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Review

An overview of the relative neutron activation analysis performed in the NAA Laboratory of the CRND using NUR reactor

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ABSTRACT

Neutron activation analysis is a highly sensitive method for multi-elemental analysis, primarily focusing on the induced radioactivity in atomic nuclei rather than the inherent chemical and physical properties of samples. This approach requires exposing the sample to neutron irradiation, typically conducted within a nuclear reactor. One of the most successful applications of Instrumental Neutron Activation Analysis (INAA) in the vicinity of the NUR reactor pertains to its use in environmental studies. It facilitates the monitoring of the distribution of trace elements (TEs) and the attribution of emission sources by analyzing samples from diverse environmental sources, including soil, air, and bioaccumulative plants collected from various locations near Algiers, Algeria. Since 2010, our laboratory has actively engaged in proficiency tests with WEPAL/IAEA, which has been instrumental in advancing and refining the methods of Neutron Activation Analysis (NAA) employed in this domain. The outcomes derived from these environmental investigations substantiate the presence of more than 30 trace elements. Comparing the enrichment factors (FEs) reveals the contribution of anthropogenic pollution, such as vehicles emitting Sb, Se, and Zn, brickyards releasing As, Co, Cr, Fe, Na, Se, Sc, Ta, and Tb, as well as soil resuspension leading to the release of Br and Zn. Additionally, our laboratory has conducted further studies in the realm of biology using the relative approach of NAA. The primary objective has been to harness the potential of NAA for early diagnosis in cases of cancer and chronic diseases. Consequently, we've examined the trace element composition in the whole blood of both healthy individuals and those afflicted by illnesses. We achieved this by subjecting lyophilized blood samples from adult subjects to simultaneous irradiation alongside an A13-IAEA blood standard. The elemental concentrations were subsequently calculated by measuring gamma rays using a gamma spectrometer. We simultaneously determines the concentrations of ten elements: Rb, Fe, Zn, Na, K, Br, Se, Sr, As and Sc.

1. Introduction

The concept of neutron activation analysis (NAA) was first introduced by von Hevesy and Levi in 1936, following the discovery of the neutron by James Chadwick in 1932 [1, 2]. For a substantial period spanning over 20 years, from the mid-1960s to the mid-1980s, NAA remained the predominant technique for analyzing trace elements in a diverse range of materials, including geological and biological samples. A comprehensive insight into the status of NAA during this era is aptly provided by Potts [3].

NAA, as a technique, offers the distinct advantage of enabling simultaneous multi-element qualitative and quantitative measurements, largely unaffected by matrix effects or interferences. It has been a cornerstone of our NAA laboratory's work, extensively applied in environmental, biological, and geological research endeavors. In particular, instrumental neutron activation analysis (INAA) has been widely adopted, as it does not necessitate post-irradiation radiochemical separations.

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INAA is acclaimed for its remarkable sensitivity in detecting and quantifying elemental constituents, even

those present in minute quantities. Some of the elements exhibit very short isotopic half-lives, on the order of minutes (e.g., Al, V, Ti), while others have half-lives extending from hours to years, including elements such as Mn, Na, La, K, As, Br, Ba, Ca, Cr, Ce, Fe, Hf, Lu, Nd, Rb, Sb, Sc, Sm, Sr, Zr, Ta Ta, Tb, Th, U, Yb and Zn.

Recognizing that the behavior of trace elements in the environment hinges on their interactions within the soil, water, and air, comprehending the fate and transport of these elements is of paramount importance for the well-being of humans, animals, plants, and soils. In this context, the NAA laboratory at CRND is dedicated to acquiring the knowledge required for assessing the presence and levels of trace elements in all environmental compartments (air, soil, vegetation) in suburban Algiers. Moreover, it strives to investigate the adverse effects of these trace elements on human health, as they can accumulate in the food chain, becoming a significant route of exposure to humans. Elevated exposure to trace elements, particularly toxic metals like mercury and lead, is a matter of serious concern due to their well-documented health risks, which encompass neurotoxicity and kidney disease from cadmium [4, 5]. On the other hand, certain trace elements are essential for human health, and deficiencies in elements such as iodine, iron, and selenium are linked to various well-documented conditions [6, 7]. In a proactive research initiative, CRND's INAA laboratory is presently engaged in exploring the early detection of cancerous and chronic diseases by leveraging nuclear techniques like neutron activation analysis. In this research area, whole blood samples from both healthy individuals and those afflicted by breast cancer are subjected to INAA for an in-depth investigation of trace elements. Breast cancer is a global health concern, being the most prevalent cancer among women worldwide, both pre- and post-menopause [8, 9 and 10]. The statistics from GLOBOCAN indicate that breast cancer is the leading cause of cancer incidence and mortality, with millions of new cases and deaths recorded in 2020 [11]. In Algeria, it is no different, with thousands of women succumbing to breast cancer each year, making it the most common cancer in Algerian women and a significant contributor to cancer cases in the country.

