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INVESTIGATION OF TWO SLAG SAMPLES USING k_0 NEUTRON ACTIVATION ANALYSIS THROUGH DIFFERENT STANDARDIZATION METHODS

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Instrumental neutron activation analysis was used to determine concentrations of several major and trace elements in two slag samples. One slag supplied by one of Steel factory and the other one by an Aluminum factory of Egypt. The aim of the present work is to study the accuracy and precision of Internal Comparator k_0 and external comparator k_0 methods in industrial application. The two slag samples together with an international reference material Soil-7 and two thin gold foils samples (one bare and the other covered with cadmium) were irradiated at the core of the Second Research Egyptian Reactor ET-RR-2 of about $13 \cdot 10^{13}$ n/(cm$^2 \cdot$s) . The elemental concentration of ^{46}Sc, ^{51}Cr, ^{60}Co, ^{65}Zn, ^{74}As, ^{82}Br, ^{85}Sr, ^{86}Zr, ^{110m}Ag, ^{122}Sb, ^{134}Cs, ^{131}Ba, ^{140}La, ^{141}Ce, ^{147}Nd, ^{153}Sm, ^{152}Eu, ^{153}Gd, ^{166}Ho, ^{169}Yb, ^{175}Hf, ^{182}Ta, ^{198}Au and ^{233}Pa (^{232}Th-series) were calculated.

Keywords: iron slag, aluminum slag, neutron activation, environmental pollutions, external comparator, internal comparator.

Introduction

The disposal of slag produced in large quantities represents a big problem, could be resolved if it used as a raw material in other industries, or it used directly in the construction and agriculture. In addition, the use of slag preserve the natural resources of raw materials, and avoid environmental problems that may result from the disposal of large quantities of waste, and to this great economic value of the solutions they provide to the costs of disposal of slag. All efforts in Egypt have focused on separating the iron from slag without paying enough attention to the slag itself.

The problem in Egypt, most types of west from many steel plants were simply dumped into neighboring desert. Processing of slag is a very important step in managing such west material. Proper processing can provide slag with high value and open new fields of application.

Also in aluminum industry before aluminum wastes are used in many applications such as production of concrete, it is very important to exactly determine the amounts of trace elements in different stage of the process [1].

Accurate elemental determination is required for slag samples before and after processing of the received by-products. Because it is critical for the quality control, there are several well-defined methods for the slag analysis. Neutron activation analysis is the most and accurate methods used in different fields such as industrial applications and quality control [2 - 3].

One important aspect of routine activation analysis is the simplification of the applied standardization [4 - 8] procedure to improve the accuracy in the calculated method. A new method using compound nuclear constants (i. e. so called k_0-factors determined experimentally with high accuracy) was developed [9 - 11] to eliminate standard preparations and errors originating from randomly selected nuclear data. The latest compilation of recommended nuclear data for use in k_0-NAA is published in the Atomic Data and Nuclear Data Tables [11].

Experiment

Two slag samples weighing 269 and 262 mg and one international reference martial Soil-7 were irradiated at the core of the Second Research Egyptian Reactor ET-RR-2**.** The cadmium ratio technique was used for the measurement of neutron flux measurements. In this technique gold foils, a bare gold foil weighing 0.00247 mg and another covered with 1 mm cadmium and weighing 0.00308 mg were irradiated the same irradiation can , and the γ-ray activities induced in the gold foils by both thermal and epithermal neutrons could be obtained.

All samples and standards were carefully weighed into small thin aluminum foil of known weight. They were irradiated in the reactor ͵s core for a period of one hour. The nuclides counting were carried out at different decay times, ranging from 5 to 30 days, in order to best detect radio nuclides of various half lives. The counting system for the measurement of the induced radioactivity in the samples and standards consisted of P-type coaxial EG&G Ortec HPGe cylinder with 100 % relative efficiency, 1.9 keV FWHM at 1.3325 MeV of ^{60}Co. A Canberra 10 thickness ultra low background lead shield with low carbon steel casing was used in

concentrations can be determined by mass.

