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FINAL REPORT ON THE SUMMER STUDENT PROGRAM

Neutron activation analysis

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Abstract

During my participation in the JINR Summer Student Program, I learned the basic theoretical principles of the neutron activation analysis. In addition, I get acquainted with the processing of experimental γ -spectra and interpreting of the obtained data to determine the quality and quantity composition of the test sample. With the aim to eliminate possible errors in the interpretation of the results, I performed the calculation allowing me to exclude the interfering reaction $^{28}\text{Si}(n, p)^{28}\text{Al}$, which introduces an error in determining the aluminum content in sample. As well the reproducibility test of experimental data was performed to study the possibility of using standards prepared from single-element standard solutions as standards in the NAA.

Introduction

Activation analysis is an analytical method for determining the qualitative and quantitative composition of objects under study by measuring the radioactive radiation of nuclei produced by nuclear reactions.^[1]

The activation of elements under the neutron irradiation has made it possible for the neutron activation analysis (NAA) to become one of the leading methods of elemental analysis.

As known, neutron is an elementary particle that is a part of the nucleus and has no electric charge. The latter property allows the neutron to freely penetrate the electron shell of the atom and interact with the nucleus of the atom, even if it moves at a very low speed. This process leads to the transformation of a stable atomic nucleus into a radioactive nucleus, which makes it possible to identify it by the emitted γ -radiation.^[2]

Depending on the method of obtaining information on the quantitative composition of the sample neutron activation analysis is divided into two types: absolute and relative.

In the relative NAA method, standards are irradiated simultaneously with the sample, the qualitative and quantitative composition of which is known in

advance.^[3] In this case, the content of the element to be determined is calculated from a simple ratio:

$$\frac{C_x}{C_{CT}} = \frac{A_x}{A_{CT}}, \quad (1)$$

where C_x and C_{CT} – the content of the element in the sample and the standard, respectively; A_x and A_{CT} – activity of the element in the sample and standard. This method was used in this paper.

In the FLNP the IBR-2 reactor is the main source of neutrons, and neutron activation analysis is performed at the radio-analytical complex REGATA.

Spectra processing

To obtain information about the qualitative and quantitative composition of the sample, it is activated, and γ -spectrum is measured on a germanium detector. Since the half-life of the produced isotopes varies from a few minutes to several thousand years, it is necessary to obtain three γ -spectra for each sample. The first one is obtained immediately after irradiation, which makes it possible to identify isotopes with half-lives of one minute to seven hour – short-lived isotopes (SLI). The second spectra are measured after three days of "cooling down" of the sample, when isotopes with short half-lives decay and nuclides with half-lives from an hour to a day show up – long-lived isotopes-1 (LLI-1). The third measurement is done in 19-21 days after irradiation, which makes it possible to determine isotopes with a half-life of more than a day more clearly – long-lived isotopes-2 (LLI-2).

The obtained spectra were processed in the GENIE2K program, which makes it possible to find full-energy-peaks; to calculate their area; to determine from the energy of the line which element it was emitted, considering possible interference reactions.

To learn how to obtain information about the qualitative and quantitative composition of the material, I was given to analyze accreditation samples, which had already been pre-treated by a local specialist.

I have processed the spectra of samples irradiated in three containers, each containing nine samples and six standards. However, as follows from formula (1), the results of standards processing for each container need to be combined into one so-called group standard. I performed this operation using the CalcConc program developed at FLNP (Fig. 1).

I have made the final calculation of the qualitative and quantitative composition of the sample using this program (Fig. 2).

When comparing the results of my processing with those of the specialist, there were differences (Fig. 3). There are several reasons for this. Large error (up to 30%) – the choice of another standard when compiling a group standard. Error up to 10% – statistical error in processing of full-energy peaks. No value – large threshold when searching for peaks (the peak was discarded during spectrum processing in GENIE2K). The error greater than 30% can be explained by the small peak area (at the level of the detection limit and, consequently, by the large error in determining the peak area).

Имя стандарта	Нуклид	Достоверность идентификации	Средне-взвешенная активность, uCi/gram	Погрешность, %	Паспортная концентрация, mg/kg	Паспортная погрешность, %	Средне-квадратичная погрешность, %
AGV2	NA-24	0,748	1,13E+03	5,29	3,11E+04	3,00	6,08
1633e	NA-24	0,758	7,99E+01	5,53	1,71E+03	3,50	6,55
2709a	NA-24	0,756	4,51E+02	5,31	1,22E+04	2,50	5,87
2711a	NA-24	0,753	4,43E+02	5,31	1,20E+04	0,01	5,31
FFA1	NA-24	0,746	8,07E+02	5,30	2,19E+04	3,70	6,47
1633c	SC-46	0,979	2,80E+01	1,98	3,76E+01	1,60	2,55
2709a	SC-46	0,979	8,49E+00	2,50	1,11E+01	1,00	2,69
2711a	SC-46	0,969	6,61E+00	2,88	8,50E+00	1,00	3,05
667	SC-46	0,977	1,05E+01	2,44	1,37E+01	5,10	5,65
AGV2	SC-46	0,977	9,42E+00	2,49	1,30E+01	7,70	8,09
FFA1	SC-46	0,976	1,88E+01	2,18	2,42E+01	4,50	5,00
1633c	FE-59	0,982	1,93E+01	3,35	1,05E+05	3,70	4,99
2709a	FE-59	0,979	6,23E+00	3,98	3,36E+04	2,10	4,50
2711a	FE-59	0,98	5,24E+00	4,21	2,92E+04	0,04	4,21
667	FE-59	0,981	9,04E+00	3,81	4,48E+04	2,20	4,40
AGV2	FE-59	0,98	9,02E+00	3,80	4,68E+04	1,90	4,25
FFA1	FE-59	0,981	8,89E+00	3,93	4,89E+04	2,90	4,89
FFA1	CO-60	0,982	1,39E+02	3,69	3,98E+01	4,30	5,66
1633e	CO-60	0,982	1,21E+02	3,52	4,29E+01	8,20	8,92
2709a	CO-60	0,983	3,99E+01	6,76	1,28E+01	1,60	6,95
2711a	CO-60	0,978	3,43E+01	7,66	9,89E+00	2,00	7,91