2. Methodology

2.1. Sampling and samples preparation for INAA

Air samples were obtained by continuously collecting total particulate matter at a flow rate of 1 m3/h. This collection was done using Whatman cellulose nitrate filters with a pore size of 0.8 μm and a diameter of 37 mm, and it was carried out with a low volume sampler (LVS) system manufactured by Millipore in Bedford, USA. You can find a detailed description of the equipment and procedures in Bouhila et al. (2015) [12]. In addition to air sampling, we used barks as biomonitors to collect samples concurrently with epiphytic lichen Xanthoria parietina. The samples were obtained by making an incision on trees at an elevation of approximately 1.5 meters above ground level. For a thorough understanding of the sampling process, please refer to Bouhila et al. (2021) [13]. Regarding blood collection, we gathered approximately 2 ml of blood from each participant, consisting of 11 breast cancer patients and 10 healthy individuals (controls). The procedures for blood collection and preparation were conducted in accordance with established protocols from previous studies [14].

2.2. INAA analysis

To conduct elemental analysis via INAA, we employed the conventional INAA relative method to detect trace elements present in the samples. Extensive experiments were conducted to analyze samples from various sources. Whenever possible, it's advisable to use Standard Reference Materials (SRM) with a similar composition to the sample matrix. For practical reasons and cost-effectiveness, we confirmed the accuracy of our INAA by utilizing common reference materials sourced from the environment for geological and plant samples. For blood samples, we employed IAEA-A13 as a reference. Detailed information regarding the qualification criteria and the significance of each element can be found in the reference sheets for each standard. In every INAA analysis, one standard served as a control, while the other was used for comparison. For elements that form long and medium-lived radioisotopes, each sample and standard reference material were weighed and encapsulated in high-purity (99.999%) aluminum foils. These were then subjected to irradiation for four hours at a thermal neutron flux of approximately 2×10^{13}n cm^{-2} s^{-1}. The precise methodologies for sample preparation and irradiation procedures can be found in our previously published works [12, 13, 15]. Following irradiation, the samples were allowed to cool for four days, after which radioactivity measurements were conducted for 5000 seconds per sample to assess medium half-life radionuclides. A second round of measurements was performed four weeks later to estimate the activity associated with long-lived radioisotopes produced (Table 1).

For elements that produce short half-life radioisotopes (Cl, Mn, and V), samples and standards were enclosed in high-density polyethylene material, known for its minimal trace

element content. The irradiation time for these samples ranged from 60 to 100 seconds, depending on the sample's origin (e.g., plant or soil). After irradiation, radioactivity measurement were typically conducted for 300 seconds.
The measurements of gamma rays were carried out usind a gamma spectrometer equipped with an HPGe detector from Canberra and Gamma Vision software, version 6.08 (EG & G ORTEC). The detector boasts a resolution of 1.90 keV on the 1332.5 keV line of 60Co, with an efficiency of approximately 30%. To ensure the quality and accuracy of our experiments, we conducted a collective analysis of NIST standard reference materials.

Table 1: An illustrative process for analyzing trace elements involving irradiation and subsequent counting

Counting #	Neutron flux ($n.cm^{-2}\ s^{-1}$)	T_i	T_d	T_c	Nuclei identified (Eγ, keV)
1	2×10^{13}	4 h	4 days	5000 s	^{82}Br (554,777), ^{140}La (1596), ^{24}Na (1369, 2754), ^{99}Mo (140.5), ^{76}As (559,1), ^{42}K (1524),^{153}Sm (103),^{175}Yb (396.3)
2	2×10^{13}	4 h	20 days	5000 s	^{141}Ce (145.4), ^{181}Hf (482.2), ^{59}Fe (1099),^{51}Cr (320), ^{134}Sc (752.63), ^{85}Sr (514), ^{65}Zn (1115), ^{60}Co (1332),^{134}Cs (604.7, 795.8), ^{160}Tb (879.4, 1178), ^{75}Se (264.7), ^{95}Zr (756.7), ^{203}Hg (279.2), ^{152}Eu (1408), ^{124}Sb (1690.7,1691), ^{86}Rb (1077), ^{182}Ta (1221.6), ^{115}Cd (527.9)
3	2×10^{13}	60-100 s		300 s	^{38}Cl (1642.4), ^{28}Al (134.58), ^{52}V (1433.9), ^{56}Mn (846.7), ^{51}Ti (319.8), ^{27}Mg (843.8)

