

Environmental monitoring used to identify nuclear signatures

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The use of environmental monitoring as a technique to identify activities related to the nuclear fuel cycle has been proposed by international organizations as an additional measure to the safeguards agreements currently in force. The specific element for each kind of nuclear activity, or “nuclear signature”, inserted into the ecosystem by several transfer paths, can be intercepted to a greater or lesser degree by different living organisms. This work demonstrates the technical viability of using pine needles as bioindicators for some nuclear signatures (Co, Ni, La, Ce, Sm, Th, and U) associated with uranium enrichment activities using high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). The concentrations of the elements whose signatures were sought and were determined in pine needle samples collected at five specific sampling locations inside the area investigated demonstrate the potential of the instrument and of the method used to identify and quantify the sought signatures present in low quantities (traces) in the evaluated matrix.

Introduction

Analysis of environmental samples is one of the important measures for strengthening the safeguard system introduced in 1996 by the International Atomic Energy Agency (IAEA). These measurements are intended to provide information on the presence or absence of undeclared nuclear activities. Nuclear activities, like any other industrial activity, release small amounts of their products into the environment. The material, which has been released, carries information on the process it arose from. Therefore, these “nuclear signatures” are supposed to be characteristic for the process from which they originated.^{1,2}

Specifically for the identification of the elements characteristic of an environment, mosses,^{3,4} lichens and fungi^{5,6} show a marked capacity for accumulating certain metals. In contrast, trees are not normally considered as good bioaccumulators, since most species cannot concentrate elements derived from the soil or air.⁷ Owing to the morphology of their leaves, however, some of them, such as the pines, have excellent “interception” characteristics, retaining contamination on the leaf surfaces.^{7,8}

Several techniques have been used for the determination of metals in environmental samples. Fluorimetry^{9,10} and neutron activation analysis¹¹ are, generally, considered as techniques demanding a relative long analysis time and also presenting a very high cost. Alpha-spectrometry¹² and atomic absorption spectrometry,⁵ widely used in this area, present low detection limits for metallic elements, but are, however, very susceptible to spectral interference effects. Owing to its low detection limits, high sensitivity and low levels of spectral interference, particularly in the high atomic mass spectral region, inductively coupled plasma

mass spectrometry has been used for the determination of metals in environmental samples.^{13,14}

The objective of this paper is to establish a non-intrusive control model for the monitoring of nuclear activities, by determination of the nuclear signatures of elements of interest present at low concentrations (traces), in pine needles (bioindicators) collected near nuclear installations using high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS). This work demonstrates the viability of using the developed experimental protocol to identify, in a non-intrusive way, the signatures in the environment. To use this same protocol for the determination of the average concentration of individual chemical elements and their trends in plants, this protocol has to be improved with respect to representative sampling¹⁵ and its uncertainties.¹⁶

Experimental

Bioindicator selection

The high specific superficial area of pine-tree leaves makes them highly efficient to remove particulate materials from the aerosol of the atmosphere. Besides this, the needles of these conifers are covered with a wax to which particles readily adhere. Therefore, the pine tree (*Pinus ellioti*) was selected as the bioindicator for this work.

Signature of interest

Mass fractions of Co, Ni, La, Ce, Sm, Th, and U were systematically measured in the collected samples. The criterion for choosing these elements, considered as a signature of interest, was the type of material usually handled in nuclear-fuel-cycle-related facilities.

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Nickel and Co are present, at high percentages, in some types of maraging steel,¹⁷ a typical material used in ultracentrifugation in isotopic enrichment facilities. Samarium and Co alloys are largely used in high performance magnets, constituting an important item in uranium isotopic separation centrifuges.¹⁸ Cerium and La are rare earth elements that are normally handled in large amounts in Zr purification facilities for the production of components used in the nuclear industry. Thorium is an element usually present at the conversion of the uranium ore to uranium hexafluoride, which is used in enrichment facilities.¹

Description of the area

Pine needle samples were collected in regions close to a location where uranium is usually handled (identified by letter E in Fig. 1). The research institutions responsible for the original emissions are the Instituto de Pesquisas Energéticas e Nucleares (IPEN) and the Centro Tecnológico da Marinha em São Paulo (CTMSP).¹⁹

To increase the probability to identify the signatures in the bioindicators, the sampling locations were selected considering the meteorological characteristics of the investigated area, the physical location of the original sources capable of emitting the signatures, and the availability of the bioindicators in the investigated area (as indicated in Fig. 1).

