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# INVESTIGATION OF WATER HYACINTH SAMPLES BY PROMPT GAMMA-RAY NEUTRON ACTIVATION ANALYSIS. A COMPARISON INDICATION OF POLLUTION IN EGYPTIAN WATER BODIES

Samples of water hyacinth (WH) collected from three different water bodies were investigated for non-essential, non-metal and rare earth elemental content using prompt gamma ray neutron activation analysis technique (PGNAA). The results showed that samples collected from Abo-Zabal drain accumulated high amounts of Sr, V, As, Sb, P, B and I both in shoots and roots. Six lanthanide elements were detected and identified with a variation in concentration between the sites studied. In general, our data revealed that the PGNAA technique is suitable for multi-elemental analyses of environmental samples and for monitoring purposes. Water hyacinth (*Eichhornia crassipes*) could also be used as a good indicator of water pollution or heavy metals built up in different water bodies. Sr/Ca ratio varies depending on plant parts and water bodies (0.07–1.11); however, the highest Sr/Ca ratios were observed in the case of drain and canal samples, which may reflect the built-up concentration of Sr in drain and Ismailia canal samples. The interactions between B and Cu, Cr and P could be a good indication of metal accumulation in the water bodies studied. The ratios of B to Cu, Cr and P showed that the accumulation of Cu, Cr and P was higher in drain samples compared to either Nile or canal samples.

## 1. INTRODUCTION

Modern instrumental multi-element methods together with automation and microcomputerization are changing the analytical service not only with respect to techniques and instrumentation employed, but also the monitoring strategies. Nuclear anlytical methods have successfully been applied to the determination of a great vari-

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ety of elements in environmental samples. Neutron activation analysis technique has been used as an excellent tool for such a purpose (BURGESS [1], ZAGHLOUL et al. [2], ABDEL-SABOUR et al. [3] and EL-TANAHY [4]). However, the analysis of complex samples by means of the reactor neutron activation technique (RNAA) usually causes some difficulties such as sample characteristics and elemental interference which produces the masking effects in the spectra and, in turn, will affect the efficiency of the analysis.

In order to overcome these problems many authors have investigated the use of prompt gamma-ray neutron activation analysis technique (PGNAA). In this technique, one can measure γ-rays emitted while the sample is being irradiated with neutrons. When the sample is irradiated with slow neutrons, the (n, γ)-reaction is usually the most dominating nuclear reaction. Following neutron capture, the obtained compound nucleus is left in an excited state with the energy essentially equal to neutron binding energy of the compound nucleus (5–11 MeV). Decay from the excited state to the ground state occurs promptly within $10^{-14}$ s, normally through several intermediate states by the emission of several gamma-rays. Although neutron capture gamma-ray spectra are complex, consisting of both high and low energy gamma-radiations, nearly every neutron capture yields gamma-rays that are potentially usable for the analysis of the capturing element. It should be mentioned that the radioactive nuclides formed by neutron capture are not necessarily the same as those used by RNAA because the product nuclei may be stable, have very short or long half-life or emit no intense gamma-radiation. For example, P and S after neutron irradiation are pure beta emitters; however, they can be determined nondestructively by capture gamma-ray analysis.

The isotopic neutron source used most widely in neutron activation analysis is Cf-252 manufactured currently by irradiating plutonium targets in a reactor. Cf-252 has a half-life of 2.65 years and decays by alpha-particle emission or by spontaneous fission giving neutron flux of $2.34 \cdot 10^{10}$ $n^{-1} \cdot s^{-1} \cdot g^{-1}$. Cf-252 neutron source with the strength of several milligrams might yield a usable thermal neutron flux of $10^{0}$ $n^{-1} \cdot cm^{2} \cdot s^{-1}$. The PGNAA facility installed recently in the Hot Labs. Center, Cairo, Egypt, has been used in the present study. Full details of the system have been reported elsewhere (ZAGHLOUL et al. [5]). The system was calibrated for the energy up to 10 MeV using standard radioactive sources, Am-241, Ba-133, Cs-137, Hg-203, Co-60 for low energy range up to 2000 keV, while the energy range from 2 to 10 MeV has been determined using the energy peaks of the prompt gamma-rays emitted in the (n, γ) reaction for the H, Fe, Cl, Mn elements. Generally, the assembly has the ability to measure instantaneously and non-destructively the complex environmental samples. Major, trace elements, rare earths and short-lived isotopes could be detected.