Note: T_i, T_d, T_c refer to irradiation time, decay time, and counting time respectively

3. Somme essential results and discussion

The concentrations of individual elements were analyzed in each sample, and we calculated the quantities of each element obtained from various sample points. Considerable variability was observed in the elemental concentrations across samples from different sources for each material. The results revealed that over 25 trace elements (including As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Eu, Fe, Gd, Hf, K, La, Mn, Mo, Na, Rb, Sb, Sc, Sm, Se, Sr, Ta, Yb, Tb, V, Zr, and Zn) were determined in geological and plant samples, as depicted in figures 1, 2, and 3. Notably, elements like Fe, Na, and Zn were found to be predominant in nearly all samples, and varying concentrations of Sr, Cr, and Br were also observed. Essential trace elements such as Cr, Fe, and Zn were present il all the samples. To assess the analytical method's efficiency and validate the results, performance metrics like Z-score, U-score, Relative Bias, and others were calculated for each assay. Furthermore, to establish the enrichment factors (EF), the concentration of target elements in the samples relative to their concentration in the Upper Continental Crust (UCC) was used as a reference. Se and Sb exhibited high EF values (> 20) for lichens and barks, signifying extremely high enrichment In comparison, elements like Cr, Cs, Sm, and Zn showed moderate enrichments (EF = 3–5), while other elements exhibited minor enrichments (EF = 1–3). The high EF values for Se and Sb strongly suggest a traffic-related origin for these elements. Notably, Zn in lichens exhibited sgnificant enrichment (EF=8.27).

The obtained concentration values allowed us to arrange the elements in descending order for various materials:

- For lichens: Fe > Na > Zn > Sr> Cr > Br > Ce > La > Co > Sc > Hf > Cs > Sb > Sm > Se > Yb > Eu > As.
- For barks: Fe > Na > Zn > Sr > Zn >Br> Cr > Ce > Hf> La > Sm > Sb > Se > Sc > Cs > Eu > Co > Yb > As.
- For air in TSP matter: Fe > Na > Sr > Zn > Br > Cr > Ce > Sb > Co > La > As > Sc > Se > Sm > Yb > Eu > Hf > Cs.
- For soil: K > Ca > Na > Hf > Sr > Tb > Zn > Cr > Ta > Ce > Cs > Sb > Br > Sm > Nd > Cd > Zr > Ag > Fe > Sc > As > Se > Co > Ga > La > Mo.
- For Blood: Na > K > Fe> Zn> Br > Br >Sc

In the case of mutual tree bark and lichen samples, the concentrations of these seven elements decreased in the following order: Fe > Na > Zn > Sr > Cr > Br > Ce. It's worth noting that Fe displayed consistent accumulation in both varieties, possibly due to longer exposure periods, each element having its unique accumulation dynamics based on environmental metal availability.

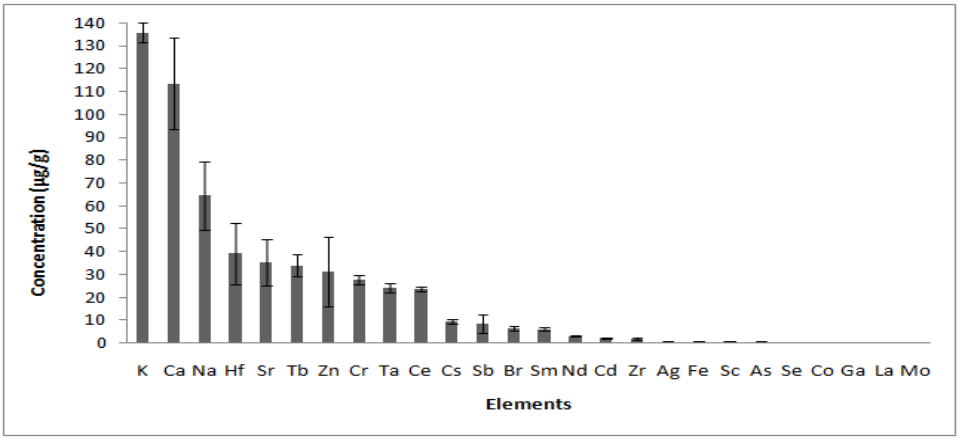

Fig 1. Average concentrations of trace elements (µg/g) in soil samples collected nearby Algiers

