Determination of metals in plant samples by using a sector field inductively coupled plasma mass spectrometer

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Abstract

The capability of pine needles to be used as bioindicators of trace metals in the environment is discussed. Samples were collected around the Instituto de Pesquisas Energéticas e Nucleares, the largest nuclear research center in South America and chosen to be the sampling target area. Results obtained for the elemental content of Th and U in samples collected nearby an uranium facility were, respectively, 0.072 and 0.042 mg kg^{-1}, while the results obtained for the La, Ce and Sm content in a sample collected in the vicinity of an extraction laboratory were, respectively, 0.22, 0.88 and 0.39 mg kg^{-1}. All these values are higher than the ones obtained with a reference sample (La 0.12; Ce 0.19, Th 0.020 and U 0.012 mg kg^{-1}), located far from the target area. Internal standardization was used to compensate the non-spectral interference of the different elements present in the sample solution matrix. The chemical elements bismuth (Bi) and indium (In) were chosen as internal standards. In order to control the accuracy of the chemical measurement process, certified samples of pine needles (NBS SRM 1575) were also analyzed. The results obtained show the capability of the investigated method in the determination of the relevant trace metals in the environment. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

At present, attention has been drawn to the development of analytical methods for measurement of trace metals in the environment (Vtorova and Markert, 1995; Markert, 1998). The concentration of some of these elements in soil samples can indicate deficiencies in their composition (Carrión et al., 1988), or contamination produced by nearby installations (Bunzl et al., 1994). In medicinal herbs, the presence and the concentration of some metals can act as an indicator of their nutritional value (Thompson and Ward, 1989). Specifically for verifying anthropogenic metal insertions in the environment, the use of environmental monitoring has been widely discussed as an alternative method to the direct measurement of these emissions in the ecosystem (Markert, 1993a). In particular, for determining the elemental status of the environment, mosses (Markert and Weckert, 1989; Markert, 1993b), lichens and fungi (Svoboda et al., 2000) show a marked ability to accumulate certain elements. The higher plants are generally poor accumulators, but possess a good interception characteristic with retention of contamination on foliar surfaces due to the plant morphology.

Environmental sampling and analysis has, since 1991, one important new feature which was introduced to aid in the detection of undeclared nuclear activities (Belew et al., 1993; Donohue and Zeisler, 1993; Efurd and Rokop, 1995; Donohue, 1998). The success of these methodologies, used as one of the main reinforcement measures for the International Atomic Energy Agency (IAEA) safeguards purposes, led to the implementation of environmental sampling as part of routine safeguards inspections in 1996.

Various techniques have been used for the determination of trace metals in environmental samples. Fluorimetric (Ghods et al., 1990) and neutron activation analysis (Machado et al., 1998) are generally time consuming and expensive techniques. Among other techniques are alpha spectrometry (Camargo and Mazzili, 1996), graphite furnace atomic absorption spectrometry (Anderson et al., 1996), which can reach lower detection limits for metallic trace elements; however, it suffers from spectral interferences, and also more recently, inductively coupled mass spectrometry (Boomer and Powell, 1987; Shiraishi et al., 1991; Bou-Rabee, 1995; Becker and Dietze, 1998; Prohaska et al., 1999; Yukawa et al., 1999).

This work describes a methodology developed for the determination of concentration of trace metals present in plants by using a sector field inductively coupled plasma mass spectrometer (ICP-MS). As a field trial, pine needles were chosen as the bioindicator whose sought property is to provide information, in a non-intrusive basis, concerning the activities developed in a nuclear site. Pine needles have been acknowledged as useful monitors of atmospheric pollution (Eriksson et al., 1989; Kuhn et al., 1995; Kurczynska et al., 1997). Their large specific surface area gives them a high scavenging efficiency for aerosol particles (Nicholson et al., 1994).

The elements chosen to be investigated are located at different positions in the periodic table of the elements. Some are metallic (Ni, Co), others lanthanides (La, Ce, Sm) and others actinides (Th, U), but all of them, in some way, are metals related to the nuclear activities developed inside the sampling target area. The metallic ones are the main constituents of maraging steels, used in enrichment facilities; lanthanides are extensively used in super magnets and, some of them, are sub-products of Zr extraction and purification plants; Th and U are elements present in the fuel cycle activities.

The sampling and treatment procedures for the pine needles samples and sample solutions to be directly analyzed in a sector field ICP-MS were established. The sensitivity and the detection limits of the method, as well as its reproducibility, were presented.

