ISSN: 2716-9227 Algerian Journal of Engineering and Technology 09 (2024) 001–007 e-ISSN: 2716-9278

Algerian Journal of Engineering and Technology

Journal homepage: https://jetjournal.org/index.php/ajet

Original Article

Non-destructive multielement analysis of airborne particles by instrumental neutron activation analysis

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ARTICLE INFO

Article history:
Received 14 January 2024
Revised 03 March 2024
Accepted 08 March 2024

Keywords:
Trace elements;
airborne particles;
Neutron activation analysis;
Metals pollution.

ABSTRACT

Instrumental neutron activation analysis (INAA) was used for the determination of the elemental composition of aerosol samples. Two samples of air of approximately 20 m^3 each one were collected of the atmosphere around the Es-Salam research reactor site in Algeria. The irradiation of the samples and reference materials was carried out during 30 s for the elements of short half-life and 06 h for the elements of medium and long half-life with a thermal neutrons flux of 1.12 10^{13} and 6.88 10^{13} n/cm²s respectively. Ge(Hp) γ-spectrometry made it possible to determine fifteen elements (Al, Cl, Mn, Ca, Cd, Br, La, Fe, Nd, Ce, Hg, Cr, Hf, Sb and Zn). The obtained results for the used reference materials almost perfectly match its certified values (Z_{score}<2).

1. Introduction

With the proliferation of industrial activities, the emission of pollutants in the atmosphere caused by anthropogenic sources increases accordingly, it contributes to the deterioration of the air quality and creates public health problems [1]. These emissions come from many sources such as the exhaust of vehicles, the smokestacks of factories, ships and coal-fired power plants, aerosols have an impact on almost all parts of the human body, depending on their composition, the degree of exposure and the size. The most impactful aerosols are very fine particles, "which can penetrate deep into the lungs and even into the bloodstream," aggravating respiratory and cardiovascular systems.

The determination of pollutants in atmospheric aerosols is an operation that is all the more delicate to carry out as the number of contained elements is large. These elements are most often toxic in trace amounts. Trace measurement techniques are varied and each of them has its own characteristics. The choice of one of them depends on the elements to be assayed, the sensitivity required, the aspect of the sample, and the exploitation that one wishes to make of the results.

INAA, XRF (X Ray Fluorescence) and PIXE (Particle-Induced X-ray Emission) are non-destructive analytical methods; ICP (Inductively Coupled Plasma), ICP-MS (Inductively Coupled Plasma Mass Spectrometry), Atomic Emission Spectroscopy (AES) and Ion Chromatography (IC) include sample dissolution operations, thus causing a possible sample contamination or loss of some of its components due to incomplete dissolution.

In any case, high sensitivity is a must-have feature. One of the most suitable nuclear techniques for the non-destructive multi-element analysis of atmospheric particles is INAA. Several works dealing with air pollution monitoring using INAA methods have been carried out successfully [2-5].

This work aims to evaluate the effectiveness of instrumental neutron activation analysis in determining the elemental composition of aerosol samples collected near the Es Salam reactor area. This would allow us to extend application fields of this method and to carry out

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Peer review under responsibility of University of El Oued.
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comparative studies on heavy metals pollution in a given site.

2. Materials and methods

2.1. Sampling

An aerosol sampling device was held at 1.5 meters above the ground. The weather conditions were constant (sunny days, temperatures between 25 and 30 °C, absence of winds). Total particles matter PM_{total} were collected onto a membrane filter type Millipore HA, 47 mm, 0.45 µm pore size; this type of filters is known for its purity and stability under irradiation, air aspiration was accomplished using a pump fitted with a flow meter, the operating airflow was 40 L/min. The total volume of air collected on each filter was around 20 to 25 m^3, blank filters and envelopes were also used for background determination.
Samples and reference materials of the medium and long half-life elements process noted MP and LP respectively, were conditioned each one in an aluminum envelope (99.9 % purity) and assembled in an aluminum capsule. Each sample of the short half-life elements process (SP) was packed in a polyethylene envelope and put in a polypropylene capsule that will be irradiated using a pneumatic system ensuring the sending and the reception of the capsule.

The thermal neutron flux gradient was monitored by using Iron samples for the MP and LP process and chloride (KCl) samples for the SP process.