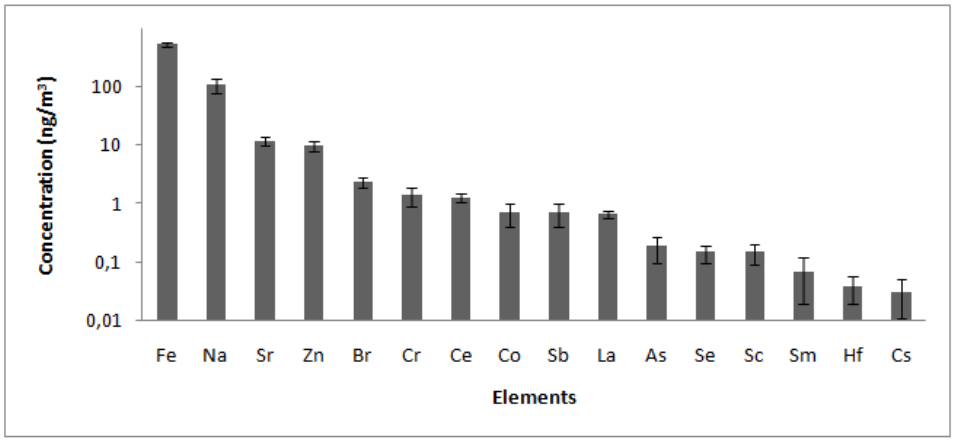

Fig 2. Average concentrations of trace elements (ng/m^3) in TSP matter samples collected nearby Algiers

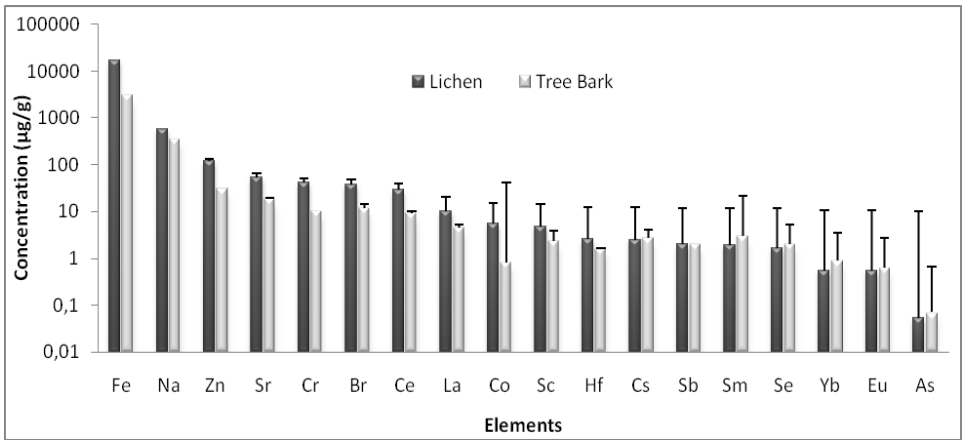

Fig 3. Average concentrations of trace elements (µg/g) in lichen and bark samples collected nearby Algiers

The analysis of blood samples holds significant value in assessing an individual's health status and identifying potential toxic elements in the body. Consequently, an extensive array of element concentrations has been scrutinized in human whole blood to ascertain any correlations with specific diseases and to gauge occupational exposure to harmful elements. Preliminary findings based on the mean concentrations of Rb, Fe, Zn, Na, K, Br, Se, Sr, As, and Sc obtained from INAA analysis of whole blood samples from cancer patients and a control group reveal varying levels of certain trace elements. The reliability of this analysis was verified by referencing the

AIEA-A13 standard material. Ten elements, namely Rb, Fe, Zn, Na, K, Br, Se, Sr, As, and Sc, were identified through this method. A statistical examination of the data strongly suggests that cancer patients exhibit lower iron levels and higher sodium levels compared to the healthy individuals tested. Chromium, Zinc, and Bromine also exhibit disparities between the two groups. While Scandium shows variations, the support for these differences is less robust. Selenium, on the other hand, does not display significant distinctions between the two groups.

4. Conclusion

To facilitate the creation of a trace elemental profile, we conducted a comprehensive assessment of elemental concentrations across various samples, revealing significant variations among them.

These results serve as a valuable reference point for establishing fingerprint profiles in future research endeavors. Our sample analyses were conducted with a stringent focus on statistical accuracy, utilizing larger sample replicas, and accounting for the elemental concentration variations within geographical and biological samples. Over the years, the outcomes of diverse investigations carried out in CRND's NAA laboratory have consistently highlighted the efficacy of this technique when applied to such samples. Moreover, they underscore the laboratory team's expertise in all aspects of this type of analysis.

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Conflict of Interest

The authors confim that they do not have any conflits of interest to disclose.

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