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Research article

Combination of NAA and TXRF: an improved method to detect elements in the moss technique

Nguyen An Son[1,*], Le Hong Khiem[2], Nguyen Thi Minh Sang[1]

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ABSTRACT

Introduction: Due to industrial development, agriculture, and urbanization, environmental pollution is a serious problem worldwide. In particular, air pollution is becoming increasingly serious. To evaluate the impact of air pollution in major cities of the country, various methods of air collection and treatment and assessment through monitoring stations are being developed. However, the main disadvantage of the installation of monitoring stations is the cost of investment for operations, maintenance, and equipment. In this study, to reduce costs, *Babular Indica* moss was chosen as a biological indicator. Two techniques, NAA and TXRF, were combined to increase the number of trace elements detected in moss samples. **Methods:** A combination of two multielement analysis techniques, NAA and TXRF, are used to detect trace elements from atmospheric deposition in Barbula indica moss collected in Bao Loc, Vietnam. **Results:** The two methods are highly complementary, allowing us to determine 42 elemental concentrations in 11 moss samples. Twenty-nine elements were identified with NAA: Na, Mg, Cl, K, Sc, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Rb, Sb, I, Cs, La, Ce, Sm, Eu, Tb, Dy, Yb, Hf, Ta, Th and U. Twenty-four elements were identified with TXRF: Al, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Y, Ag, Sn, Sb, Ba and Pb. Eleven elements were identified by both techniques. **Conclusion:** This study shows that NAA and TXRF combine efficiently and provide a more comprehensive detection of trace elements in moss samples than is possible with either technique alone.

Key words: Atmospheric deposition, Barbula indica, NAA, Trace element, TXRF

[1]*Dalat University, Dalat, Viet Nam*

[2]*Institute of Physics of Vietnamese Academy of Science and Technology, Hanoi, Viet Nam*

Correspondence

Nguyen An Son, Dalat University, Dalat, Viet Nam

Email: sonna@dlu.edu.vn

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INTRODUCTION

Mosses are effective and widely used biomonitors of atmospheric pollution because of their bioaccumulative properties. They lack a cuticle and roots and readily absorb contaminants from the atmosphere. Mosses are widespread, easy to collect and handle, and provide an inexpensive method of detecting atmospheric contaminants. The moss method was developed in the late 1960s by Rühling and Tyler [1–3] and has been used extensively in Europe and elsewhere.

Several nuclear-related analytical techniques have been applied to measure trace element concentrations in mosses. Neutron activation analysis (NAA), atomic absorption spectrometry (AAS), inductively coupled plasma–mass spectrometry (ICP–MS), total reflection X-ray fluorescence (TXRF), and proton-induced X-ray emission (PIXE) have been used to determine heavy elements [4]. The NAA technique has been used in France, India, Portugal, Ghana, Jamaica, Romania, and Russia. The ICP–MS technique has been used in France, India, Israel, and Norway. The XRF, NAA, and PIXE techniques have been used in India, Jamaica, and Ghana. However, NAA is the main analytical tool used.

In previous work, approximately 20 elements could be detected by the NAA technique on moss samples [5–7]. In some research, 30 to 36 elements were detected [8]. It is very noticeable in these studies that lead could not be detected.

The NAA sensitivity depends upon neutron flux, irradiation, decay times, and nuclear parameters of the elements being measured: magic nuclei, isotope abundance, neutron cross-section, half-life, and gamma-ray energy. The sensitivity for the determination of elements is pg to mg. As a result of NAA investigations, it is well known which elements are likely to be determined by neutron activation [9]: Mg, Si, Ti, Cr, Fe, Ni, Cu, Zn, Se, Br, Kr, Rb, Sr, Ag, Cd, I, Sr, Sb, Te, Xe, Ba, Hf, W, Re, Os, Ir, Pt, Au, Hg, Ce, Nd, Sm, Eu, Gd, Yb, and Lu.

