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Environmental monitoring as an important tool for safeguards of nuclear material and nuclear forensics

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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 safeguards organizations. The elements specific for each kind of nuclear activity, or "nuclear signatures", inserted in the ecosystem can be intercepted by different live organisms. This work demonstrates the technical viability of using pine needles as bioindicators of nuclear signatures associated with uranium enrichment activities. Additionally, it proposes the use of HR-ICP-MS to identify the signature corresponding to that kind of activities in the ecosystem. Nitric acid solutions, used to wash pine needles sampled near nuclear facilities and containing only 0.1 $\mu g \cdot kg^{-1}$ of uranium, exhibit a $n(^{235}U)/n(^{238}U)$ isotopic abundance ratio of 0.0092±0.0002, while solutions originated from samples collected at places located more than 200 km far from activities related to the nuclear fuel cycle exhibit a value of 0.0074±0.0002. Similar results were obtained for sample solutions prepared using the acid leaching process. The different values of $n(^{235}U)/n(^{238}U)$ isotopic abundance ratio obtained permit to confirm the presence of anthropogenic uranium and demonstrate the viability of using the methodology proposed in this work.

Introduction

Under international safeguards agreements, the signatory States are obligated to declare all their nuclear materials and allow the organizations to verify independently the declarations using three basic elements that, together, are destined to check if there was or was not nuclear material diversion for undeclared activities. These elements are: the nuclear material accountancy verification, the containment of the declared fissile material and the surveillance.[1,2]

From 1991, the international political situation, with the emergence of a series of international conflicts, practically forced the International Atomic Energy Agency (IAEA) safeguards system to complement its accountancy verification measures with analytical systems capable to give, firstly, an identification of "sensitive" non-nuclear materials, as the maraging steel used in the ultracentrifuge technology, and secondly, to detect radioactive emanations in effluents and in the environment, that could be considered as indicators of nuclear activities not submitted to the IAEA.[3]

The report elaborated in April of 1993 by the IAEA proposed a series of measures aiming at to enhance the confidence of the current safeguards system.[4] These measures included all the locations, declared and undeclared facilities.[5,6] In September of 1997, the IAEA Board approved the Model Protocol Additional to Safeguards Agreements, published with the name of Additional Protocol, or "INFCIRC/540 (Corrected)".[7] According to Article 9 of the Additional Protocol, Member States shall provide the AIEA with access to locations specified by the AIEA itself to carry out wide-area environmental sampling (inside and/or outside of the facility).

In the isotopic enrichment facilities, uranium is handled in the form of a gaseous compound, uranium hexafluoride (UF_6), highly hygroscopic, that reacts with water resulting in a solid compound, uranyl fluoride (UO_2F_2). In spite of the precautions taken in the uranium hexafluoride handling inside the isotopic enrichment facilities, a small fraction of this material is always emanated to the atmosphere. Uranium hexafluoride immediately reacts with the air moisture, falling over the ecosystem in the vicinity of the facility.[8,9] The uranium isotopic enrichment performed in natural material results in the production of large amounts of depleted and enriched uranium. Normally, the existence of enriched or depleted uranium in environmental samples can be considered as an evidence of a uranium isotopic enrichment facility.

In general, a bioindicator is chosen due to its capability of retaining a given signature of interest. Mosses,[10,11] lichens and fungi[12] present an extraordinary ability to accumulate certain kinds of elements. But, since we are looking for the direct dry and wet deposition of elements dispersed in the atmosphere in the aerosol form, the use of conifers as a bioindicator is considered as a good choice.[13–16] Therefore, the selected bioindicator for this work was the pine tree (*Pinnus ellioti*). This conifer was widely used as an indicator of nuclear activities, its needles have high superficial area and are covered by a wax with excellent adhering capacity.