2.2. Instrumental Neutron activation analysis (INAA)

During irradiation, the evolution of the number of radionuclides N_r is expressed by the following differential equation:

$$\frac{dN_r}{dt} = \sigma \emptyset N_n - \lambda N_r \qquad (1)$$

$$N_n = \frac{N_A m\, \theta}{M} \qquad (2)$$

where σ is the cross section of the target nuclide (cm^2); Ø the thermal neutron flux (n/cm^2 s); λ the decay constant (s^{-1}); N_n the number of atoms in the target, N_A is the Avogadro's number ; m the mass of the element in the sample (g) ; θ the isotope abundance, M the atomic mass of the element (g/mol).

The solution of Eq. 1 gives at an irradiation time t_i:

$$N_r(t) = \frac{\sigma \emptyset N_n}{\lambda}\left(1 - e^{-\lambda t_i}\right) \qquad (3)$$

Since the induced activity $A(t) = \lambda N_r(t)$ and taken into account the irradiation *(i)*, decay *(d)* and measurement *(m)* terms, and by integrating the activity over the measurement time, we can write:

$$N_d(t_m) = \frac{\sigma \emptyset N_n}{\lambda}\left(1 - e^{-\lambda t_i}\right) e^{-\lambda t_d}\left(1 - e^{-\lambda t_m}\right) \qquad (4)$$

Where, N_d is the number of nuclei decayed during the measurement time t_m.

By introducing the photon intensity factor γ with energy E for one radionuclide decay and the efficiency of the measurement chain $\xi(E)$, the total number of detected photons becomes:

$$N = \frac{\sigma \emptyset N_A m \theta \gamma \xi(E)}{\lambda M}\left(1 - e^{-\lambda t_i}\right) e^{-\lambda t_d}\left(1 - e^{-\lambda t_m}\right) \qquad (5)$$

The concentration C of each element in the sample was determined by the relative INAA method as follows:

$$C = C_{rm} \frac{N\ m_{rm}}{N_{rm}\ m} \qquad (6)$$

where C, C_{rm} are respectively the concentrations of the element in the sample and the reference material, N, N_{rm} are respectively the detected photons of the radioelement in the sample and the reference material, m and m_{rm} are the masses of the sample and the reference material, respectively.

In order to cover all the possible elements in the aerosol samples we have used four certified reference materials CRMs : stream sediments GBW07312/ GSD-12, tea leaves *GBW07605/*GSV-4, human hair GBW07601/GSH-1 and Lichen (IAEA-336); fifteen samples including blanks were prepared for SP and MP process (Table 1).

Table 1: References and masses of the used samples

N°	Sample	Mass (mg)	Analysis way
1	Filter and total PM (20 m^3 of air)	90.3	SP
2	GSD12	174.4	SP
3	Lichen (IAEA 336)	111.8	SP
4	Filter and total PM (24.18 m^3 of air)	90	MP
5	GSD12	108.3	MP
6	GSV4	98.5	MP
7	GSH1	88.3	MP
8	Lichen (IAEA 336)	143.4	MP

2.3. Irradiation

Irradiation of the samples in the reactor has been planned according to the following scheme: for medium and long period elements, the samples were irradiated during 6 hours under a thermal neutron flux of 6.88 x 10^{13} n/cm^{2}s, whereas an irradiation pneumatic system was used for the short period elements with a thermal neutron flux of 1.12 x 10^{13} n/cm^{2}s during 30 s. Decay time was 240 seconds for SP process, 5 and 21 days for MP and LP process, respectively.

Gamma-ray spectra were collected under the same conditions using Canberra Genie 2000 software at the neutron activation analysis laboratory (CRNB) with high purity germanium (hpGe) coaxial detector of 25% efficiency, FWHM of 1.8 keV at the 1332.5 keV peak of ^{60}Co. In order to determine the optimum counting conditions we have preceded short pre-collections of the totality of the samples. Irradiation, decay, counting time of γ-ray spectra and qualitative analysis of SP, MP and LP analysis process are shown in Fig. 1.

The exploitation of databases led to the qualitative analysis as shown in Table 2 [6].