Using the PGNAA technique in order to evaluate the efficiency of water hyacinth (WH) as a biological indicator of pollution was one of the objectives of our previous study (ABDEL-SABOUR et al. [6]). We indicated that WH plants showed high affinity for metal accumulation (either major ones, i.e. Na, K, Rb, Cs, Mg and Ca, or trace elements, i.e. Fe, Zn, Cu, Co, Ni, Cr, Cd, Pb and Hg) with a response to the levels of these elements in water bodies, which may suggest the good potential to use such plants as biological indicators for pollution monitoring. In this paper, we report some inessential and non-metal elements as well as lanthanide elements as affected by location (different water bodies).

## 2. EXPERIMENTAL

### 2.1. SAMPLES PREPARATION

Samples of water hyacinth collected from different three water bodies (Nile River, Ismailia Canal, Abo-Zabal drain) were collected, washed and shoots were separated

Table 1

Nuclear data used in the study

| Element | Cross-section (barn) | Gamma energies (KeV) | Intensities *I* N/100 |
|---|---|---|---|
| Sr | 1.2 | 1863.09, 897.99, 558.5 | 57.29, 27.84, 9.17 |
| B | $1.3\cdot10^{-1}$ | 478, 3367.6, 6809.41 | 33.7, 63.75 |
| P | $1.8\cdot10^{-1}$ | 636.2, 1413.1, 2154.2, 3900.3 | 12.18, 14.04, 15.2, 15.96 |
| As | 4.30 | 164.6, 1534.3, 471.9, 236.3 | 16.82, 7.18, 3.59, 2.39 |
| Sb | 5.40 | 558.4, 283.2, 232.8 | 3.25, 3.24, 2.53 |
| V | 5.04 | 645.9, 1558.4, 823.5, 2146 | 11.13, 4.3, 4.26, 4.08 |
| I | 6.20 | 133.61, 442.89, 153.02, 301.87 | 8.43, 4.38, 1.14, 1.34 |
| La | 9.14 | 218.2, 162.66, 142.3, 422.63 | 10.6, 6.0, 8.25, 5.69 |
| Pr | $1.15\cdot10^{1}$ | 178.4, 645.8, 699.8 | 11.72, 2.22, 2.08 |
| Sm | $5.8\cdot10^{3}$ | 333.4, 439.4, 505.9, 737.6, 1170.5 | 98.9, 55.5, 17.92, 11.04, 4.69 |
| Eu | $4.6\cdot10^{3}$ | 206.6, 221.6, 198.5, 191.9, 296.1 | 2.44, 2.14, 0.52, 0.54, 0.67 |
| Gd | $4.9\cdot10^{4}$ | 1186.5, 944, 199.4, 961.8, 897.3 | 10.83, 10.65, 9.5, 7.42, 6.51 |
| Tb | $2.5\cdot10$ | 75.07, 63.8, 41.9 | 10.8, 9, 5 |

from roots, thereafter the samples were dried at 70 °C for 24 h. Dry plant samples were kept in polyethylene vials and subjected to non-destructive analysis technique using the PGNAA system.

### 2.2. MEASUREMENTS

The PGNAA facility has already been installed in the Hot Labs Center 1700 S. Gamma emissions for several elements were measured by means of 4096 multichannel analyzer (canberra-35 plus). The peak analysis is completed through a prolonged computer analysis program by personal computer in conjunction with the system. The selected gamma-ray lines obtained for each sample due to (n, $\gamma$) reactions and the nuclear constants of various isotopes were as listed in table 1.

## 3. RESULTS AND DISCUSSION

Element concentrations in the collected WH samples can be measured using the prompt calculations as mentioned in detail by ZAGHLOUL et al. [5].

### 3.1. INESSENTIAL AND NON-METAL ELEMENTS

As shown in table 2, samples collected from Abo-Zabal drain accumulated higher amounts of Sr, V, As, Sb, P, B and I (either in shoots or roots) if compared with other samples taken from the river Nile or Ismailia canal.