Like human fingerprinting, nuclear material can be identified, examined, and profiled. In the new field of "nuclear forensics" the determination of isotopic and mass abundance ratios together with other chemical and physical parameters reveal the "nuclear fingerprint" of the material.[17]

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Isotopic abundance ratios of uranium are already well known.[18,19] The accurate and precise determination of isotopic abundance ratios have been made, until now, using thermal ionization mass spectrometry (TIMS) for solid samples, and gas source mass spectrometry (GS-MS) for gaseous samples. The isotopic abundance ratio measurements by instruments that have a quadrupole type analyzer, quadrupole mass spectrometer (ICP-QMS) have been described in detail in a series of technical publications. The precision and accuracy values obtained by these instruments are limited in function of the detector's lack of linearity, the background contributions and the mass discrimination effect.[20] The isotopic abundance ratio measurements performed, for the majority of the isotopes, by instruments having a quadrupole type analyzer, present precision values, defined as twice the experimental relative standard deviation between 0.5 and 10% obtained in ten consecutive measurements of the same sample. Recent publications present a significant improvement in these values, reaching less than 0.1%. Mass discrimination factors from 1 to 2% per atomic mass unity (amu) have also been frequently reported.[21,22] The use of double-focusing magnetic sectors equipped with multiple ion detectors permits the different ions to be simultaneously separated and collected, eliminating the inaccuracy resulting from the signal instability. Typical precision values obtained by this type of instrument reach 0.005 to 0.01%, values comparable to those obtained using the TIMS technique.[23–25]

The objective of this work is to present a non-intrusive control model for the verification of nuclear activities, by means of the determination of the signatures of interest (isotopic abundance ratios of uranium) present in pine needles (bioindicators), collected near a uranium enrichment facility using a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS). The acid leaching and the ultra-sound assisted acid washing methods, used to process the pine needles samples, were discussed.

Experimental

Description of the area

In order to perform a practical exercise using the presented methodology, pine needle samples were collected in regions close to a location where enriched uranium is usually handled (identified by letter E in Fig. 1).[26,27] The chosen area is located inside the "Armando Salles de Oliveira" University Campus, in São Paulo city. The sampling locations are indicated in Table 1.

Signatures to be searched

The uranium, handled in the ultracentrifugation isotopic enrichment facilities in the form of uranium hexafluoride (UF_6), may contain several natural (^{234}U, ^{235}U) or artificial (^{232}U, ^{236}U) isotopes.[28] The $n(^{235}U)/n(^{238}U)$ and $n(^{234}U)/n(^{238}U)$ isotopic abundance ratios may give evidences of a uranium isotopic enrichment process, since between certain limits their values remain constant in the nature. The average abundances of these naturally occurring isotopes are 0.00548% ^{234}U, 0.7200% ^{235}U and 99.2745% ^{238}U, in atomic percentage.[29]

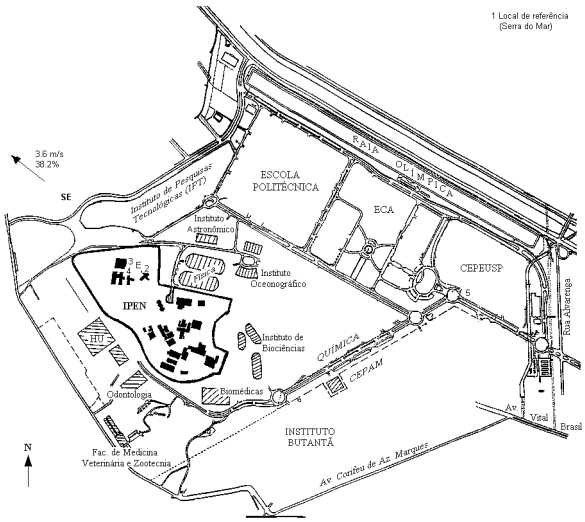

Fig.1. "Armando Salles de Oliveira" University Campus

Table1. Sampling locations of the pine needle samples

Location	Description	Distance, m	Relative position
1	Reference (Serra do Mar)	200,000	–
2	IPEN, Parking CTM-II[a]	20	SE
3	IPEN, ME,[b] front	100	NW
4	IPEN, USIPA,[c] back	300	W
5	CEPEUSP roundabout[d]	1950	E

[a] CTMSP access area, unity II.
[b] Frontal access area to ME building, Chemical Characterization Division.
[c] Back area of the Pellets Factory building.
[d] Frontal area of the USP Sports Practice Center.

The first abundance ratio $n(^{235}U)/n(^{238}U)$ is practically unaltered in the nature, the only exceptions are the uranium deposits in Oklo,[30] being located in the southeastern part of the Gabon Republic, in Africa near the equator, where the ^{235}U deficiency is due to a spontaneous fission chain reaction. So, any deviation from the natural value, comprehended between 0.7198 and 0.7202 atom percent, is a strong evidence of the existence of enriched or depleted uranium.

