ANALYSIS OF *CANOPARMELIA TEXANA* LICHENS COLLECTED IN BRAZIL BY NEUTRON ACTIVATION ANALYSIS

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Abstract

The accumulation of elements by lichens is well known. Therefore analyses of lichen samples have been carried out in order to use this kind of material in environmental studies. In this work, the epiphytic lichen *Canoparmelia texana* collected from the bark of trees was analyzed by instrumental neutron activation analysis. The preparation of samples consisted of cleaning, washing with water, lyophilization and grinding. Elements Al, As, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Eu, Fe, K, La, Lu, Mg, Mn, Mo, Na, Rb, Sb, Sc, Se, Sm, Tb, Th, Ti, U, V, Yb, and Zn were determined quantitatively by using short and long irradiations carried out under a thermal neutron flux from 10^{11} to 10^{13} n cm^{-2} s^{-1} in the IEA-R1 nuclear reactor. Radioactivity measurements were performed by using a hyperpure Ge detector. Results obtained by analyzing a sample of *Canoparmelia texana* species in replicates revealed a good precision with relative standard deviations varying from 0.5 to 15%. Also the precision and the accuracy of the method were evaluated by analyzing reference materials IAEA 336 Lichen, NIST 1575 Pine Needles and 1572 Citrus Leaves. In order to study the influence of age of the lichen, in the collection, the center and outer fraction of each sample were collected separately. For some elements the center of the lichen sample presented slightly higher concentrations than the outer fraction, indicating that the accumulation of the elements increases with the lichen age or with the length of exposure. Results obtained for lichens collected from different trees from the same sampling area showed relative standard deviations varying from 20 to about 60%.

1. INTRODUCTION

In the last years, studies on environmental pollution by trace elements have gained increasing concern and lichens have been analyzed for assessing the baseline levels of pollutants and for identifying contamination sources.

However in Brazil analytical data of pollutants obtained using biomonitors are very scarce. Most of our environmental data have been obtained by application of direct measurements by analyzing air, water or soil and this fact is requiring enormous efforts due to the great extension of the country and to the serious problems of pollution encountered, specially in big cities like São Paulo.

Consequently studies concerning trace element determinations in lichens are of great interest due to several advantages related to ease of sampling and to the particular capability of metal accumulation presented by this monitor.

Following our studies [1] of determination of trace elements in lichens, by applying neutron activation analysis, this paper presents results obtained in *Canoparmelia texana* (Tuck.) Elix & Hale collected in Brazil. The purpose of this work is to contribute for establishing adequate conditions for sampling and analysis of lichens in a further biomonitoring programme.

2. EXPERIMENTAL

2.1. Selection of lichen *Canoparmelia texana*

In biomonitoring studies, the selection of the species to be analyzed is of primordial importance [2, 3]. The *Canoparmelia texana* (Tuck.) Elix & Hale species selected in this work is an epiphytic lichen from the family of *Parmeliaceae*, very abundant in several parts of Brazilian territory, except the coast. This lichen species presents similar behaviour to *Leucanora conizeoides* (L. pityrea) well known in Europe and it grows in regions relatively polluted where other species are not present due to

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the pollution. These species which show tolerance to air pollution are of great interest to environmental studies. *Canoparmelia texana* species grows on bark of the trees and it is formed of circular thalli with radial growth. Its growth rate depends on the environmental conditions. In general, for foliose species, the growth rate is in the order of 0.5 to 5.0 mm per year [4].

2.2. Sample collection

Samples of *Canoparmelia texana* were collected from the bark of trees, at about 1.5 m from the soil and stored in paper bags. To remove the sample from the bark, a titanium knife was used.

The following samples were collected:

Sample S: About 1.0 g of lichen was collected from a same tree. This sample was used to evaluate the precision of the results that can be obtained in lichen sample analysis.

Samples CF: These samples were collected in order to study the influence of age of the lichens in their contents of the elements. In this case, in the collection, each sample was divided, in two fractions, constituted of center and peripheral parts and their analyses were performed separately.