If we chose the internal comparator element is cobalt, Eq. (1) become

$$\frac{W_a}{W_{Co}} = \frac{\left[(S.D.C.)(f+Q_0)\right]_{Co}}{\left[(S.D.C.)(f+Q_0)\right]_a} \times$$

$$\times \frac{N_A(a)}{N_A(y)} \cdot \frac{(\varepsilon_\gamma)_y}{(\varepsilon_\gamma)_a} \cdot \frac{k_{0,Au}(y)}{k_{0,Au}(a)}. \quad (3)$$

External mono-standard k_0 method [12]

If we used Au as external comparator, the concentration ρ_a of an element ''a'' is obtained using:

$$\rho_a = \frac{(N_A / t_m WSDC)_a}{(N_A / t_m WSDC)_{Au}} \cdot \frac{1}{k_{Au,a}(\alpha)} \times$$

$$\times \frac{(f + Q_{0.Au}(\alpha))}{(f + Q_{0.a}(\alpha))} \cdot \frac{\varepsilon_{\gamma,Au}}{\varepsilon_{\gamma,a}} \quad (4)$$

Where the subscript ''Au'' refers to the co-irradiated gold monitor.

Detection efficiency calibration

The detector efficiency calibration was done by using calibrated point-sources, ^{241}Am, ^{131}Ba, ^{109}Cd, ^{57}Co, ^{60}Co, ^{137}Cs, ^{152}Eu, ^{54}Mn and ^{22}Na which placed at ''reference'' position, 11.7 cm from the detector front where true coincidence effects are negligible. Fig. 1 shows the absolute detection efficiency of the used coaxial HPGe detector plotted in a logarithmic scale. In order to fit the experimental points, the energy was divided into two regions, namely 0-276 keV, 276-end keV. For the first region: a third degree polynomial was used for fitting. The second region was fitted with straight line.
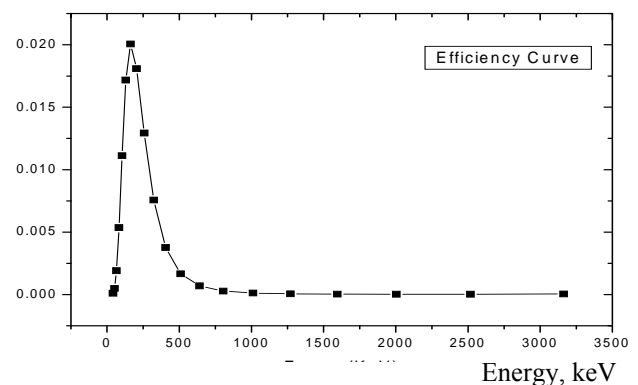
Internal comparator k_0 method [12]

The ratio of weight (W) of an element (a) to weight of the internal comparator element (y) in any irradiated sample by k_0-based internal mono standard INAA method is given by the following expression [13].

$$\frac{W_a}{W_y} = \frac{\left[(S.D.C.)(f+(Q_0(\alpha)))\right]_y}{\left[(S.D.C.)(f+(Q_0(\alpha)))\right]_a} \cdot \frac{N_A(a)}{N_A(y)} \times$$

$$\times \frac{(\varepsilon_\gamma)_y}{(\varepsilon_\gamma)_a} \cdot \frac{k_{0,Au}(y)}{k_{0,Au}(a)}, \quad (1)$$

where N_A - the net peak area under the gamma peak of interest; S - the saturation factor $\left(1-e^{-\lambda t_{irr}}\right)$; λ - the decay constant; t_{irr} - the irradiation time; D - the decay factor $e^{-\lambda t_d}$; t_d - the decay time; C - term used for correcting the decay during counting period and is given by $\frac{\left(1-e^{-\lambda t_m}\right)}{\lambda t_m}$; t_m - the measuring real time; f - the thermal to epithermal neutron flux ratio; $Q_0(\alpha)$ - the ratio of the resonance integral (I_0)-to-thermal neutron cross section (σ_0) corrected for α; α - the deviation in the real epithermal neutron spectrum $\left(\frac{1}{E^{1\pm\alpha}}\right)$ from the ideal $\left(\frac{1}{E}\right)$; (ε_γ) - the absolute detection efficiency and k_0 is a factor which is calculated from the literature $k_{0,Au}$-factors. Eq. (1) was used to calculate the elemental mass ratio in the case of core irradiation condition. When the used irradiation position has a high f-value, we can we can consider the following approximation [13]:

$$Q_0(\alpha) = Q_0, \text{ or } \alpha \approx 0.$$

So we can calculate the thermal to epithermal fluxes ratio using cadmium difference method as follows:

$$f = \frac{\varphi_{th}}{\varphi_{epi}} = Q_0\left(\frac{A_{sp(B)}}{A_{sp(Cd)}} - 1\right). \quad (2)$$

When all the major and minor elements present in the sample are amenable to NAA, the absolute

Absolute efficiency

Fig. 1. Absolute efficiency curve using ^{241}Am, ^{131}Ba, ^{109}Cd, ^{57}Co, ^{60}Co, ^{137}Cs, ^{152}Eu, ^{54}Mn and ^{22}Na standard gamma sources.

The Nuclear Data for the product isotopes are given in Table 1 and taken from Ref. [11].

Table 1. **The used nuclear data were taken from the reference**

Product isotope	Energy	$T_{1/2}$	Q_0	k_0
^{46}Sc	889.3	83.83 d	0.43	1.22
^{51}Cr	320	27.70 d	0.53	$2.6 \cdot 10^{-3}$
^{59}Fe	142.7	44.50 d	.975	$1.33 \cdot 10^{-6}$
^{60}Co	1332.5	5.271 yr	1.32	1.32
^{65}Zn	1115.5	244.3 d	1.908	$5.72 \cdot 10^{-3}$
^{76}As	563.2	26.24 h	13.6	$1.4 \cdot 10^{-3}$
^{82}Br	619.4	35.30 h	19.3	$1.45 \cdot 10^{-2}$
^{85}Sr	514	64.84 d	4.11	$9.15 \cdot 10^{-5}$
^{86}Zr	756.7	64.06 d	5.31	$1.1 \cdot 10^{-5}$
^{110m}Ag	1384	249.8 d	2.9	$1.59 \cdot 10^{-3}$
^{122}Sb	564.2	2.724 d	33	438
^{134}Cs	604	2.065 y	12.7	$4.14 \cdot 10^{-2}$
^{131}Ba	133.6	11.5 d	24.8	$3.24 \cdot 10^{-6}$
^{140}La	328.8	1.678 d	1.24	$2.87 \cdot 10^{-2}$
^{141}Ce	145.4	32.51 d	0.83	$3.66 \cdot 10^{-3}$
^{147}Nd	531	10.98 d	2	$4.56 \cdot 10^{-4}$
^{153}Sm	69.7	46.5 h	14.1	$3.25 \cdot 10^{-2}$
^{152}Eu	963.4	13.54 yr	$S_0 = 1.25$	6.46
^{153}Gd	97.4	240.4 d	0.77	$8.56 \cdot 10^{-3}$
^{175}Yb	396.3	4.185 d	0.46	$3.12 \cdot 10^{-2}$
^{175}Hf	343.4	70 d	0.78	$9.06 \cdot 10^{-3}$
^{182}Ta	100.1	114.4d	33.3	$3.18 \cdot 10^{-2}$
^{198}Au	411.8	2.695d	15.7	1
^{233}Pa (^{232}Th series)	311.9	26.97 d	11.5	$2.52 \cdot 10^{-2}$

^{151}Eu(n, γ)^{152}Eu is seriously violating the 1/v dependence. So for a 1/v thermal cross-section behavior, one has, to a good approximation [12]:

$$s_0 = \frac{2}{\sqrt{\pi}} Q_0 - 0.484 \text{ factor,}$$

where s_0 is called Westcott s_0 factor.