The TXRF sensitivity depends upon the X-ray energy source, current intensity, high voltage, and X-ray characteristics of elements in the sample. TXRF is widely used for the elemental analysis of environmental samples. Compared to other analytical techniques, such as AAS, ICP–MS, and PIXE, TXRF has the advantage of being multielemental, fast and cost-effective [10,11]. Furthermore, TXRF provides fairly

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uniform detection of trace elements and applies to a wide range of concentrations from ppm to ppb. Its main disadvantages are generally due to the X-ray energy tube in the spectrometer. The X lines of elements that have energy higher than the X-ray energy tube cannot be detected.

Using moss species in passive monitoring of atmospheric pollution depends on the regions where the moss species grow. In Europe, mosses used in biomonitoring include *Pleurozium schreberi*[5], *Scleropodium purum*[6,12], *Hylocomium splendens*[13], and *Hypnum cupressiforme*[14]. However, these moss species are rarely found in Asia. Instead, other mosses have been used: *Hypnum plumaeform* in China[15], *Hypnum plumaeforme* and *Taxithelium instratum* in Malaysia[16], *Thuidium tamariscellum* in the Philippines[17] and *Barbula indica* in Vietnam[18–20].

In this study, samples of *Barbula indica* moss were collected at different locations in Bao Loc. *Barbula indica moss* is widely distributed and easy to collect in the city. Both NAA and TXRF are used in the present investigation. These two techniques are general nondestructive, multielement techniques with high sensitivity and short analysis time. The research focused on the qualitative detection and quantitative measurement of trace elements in *Barbula indica* moss.

MATERIALS AND METHODS

SAMPLING AREAS

Bao Loc is a city in Lam Dong Province in the Central Highlands of Vietnam. It is located at 11°32'N latitude and 107°48'E longitude, covers an area of approximately 232.56 km^2, and lies approximately 846 m above sea level. Bao Loc's climate is classified as tropical with an average temperature of 21.2°C. The average rainfall is approximately 2480 mm per year. Bao Loc normally has two seasons of six months each. The dry season begins in November and ends in May, and the rainy season lasts the rest of the year.

Barbula indica moss collection was carried out once every half month from the end of the rainy season from November 2020 to March 2021. Figure 1 shows the locations of the 11 moss sample sites in Bao Loc. Sample sites were chosen where the moss was likely to have been affected by traffic, farms, or industry.

SAMPLE COLLECTION

The *Barbula indica* moss morphology and a moss powder sample are shown in Figure 2. To minimize the influence of the substrate, moss was collected from trees at least 1.5 m above the ground, and only the top green part was used for analysis. Details of the preparation sample process in the analysis of the two methods are shown in the following section.

SAMPLE PREPARATION

The collected moss samples were cleaned of soil particles, washed three times with distilled water, and then dried at 40°C for 50 hours. Afterwards, the moss samples were crushed and homogenized to a powder (~0.5 mm) in an AS 300 control analytical sieve shaker for 30 min.

For the NAA measurements, dry powdered moss samples weighing approximately 50 mg were heat-sealed in polyethylene foil bags for short-term irradiation, and powder samples weighing approximately 180 mg were packed in aluminum containers for long-term irradiation. Table 1 shows the moss sample masses.

For the TRXF measurements, powdered moss samples were ground to a particle size of 50 μm using a RETSCH MM 400^{TM} mixer mill. The powdered moss samples must be liquefied through digestion. In this investigation, the MARS 6^{TM} microwave acid digestion system was used. Approximately 0.5 g of powdered moss sample was placed into the digestion vessel, and 10 ml of HNO3 (65%) was added. The mixture was gently swirled and left to sit approximately 15 min before closing the vessel. After finishing this procedure, the moss sample was a liquid (the original sample). We then transferred 500 μl of the liquid sample to a polymer container, and gallium internal standard liquid was added until the sample reached 1 ppm gallium. The sample was then thoroughly homogenized by an automatic sample shaker. After thorough homogenization, 10 μl of the sample was transferred to a sample carrier and dried at 30°C for 3 hours.

