# DETERMINATION OF TRACE ELEMENTS IN LICHEN SAMPLES BY NEUTRON ACTIVATION ANALYSIS

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***Abstract***

*Epiphytic lichens have been used as bioindicators of environmental pollution studies because of their ability to accumulate metals present in the atmosphere at very low concentrations. In this work, experimental conditions for collection and preparation of the lichen samples as well as the experimental procedure for neutron activation analysis were established in order to obtain reliable and useful data for environmental monitoring purposes.*

*Lichen samples were collected from the barks of trees. They were first examined in a stereo microscope, cleaned and then they were washed with water, freeze-dried and ground for analysis. Out of the five species Usnea sp, Parmotrena tinctorum, Canoparmelia caroliniana, Parmotrema sancti-angeli and Canoparmelia texana analysed, the latter was chosen for this work since this species is very abundant on the Brazilian territory except for the coast.*

*The samples and synthetic standards of elements were irradiated at the IEA-R1 nuclear reactor and the concentrations of the elements Al, As, Br, Ca, Cd, Cl, Co, Cr, Cs, Fe, K, lanthanides, Mg, Mn, Na, Rb, Sb, Sc, Se, Th, U, V and Zn were determined by using short and long irradiations. Results obtained in the washed and unwashed lichen samples showed that the cleaning with water can be used in order to eliminate adhering materials. Indeed, most of elements of interest for the environmental contamination accumulated by the lichens were not removed. The study of the influence of the age of the lichen indicated that its elemental concentrations increase with its age or with the length of exposure. Results obtained for lichens collected from four different trees in the same sampling area varied from about 3.4 to 50%. The homogeneity of the sample was checked by analyzing replicates. The precision and the accuracy of the method were evaluated by analyzing IAEA 336 Lichen and NIST 1752 Citrus Leaves.*

## 1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

In Brazil, environmental pollution is a problem of increasing concern. The evaluation of the baseline levels of toxic elements and the identification of polluted areas including sources are of great interest for the environmental control authorities.

However, analytical data of trace elements pollutants obtained by using plants as biomonitors are very scarce in Brazil. Most of our environmental data are obtained by applying direct measurements in analyzing air, water or soil. This fact requires huge efforts and investments due to the great extension of the country and to the serious problems of pollution encountered, especially in big cities like São Paulo or in industrialised areas.

Taking all the above into consideration, the objective of this project is to select one or more species of suitable lichens in order to obtain baseline data of elemental concentrations in lichens from several sites with different levels of environmental contamination.

At the Radiochemistry Division of our Institute, neutron activation analysis has been actively applied for researching and monitoring of toxic and essential trace elements in biological and environmental samples.

Several biological reference materials and plant materials have been analyzed in our laboratory. Chaparro et al.[1] have analysed IAEA-336 Lichen reference material and IAEA-359 cabbage as a contribution for their certification. Also, Machado et al [2] have analysed rare earth elements in the biological reference materials Pine Needles and Spruce Needles. For quality control of the results, the Radiochemistry Division [3] has analyzed several certified reference materials such as NIST Citrus Leaves, Bowen's Kale, NIES Human Hair, SHINR-HH Human Hair, NIST Bovine Liver and Mixed Human Diet.

Biomonitors are also analyzed in our laboratory. Schuch et al.[4] determined 26 elements and natural radionuclides in environmental samples (soils, marine sediments, algae, lichens and moss) from the Brazilian Antarctic Station located in the Antarctic Peninsula. Recently, Saiki et al [5] determined 32 elements in epiphytic lichen *Canoparmelia texana* in order to compare between the results obtained for washed and unwashed samples as well as those samples collected in two different periods and from individual palm trees.

The Research Contract Projects under IAEA already developed at our Division are: **a.** "Application of neutron activation analysis to the monitoring of trace elements in Brazilian foodstuffs", **b.** "Monitoring of trace elements in environmental samples by neutron activation analysis" and **c.** "Determination of total mercury and methylmercury in human hair by radiochemical methods of analysis".

The present project is being developed in collaboration with the Instituto de Botânica da Secretaria do Meio Ambiente do Estado de São Paulo, SP.

