

ASSESSMENT OF AIR POLLUTION IN VICINITY OF PHOSPHATE FERTILIZER PLANT IN ABU-ZABAL CITY (EGYPT) USING VEGETATION AND EPITHERMAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Instrumental epithermal neutron activation analysis at the reactor IBR-2, FLNP, JINR, was used to study the major and trace elements in vegetation samples (tree leaves), collected in the agricultural land of Abu-Zabal city close to phosphate fertilizers and chemical industries. A total of 44 elements were determined in 13 vegetation samples (Na, Mg, Al, Si, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, In, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Yb, Hf, Ta, W, Th, U). Descriptive and correlation analyses were applied to the experimental data. Comparison of the results obtained with the similar data for the phosphate fertilizer in Voskresensk, (Russia) was undertaken.

INTRODUCTION

Neutron activation analysis (NAA) is one of the most advanced analytical techniques, since 2007 it has been considered the primary analytical technique [1,2]. High sensitivity, high accuracy and precision, requiring little or no elaborate sample preparation and give multi-element capability for the determination of small sample masses and for repeat analysis of the same samples. It is a non destructive and independent on the chemical state of the elements method of analysis. No sample dissolution or other processing is required that might introduce contaminants and loss of volatile elements during the packaging. Although, organic material is a significant matrix problem, especially inside many types of conventional chemical methods. The NAA is unaffected by the presence of organic material in the sample. Presented NAA-studies were performed at the Frank Laboratory of Neutron Physics (FLNP) at the Joint Institute for Nuclear Research (JINR), using "Regata" NAA-facility at the pulsed fast reactor IBR-2.

The area of investigation was the surroundings of Abu Zabal Company for fertilizers and chemical industries. The factory was established in 1974 to manufacture all kinds of phosphate fertilizers and chemicals. The fertilizer production facility produces Single Super phosphate, Triple Super phosphate, Phosphoric Acid, Ammonium Nitrate and Sulphuric Acid, the ores which are used in production of these substances are Phosphate Stone, Sulphur, Ammonium Sulphate and Potassium Sulphate. This area was chosen in order to study the

contamination level caused by this company on the agricultural land of Abu Zabal city and for a quality control on the hazards from the work of fertilizer companies in Egypt.

According to the IAEA data [3] the toxic agents that are most harmful for human health are (i) naturally occurring toxins (bacterial toxins, aflatoxins, mycotoxins, etc.), (ii) organic pollutants (petroleum products, pesticides, dioxins, etc.), (iii) radionuclides, and (iv) toxic inorganic chemical elements and their compounds. Among the latter there are, first of all, heavy metals [4]. Concentration control of heavy metals and other toxic elements in living organisms, atmosphere, soil, and vegetation and monitoring and forecasting of an increase in the pollution level over time are not only important, but vital, for assessing the environmental situation in regions exposed to a strong anthropogenic effect and for working out the environment protection strategy.

The analytical technique employed in the present study was the instrumental neutron activation analysis (INAA), which allows a simultaneous determination of more than 40 elements and which has contributed substantially to the current knowledge on the geochemistry of minor and trace elements in terrestrial and extra-terrestrial materials [5]. The sample activation with epithermal neutrons (ENAA) is advantageous for many trace elements found in the geological materials [6, 7]. The IBR-2 reactor has a high epithermal-to-thermal flux ratio, which is particularly well suited for ENAA [8], and offers the possibility of simultaneous determination of more than 40 elements in geological material [9, 10].

EXPERIMENTAL WORK

Sample Location

The Plant samples were collected along 2000 m, with separation 200 m for each one, surrounding the site under investigation as shown in the map in Figure 1. (P0) at the center of the factory and from (P1L) to (P5L) at the left side of it and from (P1R) to (P5R) at the right side, and also collect 2 samples away from the both sides of the company by 6000 m (P6L) at the left and (P6R) on the right side of the factory.



Fig. 1. The map of the Abu Zabal company for fertilizers and chemical industries and the places of plant samples collection.