TXRF TECHNIQUE

A Bruker S2 PICOFOX^{TM} spectrometer was used to collect the characteristic X-ray spectrum for each moss sample. It was operated at 50 kV high voltage with a maximum tube rating of 50 W. The characteristic details of the TXRF spectrometer are presented by[21]. The S2 PICOFOX spectrometer can detect 25 elements with K-line energy (from Al to Y) and 47 elements with L-line energy (from Ru to U).

NAA TECHNIQUE

NAA was carried out at the 500 kW Dalat research reactor (DRR) of Vietnam. Previous work established that NAA at DRR has met the requirements of multi-element analysis for 42 elements from Al to U[22].

Short irradiations were conducted for 45 s on Channel 7-1 at a thermal neutron flux of approximately 4.2×10^{12} $cm^{-2}s^{-1}$. To determine short-lived isotopes, every sample was decayed for 1-2 min and then

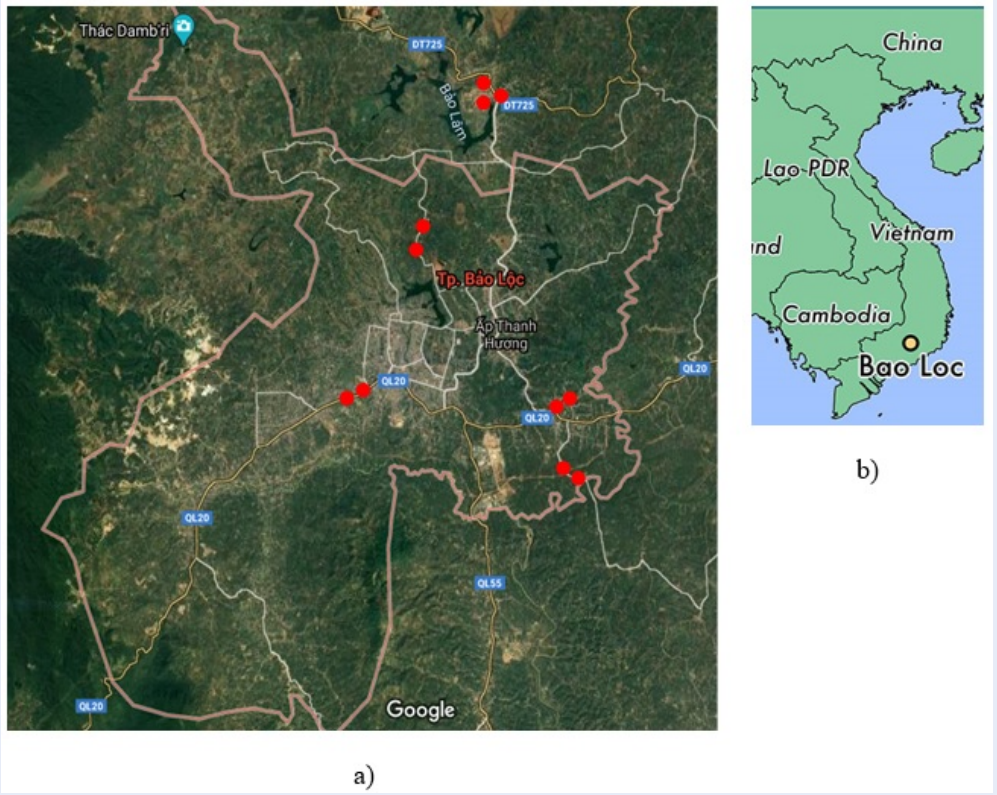

Figure 1: **a) Sampling sites in Bao Loc. b) Location of Bao Loc.**

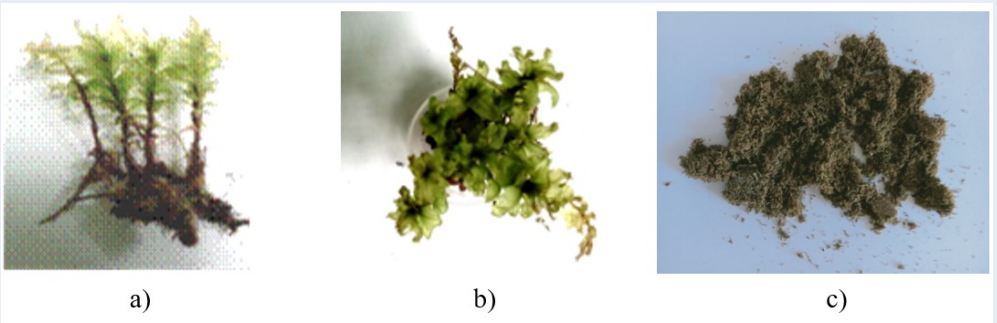

Figure 2: a) and b) Side and overhead views of *Barbula indica* moss. c) Moss powder sample

measured for 15 min. Long irradiations were conducted for 1 hour on a rotary rack at a thermal neutron flux of approximately 3.5×10^{12} $cm^{-2}s^{-1}$. The samples were allowed to decay for three days prior to counting for one hour. The moss samples were measured with a gamma-ray spectrometer on an HPGe detector with an FWHM of approximately 1.9 keV at 1332 keV and a relative efficiency of ~33%.

RESULTS

Trace element concentrations from all 11 sampling sites were analyzed using both NAA and TXRF techniques. All element concentration errors are smaller than 10%. The two techniques detected 42 elements in the moss samples. The NAA method detected 29 elements: Na, Mg, Cl, K, Sc, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Rb, Sb, I, Cs, La, Ce, Sm, Eu, Tb, Dy, Yb, Hf, Ta, Th and U, and the TXRF method detected 24

Table 1: Moss sample masses

Sample name	Short irradiation samples	Long irradiation samples (mg)
