# ANALYSIS OF Cr, Fe, Mn, Ni AND Zn FROM MOSSES BY NAA, AAS AND ICP-AES METHODS

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***Abstract.*** *Nuclear Analytical Methods can be used for research activities on environmental studies like water quality assessment, pesticide residues, global climatic change (transboundary), pollution and remediation. Heavy metal pollution is a problem associated with areas of intensive industrial activity. The moss biomonitoring technique was employed in this work to study the atmospheric deposition in Dambovita County Romania together with complementary nuclear and atomic analytical methods: Neutron Activation Analysis (NAA), Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). These high sensitivity analysis methods were used to determine the elemental composition of some samples of mosses placed in different vision areas with different pollution industrial sources. The concentrations of Cr, Fe, Mn, Ni and Zn were determined. The concentration of Fe from the same samples was determined using all these methods and we obtained a very good agreement, in statistical limits, which demonstrate the capability of these analytical methods to be applied on a large spectrum of environmental samples with the same results.*

***Keywords:*** *NAA, AAS, ICP-AES, elemental composition, mosses*

## 1. Introduction

Mosses are in particularly one of the main and effective biomonitors of atmospheric especially for heavy metal contamination because of their bioaccumulative properties [1, 2]: the heavy metal can be the intense stress factors of environmental [3, 5]. The moss groups are amenable to biomonitoring because they are widespread, easy to handle and they lack a cuticle and root system thus reflecting directly atmospheric heavy metal deposition. It is important during metal biomonitoring programs that background concentrations are established. The design of a monitoring program was involve: sampling locations, sample

collection, heavy metals to be analyzed, multi-element determination using INAA(Neutron Activation Analysis) [6,7], AAS (Atomic Absorption Spectrometry) [8] and ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometry) [4] techniques and data analysis.

The main sources of pollutants in the atmosphere are industrial processes, thermal power stations, domestic heating systems and road traffic. All of these sources are present in the territory of Dambovita County. The main polluting regional industries are: stainless steel works (Targoviste), cement and related materials production (Fieni), glass and lighting sources production (Targoviste, Fieni), chemicals materials production (Targoviste, Doicesti), coal mining and thermal power station (Doicesti), oil exploration (Targoviste, Moreni, Gaiesti).

## 2. Samples and sampling

*Sphagnum* species of moss have been considered especially suitable for monitoring heavy metal pollution due to the high caption-exchange capacity of their cell walls. Very useful results have been obtained with this type of moss in flat and spherical moss-bags. In order to optimize the assessment of atmospheric pollution in an industrial area using active biomonitoring a novel sampling design was introduced, and transplants the moss *Sphagnum girgensohnii* were deployed in parallel in order to study the uptake of a series of trace elements from the air over a defined time period. The site selected for this experiment was Dambovita County, Romania.

Samples of *Sphagnum girgensohnii* were collected from the region of Dubna town, Russia (56.44N, 37.09 E, altitude 120 m), in the frame of our protocol of collaboration with JINR-Dubna. This geographical zone is characterized by swamp landscape and extreme continental climate. Standard moss-bags of about 3 g moss (dry-weight, unwashed, cleaned, air dried) were putted in nylon nets (10 × 10 cm in size). Three moss-bags were hung in parallel by means of a T-shaped support system made of wood. Moss *Sphagnum girgensohnii* was hanged in bags at 17 different locations (Table 1), in February 2006, and analyzed by NAA, AAS and ICP-AES methods, respectively, after 1, 2 and 3 months of exposure to precipitation and wind.

Table 1. Zones of localization samples

| *Samples code* | *Zones of localization samples* |
|---|---|
| 1 | Moroieni |
| 2 | Fieni |
| 3 | Pucioasa |
| 4 | Voineşti |
| 5 | Gheboieni |
| 6 | Moreni |
| 7 | Doiceşti |
| 8 | Viforâta |
| 9 | Teiş |
| 10 | Târgovişte N-V |
| 11 | Târgovişte V |
| 12 | Târgovişte E |
| 13 | Adânca |
| 14 | Ulmi |
| 15 | Picior de Munte |
| 16 | Morteni |