Sample Preparation

A total of 13 plant samples, 500 g each were collected, washed to remove possible contaminants, dried in air for 72 hour and in an oven for 72 hours (at 70 °C) to a constant weight and ground into a powder using a mortar and pestle and meshed perfectly to pass 2 mm mesh for homogeneity. Then a portion of the prepared samples weighted and capsuled either in Al (for long irradiation) or in plastic envelope (for short irradiation).

Instrumental Neutron Activation Analysis (INAA)

The sample irradiations were performed at Frank Laboratory of Neutron Physics of the Joint Institute of Nuclear Research, Dubna, Russian Federation, at the pulsed reactor IBR 2 using epithermal neutrons. The 13 samples of about 300 mg of plants were wrapped in Polyethylene (PE) and Aluminum (Al) foils for short and long-term irradiations, respectively. The analytical scheme used has been described in detail elsewhere [11] and only a brief account is given here. To determine the short-lived isotopes, the samples were irradiated for 180 s and measured for 15 min. In case of long-lived isotopes, samples were irradiated for 4 days, repacked and measured twice using high purity germanium (HPGe) detectors, after 4–5 days and 20–23 days of decay for 30 min and 1.5 h, respectively. The data processing and determination of element concentrations were performed using software developed in FLNP JINR [12]. The element contents were determined relative to a set of certified reference materials: The total error in the determination of the concentration of 41 elements varied between 5% and 30%.

Experimental Procedure

The experimental procedure established at JINR-FLNP quantitatively determines the elemental content in samples with the comparative INAA technique. It is based on the simultaneous irradiation of the analyzed samples and standard samples for which the concentrations of the elements are known and certified. The neutron induced activity of the samples and the standards was determined from the accumulated gamma-ray spectra with the Genie-2000 software. The final result of the INAA, the concentration of different elements in the investigated samples, was determined by comparing the activity of the same isotopes in the sample and the standard. The computer program takes into account the difference in the neutron fluxes during the irradiation of the sample and the standard, the time of the irradiation and the different positions in the irradiation channel, as well as, it can analyze the results to reveal possible random errors [13].

In the relative NAA version, when the sample and the standard of identical weight are irradiated and measured under identical conditions, the concentration of the analyzed element is defined by the simple formula [14].

$$C_{\text{sam}} = C_{\text{std}} \frac{A_{\text{sam}}}{A_{\text{st}}} \quad (1)$$

When samples and standard of different weights are not irradiated and measured simultaneously, the formula is [14].

$$C_{\text{sam}} = C_{\text{st}} \frac{A_{\text{sam}}}{A_{\text{st}}} \frac{1 - \exp(-\lambda t_{\text{irr.st}})}{1 - \exp(-\lambda t_{\text{irr.sam}})} \frac{1 - \exp(-\lambda t_{\text{meas.st}})}{1 - \exp(-\lambda t_{\text{meas.st}})} \frac{\exp(-\lambda t_{\text{cool.st}})}{\exp(-\lambda t_{\text{cool.st}})} \frac{W_{\text{st}}}{W_{\text{sam}}} \frac{\Phi_{\text{st}}}{\Phi_{\text{sam}}} \quad (2)$$

where, C_{sam} , C_{st} are the concentration of the elements in the sample and the standard; A_{sam} , A_{st} are the measured activity of the sample and the standard in (Bq); W_{sam} , W_{st} are the weights of the sample and the standard; Φ_{sam} and Φ_{st} are the neutron fluxes ($\text{n/cm}^2 \cdot \text{s}$) on the sample and

the standard; t_{irr} , t_{meas} and t_{cool} are the sample irradiation, measurement and cooling times (s), respectively.

Detection System Setup

The energy and intensity of various gamma ray lines have been measured using CANBERRA coaxial (HPGe) detector Model number GC3018 of relative efficiency 30% coupled to a 16384 channel analyzer. The full width at half maximum (FWHM) was found to be 1.8 keV for ^{60}Co –1.33MeV gamma ray line. The spectrum acquired with Genie 2000 data acquisition and analysis software made by Canberra using its automatic peak search and peak area calculations, along with changes in the peak fit using the interactive peak fit interface when necessary to reduce the residuals and error in the peak area values.