Samples LQ: Four samples were collected on the same day from four individual trees in the surroundings of IPEN-CNEN/SP, located at the Campus of São Paulo University, SP, within an area of about 350 m^2. These samples were analyzed to study the variation in the element concentrations within one sampling site.

2.3. Preparation of the samples for analysis

In order to remove eventual bark substrates or other extraneous materials, the lichen samples were cleaned by using an Olympus zoom stereo microscope model SZ 4045. Then, they were washed in distilled water for about 5 min and placed on filter papers for drying at room temperature. The samples were also freeze-dried for about 8 hours under a pressure of about 4×10^{-2} mbar and in this process a mean weight loss of about 13% was found. The fine powder of lichen sample was obtained by grinding, manually, in an agate mortar.

2.4. Preparation of synthetic standards of elements

Stock solutions of the elements were individually prepared by dissolving metals, oxides or salts of the elements with adequate reagents and then diluted using distilled water in a quartz apparatus. High purity or spectroscopically pure reagents were used to prepare these standard solutions. Single or multielement solutions were prepared by mixing appropriate amounts of stock solutions. These solutions were then pipetted onto sheets of 35 x 12 mm Whatman n° 40 filter paper using an Eppendorf pipette. After drying in a dessicator at room temperature, filter papers were folded, placed into polyethylene bags previously cleaned using diluted HNO_3 solution and distilled water, being these bags heat-sealed.

2.5. Procedure used for neutron activation analysis

About 150 mg of each sample were weighted in polyethylene bags and irradiated together with the standards. Two separate irradiations were performed to determine a large number of elements. Irradiations of 5 minutes under a thermal neutron flux of 4.25×10^{11} n cm^{-2} s^{-1} from the IEA-R1 nuclear reactor were carried out to determine Al, Br, Cl, K, Mg, Mn, Na, Ti, and V. Longer irradiations of 16 hours under a neutron flux of 10^{13} n cm^{-2} s^{-1} were done to determine As, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, Fe, La, Lu, Mo, Rb, Sb, Sc, Se, Sm, Tb, Th, U, Yb, and Zn.

Irradiated samples and standards were placed on stainless steel planchets and after adequate decay times, they were measured using an EG & G Ortec Model GMX20190 Ge detector with a resolution (FWHM) of 0.80 keV at 122 keV [57]Co and 1.80 keV at 1332 keV [60]Co. The detector was coupled to an EG & G Ortec 918A Multichannel Buffer and this one to a microcomputer. Samples and standards were measured at least twice after different decay times. Analyses of gamma spectra were carried out by using VISPECT [5] software and the concentrations of the elements were calculated by comparative method.

TABLE I. ELEMENTAL CONCENTRATIONS IN *CANOPARMELIA TEXANA*
(Concentrations in µg/g unless otherwise indicated)