2. Experimental

The environmental plant tissues, including a pine needles standard material, 'National Bureau Standard of Reference Material 1575' (NIST: SRM 1575 Pine Needles), were digested by an acid digestion method (Feinberg, 1991; Sinquin et al., 1993) in a microwave oven. In addition, a

comparison by the conventional method of dry ashing for sample digestion was also included. The analytic method used for the elemental determination by ICP-MS in the solutions originated from both of the digestion methods which need the establishment of an external standard calibration curve, relating the expected value of the observed signal to the analyte amount (Cheatham et al., 1993; IUPAC, 1998a). In this method, it is also necessary to compensate the matrix effects arising mainly from the non-spectral interferences. This can be done using the addition of internal standards to the solutions.

2.1. Area description

The pine needles samples for the field trial were collected inside the Cidade Universitária 'Armando Salles de Oliveira' campus in São Paulo city, capital of the São Paulo State. The Cidade Universitária complex is approximately 5.5 km^2 and its nearby lands have mainly urban characteristics. Inside its limits, almost all of the educational units of the Universidade de São Paulo (USP), and some research institutes, as the Institute de Pesquisas Tecnológicas de São Paulo (IPT), Instituto Butantã and Instituto de Pesquisas Energéticas e Nucleares (IPEN) can be found. In order to make the trial more representative, some samples were collected inside the nuclear research institute, chosen to be the sampling target area, and one far away from these, to be used as a reference sample.

2.2. Instrumentation

A sector field, 27 MHz, ICP-MS system from Finnigan MAT (Bremen, Germany), with a magnetic sector followed by an electrostatic analyzer (ESA) in reverse Nier−Johnson geometry, was used for the experiments. The introduction of the sample solutions in the equipment was made with the aid of an automatic liquid sample introduction system (Gilson 222, Villiers Reads Bel, France). The sample delivery to the equipment nebulizer, as well as to the washing station of the automatic samples introduction system, was done with the aid of a four-channel head peristaltic pump (Perimax 1274, Petec GmbH, Erding, Germany). A summary of the operating conditions of the HR-ICP-MS is given in Table 1.

The data were generated, in the equipment, in a sequential mode, in such a way that the result obtained for each isotope represents the average of 10 measurements, each one repeated six times, totaling 60 measures for each investigated element.

2.3. Reagents

The standard solutions were prepared using 1000 $\mu g\ g^{-1}$ solutions of elemental standards Spex® (Spex Industries, Edison, NJ, USA). The water used in the dilutions, with a conductivity of 18 MΩ cm, was produced in a water purifying system (Milli Q, Millipore, Molsheim, France). For the samples preparation and standards dilution, Suprapur® nitric acid (Merk, Darmstad, Germany) was used.

Table 1
Operating parameter settings for the Finnigan MAT ELEMENT ICP-MS

Forward rf power	1300 W
Coolant gas flow rate	15 l min^{-1}
Auxiliary gas flow rate	0.98 l min^{-1}
Nebulizer gas flow rate	Tuned for maximum $^{115}In^+$ signal
Nebulizer	Meinhard
Ion sampling depth from load coil	Tuned for maximum $^{115}In^+$ signal
Sampling cone	1.0 mm aperture
Skimmer cone	0.75 mm aperture
Lens voltages	Tuned for maximum $^{115}In^+$ signal
Mass resolution	300
Scan mode	E-Scan (ESA)

2.4. Sample preparation

All the samples were submitted to the same sampling process. The pine needles were sampled in the same day, being used disposable polypropylene gloves. All the leaves were detached without their stem. In the laboratory, the plant tissues were placed in beakers, covered with watch glasses and dried for a period of 12 h in an oven at 110°C. The samples were composed of several needles of each pine tree used as a sampling point, totaling approximately 10 g of dry material, that were conditioned in polypropylene bags. Later, these samples were triturated, homogenized and subdivided using the coning and quartering method.

2.4.1. Dry ashing

A representative aliquot of the previously dried sample (approx. 3 g), was carefully weighed in a quartz beaker and calcined for 8 h at 500°C. The muffle furnace temperature was gradually increased from 100 to 500°C at 1-h intervals. The recipient was cooled and approximately 0.1 g of its content was transferred to a Teflon® beaker of 50 ml, in which 5 ml of 8 N nitric acid were added. The solution was evaporated, transferred to a volumetric flask and diluted to 10 ml with water. The final concentration of the solution was adjusted to 500 μg ash ml^{-1} with 0.3 mol l^{-1} nitric acid.