RESULTS AND DISCUSSION

Figure 2, shows a typical spectrum for sample P0 irradiated for short time 3 minutes as obtained by gamma spectrometer with HPGe detector while Table 1, contains the obtained results of the concentrations in all plant samples.

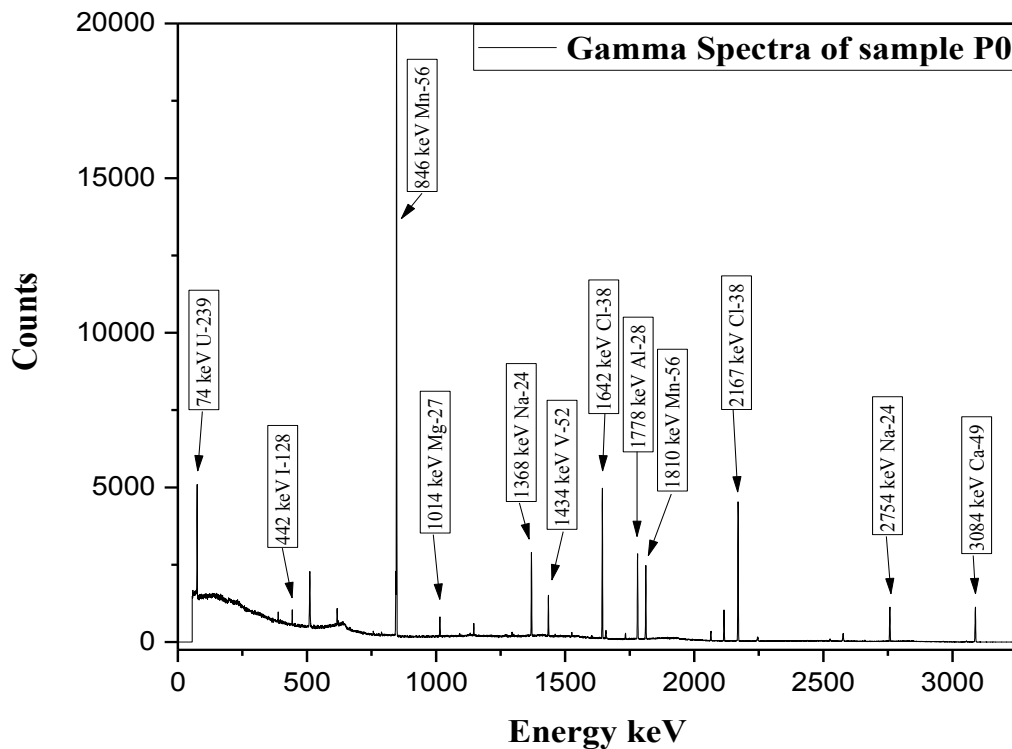


Fig. 2. Gamma spectrum of the plant sample at position P0 irradiated for short time.

The elements generally most frequently associated with pollution are Nickel (Ni), Cobalt (Co), Copper (Cu), Chromium (Cr), Zinc (Zn), Arsenic (As). These elements have been observed several studies in the Egyptian part of the Nile watershed at contents clearly exceeding the natural levels, confirming significant pollution at the local level [15-19] In the present work Ni, Co, Zn, Cu, Cr and As were among the studied elements.

Table 1. The concentration of the elements in the 13 samples by (ppm)