Element	Sample S (r = 1)		Sample LQ (r = 4)		
	Mean ± s	(n)[b]	Mean ± s	$S_{r (\%)}$	Range
Al	2120 ± 125	(3)	3433 ± 415	12.1	3140 - 3727
As (µg/kg)	769 ± 7	(3)	904 ± 496	54.9	272 - 1347
Br	16.3 ± 2.9	(5)	10.2 ± 6.7	65.6	2.5 - 14.8
Ca (%)	2.96 ± 0.25	(3)	4.5 ± 2.5	56.9	3.5 -17.7
Cd (µg/kg)	1486 ± 95	(3)	2495 ± 1326	52.0	978 - 3727
Cl	520 ± 15	(5)	243 ± 81	33.0	181 - 362
Co (µg/kg)	1745 ± 238	(3)	1720 ± 558	32.4	1003 - 2257
Cr	4.6 ± 0.2	(2)	5.3 ± 2.9	54.5	2.1 - 7.7
Cs (µg/kg)	193 ± 4	(3)	202 ±127	62.8	75 - 340
Cu	11.1 ± 1.9	(3)	19.2 ± 8.1	42.2	14 - 25
Eu (µg/kg)	68 ± 3	(3)	61 ± 32	52.0	31 - 90
Fe	1598 ± 44	(3)	1732 ± 1089	62.9	971 - 2747
K	1666 ± 51	(3)	1477 ± 484	32.8	846 - 1926
La	3.41 ± 0.05	(3)	3.0 ± 1.4	48.0	1.7 – 4.4
Lu(µg/kg)	17.9 ± 2.1	(3)	16.4 ± 10.7	65.2	8.2 - 26.5
Mg	1419 ± 204	(5)	1122 ± 694	61.2	283 - 1946
Mn	70 ± 4	(5)	103.9 ± 56.3	54.4	41.6 - 148.1
Mo	1.07 ± 0.12	(3)	0.94 ± 0.26	27.2	0.68 - 1.17
Na	127 ± 7	(5)	61.6 ± 19.3	31.3	35 - 76
Nd	2.21 ± 0.01	(3)	2.2 ± 1.0	46.9	1.2 - 3.2
Rb	9.37 ± 0.03	(2)	6.7 ± 3.1	46.0	3.8 - 9.9
Sb (µg/kg)	455 ± 21	(3)	536 ± 243	45.3	245 - 774
Sc (µg/kg)	277 ± 26	(3)	324 ± 208	64.2	118 - 515
Se (µg/kg)	245 ± 32	(3)	322 ± 175	54.4	116 - 487
Sm (µg/kg)	339.6 ± 3.3	(3)	310 ± 165	53.1	164 - 477
Tb (µg/kg)	44.3 ± 3.2	(3)	43.6 ± 23.1	52.9	22 - 66
Th (µg/kg)	525 ± 27	(3)	535 ± 358	66.9	194 - 922
Ti	179 ± 11	(5)			
V	5.5 ± 0.4	(5)	5.0 ± 2.7	53.1	2.2 - 8.0
Yb (µg/kg)	96 ± 14	(3)	96.3 ± 51.9	53.9	49 - 152
Zn	98.0 ± 1.2	(3)	99.6 ± 32.4	32.5	68 - 135

a - r indicates number of samples analyzed

b - n indicates number of determinations

2.6. Analysis of certified reference materials

Three certified reference materials, IAEA 336 Lichen, NIST 1572 Citrus Leaves and NIST 1575 Pine Needles were analyzed for the evaluation of the accuracy of the method. They were analyzed by applying the same experimental conditions used in lichen analyses. The moisture content in these reference materials was ascertained by drying in accordance with the producer's recommendations. The following values (in percent) of the weight loss were found and used for correcting the final results: 7.1 for Lichen, 4.9 for Citrus Leaves and 5.2 for Pine Needles.

3. RESULTS AND DISCUSSION

Table 1 presents results obtained by analyzing sample S, in replicates, as well as the results found in four samples codified LQ. Results obtained for sample S show a good precision for most of elements with relative standard deviations varying from 0.3 to 14.6%. These findings indicate that the procedure adopted for lichen sample preparation and homogenization was adequate. The results

TABLE II - ELEMENTAL CONCENTRATIONS IN TWO FRACTIONS OF SAMPLES CF (C- CENTRAL FRACTION, F- PERIPHERAL FRACTION)
(Results in µg/kg unless otherwise indicated)