## 2. METHODS

### 2.1. Collection of lichen samples and preparation for analysis

Lichen samples were carefully collected from the barks of trees at the height of about 1.5 m from the ground using a titanium knife and stored in paper bags. In the laboratory the samples were firstly examined under an Olympus zoom stereo microscope model SZ4045 and cleaned in order to remove eventual bark substrates or extraneous materials. Then, they were washed in distilled water to remove dust and sand. In this washing procedure the lichen samples were immersed in the water for about 5 min and then they were placed on filter papers to be freeze- dried for 16 h under a pressure of about $4.10^{-2}$ mbar. The fine powder of lichen sample was obtained by manual grinding in an agate mortar.

### 2.2. Samples collected for this work

Lichen samples utilized in this work were collected mainly from the palm trees at the Campus of the University of São Paulo, SP and in Jardim Botânico located inside State Park of Fontes do Rio Ipiranga, SP. The following species of epiphytic lichens were collected: *Canoparmelia texana* (Tuck) Elix & Hale, *Canoparmelia caroliniana* (Nylander) Elix & Hale, *Parotrema sancti angeli* (Lynge) Hale, *Parmotrema tinctorum* (Nylander) Hale and *Usnea sp*.

### 2.3. Procedure for instrumental neutron activation analysis

About 100 to 150 mg of material were weighed in polyethylene envelopes previously washed in diluted nitric acid solution and distilled water. The standards were prepared by pippeting aliquots of 50 or 100 μL of multielement or single element standards onto a small sheet of Whatman No. 41 filter paper.

Samples and standards were irradiated together at the IEA-R1 research nuclear reactor. Short irradiations of 5 min for determining Al, Cl, Mg, Mn, Na, Ti and V were carried out by using a pneumatic transfer system facility under a thermal neutron flux of $4.10^{11} n.cm^{-2}.s^{-1}$. Long irradiations of 16 h under a thermal neutron flux of about $10^{13}$ n $cm^{-2}$ $s^{-1}$ were for As, Br, Ca, Cd, Co, Cr, Cs, Fe, Hf, K, lanthanides, Rb, Sb, Sc, Se, Th, U and Zn determinations. After adequate decay times, gamma ray measurements were performed using a hyperpure Ge detector. Samples and standards were measured at least twice after different decay times. Analyses of gamma spectra were carried out using appropriate software and the elemental concentrations were calculated by comparative method.

## 3. RESULTS AND DISCUSSION

### 3.1. Analysis of different lichen species

Results obtained in the five lichen species collected in the Jardim Botânico presented in TABLE I indicate that *C. caroliniana* shows that the concentration means of various elements are slightly higher than those obtained by other four species: *C. texana, P. tinctorium, P. sancti angeli* and *Usnea sp. C. texana* was chosen for this work since it is very abundant in several parts of Brazilian territory with the exception of the coast. Also this species has the same behaviour as *Lecanora conizaeoides* (L. pityrea) well known in Europe and it grows in relatively polluted regions where other species are not present. The species showing tolerance to air pollution are of great interest for environmental studies. The *C. texana* is an epiphytic lichen from the family of Parmeliaceae and it grows on tree barks and on rocks. This foliose species is formed of circular thalli with radial growth and its growth rate depends on the environmental conditions

### 3.2. Analysis of washed and unwashed lichen

TABLE II shows the results obtained from washed and unwashed lichens collected from the same palm tree. The unwashed sample presented concentrations of most elements of the same magnitude or slightly higher than the washed ones. However, within the experimental errors these results show no significant difference, with the exception of the following elements: Al, K, Na, Se and Ti. These results indicate that the washing procedure can be used to eliminate adhering materials, since most of the elements retained by the lichens and which are of interest for environmental contamination were not removed. The results of analytical reproducibility presented in TABLE II indicate a good precision for most of the elements, with relative standard deviations varying from 3.6 to 15%. These findings indicate that the procedure adopted for lichen sample preparation and homogenization was adequate.

### 3.3. Analyses of lichen samples with different ages or lengths of exposure

Samples collected in order to study the influence of the age of the lichen on their contents of the elements were codified CF. The results obtained in five CF samples presented in TABLE III show that most elements present slightly higher concentrations in the central fraction than in the peripheral part. For the elements Co, K, Mn, Rb and Zn both fractions presented very close concentrations. These results indicate that the accumulation of the elements in C. texana increases with the age of the lichen 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 of the same age or with the same length of exposure.