Sample	Na	Mg	Al	Si	S	Cl	K
P0	2640	6190	756	15800	4040	11000	8010
P1R	529	4010	370	35600	3060	12600	24100
P2R	634	1590	385	14300	3730	10600	19300
P3R	173	1440	311	12600	3050	10300	17700
P4R	455	4770	2030	21900	5800	8940	23100
P5R	339	3320	1630	18700	5770	6500	27200
P6R	374	2880	1250	17100	2510	4080	27700
P1L	1650	2900	581	20500	7250	10900	26000
P2L	1470	2110	938	7210	3030	4300	15200
P3L	384	3350	1840	18700	2650	3430	23900
P4L	2380	4300	1510	18800	1860	5530	17000
P5L	1120	3620	1390	18200	2270	6240	20000
P6L	269	3310	1000	13900	2110	1580	17900
Sample	Ca	Sc	Ti	V	Cr	Mn	Fe
P0	51500	0.352	39.4	12.3	6.79	293	835
P1R	36500	0.178	16.8	3.05	2.77	79.8	436
P2R	5030	0.0663	57.4	1.15	6.49	114	330
P3R	6000	0.0578	20.8	0.512	2.31	45.9	392
P4R	39300	0.6	223	4.86	5.33	129	2070
P5R	27400	0.402	154	3.63	4.03	104	1400
P6R	17700	0.363	130	2.95	4.65	97.6	1330
P1L	7240	0.158	62.5	1.83	5.77	307	1920
P2L	14100	0.246	72.4	2.39	3.92	155	725
P3L	30400	0.51	219	4.31	3.76	126	1760
P4L	36400	0.328	157	3.12	3.71	47	1300
P5L	32800	0.342	147	3.1	3.63	32.1	1280
P6L	39100	0.218	97.1	2.24	2.81	52.3	870
Sample	Ni	Co	Cu	Zn	As	SE	BR
P0	13.9	2.26	7.01	60.3	3	0.575	30.4
P1R	6.98	0.437	6.37	21.9	0.833	0.256	19.8
P2R	3.71	0.144	44.5	20.5	0.225	0.168	34.7
P3R	33.1	0.206	7.93	23.3	0.19	0.1	12.2
P4R	8.36	0.851	6.15	35.6	0.499	0.15	20.9
P5R	4.3	0.662	6.92	50.3	0.519	0.145	23.3
P6R	14.9	0.592	11.3	38.6	0.315	0.202	25
P1L	12.1	2.22	113	91.9	1.27	0.343	15
P2L	6.69	0.375	14.1	27.3	0.555	0.394	20.4
P3L	3.93	0.871	7.14	41.4	0.856	1.11	26.9
P4L	2.3	0.577	5.38	26.4	0.451	0.125	14.8
P5L	2.1	0.548	5.77	23	0.363	0.107	28.6
P6L	1.79	0.381	2.97	25.2	0.263	0.109	9.87