Elements	CF 1		CF 2		CF 3		CF 4		CF 5	
	C 1	F 1	C 2	F 2	C 3	F 3	C 4	F 4	C 5	F 5
Al (µg/g)	1099 ± 10[a]		3410 ± 63	2056 ± 28	1431 ± 56	631 ± 24	2544 ± 49	1393 ± 20	3187 ± 54	927 ± 14
As	914 ± 11		982 ± 9	846 ± 10	563 ± 9	304 ± 7	879 ± 7	607 ± 7	876 ± 10	684 ± 10
Ca (%)	8.99 ± 0.07		12.31 ± 0.09	9.07 ± 0.06	13.13 ± 0.09	9.27 ± 0.07	5.26 ± 0.04	4.01 ± 0.03	4.80 ± 0.03	2.03 ± 0.01
Cd (µg/g)	3.3 ± 0.2	2.3 ± 0.1	2.7 ± 0.1	2.5 ± 0.1	2.4 ± 0.1	1.4 ± 0.1	3.1 ± 0.2	2.1 ± 0.1	2.5 ± 0.2	1.2 ± 0.1
Ce	8367 ± 24	5616 ± 16	7003 ± 20	5156 ± 19	3532 ± 16	1817 ± 13	6935 ± 25	3996 ± 14	7469 ± 21	2521 ± 14
Cl (µg/g)	208 ± 1	176 ± 5	265 ± 7	166 ± 4	143 ± 4	172 ± 4	210 ± 9	186 ± 4	224 ± 5	158 ± 3
Co	1570 ± 6	1739 ± 22	639 ± 10	1793 ± 27	1949 ± 30	1258 ± 18	1452 ± 21	1452 ± 21	1465 ± 21	1314 ± 19
Cr	8691 ± 70	5186 ± 45	7410 ± 56	6379 ± 51	4371 ± 40	2116 ± 24	6975 ± 56	4604 ± 40	7490 ± 60	3711 ± 32
Cs	260 ± 5	159 ± 4	405 ± 6	358 ± 5	139 ± 4	128 ± 4	188 ± 4	127 ± 3	308 ± 4	192 ± 3
Eu	100 ± 1	66 ± 1	81 ± 1	55 ± 1	40 ± 1	39 ± 1	71 ± 1	43 ± 1	84 ± 1	32 ± 1
Fe (µg/g)	3007 ± 22	1844 ± 13	2616 ± 17	1893 ± 13	1027 ± 7	480 ± 4	1656 ± 11	974 ± 7	1865 ± 13	675 ± 5
K (µg/g)	1497 ± 10	1249 ± 12	2380 ± 12	3611 ± 21	4411 ± 176	4116 ± 17	2538 ± 11	3623 ± 15	3516 ± 21	4888 ± 24
La	4647 ± 21	2935 ± 15	3640 ± 16	2657 ± 13	2011 ± 10	942 ± 6	3355 ± 12	2062 ± 9	4161 ± 15	1378 ± 7
Lu	28.3 ± 0.3	17.8 ± 0.2	24.8 ± 0.2	16.1 ± 0.3	12.4 ± 0.3	5.0 ± 0.3	20.4 ± 0.2	10.5 ± 0.2	18.7 ± 0.3	10.4 ± 0.3