Instrumentation

The HR-ICP-MS instrument used in this project is a Finnigan MAT, Element, (Germany). It includes a double-focusing ion analyzer, with reverse geometry and can be operated at three nominal resolution values: 300, 3000 and 7500.²⁰

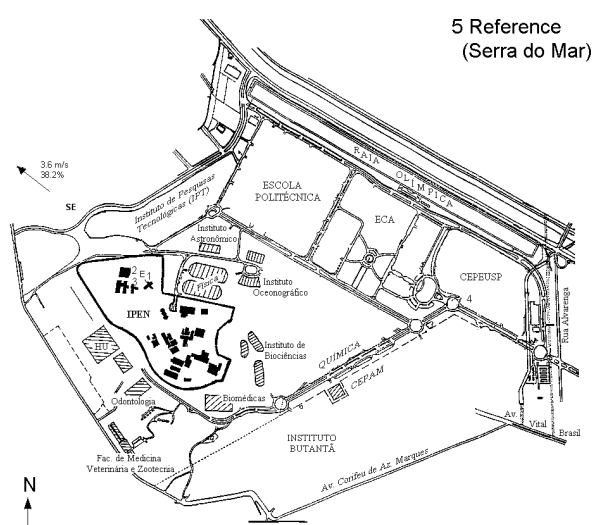


Fig. 1. "Armando Salles de Oliveira" University Campus

Reagents

Analytical grade acids (Suprapur®, Merck, Germany) and purified water produced using a Milli Q (Millipore, France) system were used for dilution and digestion. The solutions injected into the HR-ICP-MS were prepared in 0.29 mol·l⁻¹ HNO₃. Washing solutions, such as 0.98 mol·l⁻¹ HNO₃ or 0.99 mol·l⁻¹ HCl, were used between each sample analysis to reduce memory effects. All dilutions were performed gravimetrically to avoid uncertainties introduced by the expansion of glassware with increasing temperature.

Sampling

The pine needles were collected at an average height of 2 meters, as prescribed by ERIKSON et al.²¹ Double polystyrene gloves were used to avoid contamination. Whenever possible, needles were detached from their stem. About 300 g of needles were collected for each sample. Sample treatment was either performed on the same day or the samples were frozen for later use.

Sample treatment

100 g of pine needles were dried in an oven at 110 °C, for up to 54 hours, until constant mass was reached (i.e., a mass difference between two weighings of less than 0.05 g was obtained). The dried needles were then packed in polyethylene vials and stored in a desiccator. NIST SRM 1575 was processed in parallel with the samples and with the blank solutions for quality control.

A closed vessel microwave digestion²² was performed to dissolve ca. 0.5 g of dried pine needles in HNO₃ media. A nominal power of 630 W was applied using a MARS 5 microwave oven (CEM Co., USA). The digested solutions were spiked by ¹¹⁵In and ¹⁹³Ir internal standards. After digestion, samples were cooled to room temperature, transferred to polyethylene bottles and diluted by water to 125 ml.

All the necessary precautions required when measuring low concentrations were implemented as described elsewhere.²³

Measurements

Five solutions with concentrations close to 0.2, 0.5, 1.0, 5.0 and 10 µg·l⁻¹ were used as reference material²⁴ for the construction of the calibration functions²⁵ of the elements studied in this work. The complete optimization of the instrument and the methodology used to evaluate the uncertainties associated with each stage of the dilution process was described elsewhere.²⁶

Results and discussion

Table 1 presents the elemental concentration obtained for each measured element of the certified reference and its confidence interval ($\pm a$).²⁷

Table 2 presents the results obtained and the respective estimated global uncertainties. Analysis of the data of Table 2 permits the identification of a location at which all the elemental sample concentrations are very low (Location No. 5), and another where the majority of these concentrations are relatively high (Location No. 4).

Table 1. Mass fractions (in $\text{mg}\cdot\text{kg}^{-1}$) obtained for the validation sample (NIST SRM 1575)²⁷ compared with the values provided in the NIST certificate

Element	Present work	Certificate
Co	0.12 ± 0.01	(0.1)
Ni	3.1 ± 0.4	(3.5)
La	0.15 ± 0.02	(0.2)
Ce	0.22 ± 0.02	(0.4)
Sm	0.02 ± 0.01	ND
Th	0.031 ± 0.004	0.037 ± 0.003
U	0.023 ± 0.005	0.020 ± 0.004

All results are related to dry mass. Expanded uncertainties (U , with coverage factor $k=2$, for a level of confidence of approximately 95%) and confidence intervals are provided for our experimental data and certificate values, respectively. Informative values are given in brackets. Sm was not determined by NIST.