Sample	Rb	Sr	Zr	In	Sn	Sb	I
P0	3.27	322	6.46	0.0668	0.56	0.158	2.62
P1R	14.1	190	7.27	0.063	0.49	0.0853	0.854
P2R	5.82	95.3	6.15	0.0622	0.26	0.192	0.23
P3R	4.81	44	4.93	0.0969	0.378	0.117	0.138
P4R	6.34	266	8	0.0455	0.549	0.439	0.351
P5R	5.22	179	7.36	0.0593	0.452	0.573	0.492
P6R	4.49	163	4.1	0.0419	0.478	0.897	0.601
P1L	10.1	34.6	3.41	0.0538	2.01	0.17	0.311
P2L	5.05	135	6.18	0.0522	0.539	0.184	0.375
P3L	5.05	172	4.62	0.0534	0.416	0.0899	0.399
P4L	4.35	401	10.6	0.0624	0.413	1.16	0.401
P5L	4.88	230	6.85	0.072	0.408	0.512	0.357
P6L	10.8	146	2.01	0.0648	0.383	0.0814	0.174
Sample	Ba	Cs	La	Ce	Nd	Sm	Eu
P0	31.9	0.0277	1.04	2.65	1.74	0.0431	0.164
P1R	15.7	0.0315	0.509	1.18	0.746	0.048	0.0946
P2R	14.2	0.0108	0.178	0.424	1.32	0.0287	0.0638
P3R	7.5	0.00541	0.155	0.27	0.226	0.0171	0.0743
P4R	45.7	0.0429	1.07	2.95	1.97	0.263	0.0685
P5R	32.2	0.037	0.822	1.1	0.372	0.117	0.0994
P6R	21.4	0.0307	0.736	1.35	0.322	0.104	0.0263
P1L	13.8	0.039	0.579	0.926	0.558	2.4	0.0713
P2L	13.3	0.0218	0.624	1.04	0.566	0.0955	0.0314
P3L	23.8	0.0512	0.806	1.56	0.973	0.132	0.105
P4L	25.8	0.0405	0.635	1.35	0.705	0.0995	0.0928
P5L	39.5	0.0356	0.666	1.31	1	0.103	0.0715
P6L	33	0.0262	0.392	0.775	0.618	0.0615	0.0741
Sample	Tb	Dy	Tm	Yb	Hf	Ta	W
P0	0.028	0.621	0.0437	0.158	0.0407	0.00585	0.0439
P1R	0.0155	0.494	0.0352	0.128	0.0238	0.00443	0.0394
P2R	0.00299	0.236	0.0193	0.124	0.0172	0.00386	0.0595
P3R	0.00239	0.214	0.0237	0.0673	0.0237	0.00435	0.0246
P4R	0.0313	0.256	0.0268	0.147	0.214	0.0445	0.131
P5R	0.0208	0.237	0.0137	0.0673	0.155	0.0311	0.0747
P6R	0.0186	0.207	0.0179	0.0794	0.139	0.0291	0.0964
P1L	0.0162	0.293	0.00771	0.0828	0.0372	0.0118	0.056
P2L	0.0168	0.212	0.0131	0.0351	0.113	0.025	0.0448
P3L	0.0266	0.241	0.0187	0.0598	0.168	0.0381	0.0678
P4L	0.0195	0.149	0.00971	0.0319	0.183	0.038	0.105
P5L	0.019	0.228	0.00646	0.0496	0.199	0.0386	0.0724
P6L	0.0111	0.18	0.00957	0.0521	0.0801	0.0189	0.0529

Sample	Th	U
P0	0.0837	22.5
P1R	0.0546	7.3
P2R	0.0252	1.03
P3R	0.0325	0.0825
P4R	0.194	2.2
P5R	0.173	0.36
P6R	0.0827	0.307
P1L	0.0689	0.64
P2L	0.13	0.489
P3L	0.204	0.14
P4L	0.191	0.126
P5L	0.16	0.14
P6L	0.0921	0.0545

Figures 3-10 show the concentration distributions of Na, S, Cl, Mn, V, Ni, Zn, Cu, As, Co, Cr and U at different plant sample positions, where the number 0 refer to P0-position and those from 2 to 10 indicate the positions from P1L (200 m left of the factory) to P5L (after 1000 m left), respectively, with a step of 200 m; -2 to -10 indicate the positions from P1R (200 m right of the factory) to P5R (after 1000 m right), respectively, with a step of 200 m; numbers 12 and -12 indicate the positions P6L (after 6000 m left) and P6R (after 6000 m right), respectively.

It became clear that the highest concentrations of these elements are at the center of the factory and they are decreasing by increasing the distance from it. This shows also the level of influence of the emissions from the fertilizer company on the agricultural land of Abu-Zabal city.

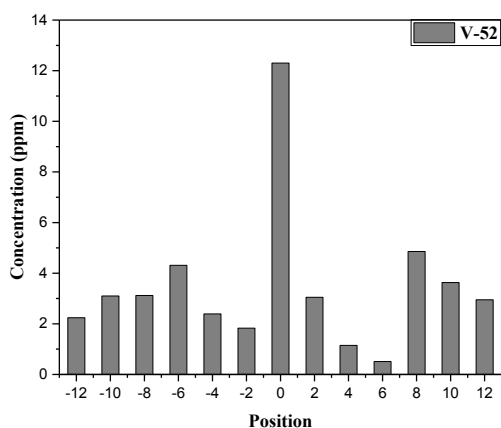


Fig. 3. The concentration distribution of V for different sample position.