Mg (µg/g)	1372 ± 177	1197 ± 149	1617 ± 172	1413 ± 148	796 ± 112	778 ± 89	1736 ± 149	1161 ± 119	1703 ± 165	1078 ± 104
Mn (µg/g)	108 ± 1	124 ± 2	116 ± 1	130 ± 2	54.3 ± 0.6	49.1 ± 0.6	85 ± 1	117 ± 1	103 ± 1	96 ± 1
Mo	1630 ± 101	1119 ± 79	1394 ± 85	1102 ± 74	757 ± 71	449 ± 62	829 ± 69	631 ± 63	893 ± 82	408 ± 63
Nd	3368 ± 41	2237 ± 30	2464 ± 32	1801 ± 40	1225 ± 43	670 ± 43	2525 ± 33	1399 ± 28	2664 ± 39	1019 ± 61
Rb (µg/g)	7.9 ± 0.1	6.4 ± 0.1	14.5 ± 0.2	18.9 ± 0.2	8.2 ± 0.1	8.4 ± 0.1	11.9 ± 0.2	14.3 ± 0.2	10.7 ± 0.1	11.4 ± 0.12
Sb	763 ± 4	525 ± 3	574 ± 3	490 ± 3	284 ± 2	161 ± 3	466 ± 2	352 ± 2	480 ± 3	244 ± 2
Sc	539 ± 2	331 ± 1	460 ± 2	321 ± 1	195 ± 1	190.4 ± 0.9	359 ± 2	194 ± 1	416 ± 2	136.8 ± 0.7
Se	435 ± 20	316 ± 16	379 ± 20	317 ± 17	245 ± 17	202 ± 15	331 ± 17	210 ± 11	311 ± 17	183 ± 13
Sm	544.7 ± 0.8	376.8 ± 0.8	403.4 ± 0.9	291.8 ± 0.7	206.2 ± 0.7	105.6 ± 0.5	347.2 ± 0.8	208.1 ± 0.5	413.1 ± 0.9	149.5 ± 0.6
Tb	78 ± 3	49 ± 3	57 ± 3	41 ± 3	32 ± 3	29 ± 3	54 ± 3	24 ± 2	63 ± 3	20 ± 2
Th	971 ± 3	561 ± 2	760 ± 3	593 ± 3	315 ± 2	137 ± 2	601 ± 3	334 ± 2	693 ± 3	210 ± 2
Ti (µg/g)	220 ± 37	132 ± 22	302 ± 36	163 ± 21	200 ± 16	39 ± 8	178 ± 28	131 ± 19	220 ± 29	81 ± 17
U	197 ± 14	195 ± 17	179 ± 15	135 ± 13	128 ± 13	71 ± 10	150 ± 13	107 ± 12	180 ± 15	69 ± 11
V (µg/g)	2.9 ± 0.2	2.1 ± 0.1	7.6 ± 0.4	4.5 ± 0.2	2.6 ± 0.2	1.12 ± 0.08	6.2 ± 0.4	3.8 ± 0.2	5.9 ± 0.4	2.5 ± 0.2
Yb	203 ± 6	119 ± 4	168 ± 4	116 ± 5	85 ± 6	57 ± 5	150 ± 6	82 ± 4	130 ± 5	148 ± 5
Zn (µg/g)	113.7 ± 0.5	117.2 ± 0.5	131.9 ± 0.6	165.8 ± 0.8	115.5 ± 0.5	106.3 ± 0.5	121.8 ± 0.4	137.5 ± 0.5	111.4 ± 0.5	97.3 ± 0.4