### 3.4. Analysis of samples collected from different individual trees

In order to evaluate the variation in the elemental concentrations in lichens collected within one sampling site of about 350 $m^2$, four lichen samples were collected from individual palm trees and analyzed. TABLE IV shows the means and range values of the elemental concentrations obtained for samples from different trees. In general, the relative standard deviations of these results varied from 3.4 to about 50%. In order to reduce this relative standard deviation, it is necessary to increase the number of samples to be collected in the same sampling area.

### 3.5. Analysis of certified reference materials

The analytical results for IAEA 336 Lichen and NIST 1572 Citrus Leaves are given in Table V 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. Also, the relative standard deviations obtained for most elements in reference materials were lower than 15% generally considered a good result in trace analysis.

Results obtained in this work indicated the feasibility in using C. texana as biomonitor 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.

## ACKNOWLEDGMENTS

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TABLE I. ANALYSIS OF DIFFERENT LICHEN SPECIES COLLECTED IN THE JARDIM BOTÂNICO, SP.

| Element | *Canoparmelia texana* | *Canoparmelia caroliniana* | *Parmotrema tinctorium* | *Parmotrema sancti angeli* | *Usnea sp.* |
|---|---|---|---|---|---|
| Al, µg/g | 426 ± 17 | 1640 ± 362 | 748 ± 216 | 981 ± 624 | 876 ± 423 |
| As, µg/kg | 274 ± 7 | 712 ± 103 | 287 ± 91 | 455 ± 40 | 923 ± 261 |
| Br, µg/g | 1.3 ± 0.4 | 15.6 ± 0.9 | 10 ± 6 | 6 ± 2 | 11 ± 7 |
| Ca, % | 1.96 ± 0.06 | 5.2 ± 1.7 | 0.23 ± 0.06 | 1.1 ± 0.2 | 0.8 ± 0.6 |
| Cd, µg/g | 0.80 ± 0.04 | 1.9 ± 0.7 | 0.51 ± 0.05 | 0.44 ± 0.07 | 0.8 ± 0.3 |
| Ce, µg/g | 1.70 ± 0.01 | 4.0 ± 0.9 | 0.24 ± 0.06 | 1.9 ± 1.0 | 3.1 ± 0.5 |
| Cl, µg/g | 499 ± 11 | 357 ± 37 | 386 ± 183 | 718 ± 202 | 139 ± 9 |
| Cr, µg/g | 1.76 ± 0.02 | 5.62 ± 0.05 | 3.6 ± 1.3 | 5.1 ± 3.1 | 4.7 ± 3.1 |
| Fe, µg/g | 366 ± 3 | 1515 ± 357 | 764 ± 333 | 1016 ± 565 | 1078 ± 787 |
| K, µg/g | 1491 ± 72 | 709 ± 315 | 2477 ± 681 | 2216 ± 638 | 3452 ± 1013 |
| La, µg/g | 0.936 ± 0.04 | 2.4 ± 0.5 | 1.1 ± 0.3 | 0.96 ± 0.35 | 1.7 ± 0.3 |
| Mg, µg/g | 570 ± 54 | 696 ± 140 | 484 ± 117 | 734 ± 166 | 882 ± 72 |
| Mn, µg/g | 11.4 ± 0.2 | 43 ± 29 | 17 ± 8 | 14 ± 3 | 25 ± 5 |
| Na, µg/g | 33.9 ± 0.8 | 89 ± 20 | 48 ± 7 | 58 ± 33 | 75 ± 33 |
| Rb, µg/g | 9.1 ± 0.1 | 5.1 ± 0.6 | 12 ± 2 | 22 ± 2 | 15 ± 4 |
| Sb, µg/kg | 192 ± 1 | 437 ± 29 | 365 ± 118 | 489 ± 183 | 686 ± 307 |
| Sc, µg/kg | n.d. | 216 ± 5 | 88 ± 24 | 163 ± 100 | 221 ± 77 |
| Se, µg/kg | 104 ± 9 | 198 ± 62 | 178 ± 52 | 244 ± 30 | 376 ± 164 |
| Sm, µg/kg | 113 ± 1 | 230 ± 38 | 223 ± 93 | 164 ± 62 | 170 ± 34 |
| Th, µg/kg | 83 ± 1 | 388 ± 47 | 189 ± 76 | 245 ± 158 | 278 ± 216 |
| Ti, µg/g | 47 ± 7 | 114 ± 49 | 71 ± 23 | 105 ± 81 | 103 ± 45 |
| V, µg/g | 1.26 ± 0.08 | 5.3 ± 2.4 | 2.5 ±0.9 | 3.2 ± 1.5 | 3.2 ± 2.6 |
| Zn, µg/g | 66.1 ± 0.2 | 94 ± 38 | 62 ± 20 | 41 ± 2 | 67 ± 13 |