Table 2. Mass fractions (in $\text{mg}\cdot\text{kg}^{-1}$) of the elements of interest in the different sampling locations, measured using HR-ICP-MS

Element	Location 1	Location 2	Location 3	Location 4	Location 5
Co	0.19 ± 0.02	0.31 ± 0.04	0.29 ± 0.03	0.49 ± 0.06	0.11 ± 0.01
Ni	1.1 ± 0.1	2.9 ± 0.4	5.5 ± 0.7	3.1 ± 0.4	0.37 ± 0.04
La	0.82 ± 0.04	0.46 ± 0.05	0.43 ± 0.04	0.59 ± 0.06	0.09 ± 0.01
Ce	3.9 ± 0.2	1.2 ± 0.1	0.87 ± 0.09	1.3 ± 0.1	0.21 ± 0.02
Sm	0.16 ± 0.02	0.05 ± 0.01	0.03 ± 0.01	0.06 ± 0.01	0.01 ± 0.01
Th	0.12 ± 0.01	0.12 ± 0.01	0.09 ± 0.01	0.18 ± 0.02	0.03 ± 0.01
U	0.042 ± 0.005	0.035 ± 0.002	0.028 ± 0.003	0.018 ± 0.002	0.004 ± 0.002

Expanded uncertainties ($k=2$) are provided. Results are related to dry mass.

Location No. 5 was chosen as the reference site since it is situated 200 km away from urban/nuclear activities (at Serra do Mar) that could be considered responsible for the anthropogenic insertion of some of the signatures sought in the environment. The results obtained are of the same order of magnitude as those presented in Table 1.

Location No. 4, in spite of being situated far from the emission point and at a geographical position unfavorable relative to the predominant winds in the investigated area, presented very high values for the majority of the sought signatures. This fact is possibly related to the position of this sampling location, close to the University Campus. Signs of high urban activity without signatures related to the nuclear fuel cycle were expected.

Results obtained at location No. 1 presented relatively higher values for La, Ce, Sm and U. These results were expected, since this location is situated very close to the facilities that handle this kind of material (about 20 m), in spite of its unfavorable situation relative to the predominant wind direction in the area. The presence of uranium and rare earth elements in amounts greater than those measured in the samples

collected at other locations (Nos 2, 3 and 4) is a strong indication that these elements are handled in the vicinity of this sampling site.

For the metallic elements (Co and Ni) no relevant information can be extracted from the results. Intense industrial activity close to the sampling locations, with the transfer of the characteristic signatures to the ecosystem would be necessary for subsequent detection of these elements.

Conclusions

Today, the control of activities related to the production of arms of mass destruction are the object of intense discussion. The inspection of locations where it is suspected that undeclared activities have occurred strongly relies on the agreement of those under suspicion, which is often impossible to obtain. This work clearly shows that the use of ultra-trace analytical techniques together with the selective collection of environmental samples can serve effectively as an important strategy for the identification of these activities without, necessarily, depending on the authorization of the operators of the installation.

Results obtained for pine needle samples collected at five specific sampling locations inside the investigated area presented a dispersion that could be attributed to the heterogeneity of the pine trees from which they were removed. This is most likely caused by seasonal variations in their physiological and metabolic processes. Variations of this kind are influenced by the classic abiotic factors, such as soil, light, pluviometric precipitations and winds. This conclusion is also valid for the case of an individual evaluation of each sampling location. For a global evaluation, in which the locations were chosen in a strategic way (considering geographical and the meteorological factors), the results obtained presented the expected behavior depending on their routes in the ecosystem: decreasing concentrations of U, Th and rare-earth elements were observed with increasing distance from the emission point.

Although not contributing directly to the detection of the group of indicators characteristic of nuclear activities, the results obtained for the other elements demonstrated the viability of applying the methodology to the identification of the insertion of these signatures into the ecosystem.

Uranium presents the lowest elemental concentration in the bioindicator. Results with greater precision could be obtained by the use of processing methods involving the concentration, purification and separation of the uranium present in the solutions.²⁸

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