| | |
|---|---|
| 17 | Tărtăşeşti |

## 3. Experimental

### 3.1. NAA (Neutron Activation Analyses)

NAA (Neutron Activation Analyses) were performed at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. Following exposure, the moss was removed from the nylon net, manually homogenized and dried in a thermostat oven at $40^0$ C for 48 h. Conventional and epithermal NAA at the IBR-2 pulsed fast reactor FLNP JINR Dubna, Russia (Frontasyeva and Pavlov, 2000, [7]), were used to determine concentrations of following elements: Cr, Mn, Ni, Fe, Zn. Two kinds of analysis were performed: long irradiation for 100 hours in Ch1 was used to determine elements associated with long-lived radionuclide Cr, Fe, Ni and Zn) and short irradiation for 2 minutes in Ch2 was used for short-lived radionuclide (Mn). Gamma-ray spectra were recorded four times using a high-purity Ge detector; after decay periods of 5 minutes and 10 minutes following the short irradiation, and after 5 days and 13 days following the long irradiation. The quantity of radioactive nuclides is determinate by measuring the intensity of the gamma characteristic gamma-ray line in spectra.

### 3.2. AAS (Atomic Absorption Spectrometry)

The AAS is the most widely utilized method today for quantitative element analysis. The detection limit in AAS is up to about one ppt under optimum experimental conditions. A material sample, in a liquid solution, is atomized, through rapid heat application and placed in the radiation path of several elements – specific light sources. The atoms of sample absorb the wavelength corresponding to their excitation energy, thus reducing the radiated energy. The concentration of element can be determinate with the aid of Lambert-Beer law [9] through wavelength dispersive measurement of this reduction. The Lambert –Beer law give the value of absorbance from each element of sample. The absorbance is proportional with the element concentration. The Atomic Absorption Spectrometer used by us is an AAS-AVANTA GBC with hollow cathode lamp (HCL). Measurements were made separately for each element of interest from sample using the calibration curve – absorbance versus concentration.

### 3.3. ICP-AES (Inductively Coupled Plasma- Atomic Emission Spectrometry)

ICP-AES (Inductively Coupled Plasma- Atomic Emission Spectrometry) method is based on the fact that the atoms and ions produced in the plasma are excited and emit light. The intensity of light emitted at wavelengths characteristic of the particular elements of interest is measured and related to the concentration of each element from samples.

The ICP-AES spectrometer used by us is a Baird ICP2070 - Sequential Plasma Spectrometer.

The AAS and ICP-AES techniques were applied in the determination of Fe concentration in the same sample of moss *Sphagnum girgensohnii.*

For the AAS and ICP-AES analysis, portions of about 0.4 g moss were decomposed with 4mL of concentrated nitric acid in a microwave oven. The extracts were then filtered and distilled water was added to a total volume of 25 mL. The presence of possible contaminants during the digestion process was controlled using blanks. Accuracy was checked by analysis of three replicates of references material IAEA 336, lichen.

## 4. Results and discussion

The analytical performance was checked by the regular analyses of the standard reference materials (SRM IAEA-336, lichen and moss) issued by the International Atomic Energy Agency [10].

The concentration values obtained in our study are presented in Tables 2 and 3, together with the concentration values of elements in SRM IAEA-336 [10].

Table 2. The mean values of elemental concentration (mg/kg) determined in mosses by NAA

| *Samples code* | *Cr* | *Mn* | *Ni* | *Zn* |
|---|---|---|---|---|
| 1 | 0.95±0.25 | 198.67±9.87 | 1.80±0.22 | 19.00±0.70 |
| 2 | 1.60±0.53 | 202.37±10.05 | 2.30±0.48 | 66.59±2.51 |
| 3 | 2.04±0.29 | 157.23±8.28 | 2.28±0.25 | 110.38±3.57 |
| 4 | 1.54±0.56 | 177.40±8.81 | 2.19±0.41 | 21.20±0.93 |
| 5 | 1.85±0.54 | 155.37±8.13 | 2.63±0.40 | 21.75±0.94 |
| 6 | 0.73±0.63 | 179.15±8.33 | 2.76±0.58 | 352.62±13.75 |
| 7 | 3.06±0.76 | 178.70±9.35 | 1.93±0.47 | 51.19±2.25 |
| 8 | 1.66±2.29 | 859.93±44.43 | 2.06±1.03 | 32.52±2.35 |
| 9 | 2.49±0.29 | 148.00±7.75 | 2.04±0.21 | 24.98±0.88 |
| 10 | 7.08±1.72 | 182.97±9.58 | 1.97±0.63 | 33.02±2.03 |
| 11 | 26.17±1.97 | 164.83±8.24 | 5.62±0.84 | 121.93±5.12 |
| 12 | 13.08±1.47 | 274.97±13.66 | 3.61±0.57 | 63.31±2.66 |
| 13 | 1.76±0.79 | 188.23±9.35 | 2.07±0.54 | 43.60±2.03 |
| 14 | 8.64±0.81 | 157.70±8.04 | 2.80±0.25 | 40.22±1.35 |
| 15 | 3.69±1.01 | 608.50±31.64 | 3.31±0.93 | 97.98±5.16 |
| 16 | 1.12±0.97 | 184.33±9.65 | 1.20±0.55 | 23.53±1.47 |
| 17 | 1.09±2.33 | 189.13±9.46 | 0.94±0.55 | 48.84±2.62 |
| SRM -336, [10] | 1.06±0.092 | 246±2.9 | 3.5±0.35 | 30.4±1.4 |