The second abundance ratio $n(^{234}U)/n(^{238}U)$ varies in the nature. ^{234}U is a ^{238}U decay product. In samples undisturbed by nature, ^{234}U and ^{238}U are present in secular equilibrium. However, the natural uranium may be slightly enriched or depleted in the ^{234}U isotope in relation to its equilibrium value with ^{238}U. Ocean waters have, for example, an ^{234}U abundance ratio about 15% higher than the equilibrium value with ^{238}U.[31]

The ^{236}U does not exist in nature, being produced by ^{235}U neutron capture. The ^{236}U presence normally identified through $n(^{236}U)/n(^{238}U)$ isotopic abundance ratio measurement, clearly indicates, therefore, the handling of previously irradiated material, fact that does not necessarily mean the presence of a material subject to an isotopic separation process.

As a consequence, the most specific approach to be used to detect uranium isotopic enrichment activities is the measurement of the $n(^{235}U)/n(^{238}U)$ isotopic abundance ratio, followed by the detection of the presence of the ^{236}U isotope through the measurement of the $n(^{236}U)/n(^{238}U)$ abundance ratio.[32]

Instrumentation

The HR-ICP-MS instrument used is a Finnigan MAT, ELEMENT, (Bremen, Germany). This instrument presents a double-focusing ion analyzer, with reverse geometry (Nier-Johnson): a magnetic analyzer is followed by an electrostatic analyzer and can operate in three nominal resolution values: 300, 3000 and 7500.[33–35]

Reagents

Analytical grade acids (Suprapur® from Merk, Germany) and purified water produced using a Milli Q (from Millipore, France) system were used for dilutions and digestions. The solutions injected into the HR-ICP-MS were prepared in 0.29 mol·l^{-1} HNO_3. Washing solutions, such as 0.98 mol·l^{-1} HNO_3 and 0.99 mol·l^{-1} HCl, were used between each sample analysis to reduce memory effects.

Contamination control

In order to reduce the risk of contamination (of external origin or cross contamination between the samples), extremely severe measures were adopted to assure that materials used during the sampling execution were sufficiently cleaned and that all the sample handling and processing were conducted in extraordinary clean ambient. All these precautions contributed to obtain blank solutions with extremely low concentration values. All the aspects related to the quality assurance of the obtained results were incorporated in the execution of this work and are described in Reference 36.

Sample processing

The sampling and driyng process of the pine needles was also described in a previous work.[37] Two different methods were used to process the samples: (1) acid leaching and (2) ultra-sound assisted acid washing. In the first method, NIST SRM 1575 was processed in parallel with the samples and with the blank solutions for quality control.

Acid leaching processing: A 10 g aliquot of the dry pine needles was transferred to 250-ml quartz beakers, covered with a quartz plate and placed into a muffle furnace. The pine needle sample was ashed at 350 °C for 12 hours. The ashing process continues now at 550 °C for 24 hours. The ash was transferred to a 50 ml Teflon® beaker and 15 g of Suprapur® HNO_3 and HCl were added. The beaker was inserted into an aluminum block and placed on a hot plate at 150 °C for 2 hours. The beaker was removed from the hot plate and cooled to room temperature. The supernate was transferred to a polystyrene centrifuge tube and centrifuged at 3000 rpm for 3 minutes. The supernate was transferred to a clean Teflon® beaker and evaporated to dryness. About 15 g of Suprapur® 8 mol·kg^{-1} HNO_3 were added to the first beaker residue, heated, transferred to the centrifuge tube containing the residue and centrifugated again. The rinses were also transferred to the clean Teflon® beaker that was heated before. The dry sample was redissolved in Suprapur® HNO_3 and purified water until an acid concentration of approximately 0.3 mol·kg^{-1}. Uranium was present in concentrations from 0.80 to 3.50 μg·kg^{-1} in these solutions.