TABLE II RESULTS OF WASHED AND UNWASHED LICHENS

| Element | Lichen Sample | | Variation between Washed and Unwashed (%) | Analytical Reproducibility (%) |
|---|---|---|---|---|
| | Washed | Unwashed | | |
| Al, µg/g | 1629 ± 68 | 1947 ± 84 | 16.3 | 6.1 |
| As, µg/kg | 375 ± 5 | 408 ± 4 | 8.0 | 9.6 |
| Br , µg/g | 3.15 ± 0.01 | 2.91 ± 0.01 | 8.2 | 4.8 |
| Ca, % | 4.70 ± 0.03 | 4.54 ± 0.03 | 3.5 | 8.1 |
| Cd, µg/kg | 1099 ± 32 | 1120 ± 42 | 1.9 | 13.7 |
| Cl, µg/g | 428 ± 17 | 510 ± 20 | 1.6 | 4.9 |
| Co,µg/kg | 304 ± 3 | 284 ± 4 | 7.0 | 8.6 |
| Cr , µg/g | 24.1 ± 0.1 | 23.6 ± 0.1 | 2.1 | 4.2 |
| Cs, µg/ kg | 270 ± 4 | 272 ± 5 | 0.7 | 6.2 |
| Fe, µg/g | 938 ± 4 | 877 ± 7 | 6.9 | 9.6 |
| Hf, µg/kg | 345 ± 3 | 322 ± 3 | 7.1 | 8.0 |
| K, µg/g | 1353 ± 14 | 3216 ± 16 | 57.9 | 6.4 |
| La, µg/g | 2.667 ± 0.008 | 2.602 ± 0.008 | 2.5 | 3.6 |
| Ce, µg/g | 4.71 ± 0.04 | 4.74 ± 0.04 | 0.6 | 5.7 |
| Nd, µg/g | 1.88 ± 0.10 | 1.68 ± 0.09 | 11.9 | 9.7 |
| Sm, µg/kg | 268.4 ± 0.5 | 272.3 ± 0.4 | 1.4 | 10.6 |
| Eu, µg/kg | 46.2 ± 0.9 | 45.9 ± 0.9 | 0.6 | 9.8 |
| Tb, µg/kg | 23.9 ± 2.1 | 25.5 ± 2.0 | 6.3 | 12.2 |
| Yb, µg/kg | 56.6 ± 5.0 | 59.3 ± 5.8 | 4.5 | 10.7 |
| Lu, µg/kg | 13.6 ± 0.4 | 14.1 ± 0.4 | 3.5 | 7.9 |
| Mg, µg/g | 864 ± 88 | 988 ± 103 | 12.5 | 14.8 |
| Mn, µg/g | 35.4 ± 0.5 | 37.4 ± 0.5 | 5.3 | 3.6 |
| Na, µg/g | 106 ± 6 | 148 ± 7 | 28.4 | 10.4 |
| Rb, µg/g | 14.0 ± 0.1 | 13.4 ± 0.1 | 4.5 | 10.0 |
| Sb, µg/kg | 410.5 ± 1.4 | 430.3 ± 1.6 | 4.8 | 12.1 |
| Sc, µg/kg | 289.5 ± 0.6 | 289.2 ± 0.8 | 0.1 | 3.3 |
| Se, µg/kg | 178 ± 18 | 229 ± 20 | 22.3 | 12.1 |
| Th, µg/kg | 311 ± 2 | 337 ± 2 | 7.7 | 2.9 |
| Ti, µg/g | 158 ± 27 | 130 ± 28 | 21.5 | 2.9 |
| U, µg/kg | 144 ± 2 | 154 ± 2 | 6.5 | 12.4 |
| V, µg/g | 4.3 ± 0.3 | 4.2 ± 0.3 | 2.3 | 6.2 |
| Zn, µg/g | 95.9 ± 0.4 | 99.9 ± 3.7 | 4.0 | 6.0 |