2.4.2. Microwave-assisted acid digestion

Approximately 0.5 g of dry pine needles were weighed and carefully transferred to Teflon® tubes belonging to a microwave oven (MDS 2000, CEM Corporation, Matthews, NC, USA). After this, 15 ml of concentrated nitric acid were added. The tubes were closed and irradiated with a nominal power of 630 W during a period of 45 min. At the end of the irradiation cycle, the samples were cooled to the room temperature, transferred to a volumetric flask and diluted to 25 ml with water. Later on, these solutions were diluted again with water until the final concentration of 5500 μg of dry material ml^{-1}.

In order to control the accuracy of both methods, the NIST: SRM 1575 Pine Needles were submitted to both digestion processes. All the blank solutions were processed together with the samples. For the material and instrument cleaning, a solution of 1 mol l^{-1} nitric acid was used.

3. Results and discussion

3.1. Selection of the measured isotopes

The elements chosen to act as signatures of nuclear activities in the bioindicators in the field trial are Ni, Co, La, Ce, Th and U. Most of them have more than one isotope, in these cases, the selection of the isotope to be measured relapsed on the most abundant, or in that more abundant with no isobaric interference, as indicated in Table 2.

3.2. Calibration

The method of external standard calibration was chosen for the accomplishment of the measurement results in the HR-ICP-MS. The calibration graphs were obtained by a linear calibration model using five working multi-elemental standard solutions, with concentrations of 0.2, 0.5, 1.0, 8.0 and 10 μg l^{-1}, all of them in 0.3 mol l^{-1} nitric acid solutions, prepared from the elemental standard Spex® solutions. Considering that the un-

Table 2

Sensitivity and detection limit of the analytes in the equipment, observed during the measurements (assuming 10 μg l^{-1} solution)

Element	Isotope		Detection limit[b] (pg ml^{-1})	Sensitivity $\times 10^4$ (cps ng^{-1} ml^{-1})
	Ion	P[a] (%)		
Cobalt	^{59}Co$^+$	100	3	3
Nickel	^{60}Ni$^+$	26.23	60	0.7
Lanthanum	^{139}La$^+$	99.91	0.3	11
Cerium	^{140}Ce$^+$	88.48	0.4	9
Samarium	^{149}Sm$^+$	13.83	1.5	6
Thorium	^{232}Th$^+$	100	0.6	14
Uranium	^{238}U$^+$	99.27	0.7	17

[a] Representative isotopic abundance (at.%) (IUPAC, 1998b).

[b] Detection limit calculated at the 98% confidence level.

certainties associated to the working multi-elemental standard solutions concentration are small and, consequently, can be neglected compared with those associated to the measured signal obtained in the HR-ICP-MS, the parameters corresponding to the intercept and the slope of the calibration function can be estimated by the Gaussian (normal) last squares algorithm. The obtained calibration graphs were all of excellent quality, always presenting the correlation coefficient $R^2 > 0.999$.

3.3. Internal standard

Matrix interference arise from components in the sample that might cause a depression of the measured signal. This effect can be reduced through dilution of the samples. However, this procedure presents the disadvantage of increasing the measurement uncertainty, once the intensity of the signal proportionally decreases. Internal standardization was, therefore, chosen to correct this matrix effect. An internal standard must fulfill the following requirements: its contents, in the samples, must be negligible, it must behave similarly to the element to be analyzed, and it should be mono-isotopic. In a general way, these qualities can be summarized in the fact that the used internal standard should have an atomic mass as close as possible to that of the element to be analyzed (Igarashi et al., 1989). From several available options ([115]In, [159]Tr, [165]Ho, [193]Ir, [205]Tl and [209]Bi), [115]In was chosen to be used as internal standard for the analysis of the elements with low atomic masses (Co, Ni, La, Ce and Sm) and [209]Bi, for the analysis of elements with high atomic masses (Th and U). These internal standards, in the concentration of 1 μg l^{-1}, were added to all the analyzed solutions.

3.4. Detection limits and sensitivity

The detection limit was calculated as being equal to three times the experimental standard deviation of 10 non-consecutive blank analyses (Milli Q water), performed with the working multi-elemental standard solution of 10 μg l^{-1}

(Date and Gray, 1989). The detection limits are a function not only of the blank quality, but also of the equipment detection sensitivity for the several investigated elements. Mean values of the equipment sensibilities and detection limits, obtained during the period in which the measurements were done, are also given in Table 2.