Ultra-sound assisted acid washing processing: A 10 g of the previously dry pine needles were placed into a Pyrex® beaker with approximately 200 g of 0.29 mol·kg^{-1} Suprapur® HNO_3. The obtained solution was irradiated in an ultra-sound system (Thornton T14, Inpec Eletrônica LTDA, Vinhedo, SP, Brazil) during 15 minutes, at the temperature of 25 °C (without temperature increase). The supernates were transferred to polypropylene bottles for storage. Aliquots of 10 g taken from these bottles are transferred to polystyrene centrifuge tubes and centrifuged during 3 minutes, at a rotation speed of 3000 rpm and introduced directly in the HR-ICP-MS for isotopic analysis. These solutions

presented a lower uranium content ranging from from 0.01 to 0.10 μg·kg^{-1}.

Measurement procedure

All the parameters that influence the isotopic abundance ratio measurements were carefully optimized using 0.94±0.05 μg·kg^{-1} uranium working isotopic standard solution from NBL CRM U015. The characteristics of the instrument used and the measurement parameters optimized for the uranium isotopes are presented in Table 2. The determination of the $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$, and $n(^{236}U)/n(^{238}U)$ abundance ratios in the pine needle sample solutions follows a procedure presented in Fig. 2. The isotopic abundance ratio for the isotope of interest, $R_{i/238}$, for $i = 234$, 235, 236 was obtained by:

$$R_{i/238} = K \cdot R_{\text{measured}} \quad (1)$$

where K is the mass discrimination factor and R_{measured} is the value corresponding to the isotopic abundance ratio obtained by the instrument. The final result is the average of three independent analyses of the same sample. All uncertainties were calculated according to the ISO Guide,[38] using a coverage factor of k=2, and explained in previous works.

Results and discussion

The results included a restricted set of sampling points (points 1, 2, 3, 4 and 5), selected in a way to characterize the applicability of the procedure used as a tool for the identification of uranium isotope enrichment activities. Location No. 1 was chosen as the reference site since it is situated at 200 km from nuclear activities that could be considered responsible for the anthropogenic insertion of some of the signatures sought in the environment.

The values obtained for the $n(^{236}U)/n(^{238}U)$ isotopic abundance ratios were below the detection limit of the instrument in the majority of the sample solutions. The results obtained for the $n(^{234}U)/n(^{238}U)$ isotopic abundance ratio in the sample solutions obtained using the two distinct processing methods did not provide any additional or different information from those obtained for the $n(^{235}U)/n(^{238}U)$ isotopic abundance ratio that present smaller uncertainties.

Tables 3 and 4 presents the isotopic abundance ratio measurements in the acid leaching sample solutions, associated to the respective expanded uncertainties u. For both tables, the sampling locations Nos 1, 2 and 5 can be considered as having uranium with isotopic abundance ratio equivalent to a material of natural origin. The SRM 1575 reference material submitted to the same processing and measurement procedures, presents an isotopic abundance ratio equivalent to those found in material with natural isotopic composition. Solutions obtained from the samples collected at the sampling locations Nos 3 and 4 indicate a variation in the isotopic ratios. These results were expected, since these locations are situated very close to the facilities that handle enriched uranium, furthermore, are located in a favorable situation relative to the predominant wind direction in the area. Figure 3 and 4 present graphically the results compiled in the tables. The dotted line corresponds to the natural isotopic abundance ratio, according to the value stated by the IUPAC.[29]

The results of the isotopic abundance ratios measured in the solutions obtained from the pine needles washing with a 0.29 mol·kg^{-1} HNO_3 solution, are shown in Tables 5 and 6. No information is available about the SRM 1575 abundance ratios. The conclusions are the same as in the previous case, except for location No. 2, that in this case shows a higher enrichment. The value obtained from the superficial washing of the pine needles provides information related to the uranium deposition over the needles while in the acid leaching method, all the uranium present in the sample is digested together. If the deposition is small, the material and isotopic balance of the uranium present in the needles can mask the final interpretation of the result. This processing method seems to be more sensitive.

