two determinations and for other elements three determinations.

3. CONCLUSIONS

The results obtained in this study indicated that element concentrations in tree barks depend on its species since the retention of aerosol matter is dependent on the bark surface porosity. Overall, the results indicated the possibility of using two arboreal species, Sibipiruna and Tipuana although they showed different retention capacity. In this regard in biomonitoring studies, it is important to choose a same tree species or either first to make intercalibration of the element accumulation between the species. Besides, to obtain a representative sample it is relevant to collect barks around the trunk as well as to take the same thickness of outer layer for the analysis since there are differences between outer and inner layer element

concentrations. The grinding process used in preparation of the sample was adequate since the replicate analysis showed homogeneity of prepared sample.

The findings of this preliminary study can be used in the standardization of sampling, in tree bark treatment as well as the INAA and GF AAS procedures presented allow obtaining reliable data for analyzing bark samples.

ACKNOWLEDGMENTS

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