2.4. Gamma spectrometry

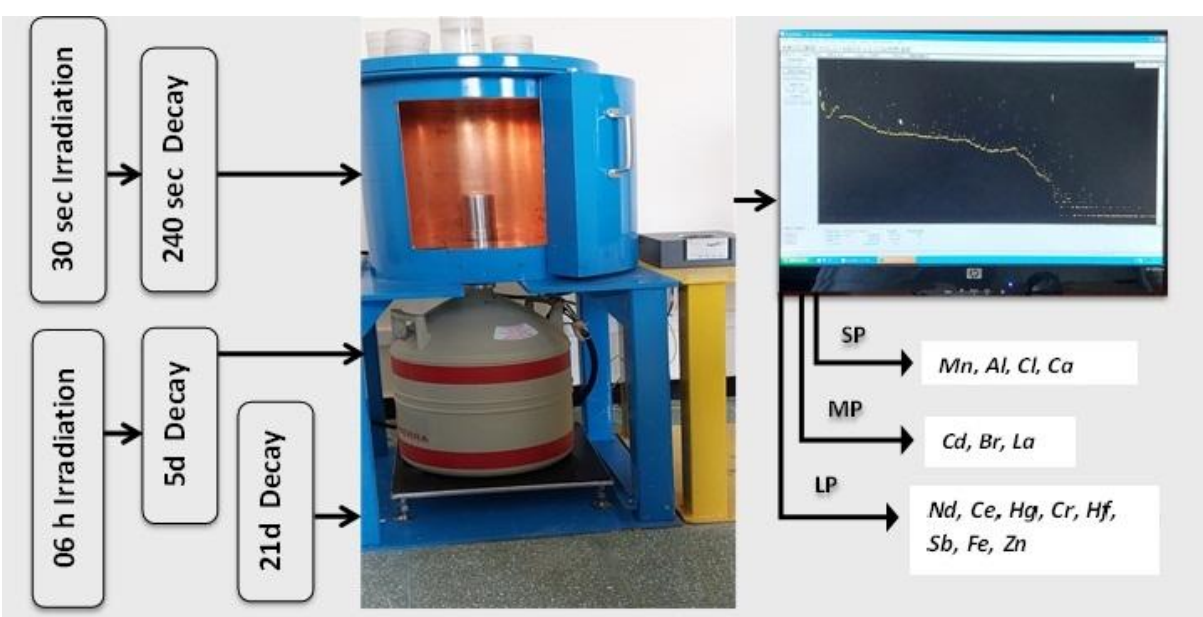

Fig 1. Instrumental Neutron activation analysis process

Table 2 : Qualitative analysis of aerosol particles

Element	Isotope	Radio-isotope	γ-ray peak (keV)	Analysis way
Al	^{27}Al	^{28}Al	1779	S.P
Br	^{81}Br	^{81}Br	554	M.P
Ca	^{48}Ca	^{49}Ca	3084	S.P
Cd	^{114}Cd	^{115}Cd	527.56	M.P
Ce	^{140}Ce	^{141}Ce	145.4	L.P
Cl	^{37}Cl	^{38}Cl	1642.71	S.P
Cr	^{50}Cr	^{51}Cr	320	L.P
Fe	^{58}Fe	^{59}Fe	1099	L.P
Hf	^{180}Hf	^{181}Hf	482	L.P
Hf	^{180}Hf	^{181}Hf	482	L.P
La	^{139}La	^{140}La	486.77	M.P
Mn	^{55}Mn	^{56}Mn	847.05	S.P
Nd	^{146}Nd	^{147}Nd	91	L.P
Sb	^{123}Sb	^{124}Sb	602.8	L.P
Zn	^{64}Zn	^{65}Zn	1115.66	L.P

3. Results and discussion

The relative method led to the determination of fifteen elements, namely: Mn, Cl, Al and Ca using the short period way, the medium period way led to the determination of Br, Cd and La, the remaining elements (Nd, Ce, Hg, Cr, HF, Sb, Fe and Zn) were analyzed by the long period way. It should be noted that our method showed a high sensitivity reaching values of the order of 3.4 10^{-11} g/m^3 for Mercury, for example. In Fig. 2, we show, as an indication, the gamma spectrum obtained for the MP way.