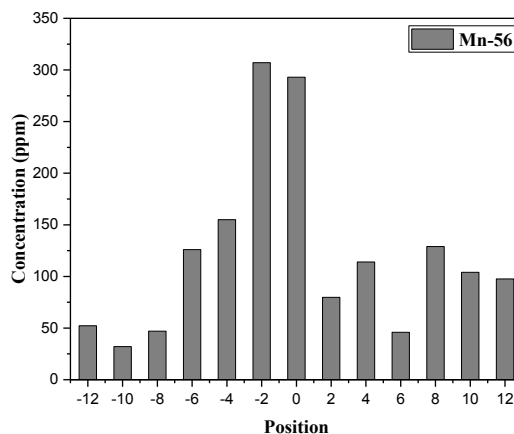


Fig. 4. The concentration distribution of Mn for different sample position.

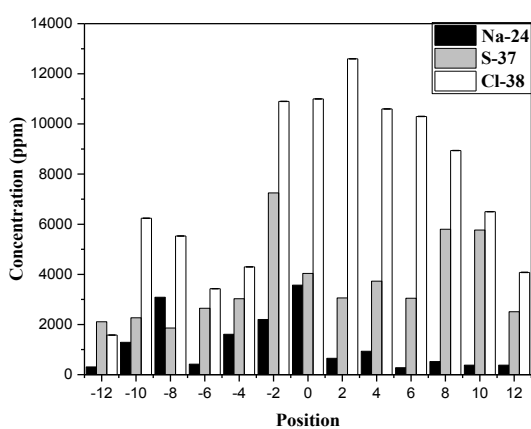


Fig. 5. The concentration distribution of Na, S and Cl for different sample position.

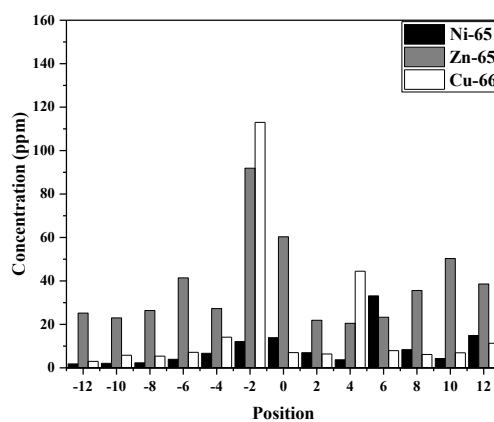


Fig. 6. The concentration distribution of Ni, Zn and Cu for different sample position.

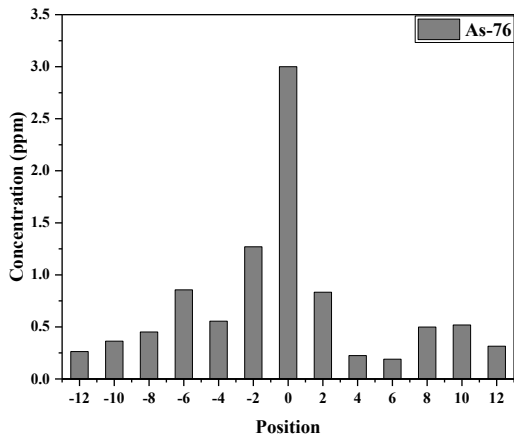


Fig. 7. The concentration distribution of As for different sample position.

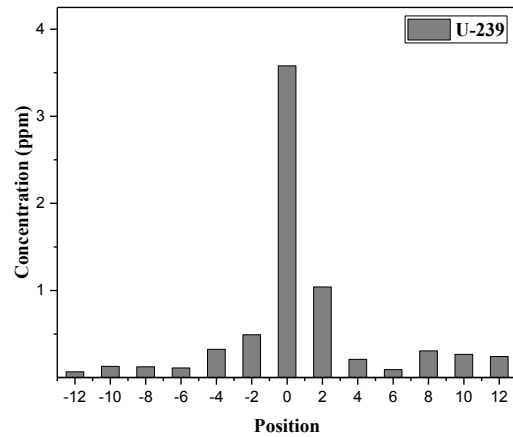


Fig. 8. The concentration distribution of U for different sample position.