3.5. Precision and accuracy

The internal precision and the accuracy of the method, obtained during the period of measurements, can be evaluated through the measurement results of the analysis of standard NIST: SRM 1575 Pine Needles. The standard was submitted to both digestion processes. The measurement results, for each element, corresponding to each process, are presented in Table 3, together with results obtained by other authors (Date and Gray, 1989; Gladney, 1980; Machado et al., 1998) for the same standard.

3.6. Recovery tests

Recovery measurements were conducted in samples submitted to each of the two investigated digestion methods. Using the working multi-elemental standard solutions, approximately 1.0 μg g^{-1} of each investigated element were added to the samples prior digested by the microwave assisted acid digestion method (type A samples) and 0.6 μg g^{-1} to those prepared using the dry ashing method (type B samples). The average percent recovery for each method showed that the dry ashing method had a lowest percent recovery at 70–90%. The microwave-assisted acid digestion method had average percent recoveries of 75–98%, as it can be observed in Fig. 1. Ultimately, the percent recovery of a spike sample should be as close to 100% as possible but typical values were 80–90% for dry ashing and 83–99% for the microwave-assisted acid digestions (Alvarado et al., 1996).

Since the obtained results, either for precision or recovery, are better for the microwave-assisted acid digestion method, this one was used for digestion of the real samples.

Table 3
Measurement results for the concentration $c(E)$, in mg kg^{-1} dry matter, of the investigated elements in NIST: SRM 1575 Pine Needles

| Element | Dry ashing | | Microwave digestion | | Machado et al., 1998 | Date and Gray, 1989 | Gladney, 1980 | Certified value[c] |
	$c(E)$[a]	R.S.D.[b]	$c(E)$	R.S.D.	$c(E)$	$c(E)$	$c(E)$	$c(E)$
Co	0.105	5	0.103	2	ND[d]	0.0788	0.132	(0.1)[e]
Ni	2.3	2	2.4	2	ND	3.04	2.2	(3.5)
La	0.12	5	0.17	4	0.176 ± 0.019[f]	ND	0.14	(0.2)
Ce	0.20	3	0.28	3	0.367 ± 0.018	0.19	ND	(0.4)
Sm	0.05	3	0.03	6	0.026 ± 0.002	ND	ND	ND
Th	0.022	4	0.041	3	ND	ND	0.034	0.037 ± 0.003
U	0.015	5	0.020	3	ND	ND	0.015	0.020 ± 0.004

[a] Elemental content related to the dry weight, for $n = 3$ replicates.
[b] Relative standard deviation (%), obtained for 10 acquisitions.
[c] NIST, certified values with significant level of $\alpha = 0.05$.
[d] ND, not determined.
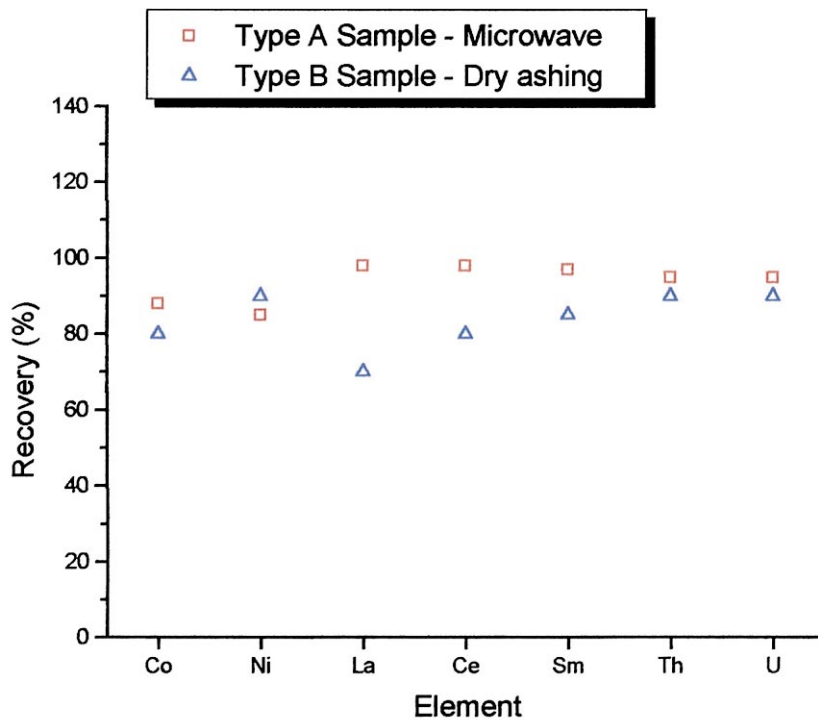[e] Reference values, not certified.
[f] Mean $\pm$ standard deviation.