BL01	47.41	148.27
BL02	54.27	139.03
BL03	57.16	189.55
BL04	47.16	150.33
BL05	72.94	159.75
BL06	55.86	151.29
BL07	44.07	152.33
BL08	61.07	181.01
BL09	65.78	156.47
BL10	62.63	156.81
BL11	47.08	121.53
IAEA-392 sample	55.69	111.89

elements: Al, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Y, Ag, Sn, Sb, Ba and Pb. Eleven elements (Cl, K, V, Cr, Mn, Fe, Co, Zn, Br, Rb and Sb) were detected by both methods. The results are consistent between the techniques.

Our results can be compared with previous studies in Vietnam that also use Barbula indica moss but with different detection techniques. In Table 2, the mean elemental concentrations in moss samples from our work are compared with previous studies by Doan Phan [19] and Khiem [20]. The comparison shows that the number of elements in our research is greater than that in previous studies, despite Ho Chi Minh City (the largest city of Vietnam) and Hanoi (the capital of Vietnam) having more pollution sources.

Table 2: Comparison between our results and previous, single-method studies in Vietnam

No.	Element	Element concentration in mg/kg			
		Our work		Ref.19	Ref.20
		NAA	TXRF	INAA	PIXE
1	Na	304	–	953	–
2	Mg	684	–	1486	3838
3	Al	–	3,236	4,600	9911
4	P	–	662	–	1172
5	S	–	1,683	–	2,987
6	Cl	696	682	1,527	1368
7	K	914	925	15,000	11,881
8	Ca	–	854	11,600	17,877
9	Sc	1.89	–	–	–
10	Ti	–	337	333	676
11	V	4.91	5.5	8.46	–
12	Cr	6.61	6.32	12.57	28
13	Mn	118	102	80	137
14	Fe	2,887	3,105	4,653	6,127
15	Co	2.01	1.97	–	–
16	Ni	–	3.24	5.47	4.40
17	Cu	–	16.59	–	21.9
18	Zn	371	413	186	285
19	As	5.67	–	3.13	7.9
20	Se	0.28	–	–	–
21	Br	5.14	3.43	10.3	9.9
22	Rb	3.27	2.91	–	171
23	Sr	–	46	–	147
24	Y	–	8.24	–	–
25	Ag	–	61	–	–
26		–	92	–	–
27		43.36	46.63	1.1	–
28	I	7.41	–	–	–
29	Cs	1.13	–	2.69	–
30	Ba	–	45.44	80.67	1268
31	La	6.89	–	–	–
32	Ce	14.23	–	7.37	–
33	Sm	1.43	–	0.67	–
34	Eu	0.24	–	–	–
35	Tb	0.26	–	0.11	–
36	Dy	1.24	–	–	–
37	Yb	0.63	–	–	–
38	Hf	0.69	–	–	–
39	Ta	0.22	–	–	–
40	Pb	–	4.14	–	89.8
41	Th	2.29	–	1.38	–
42	U	3.08	–	0.65	–