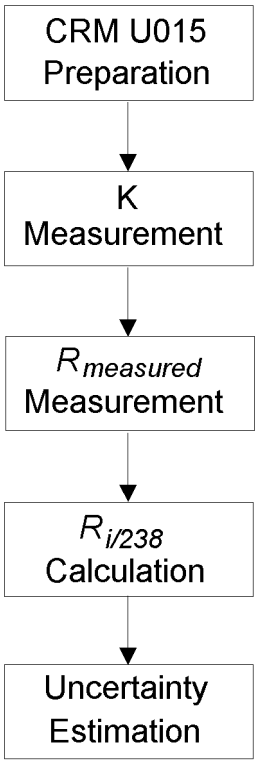

Fig.2. Isotopic abundance ratio measurement in samples

Table 2. Characteristics of the instrument used and measurement parameters optimized for the uranium isotopes

Instrument	Element ICP-MS
Resolution	300
Nebulizer	Meinhard type
Spray chamber	Scott, cooled
Instrument sensitivity for U	$2.2 \cdot 10^6$ ions·s^{-1}·µg^{-1}·kg
Detection limit for U	0.1 pg·g^{-1}
Sample uptake*	1.0 ml·min^{-1}
Total analysis time	6 minutes
Ion detection	SEM (Secondary electron multiplayer)
Correction for the dead time	21 ns
Acquisition mode	Electrostatic scan (E-scan)
Mass range	234–238
Integration time per isotope	0.15 seconds
Integration window	5% of the peak width
Number of sample per window	15
Number of scans	600
Number of isotopes measured	4
Residence time in the magnet	0.001 seconds
Sample time	0.010 seconds
Samplings per peak	300
Typical mass discrimination factor	1.01

* Value optimized at each analysis performed.

Table 3. $n(^{234}U)/n(^{238}U)$ isotopic abundance ratios obtained for the samples submitted to the acid leaching processing method and respective estimated uncertainties

Location	$n(^{234}U)/n(^{238}U)$	u_c	u*	u, %
1	0.000066	0.0000042	±0.000008	±12.1
2	0.000066	0.0000030	±0.000006	±9.1
3	0.000076	0.0000033	±0.000007	±9.2
4	0.000088	0.0000029	±0.000006	±6.8
5	0.000073	0.0000030	±0.000006	±8.2
SRM 1575	0.00006	0.0000063	±0.00001	±16.6

* Resulting from the product of the combined uncertainty by a coverage factor $k = 2$, for a level of confidence of approximately 95%.

Table 4. $n(^{235}U)/n(^{238}U)$ isotopic abundance ratios obtained for the samples submitted to the acid leaching processing method and respective estimated uncertainties

Location	$n(^{235}U)/n(^{238}U)$	u_c	u*	u, %
1	0.0072	0.000056	±0.0001	±1.4
2	0.0072	0.000062	±0.0001	±1.4
3	0.0079	0.000056	±0.0001	±1.3
4	0.0101	0.000089	±0.0002	±1.9
5	0.0072	0.000057	±0.0001	±1.4
SRM 1575	0.0073	0.000079	±0.0002	±2.7

* Resulting from the product of the combined uncertainty by a coverage factor $k = 2$, for a level of confidence of approximately 95%.

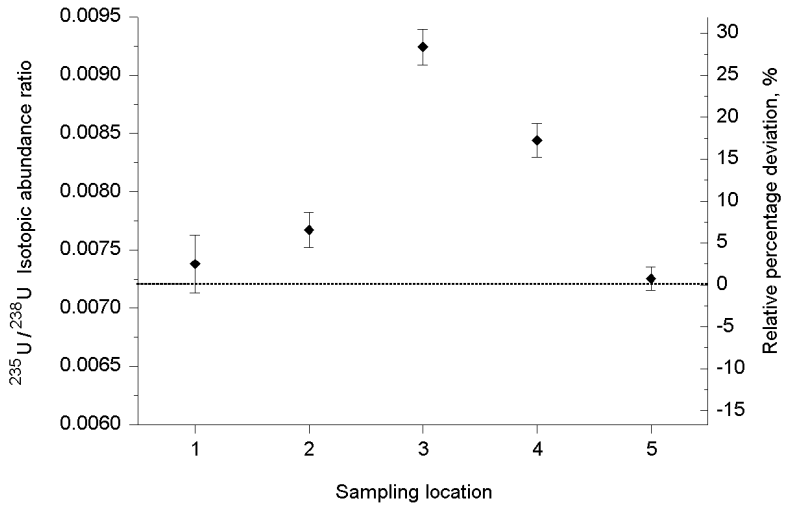

Fig. 3. Isotopic abundance ratios obtained for the samples submitted to the ultra-sound assisted acid washing processing method and respective estimated uncertainties