Fig. 1. Recovery of 1.0 μg g^{-1} of each element added to the sample A, and of 0.6 μg g^{-1} added to the sample B.

3.7. Analytical results

In order to verify the applicability of the method investigated in this paper, a field trial campaign was performed evaluating the behavior of three

pine needles trees potentially acting as bioindicators inside the Cidade Universitária campus. The first two samples, named Sample 1 and Sample 2, were collected inside the target area; the third one, the reference Sample 3, was collected approximately 2000 m from this center, upwind, in

Table 4
Elemental analysis of the pine needles samples digested by the microwave assisted acid digestion method, with elemental content $c(E)$, given in mg kg^{-1} dry matter

Element	Sample 1		Sample 2		Sample 3	
	$c(E)$[a]	R.S.D.[b]	$c(E)$	R.S.D.	$c(E)$	R.S.D.
Cobalt	0.07	3	0.05	3	0.04	4
Nickel	0.6	2	0.5	2	0.4	3
Lanthanum	0.16	5	0.17	5	0.09	6
Cerium	0.27	7	0.73	6	0.16	7
Samarium	0.014	4	0.039	4	0.013	4
Thorium	0.042	5	0.015	6	0.020	3
Uranium	0.072	4	0.055	5	0.012	7

[a] Elemental content related to the dry weight, for $n = 3$ replicates.
[b] Relative standard deviation (%), obtained for 10 acquisitions.

an urban area of the campus. These three samples were digested by the microwave assisted acid digestion method and analyzed with the HR-ICP-MS. The measurement results for the concentration of the investigated elements in each one of the samples, with the associated internal relative standard uncertainty expressed as a relative standard deviation, are shown in Table 4.

It is possible to identify, in the obtained measurement results, a relative higher content of La, Ce and Sm in Sample 2, collected inside the nuclear research center, that may be due to anthropogenic element insertions in the environment produced by a rare earth extraction laboratory located nearby the sampled tree. The same can be observed in the thorium and uranium content of Sample 1, collected near an uranium facility in the center. These values are, respectively, approximately seven and two times higher than the values obtained for the measured concentration of thorium and uranium in the reference Sample 3, located far away and upwind. The La and Ce contents obtained in Sample 1 are slightly high also. This may be the result of the higher content of the two first elements present in the material handled in the extraction laboratory and that was not so far from the facility. The presence of Sm in this sample was not observed in the same magnitude. The amount of this element in the handled material is very small and its effect in the environment cannot be observed far from the laboratory. In respect of the metallic (Ni, Co,) content of the samples collected in the target area (Sample 1 and 2), no significant differences were obtained if compared with those values obtained for the reference sample tree (Sample 3).

4. Conclusion

The measurement results obtained for the concentration of the investigated elements in the samples collected in the field trial indicate that pine needles can be used as bioindicators of the investigated trace metals in the environment. Using the ability of a bioindicator to retain the elements of interest it was possible to identify, outside facilities, the elements routinely manipu-

lated at that nuclear site. The widespread distribution of the pine inside the Cidade Universitária campus suggests that it can provide a suitable sampling matrix for evaluation contaminants handled by the facilities located inside the sampling target area.

The measurement results obtained for the element content in the NIST: SRM 1575 Pine Needles standard, digested by both methods, used to control the accuracy of the measurements, show quite similar results, without any significant difference between them and in accordance with those obtained in literature.

Two methods have been tested for the dissolution of pine needles samples. The microwave-assisted acid digestion method is very promising, with a relative higher percent recovery, very short digestion time, lower required supervision and a lower potential for contamination, and was chosen as the method to be used with the real samples.

The sector field ICP-MS promises to be a powerful tool for the determination of low level concentrations of the investigated elements in pine needle samples and thereof, to identify anthropogenic insertions in the environment. This technique has many advantages, such as high sample throughput and simplicity if compared with the conventional methods of analysis that are much more time-consuming in both instrumental adaptations and measuring procedures, and often require higher level of chemical and operator skills.

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