DISCUSSION

In Table 2, the results were compared with those of some previous studies. It is clear that the number of elements when combining the two methods is greater than that when using the other single methods.

In the Doan Phan [19] study, instrumental neutron activation analysis (INAA) using the IBR-2 nuclear reactor at the Joint Institute for Nuclear Research in Dubna (Russia) was carried out for moss samples from Hue, Hoi An and Ho Chi Minh City. It found 13 fewer elements (P, S, Cu, Rb, Y, Ag, Sn, I, Eu, Dy, Yb, Hf, Pb) than our work. In particular, some elements that are usually evaluated in air quality studies were not detected by Doan Phan [19]. The results differ for two main reasons: the abovementioned elements have low thermal cross sections and low isotope abundances in nature. Therefore, the NAA technique could not detect them effectively, whereas TXRF could.

Table 2 shows that we detected 22 elements not found by Khiem [20] in Hanoi: Na, Sc, V, Co, Se, Y, Ag, Sn, Sb, I, Cs, La, Ce, Sm, Eu, Tb, Dy, Yb, Hf, Ta, Th and U. They detected two elements that we did not, Si and Zr. The disadvantages and limitations of the PIXE technique depend on the proton cross section and isotope abundances.

CONCLUSION

This investigation combined NAA and TXRF techniques to identify 42 chemical elements in Barbula indica moss. The 29 elements identified with the NAA technique are Na, Mg, Cl, K, Sc, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Rb, Sb, I, Cs, La, Ce, Sm, Eu, Tb, Dy, Yb, Hf, Ta, Th and U. The 24 elements detected by TXRF are Al, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Y, Ag, Sn, Sb, Ba and Pb. Eleven elements, Cl, K, V, Cr, Mn, Fe, Co, Zn, Br, Rb and Sb, were detected by both techniques.

The NAA and TXRF techniques complement each other well, increasing the number of trace elements detected in moss samples and providing more information from biomonitoring surveys. Each analytical method has its own disadvantages when combining analytical methods, so the combination of NAA and TXRF improved the method to detect elements in the moss technique. The two techniques also provide a reliable method for determining atmospheric deposition in moss samples.

ABBREVIATIONS

AAS: Atomic Absorption Spectrometry

ICP-MS: Inductively Coupled Plasma–Mass Spectrometry

INAA: Instrument Neutron Activation Analysis

FWHM: Full width at half maximum

HPGe: High Purity Germanium

NAA: Neutron Activation Analysis

PIXE: Proton-Induced X-Ray Emission

TXRF: Total X-ray Reflection Fluorescence

XRF: X-ray Reflection Fluorescence

CONFLICT OF INTERESTS

The authors declare no potential conflict of interest regarding the publication of this work. In addition, ethical issues, including plagiarism, informed consent, misconduct, data fabrication and falsification, double publication and submission, and redundancy, have been completely witnessed by the authors.

AUTHORS' CONTRIBUTIONS

Le Hong Khiem, Nguyen An Son, Nguyen Thi Minh Sang suggested the research plan. Nguyen Thi Minh Sang proposed and implemented the experiment. Le Hong Khiem, Nguyen An Son, Nguyen Thi Minh Sang compiled the data, prepared and completed the manuscript.

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