TABLE III - ELEMENTAL CONCENTRATIONS IN TWO FRACTIONS OF THE SAME SAMPLE CF (C- CENTRAL FRACTION WITH GREAT LENGTH OF EXPOSURE, F- PERIPHERAL FRACTION WITH SHORT LENGTH OF EXPOSURE). (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) | | | 3410 ± 63 | 2056 ± 28 | 1431 ± 56 | 631 ± 24 | 2544 ± 49 | 1393 ± 20 | 3187 ± 54 | 927 ± 14 |
| As | 1099 ± 10[a] | 914 ± 11 | 982 ± 9 | 846 ± 10 | 563 ± 9 | 304 ± 7 | 879 ± 7 | 607 ± 7 | 876 ± 10 | 684 ± 10 |
| Ca (%) | 8.99 ± 0.07 | 6.23 ± 0.05 | 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 IV. RESULTS FOR LICHENS COLLECTED FROM DIFFERENT PALM TREES ON THE SAME SITE

| Element | *Canoparmelia texana* | |
|---|---|---|
| | Mean ± s(sr) | Range |
| Al, µg/g | 2360 ± 598(25) | 1687 - 2936 |
| As, µg/kg | 737 ± 194(26) | 436 - 826 |
| Br, µg/g | 14 ± 6(42) | 8.7 - 21.5 |
| Ca, % | 2.5 ± 0.5(18) | 1.86 - 2.92 |
| Cd, µg/kg | 1779 ± 576(32) | 1023 - 2426 |
| Cl, µg/g | 605 ± 135(22) | 462 - 761 |
| Co, µg/kg | 409 ± 123(30) | 262 - 560 |
| Cr, µg/g | 5.0 ± 1.8(36) | 3.2 - 7.5 |
| Cs, µg/kg) | 325 ± 185(57) | 131 - 575 |
| Fe, µg/g | 1197 ± 789(41) | 740 - 1870 |
| Hf, µg/kg | 342 ± 167(49) | 239 - 590 |
| K, µg/g | 1412 ± 362(26) | 1064 - 1785 |
| La, µg/g | 3.7 ± 2.3(63) | 1.93 - 7.22 |
| Ce, µg/g | 6.1 ± 2.5(41) | 3.5 - 9.6 |
| Nd, µg/g | 2.36 ± 1.40(59) | 1.24 - 4.41 |
| Sm, µg/kg | 372 ± 158(42) | 229 - 596 |
| Eu, µg/kg | 76 ± 48(48) | 36 - 145 |
| Tb, µg/kg | 40 ± 25(62) | 18 - 76 |
| Yb, µg/kg | 106 ± 53(50) | 66 - 184 |
| Lu, µg/kg | 19 ± 10(51) | 12.2 - 33.8 |
| Mg, µg/g | 1870 ± 440(23) | 1363 - 2239 |
| Mn, µg/g | 97.3 ± 50.2(51) | 49.1 - 165.1 |
| Na, µg/g | 143 ± 56(39) | 81 - 216 |
| Rb, µg/g | 6.9 ± 1.3(20) | 4.99 - 8.20 |
| Sb, µg/kg | 560 ± 202(36) | 392 - 851 |
| Sc, µg/kg | 365 ± 153(42) | 228 - 574 |
| Se, µg/kg | 271 ± 79(42) | 162 - 343 |
| Th, µg/kg | 605 ± 258(43) | 419 - 985 |
| Ti, µg/g | 197 ± 94(47) | 110 - 331 |
| U, µg/kg | 167 ± 58(3.4) | 38 - 270 |
| V, µg/g | 8.1 ± 2.2(27) | 5.4 - 10.8 |
| Zn, µg/g | 94.7 ± 24.1(25) | 60.5 - 113.5 |