Results and discussion

A portion of gamma ray spectrum of IAEA Soil-7 reference material which used to calculate the concentration of Cobalt in the two slag samples is shows in Fig. 2. Non-shaded peaks refer to the background spectrum.
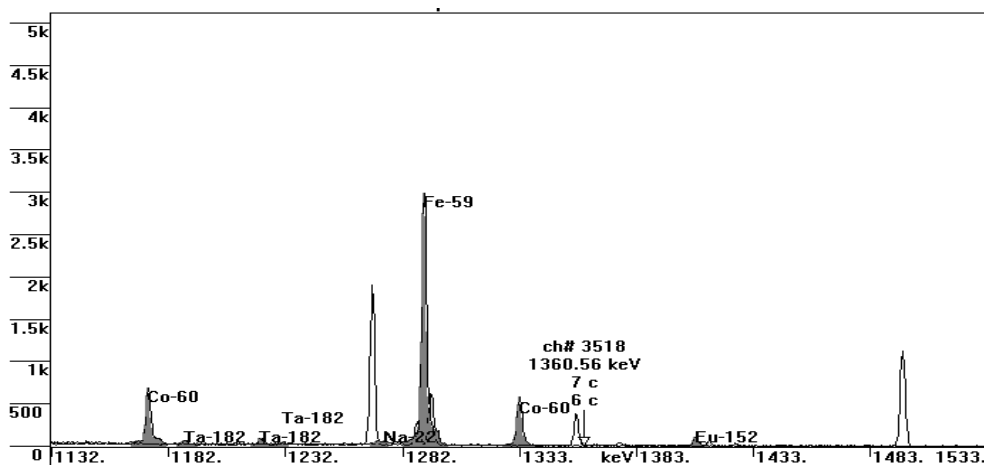

Fig. 2. A portion of gamma ray spectrum of IAEA Soil-7 reference material.

In order to study the accuracy and precision of the used methods, the concentration percentage values of seven elements: Cr, Cs, Eu, Fe, Hf, Sc and Zr have been estimated using the data of the delayed gamma-ray spectra applying both Internal Comparator k_0 and External Comparator k_0 methods as reported in Table 2.

Table 2. **Comparison of elemental concentrations (ppm) of IAEA Soil-7 using internal and external comparator method**

Product element	Energy, keV	Elemental concentrations using external comparator method	Elemental concentrations using internal comparator method	The Proper values of elemental concentration in Soil-7 [14]	
				Confidence Interval	Recommended value
Cr	320	49.3 ± 1.2	48.81 ± 2.5	49 - 74	60
Cs	604.7	4.83 ± 0.14	4.73 ± 0.16	4.9 - 6.4	5.4
Eu	963	1.2 ± 0.04	1.18 ± 0.05	0.9 - 1.3	1
Fe	1099	25300 ± 506	24829 ± 774	25700 - 26300	25700
Hf	482	4.81 ± 0.12	4.10 ± 0.16	4.8 - 5.5	5.1
Sc	889	7.77 ± 0.09	7.62 ± 0.2	6.9 - 9	8.3
Zr	756	186 ± 5	181.4 ± 7	180 - 201	185