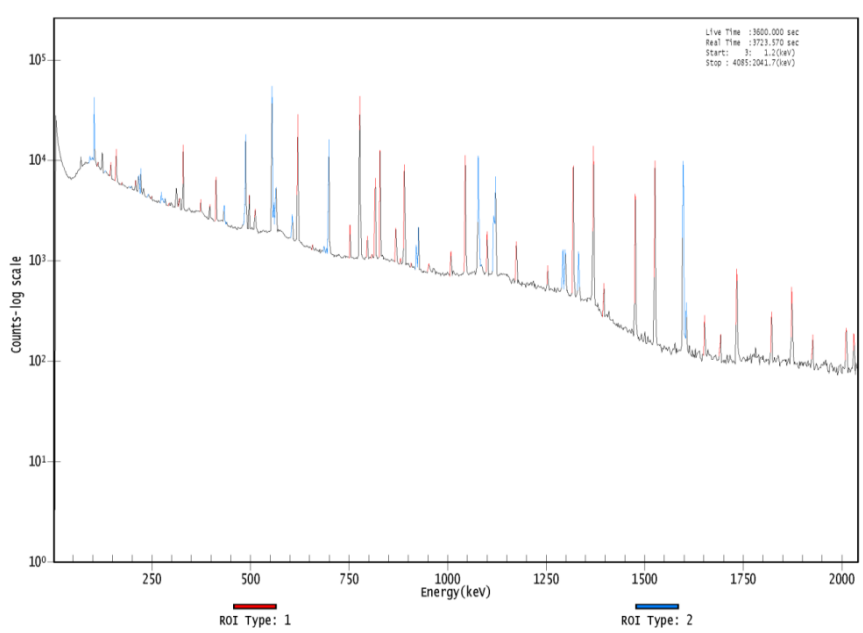

Fig 2. Gamma Ray spectrum of the aerosol sample (MP way)

The Occupational safety and health administration (OSHA) provided global air quality guidelines with a recommended maximum level of pollutants. The average amounts of determined heavy metals Mn, Cd, Hg, Cr, Zn and Fe were much lower than the average inhalable limits set by OSHA which are 0.02, 0.005, 0.025, 0.005, 5 and 5 mg/m^3, respectively. With an average concentration of 253.4 ng/m^3, iron (Fe) represents about 2.5% of the mass of PM (10 µg/m^3) which was expected because of its abundance in the Earth's crust.

The measured concentrations are shown in Table 3.

Table 3: Elemental composition of the aerosol samples

Element	Concentration (ng/m^3)
AL	53.3± 5.1
Br	0.46 ±0.05
Ca	360 ±63
Cd	9.8 ± 3.03
Ce	40.6 ±17.3
Cl	287.6±21.2
Cr	0.45 ±0.05
Fe	253.4 ±18.9
Hf	0.07 ±0.03
Hg	0.034 ±0.002
La	101.5 ±8.6
Mn	0.69 ±0.08
Nd	1.67±0.02
Sb	0.34 ±0.03
Zn	4.2±0.2

In addition, and according to WHO recommendations in terms of the PM pollution limits for short and long terms, air quality in the studied area (PM_{Total} =10 µg/m^3) can be categorized as fair (levels above 5 and not exceeding 10 µg/m^3).

3.1 Enrichment Factor

The enrichment factor (EF) is used to assess the anthropogenic contribution. It represents the ratio of an element's concentration to that of the chosen element of reference in the sample, all divided by the same ratio in a reference material [7].

Because of its reliable determination, zinc was chosen in this study as an element of reference [8]. The EF was calculated as follows:

$$EF = \frac{\left(X/_{Zn}\right)_{Sample}}{\left(X'/_{Zn'}\right)_{Reference}} \qquad (7)$$

where X and Zn are the concentrations of the element and zinc in the aerosol sample, X' and Zn' are the concentrations of the element and zinc in the certified reference material CRM (Lichen IAEA-336).

For EF values close to unity, the crustal source is the predominant source [9], the enrichment is moderate when 5<EF<10, from severe to very severe between 10 and 50 and extremely severe when EF>50 [10,11].

The enrichment factor values for determined elements are summarized in table 4, elements with EF lower than 5 such as Mn, Cl, Al, Br, Hg, Cr and Fe are considered to be of crustal origin, Enrichment factors of Nd and Sb have coherently low enrichment factors, while Cd, La and Ce with an EF greater than 100 derived from anthropogenic sources.