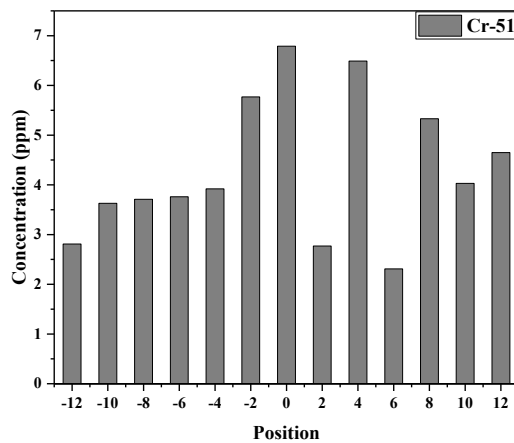


Fig. 9. The concentration distribution of Cr for different sample position.

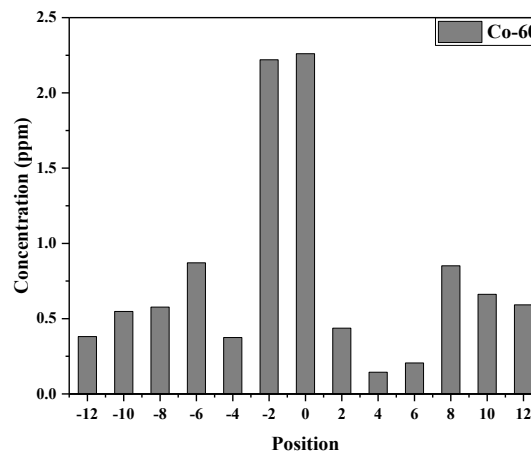


Fig. 10. The concentration distribution of Co for different sample position.

Table 2 shows the mean, minimum and maximum values of the plants samples for Ni, Co, Cu, Zn, As and Cr heavy elements and also shows the value of “Reference plant” by Markert [20] follows the idea of the “Reference man“ by the International Commission of Radiological protection, which gives a model of a human (with averaged parameters) to be used for calculations and predictions in the field of radiation safety. In the same way, the “Reference plant” is based on the analysis of many plant species, but gives reference values for the concentration of chemical elements. It is a common practice to use the “Reference plant” as a standard for comparison, on which to base the decision if the studied plant has a relatively low or relatively high concentration of a certain element. Also Kabata-Pendias and Pendias [21] have given the approximate concentration of some elements found in plant leaf tissue, giving their range of toxicity to excessive in Table (2).

A comparison of the results on the concentration of some elements, obtained in this work, with similar data for distance 200 m from the Phosphate fertilizer factory in Voskresensk (Russia) [22], is shown in **Table 3**.

Table 2. The mean, stander deviation, minimum, maximum, reference plant, toxic elements and excessive concentration in (mg/km) in plants samples.

	Ni	Co	Cu	Zn	As	Cr
Mean	8.78	0.78	18	37	0.72	4.31
Minimum	1.79	0.144	2.97	20.5	0.19	2.31
Maximum	33.1	2.26	113	91.9	3	6.79
Reference plant [20]	1.5	0.2	10	50	0.1	1.5
Toxic [21]	0.1-5	0.02-1	5-30	27-150	1-1.7	0.1-0.5
Excessive [21]	10-100	15-50	2-100	100-400	5-20	5-30

Table 3. Comparison with data for a phosphate fertilizer in Russia, in (ppm).

Elements	Abu-Zabal	Russia [22]
Ca	21870	11000
Sc	0.16	0.5
Cr	4.27	19.3
As	1.05	5.3
Sr	112.3	186
Sb	0.12	2.6
La	0.54	8
Ce	1.05	10.2
Sm	1.22	0.9
Eu	0.082	0.4
Th	0.061	0.6

CONCLUSIONS

The Neutron Activation Analysis has proved to be a very effective method for analyzing trace elements in plants. More important is the fact that the basic major elements, which are universally presented in plants samples, are clearly identified in percentage of their concentrations (ppm). At the same time, the distribution of potential polluting elements, such as Ni, Cu, Co, Cr, Zn and As, are presenting a systematic increase in the region of Phosphate fertilizer factories.

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