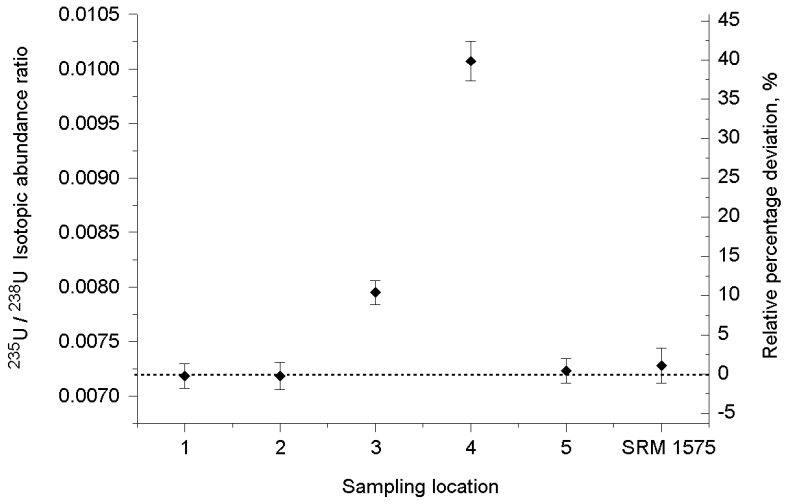

Fig. 4. Isotopic abundance ratios obtained for the samples submitted to the acid leaching processing method and respective estimated uncertainties

Table 5. $n(^{234}U)/n(^{238}U)$ isotopic abundance ratios obtained for the samples processed by the ultra-sound assisted acid washing method and respective estimated uncertainties

Location	$n(^{234}U)/n(^{238}U)$	u_c	u*	u, %
1	0.00006	0.0000134	±0.00003	±50
2	0.000063	0.0000043	±0.000009	±14
3	0.00008	0.0000059	±0.00001	±12
4	0.00007	0.0000066	±0.00001	±14
5	0.000060	0.0000047	±0.000009	±15

* Resulting from the product of the combined uncertainty by a coverage factor $k = 2$, for a level of confidence of approximately 95%.

Table 6. $n(^{235}U)/n(^{238}U)$ isotopic abundance ratios obtained for the samples submitted to the ultra-sound assisted acid washing processing method and respective estimated uncertainties

Location	$n(^{235}U)/n(^{238}U)$	u_c	u*	u, %
1	0.0074	0.000123	±0.0002	±2.7
2	0.0077	0.000075	±0.0002	±2.6
3	0.0092	0.000077	±0.0002	±2.2
4	0.0084	0.000073	±0.0001	±1.2
5	0.0073	0.000050	±0.0001	±1.4

* Resulting from the product of the combined uncertainty by a coverage factor $k = 2$, for a level of confidence of approximately 95%.

Conclusions

The results presented in this work confirm the possibility of substituting the traditional method of acid leaching, used to process this kind of sample, by a simple, fast and effective method, capable of providing results with the same quality.

It was possible to verify that the existence of a uranium compound with physical and chemical properties very particular (UF_6), massively used in uranium isotopic enrichment facilities, makes available an unmistakable and characteristic signature, the $n(^{234}U)/n(^{238}U)$ and $n(^{235}U)/n(^{238}U)$ isotopic abundance ratios, in the adjacent ecosystem.

The presented methodology confirmed, in an effective and simple way, the possibility of identifying activities related to the uranium isotopic enrichment through the measurement of the uranium isotopic abundance ratios using an HR-ICP-MS, in acid solutions obtained from the washing of pine needles.

The acid leaching method produced solutions, which uranium isotopic abundance ratio values presented the lowest associated uncertainties. However, it demands a lot of hand labor, time and the handling of chemical products in aggressive conditions.

The ultra-sound assisted acid washing method resulted in solutions which measurement results of the uranium isotopic abundance ratios were similar to those obtained for the acid leaching method. It is faster and requires a minimum amount of chemicals and glassware material. Its disadvantage is that it presents a high risk of external uranium contamination in the sample processing.

The work presented also represents a contribution in the safeguards and nuclear forensics area, confirming the technical viability and presenting a system capable of providing, through the use of the environmental monitoring, signs and evidences of enriched uranium handling in determined areas, fact that is intimately related to the isotopic enrichment activities.

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