Table 4: Enrichment factor (EF) values for determined elements in the studied area

Element	EF
Al	0.56
Br	0.26
Cd	599.9
Ce	227.7
Cl	1.09
Cr	3.04
Fe	4.2
Hg	1.2
La	1102
Mn	0.08
Nd	19.9
Sb	33.4

3.2 Evaluation and validation of results

Quality assurance methods are pre-established and cover the entire neutron activation analysis process, including sample preparation, calibration of the spectrometry chain, irradiation, collection of spectra and internal quality control [12-14]. Table 5 gives a comparison of the obtained results for two certified reference materials (IAEA-336 and GSH-1) to the corresponding certified values, the statistical parameters Z-score and relative bias (RB) were calculated using the following equations :

$$Z_{score} = \frac{|x_{lab} - x_{ref}|}{\sigma_{ref}} \quad (8)$$

$$Relative\ bias\ (RB) = \frac{|x_{lab} - x_{ref}|}{x_{ref}} \times 100\% \quad (9)$$

where x_{lab}, x_{ref}, and σ_{ref} are the laboratory results, the mass fraction of the element in the reference material and the standard uncertainty respectively.

Table 5: Validation of obtained results based on Lichen (IAEA-336) and human hair (GSH-1) reference materials

Element	Lichen-IAEA336				Human hair -GSH1			
	Certified values	Calculated values	Z_{score}	RB	Certified values	Calculated values	Z_{score}	RB
Al	680±110	710±83	0.2	4.4	ND	ND	-	-
Br	12.9±1.7	10.8±1.2	1.2	16.2	0.36*	0.41±0.07		13.8
Ca (%)	ND	ND	-	-	0.29±0.03	0.36±0.06	2.3	24.1
Cd	0.117±0.017	0.166±0.02	2.8	41.8	0.11±0.03	0.17±0.012	2	54.5
Ce	1.28±0.17	1.35±0.14	0.4	5.4	0.12±0.03	0.16±0.013	1.3	33.3
Cl	1900±300	1466±215	1.4	22.8	ND	ND	-	-
Cr	1.06±0.17	1.29±0.11	1.3	21.7	0.37±0.03	0.46±0.06	3	24.3
Fe	430±50	451±37	0.4	4.8	54±10	49±8	0.5	9.2
Hg	0.2±0.04	0.135±0.02	1.6	32.5	0.36±0.08	0.28±0.05	1	22.2
La	0.66±0.1	0.93±0.15	2.7	40.9	0.049±0.011	0.077±0.008	2.5	57.1
Mn	63±7	56±5	1	11.1	6.3±0.8	5.4±0.75	1.1	14.2
Nd	0.6±0.18	0.75±0.14	0.8	25	ND	ND	-	-
Sb	0.073±0.01	0.055±0.01	1.8	24.6	0.095±0.016	0.082±0.012	0.8	13.6
Zn	30.4±3.4	28.5±4.2	0.5	6.2	190±9	163±12	3	14.2

* : Proposed value
ND : Not determined

The laboratory effectiveness is considered satisfactory if $Z_{score} \leq 2$, debatable for $2 < Z_{score} < 3$, and unsatisfactory for $Z_{score} \geq 3$ [15]. The obtained results almost perfectly match the certified values of the used reference material [14].

4. Conclusion

The high thermal neutrons flux was favorable for the determination of fifteen elements (Al, Cl, Mn, Ca, Cd, Br, La, Fe, Nd, Ce, Hg, Cr, Hf, Sb and Zn) with high precision in air filters and blank filter materials.

Enrichment factor analysis revealed that Cd, La and Ce with an EF greater than 100 derived from anthropogenic sources which would constitute a way of investigation in terms of monitoring these metal concentrations in the studied area.

Values for Z_{score} indicated a satisfactory laboratory performance since the obtained results almost perfectly match the certified values of the used reference materials.

In order to extend the range of elements to be analyzed and to improve the accuracy of the method, it is recommended to increase the volume of the collected air samples, the irradiation time and the use of standards better suited to this type of analysis.

Acknowledgement

The authors thank the Algerian Energy Commission for its support during the realization of this work.

Conflict of Interest

All authors certify that there is no conflict of interest.

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Recommended Citation

Ararem A, Slamene H, Dendene O. Non-destructive multielement analysis of airborne particles by instrumental neutron activation analysis. *Alger. J. Eng. Technol. 2024, 9(1): 1-7.* https://doi.org/10.57056/ajet.v9i1.151

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