Table 2

Element concentrations in water hyacinth samples (mg/kg)

| Location | Plant part | Sr | B | P | As | Sb | V | I |
|---|---|---|---|---|---|---|---|---|
| Nile river | shoot | 1.6 | 1.71 | 2.7 | 0.56 | 0.56 | 0.79 | 0.43 |
| | root | 4.2 | 5.10 | 9.2 | 1.50 | 2.00 | 2.71 | 1.50 |
| Ismailia canal | shoot | 2.9 | 1.65 | 5.4 | 0.80 | 1.25 | 0.88 | 0.59 |
| | root | 8.3 | 5.51 | 18.1 | 2.20 | 4.12 | 2.91 | 1.98 |
| Abo-Zabal drain | shoot | 4.8 | 2.10 | 5.7 | 1.20 | 2.64 | 1.91 | 0.67 |
| | root | 15.3 | 7.20 | 19.2 | 3.50 | 8.80 | 6.51 | 2.25 |

Strontium concentrations in plant samples ranged from 1.6 to 15.3 ppm. Its highest values were determined in roots and the lowest values in shoots. The common Sr levels varied from 1.5 to 1500 ppm for different plants as reported by BOWEN [8]. Since the Sr to Ca ratio seems to be relatively stable in the biosphere (PENDIAS and PENDIAS [9]), it is commonly used for the identification of built-up concentration of Sr in a particular environment. As shown in table 3, Sr/Ca ratios vary, depending on the plant part and water body (0.07–1.11); however, the highest Sr/Ca ratios were observed in the case of drain and canal samples, which may reflect the built-up concentration of

Sr in drain and Ismailia canal samples. The Sr/P and Sr/Mg ratios confirm this finding as shown in table 3.

Table 3

Selected metal ratios as indication of accumulation

| Location | Plant part | Sr/Ca | Sr/Mg | Sr/P | B/Cu | B/Cr | B/P |
|---|---|---|---|---|---|---|---|
| Nile river | shoot | 0.07 | 0.39 | 0.59 | 0.31 | 1.54 | 0.63 |
| | root | 0.59 | 0.32 | 0.46 | 0.34 | 1.59 | 0.55 |
| Ismailia canal | shoot | 0.12 | 0.45 | 0.54 | 0.15 | 1.03 | 0.31 |
| | root | 1.11 | 0.39 | 0.46 | 0.18 | 1.45 | 0.30 |
| Abo-Zabal drain | shoot | 0.63 | 0.65 | 0.84 | 0.13 | 0.91 | 0.37 |
| | root | 0.68 | 0.59 | 0.80 | 0.15 | 1.06 | 0.38 |

Boron is important for the metabolism of plants as it is believed that this element plays the most significant role in the translocation of sugars. The averages of the boron content in plants grown under natural conditions are reported to be 5.7 ppm for monocot plants and 37 ppm for dicot plants (PENDIAS and PENDIAS [9]). Our results showed that boron concentration ranged from 1.7 to 7.2 ppm. It was reported that this element interacts with copper, chromium and phosphorus (LEAL et al. [10], BARLETT and PICARELLI [11] and PRATHER [12]). Thus the ratios of the boron to the elements specified could be a good indication of metal accumulation in the water bodies studied. All the ratios of boron to copper, chromium and phosphorus showed that the accumulation of copper, chromium and phosphorus was higher in drain samples compared to either Nile or canal samples (table 3).

Phosphorus is a major nutrient and plants adsorb it in the readily available form, therefore, the increase in its uptake means the increase in the available phosphorus concentration in the growing media. Table 2 shows that the content of phosphorus in plants increased by twofold in the samples collected from either the drain or the canal in comparison to Nile samples. This may clearly indicate that both the drain water and Ismailia canal water are enriched with phosphorus which will cause the deterioration of water quality.

Arsenic is a constituent of most plants, but little is known about its biochemical role. Several reports showed a linear relationship between the arsenic content in the plants and its levels in the soil. Concentrations of arsenic in plants grown on uncontaminated soils vary from 0.009 to 1.5 mg/kg with leafy plants being in the upper range (OAKES et al. [13], SHACKLETTE [14] as well as KITAGISHI and YAMANE [15]). If the arsenic content in the WH samples is considered, it is clearly seen that its range varied from 0.56 to 1.2 in shoots and from 1.5 to 3.5 mg/kg in roots. Arsenic levels in drain samples was two- or threefold as high as its levels in Nile samples which may suggest a potential pollution problem. It was reported that excessive levels of arsenic in plants grown in contaminated sites were ranged from 0.26 to 387 mg/kg, depending on the location, pollution source and plant species (LINZON et al. [17] and CHISHOLM [16]).