a- uncertainty calculated using statistical counting errors of sample and standard.

TABLE III: ELEMENTAL CONCENTRATIONS IN REFERENCE MATERIALS

Element	Reference material [a]	This work [c]	Ref. [6-7]	Element	Reference material [a]	This work [c]	Ref. [6-7]
Al (μg/g)	1	702 ± 18	680(570 - 780)[b]	Tb (μg/kg)	1	17 ± 3	7-13[b]
	2	112 ± 11	92 ± 15		2	9.5 ± 0.1	
					3	4.4 ± 0.4	(5)
As(μg/kg)	1	699 ± 25	640(650-720)	Yb(μg/kg)	1	37.1 ± 1.8	
	2	3174 ± 44	3100 ± 300		2	8.37 ± 0.06	
	3	196 ± 14	210 ± 40		3	11.9 ± 1.4	12[b]
Br (μg/g)	1	11± 1	12.9(11.2-14.6)	Lu (μg/kg)	1	6.5 ± 0.7	
	2	7.7 ± 1.3	8.2[b]		2	1.3 ± 0.4	
	3	6.9 ± 0.3	9 [b]		3	1.85 ± 0.26	2[b]
Ca (μg/g)	1	2895 ± 100	2600(2400-3300)[b]	Mg (μg/g)	1	721 ± 104	610(500-710)[b]
	2	36179 ±751	31500 ± 1008		2	6249 ± 269	5800 ± 301
	3	4037 ± 134	4100 ± 201				
Cd(μg/kg)	1	172 ± 72	117(100-134)	Mn (μg/g)	1	64.7 ± 2.7	64(57-71)
	3	279 ± 21	<500		2	21 ± 2	23 ± 2
					3	607 ± 47	675 ± 15
Cl (μg/g)	1	1805 ± 77	1900(1650-2200)[b]	Mo(μg/kg)	1	480 ± 42	
	2	395 ± 12	414[b]				
Co(μg/kg)	1	285 ± 28	290(250-330)	Na (μg/g)	1	323 ± 7	320(280-360)
	2	30.2 ± 2.1	20[b]		2	173 ± 4	160 ± 21
	3	177 ± 31	100[b]		3	16.0 ± 1.2	
Cr (μg/g)	1	1100 ± 400	1030(800-1170)[b]	Rb (μg/g)	1	1.80 ± 0.01	1.72(1.52-1.92)
	2	762 ± 26	800 ± 200		2	4.8 ± 0.2	4.84 ± 0.06
	3	2658 ± 152	2600 ± 200		3	11.2 ± 0.3	11.7 ± 0.1
Cs(μg/kg)	1	121 ± 7	110(97-123)	Sb (μg/kg)	1	86 ± 3	73(63-83)
	2	99.0 ± 1.4	98[b]		2	56 ± 9	40[b]
	3	132 ± 5			3	209 ± 14	200[b]
Fe (μg/g)	1	518 ± 23	425(380-470)	Sc (μg/kg)	1	168 ± 11	170(148-192)
	2	99 ± 13	90 ± 9		2	9.8 ± 0.4	10[b]
	3	192 ± 16	200 ± 10		3	38.1 ± 2.3	30[b]
K (μg/g)	1	1940 ± 362	1840(1640-2040)	Se (μg/kg)	1	243 ± 25	220(180-250)
	2	20947± 1454	18200 ± 600		2	51.1 ±6.5	25[b]
	3	4112 ± 476	3700 ± 200		3	73.6 ± 5.1	
La(μg/kg)	1	630 ± 31	660(550-760)[b]	Th (μg/kg)	1	145 ± 9	140(120-160)[b]
	2	182 ± 27	190[b]		2	13.6 ± 1.3	
	3	190 ± 15	200[b]		3	38.5 ± 2.9	37 ± 3
Ce(μg/kg)	1	127 ± 5	127(109-144)	Ti (μg/g)	1	69.7 ± 8.7	
	2	388 ± 46	280[b]				
Nd(μg/kg)	1	762 ± 68	(500-1000)[b]	U (μg/g)	3	19.1 ± 1.2	20 ±4
	2	279 ± 10					
Sm(μg/k)	1	110 ± 8	106(92-120)	V (μg/g)	1	1.42 ± 0.08	1.5(1.2-1.7)[b]
	2	52.1 ± 3.4	52[b]				
	3	28 ± 1	30[b]				
Eu(μg/kg)	1	24.7 ± 1.8	23(19-27)[b]	Zn (μg/g)	1	34.3 ± 2.1	31.5(28-35)
	2	11.7 ± 1.2	10[b]		2	30.6 ± 1.1	29 ± 2
	3	6.4 ± 0.8	6[b]		3	65.6 ± 9.9	

a – 1- IAEA 336 Lichen; 2- NIST 1572 Citrus Leaves; 3- NIST 1575 Pine Needles.

b - indicates information values

c – mean and standard deviation obtained in n determinations (3≤n≤5)

obtained for sample LQ exhibit considerable variability of the elemental concentrations within one sampling area. The relative deviations of these results varied from 12 to about 60%.

Analytical results obtained for samples CF presented in Table II show that most the elements present slightly higher concentrations in the central fraction than in the peripheral part. For the elements Co, K, Mn, Rb, and Zn both of the fractions presented very close concentrations. These results indicate that the accumulation of the elements in *Canoparmelia texana* increases with the lichen age or with the length of exposure. Therefore the variation of the element concentrations in *Canoparmelia texana* within one sampling site may probably be reduced by collecting samples with the same age or the same length of exposure.

The analytical results for IAEA 336 Lichen, NIST 1572 Citrus Leaves and NIST 1575 Pine Needles are given in Table III together with literature values for comparison. Most of our results are in good agreement with these certified values with relative errors lower than 15%. The less accurate result was obtained for Al in NIST 1572 Citrus Leaves reference material. For some elements there are no certified values and in these cases, results presented here constitute a contribution for their certification. Also the relative standard deviations obtained for most elements in reference materials were lower than 15% which is generally considered a good result in trace analysis.

Results obtained in this work indicated the feasibility in using *Canoparmelia texana* as bioindicator of environmental pollution. From the results obtained for precision and accuracy it was confirmed that instrumental neutron activation analysis is one of the most adequate method for environmental studies.

ACKNOWLEDGEMENTS

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