To study the accuracy of the used method in industrial applications, two slag samples were irradiated and the elemental concentrations were measured. Tables 3 and 4 indicate the elemental concentration of 23 elements in aluminum slag sample and 19 elements in iron slag sample. Figs. 3 and 4 show elemental concentration comparison values (using the two comparator method in mg/kg) of aluminum and iron slag samples respectively.
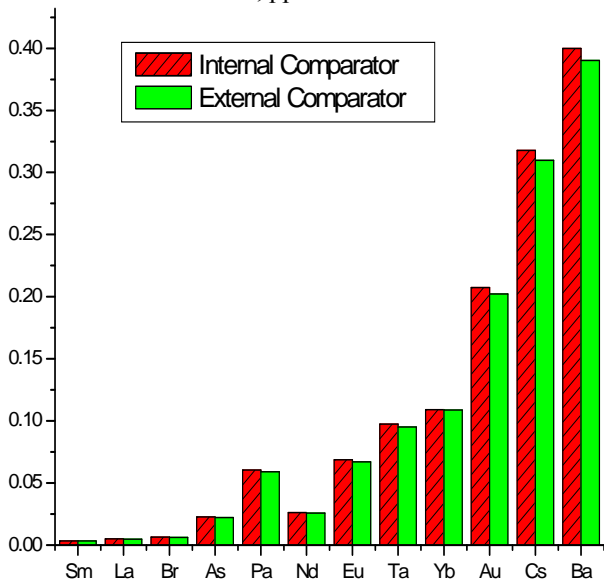
Table 3. **The elemental concentrations values of aluminum slag sample using external and internal mono standard method (ppm)**

Product isotope	Internal comparator (Co) method	External comparator (Au) method	Standard deviation
^{46}Sc	0.7569	0.7384	0.013
^{51}Cr	900.44	878.39	15.59
^{59}Fe	4147.00	4045.5	71.77
^{65}Zn	246.02	240.00	4.25
^{74}As	0.0227	0.0221	0.00042
^{82}Br	0.0064	0.0062	0.00014
^{85}Sr	0.2264	0.2208	0.00396
^{86}Zr	495.74	483.60	8.58428
^{110m}Ag	0.6311	0.6311	0
^{122}Sb	1.4600	1.4201	0.028
^{134}Cs	0.3177	0.3098	0.005
^{131}Ba	0.4000	0.3903	0.006
^{140}La	0.0050	0.0048	0.00014
^{141}Ce	4.5433	4.4321	0.078
^{147}Nd	0.0263	0.0256	1.142
^{153}Sm	0.0032	0.0032	0
^{152}Eu	0.0687	0.0670	0.0012
^{153}Gd	17.628	17.197	0.304
^{169}Yb	0.1090	0.1088	0.0001
^{175}Hf	2.1436	2.0911	0.037
^{182}Ta	0.0974	0.0950	0.0017
^{198}Au	0.2073	0.2022	0.003
^{233}Pa(^{232}Th series)	0.0604	0.0589	0.001

Table 4. **The elemental concentration values of iron slag sample using external and internal mono standard method (ppm)**

Product isotope	Internal comparator (Co) method	External comparator (Au) method	Standard deviation
^{46}Sc	1.1301	1.1091	0.01485
^{51}Cr	136.86	134.31	1.80312
^{59}Fe	5237.3	5139.9	68.8722
^{65}Zn	1586.4	1556.9	20.85965
^{74}As	3891.9	3819.5	51.19453
^{85}Sr	0.3753	0.3683	0.00495

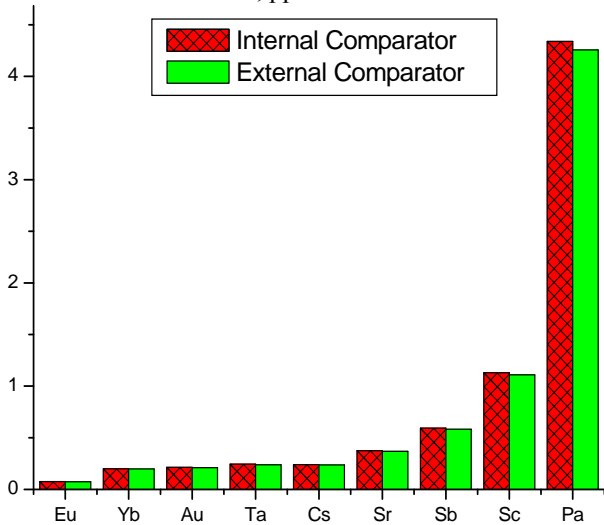| Product isotope	Internal comparator (Co) method	External comparator (Au) method	Standard deviation
^{86}Zr	64.713	63.510	0.85065
^{122}Sb	0.593	0.5816	0.00806
^{134}Cs	0.2412	0.2365	0.00332
^{131}Ba	255.4	250.65	3.35876
^{140}La	3.160	3.1020	0.04101
^{141}Ce	4.3916	4.3100	0.0577
^{152}Eu	0.0744	0.0730	0.00099
^{153}Gd	22.865	22.440	0.30052
^{169}Yb	0.1993	0.1989	0.0003
^{175}Hf	1.8097	1.7761	0.0237
^{182}Ta	0.245	0.2376	0.0052
^{198}Au	0.2139	0.2100	0.0028
^{233}Pa(^{232}Th series)	4.3381	4.2570	0.0573