Antimony is considered as inessential metal and is known to be easily taken up by plants if present in soluble forms. The concentration of antimony in the WH samples ranged between 0.56 and 8.8 mg/kg, which was lower than reported by SHACKLETTE et al. [18] in shrubs and trees grown in mineralized areas (the range from 7 to 50 mg/kg).

Vanadium content in the WH samples ranged from 0.79 to 6.51 mg/kg. SHACKLETTE et al. [18] reported the range of vanadium levels in plants to be from 5 to 50 mg/kg.

Iodine has not been shown to be essential for plants. It was reported that terrestrial plants contain lower concentrations of iodine (0.005–10.4 mg/kg) than marine plants which concentrate from 53 to 8800 mg of iodine/kg (SHACKLETTE and CUTHBERT [19] ). Our results showed low levels of iodine (from 0.43 to 2.25 mg/kg), and the highest iodine concentration was measured in the WH drain samples.

## 3.2. LANTHANIDES

Table 4

Lanthanide contents in shoots and roots (μg/g)

| Location | Plant part | La | Pr | Sm | Eu | Gd | Tb |
|---|---|---|---|---|---|---|---|
| Nile river | shoot | 0.20 | 1.56 | 0.22 | ND | 0.52 | 0.24 |
| | root | 0.71 | 5.12 | 0.71 | 0.21 | 1.80 | 0.70 |
| Ismailia canal | shoot | 0.26 | 0.27 | 0.48 | ND | 1.11 | 0.27 |
| | root | 0.82 | 0.90 | 1.60 | 0.25 | 3.73 | 0.90 |
| Abo-Zabal drain | shoot | 0.42 | 0.34 | 0.28 | 0.13 | 0.67 | 0.34 |
| | root | 0.41 | 1.11 | 0.94 | 0.42 | 2.21 | 1.11 |

In literature, there is not enough data about lanthanides because it is difficult to determine them. Taking advantage of PGNAA, six lanthanide elements were identified and measured as shown in table 4. The drain samples showed higher amounts of La, Eu and Tb, where as in the Ismailia canal samples the concentrations of Sm and Gd were the highest. WH samples selected from the Nile river showed higher Pr levels compared to other sites.

## 4. CONCLUSION

In conclusion, PGNAA technique is very suitable for multi-elemental analysis of environmental samples and for monitoring purposes. Water hyacinth samples can be used as a good pollution indicator since it reflects the accumulation of major, trace element and non-metal elements as well as lanthanides. However, further research program is needed to investigate the relations between different environmental components, WH pollution prediction and monitoring purposes.

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## BADANIE PRÓBEK HIACYNTA WODNEGO METODĄ NEUTRONOWEJ ANALIZY AKTYWACYJNEJ. PORÓWNAWCZE WSKAŹNIKI SKAŻENIA WÓD W EGIPCIE

W próbkach hiacynta wodnego (*Eichhornia crassipes*) pobranych z trzech stanowisk badano metodą neutronowej analizy aktywacyjnej zawartość pierwiastków, które nie są niezbędne dla roślin, pierwiastków niemetalicznych i lantanowców. Wyniki pokazały, że w próbkach korzeni i łodyg pobranych z kanału ściekowego Abo-Zabal były zakumulowane duże ilości strontu, wanadu, arsenu, antymonu, fosforu, boru i jodu. Wykryto i zidentyfikowano sześć lantanowców, których stężenie zmieniało się w zależności od stanowiska. Można stwierdzić, że otrzymane dane potwierdzają przydatność wybranej metody do analizy wielu pierwiastków znajdujących się w środowisku i do monitoringu skażeń wody. Okazało się również, że wodny hiacynt jest dobrym wskaźnikiem skażenia wody metalami ciężkimi. Stosunek Sr/Ca zmienia się w zależności od badanej części rośliny i zbiornika wodnego (0,07–1,11). Najwyższe jego wartości stwierdza się jednak w przypadku próbek pobranych z kanału i ścieku, co może odzwierciedlać stężenia strontu w wodzie. Oddziaływania między borem a miedzią oraz chromem a fosforem także mogą być dobrym wskaźnikiem stężenia metali w wodzie. Wszystkie stosunki B/Cu i Cr/P były większe w próbkach z kanału ściekowego Abo-Zabal niż w próbkach z Nilu i kanału Ismailia.