s - standard deviation; $s_r$ - relative standard deviation

TABLE V. ELEMENTAL CONCENTRATIONS IN REFERENCE MATERIALS

| Elements | IAEA 336 Lichen | | NIST 1572 Citrus Leaves | |
|---|---|---|---|---|
| | This work | Ref [6] | This work | Ref.[7] |
| Al, µg/g | 702 ± 18* | 680(570-780)[a] | 112 ± 11 | 95 ± 15[c] |
| As, µg/kg | 699 ± 25 | 640(650-720)[b] | 3174 ± 44 | 3100 ± 300[c] |
| Br, µg/g | 11 ± 1 | 12.9(11.2-14.6)[a] | 7.7 ± 1.3 | 8.2[d] |
| Ca, µg/g | 2895 ± 100 | 2600(2400-3300)[b] | 36179 ± 751 | 31500 ± 1008[c] |
| Cd, µg/kg | 172 ± 72 | 117(100-134)[a] | | |
| Cl, µg/g | 1805 ± 77 | 1900(1650-2200)[b] | 395 ± 12 | 414[d] |
| Co, µg/kg | 285 ± 28 | 290(250-330)[a] | 30.2 ± 2.1 | 20[d] |
| Cr, µg/kg | 1100 ± 400 | 1030(800-1170)[b] | 762 ± 26 | 800 ± 200[c] |
| Cs, µg/kg) | 121 ± 7 | 110(97-123)[a] | 99.0 ± 1.4 | 98[d] |
| Fe, µg/g | 518 ± 23 | 425(380-470)[a] | 99 ± 13 | 90 ± 9[c] |
| K, µg/g | 1940 ± 362 | 1840(1640-2040)[a] | 20947 ± 1454 | 18200 ± 600[c] |
| La, µg/kg | 630 ± 31 | 660(550-760)[b] | 182 ± 27 | 190[d] |
| Ce, µg/kg | 1270 ± 50 | 1270(1090-1440)[a] | 388 ± 46 | 280[d] |
| Nd, µg/kg | 762 ± 68 | | 279 ±10 | |
| Sm, µg/kg | 110 ± 8 | 106(92-120)[a] | 52.1 ± 3.4 | 52[d] |
| Eu, µg/kg | 24.7 ± 1.8 | 23(19-27)[b] | 11.7 ± 1.2 | 10[d] |
| Tb, µg/kg | 17 ± 3 | | 9.5 ± 0.1 | |
| Yb, µg/kg | 37.1 ± 1.8 | | 8.37 ± 0.06 | |
| Lu, µg/kg | 6.5 ± 0.7 | | 1.3 ± 0.4 | |
| Mg, µg/g | 721 ± 104 | 610(500-710)[b] | 6249 ±269 | 5800 ±301[c] |
| Mn, µg/g | 64.7 ± 2.7 | 64(57-71)[a] | 21 ± 2 | 23 ± 2[c] |
| Na, µg/g | 323 ± 7 | 320(280-360)[b] | 173 ± 4 | 160 ± 21[c] |
| Rb, µg/g | 1.80 ± 0.01 | 1.72(1.52-1.92)[a] | 4.8 ± 0.2 | 4.84 ± 0.06[c] |
| Sb, µg/kg | 83 ± 3 | 73(63-83)[a] | 56 ± 9 | 40[d] |
| Sc, µg/kg | 138 ± 11 | 170(148-192)[a] | 9.8 ± 0.4 | 10[d] |
| Se, µg/kg | 243 ± 25 | 220(180-160)[a] | 51.1 ± 6.5 | 25[d] |
| Th, µg/kg | 145 ± 9 | 140(120-160)[b] | 13.6 ± 1.3 | |
| Ti, µg/g | 69.7 ± 8.7 | | | |
| V, µg/g | 1.42 ± 0.08 | 1.5(1.2-1.7)[b] | | |
| Zn, µg/g | 34.3 ± 2.1 | 31.5(28-35)[a] | 30.6 ± 1.1 | 29 ± 2[c] |

* - arithmetic mean and standard deviation of n determinations ($3 \leq n \leq 5$)

a - recommended values and confidence interval; b - information values and confidence interval

c - certified values; d - information values