Fig. 3. Elemental concentration comparison values of aluminum slag samples using two comparator method (mg/kg).
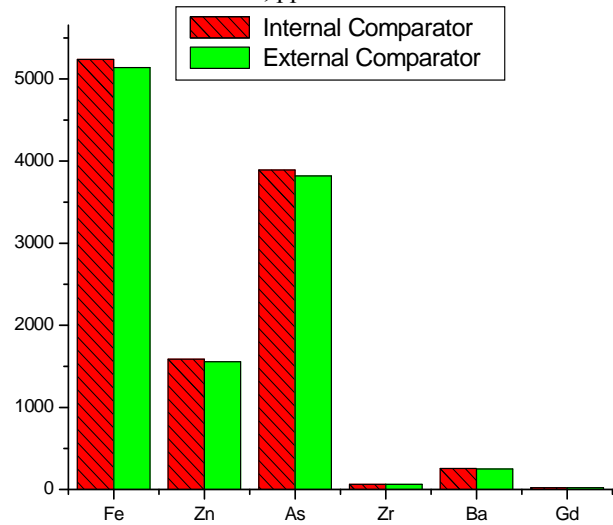

Fig. 4. Elemental concentration comparison values of iron slag samples using two comparator methods (mg/kg).

Fig. 5 gives elemental concentrations comparison values of aluminum and iron slag samples using internal comparator method.
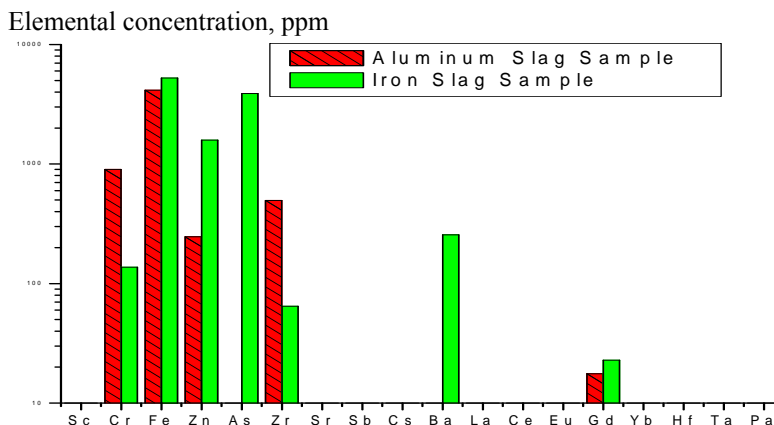
Elemental concentration, ppm

Fig. 5. Elemental concentration comparison values of aluminum and iron slag samples using internal comparator method (mg/kg).

The above results indicate that Aluminum and Iron slag concentrations differ manly in Cr, Fe, Zn, As, Ba and Gd. Iron slag is more polluted in arsenic, protactinium, while aluminum slag is more polluted in chromium and zirconium.

Conclusion

For industrial application it is very convenient to investigate trace elements content in different industrial stage. In this work, the nondestructive multi-elements neutron activation analysis technique was applied to identify the elemental constitute of two slag samples using k_0 method through two different standardization methods (Internal and external Comparator Method). The results indicate that, the used method gives good accuracy and

precision as the relative method, if all the reactor parameters are accurately determined.

As an industrial application 25 elements in slag samples are calculated. The identified elements are: Sc, Cr, Fe, Zn, As, Br, Sr, Zr, Ag, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Yb, Hf, Ta, Au and Pa.