In the next diagrams (Figures.1 - 4) are presented the comparison between the values concentrations in mosses obtained by us and the concentration from standard reference material [10].

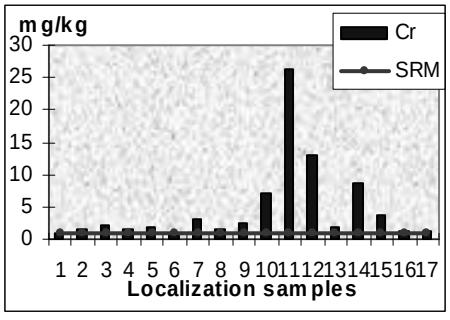


**Figure 1. The comparison between the Cr concentrations from moss determinate by NAA and the concentration from standard reference material**

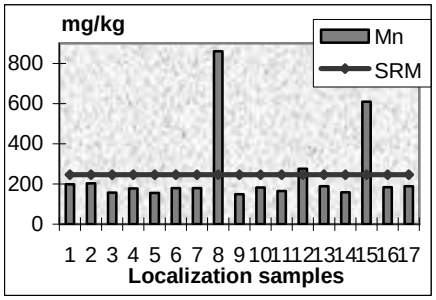


**Figure 2. The comparison between the Mn concentrations from moss determinate by NAA and the concentration from standard reference material**

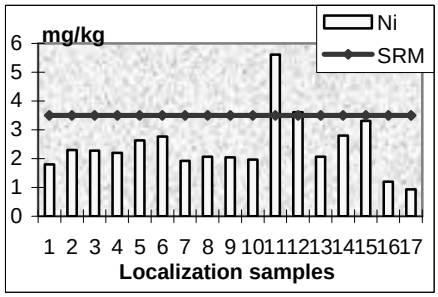


**Figure. 3. The comparison between the Ni concentrations from moss determinate by NAA and the concentration from standard reference material**

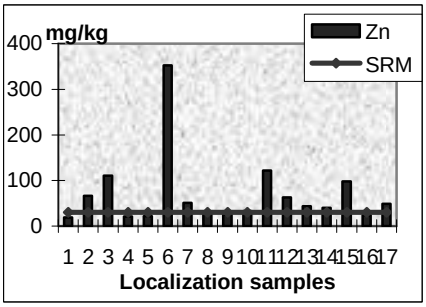


**Figure. 4. The comparison between the Zn concentrations from moss determinate by NAA and the concentration from standard reference material**

In the last part of our experiment we applied the NAA, AAS and ICP-AES methods in determination of the Fe concentration from the same type of samples: moss *Sphagnum girgensohnii.*

The comparisons of results are given in Table 3 and Figure 5.