The results show a good agreement between the two standardization methods. For routine work, it is recommended to use the internal comparator method, if at least one major or minor element is known and the irradiation parameters are steady at all time for the used irradiation positions. Internal comparator method helps in reducing radioactive waste and radiation exposure resulting from irradiation of gold monitor.

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ДОСЛІДЖЕННЯ ДВОХ ЗРАЗКІВ ШЛАКІВ З ВИКОРИСТАННЯМ k_0 НЕЙТРОННОГО АКТИВАЦІЙНОГО АНАЛІЗУ РІЗНИМИ МЕТОДАМИ СТАНДАРТИЗАЦІЇ

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Промисловий метод нейтронного активаційного аналізу застосовано для дослідження концентрації різних основних та супутніх елементів у двох зразках шлаків. Один зразок шлаку надано сталеплавильним заводом, а другий - алюмінієвим заводом у Єгипті. Метою даної роботи є вивчення надійності та точності k_0-методів внутрішнього та зовнішнього компараторів при промисловому застосуванні. Два зразки шлаку разом з еталонним матеріалом Soil-7 та двома тонкими зразками золотої фольги (один чистий, а другий покритий кадмієм) опромінювались в активній зоні другого дослідницького реактора Єгипту ET-RR-2 при потоці $13 \cdot 10^{13}$ нейтрон/(см$^2 \cdot$ с). Одержано концентрації таких елементів: ^{46}Sc, ^{51}Cr, ^{60}Co, ^{65}Zn, ^{74}As, ^{82}Br, ^{85}Sr, ^{86}Zr, ^{110m}Ag, ^{122}Sb, ^{134}Cs, ^{131}Ba, ^{140}La, ^{141}Ce, ^{147}Nd, ^{153}Sm, ^{152}Eu, ^{153}Gd, ^{166}Ho, ^{169}Yb, ^{175}Hf, ^{182}Ta, ^{198}Au and ^{233}Pa (^{232}Th ланцюжок).

Ключові слова: залізний шлак, алюмінієвий шлак, активація нейтронами, забруднення навколишнього середовища, зовнішній компаратор, внутрішній компаратор.

ИССЛЕДОВАНИЯ ДВУХ ОБРАЗЦОВ ШЛАКОВ С ИСПОЛЬЗОВАНИЕМ k_0 НЕЙТРОННОГО АКТИВАЦИОННОГО АНАЛИЗА РАЗНЫМИ МЕТОДАМИ СТАНДАРТИЗАЦИИ

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Промышленный метод нейтронного активационного анализа применен для исследования концентрации различных основных и сопутствующих элементов в двух образцах шлаков. Один образец шлака был предоставлен сталеплавильным заводом, а второй – алюминиевым заводом Египта. Целью настоящей работы является изучение надежности и точности k_0-методов внутреннего и внешнего компараторов при промышленном применении. Два образца шлака совместно с эталонным материалом Soil-7 и два тонких образца золотой фольги (один чистый, а второй покрытый кадмием) облучались в активной зоне второго исследовательского реактора Египта ET-RR-2 при потоке $13 \cdot 10^{13}$ нейтрон/(см$^2 \cdot$ с). Получены концентрации следующих элементов: ^{46}Sc, ^{51}Cr, ^{60}Co, ^{65}Zn, ^{74}As, ^{82}Br, ^{85}Sr, ^{86}Zr, ^{110m}Ag, ^{122}Sb, ^{134}Cs, ^{131}Ba, ^{140}La, ^{141}Ce, ^{147}Nd, ^{153}Sm, ^{152}Eu, ^{153}Gd, ^{166}Ho, ^{169}Yb, ^{175}Hf, ^{182}Ta, ^{198}Au and ^{233}Pa (^{232}Th цепочка).

Ключевые слова: железный шлак, алюминиевый шлак, активация нейтронами, загрязнения окружающей среды, внешний компаратор, внутренний компаратор.