Table 3. The mean values of Fe concentration (mg/kg) determined in mosses by NAA, AAS and ICP-AES methods

| *Samples code* | *Fe* | | |
|---|---|---|---|
| | *NAA* | *AAS* | *ICP-AES* |
| 1 | 430.10±27.38 | 436.14 ± 55.82 | 469.33±70.39 |
| 2 | 579.23±46.15 | 571.41 ± 51.42 | 617.67± 92.65 |
| 3 | 601.47±32.88 | 589.43 ± 42.52 | 645.00±96.75 |
| 4 | 549.27±43.94 | 545.68 ± 49.11 | 609.00±121.35 |
| 5 | 582.77±44.48 | 555.79 ± 40.03 | 577.67±101.65 |
| 6 | 503.65±42.56 | 504.72 ± 50.66 | 519.00± 83.86 |
| 7 | 550.43±49.54 | 565.37 ± 45.23 | 521.33±100.98 |
| 8 | 528.87±126.40 | 561.23 ± 39.28 | 496.67± 95.60 |
| 9 | 595.93±33.77 | 558.14 ± 50.23 | 562.33± 91.48 |
| 10 | 577.97±97.10 | 585.76 ± 35.14 | 611.67± 87.80 |
| 11 | 2056.33±128.86 | 1939.01±155.12 | 2038.33±93.45 |
| 12 | 1397.43±91.30 | 1286.72 ± 102.94 | 1332.33±65.91 |
| 13 | 513.10±60.89 | 502.36 ± 40.19 | 532.00± 87.85 |
| 14 | 963.60±47.22 | 946.12 ± 75.69 | 986.00± 84.38 |
| 15 | 951.63±120.22 | 962.86 ± 77.03 | 983.67±111.28 |
| 16 | 487.10±68.36 | 483.93 ± 43.55 | 475.00± 91.06 |
| 17 | 377.20±64.31 | 307.95 ± 23.40 | 345.00± 86.57 |
| SRM-336, [10] | 430±10.75 | | |

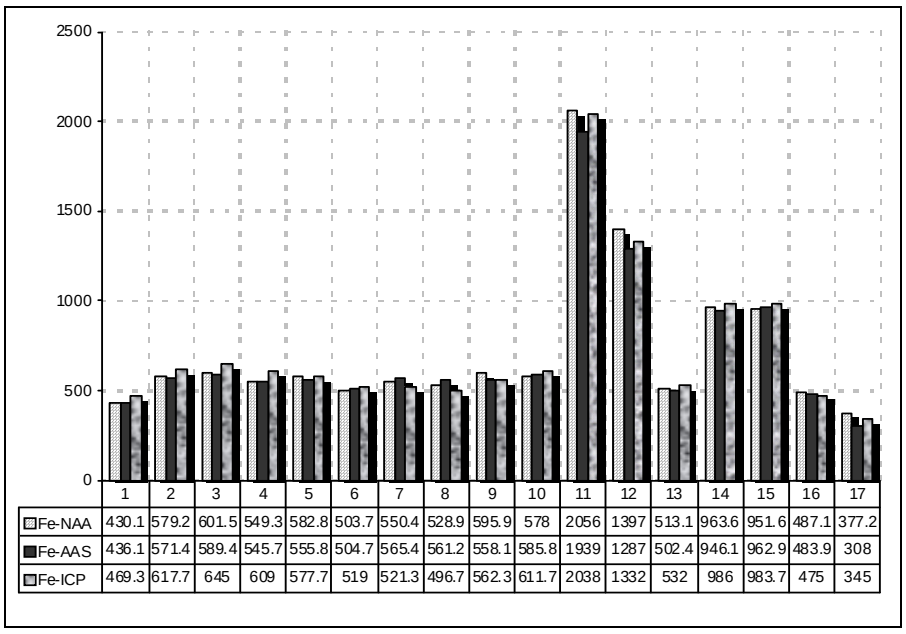


**Figure. 5. Comparison value of Fe concentrations determinate by NAA, AAS and ICP-AES, respectively**

## Conclusions

We can concluded that it is a very good agreement, in statistical limits between the concentrations values of Fe determined with NAA, AAS and ICP-AES analytical techniques applied on the same type of mosses samples (table 3 and Figure 3).

A high concentration of Cr (26 mg/kg) was found in the samples transplanted in Targoviste zones, which can be explained by the presence of a steel processing plant. Also, from the same reason we can explain the high content of Fe (2056 mg/kg) Ni (5.62 mg/kg) and Zn (126.4 mg/kg) in moss samples transplanted also in Targoviste zones.

This study is the first attempt to apply the moss-bag technique to a region scale in Romania.

Our results demonstrate the capability of these analytical methods to be applied on a large spectrum of environmental samples.

The results from this study will be used for establishing correlation between environmental and epidemiological data in the examined area

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