Fig. 1. The window for editing a group standard sample.

Имя образца	SLI-2	LLI-1	LLI-2	Na			Mg			Al			Cl		
				LLI-1			SLI-2			SLI-2			SLI-2		
				Conc, $\mu\text{g/g}$	Err, %	MDC, $\mu\text{g/g}$	Conc, $\mu\text{g/g}$	Err, %	MDC, $\mu\text{g/g}$	Conc, $\mu\text{g/g}$	Err, %	MDC, $\mu\text{g/g}$	Conc, $\mu\text{g/g}$	Err, %	MDC, $\mu\text{g/g}$
v-01	1006161. CON	7108041. CON	7207435. CON	151	8,3	0,541	1390	5,5	66,9	344	3,6	2,14	37	20,5	6,43
v-02	1006162. CON	7108042. CON	7207436. CON	105	8,3	0,578	550	13,1	68,4	401	3,9	3,27	63	17,4	6,07
v-03	1006163. CON	7108043. CON	7207437. CON	112	8,3	0,587	990	9,5	47	297	3,5	0,832	51	21,7	4,3

Fig. 2. Element of the final sample-processing table.

№	Na-24				Deviation, %
	My		Specialist		
	Average	Stat. Deviation	Average	Stat. Deviation	
1	1057	9,34	991	12,02	6,68
2	5200	1,92	5165	21,21	0,68
3	10433	1,11	10200	100,00	2,29
4	3967	152,75	4083	165,03	2,86
5	27200	100,00	26850	70,71	1,30
6			16967	152,75	
7	4333	152,75	4113	230,29	5,35
8	293	23,09	252	3,54	16,63
9	2670	165,23	2345	21,21	13,86
№	Co-58				Deviation, %
	My		Specialist		
	Average	Stat. Deviation	Average	Stat. Deviation	
1	39,50	16,11	59,67	14,01	33,80
2	24,33	15,56	30,80	10,10	21,00
3	37,67	6,68	46,25	0,35	18,56
4			7,20		
5	25,67	1,53	23,77	2,54	7,99
6	28,10	5,91	28,30	6,34	0,71
7	38,67	6,11	46,25	0,35	16,40
8					
9	39,67	5,03	46,67	7,82	15,00

Fig. 3. Comparison of my results with those of a specialist.

Interfering reactions

Interfering reactions are reactions in which the same final nuclides are formed from different starting nuclides. These reactions lead to large errors in determining the activity of the samples.

Considered the following interfering reactions:



Reaction (3) contributes to the gamma spectrum, which leads to incorrect information about the aluminum content in the original sample.

To solve this problem, the isotopic composition of silicon was analyzed in the first place, from which it was seen that only two of its isotopes are found in nature: ^{28}Si and ^{29}Si , the relative abundance of which on Earth is 92.23% and 4.67%, respectively. Therefore, at the same time as reaction (3) there is a reaction:



that causes the line with an energy of 1273 keV in the γ -spectrum belonging to ^{29}Al .

Then we have performed activation of a silicon dioxide standard without aluminum content and obtained γ -spectrum. We know that the activity of an isotope is related to the photo-peak area as follows:

$$A = \frac{\lambda S}{E_{ff} \theta m (1 - e^{-\lambda t_{irr}})(1 - e^{-\lambda t_m}) e^{-\lambda t_{cool}}}, \quad (5)$$

in which λ – decay constant; S – peak area in the γ -spectrum, E_{ff} – γ -quantum detection efficiency; θ – probability of emission of the γ -line; m – nuclide mass; t_{irr} – irradiation time; t_m – measuring time; t_{cool} – time between irradiation and measurement.

Formula (5) makes it possible to calculate the ratio of isotope activities ^{28}Al и ^{29}Al , which will be constant in all samples:

$$\frac{A_{^{28}\text{Al}}}{A_{^{29}\text{Al}}} \cong 2,05. \quad (6)$$

The obtained coefficient will allow considering the contribution of reaction (3) to the γ -peak of ^{28}Al with an energy of 1778.8 keV in the presence of peak ^{29}Al in future measurements.

Reproducibility

The relative NAA method uses standards, which can be solid or liquid. While for solid standards the mass error is well defined (mass measurement error), for

liquid standards it is an issue. So, the standards are activated the same conditions with the same neutron flux density, "cooling down" and measurement times, this allows the reproducibility of liquid standards to be examined.

To check the reproducibility of the obtained values, we used the Romanowsky criterion, as one of the simplest and sufficiently accurate methods of determining the "blunders" of the measurement:

$$\beta_{calc} = \left| \frac{\bar{x} - x_i}{\sigma} \right|, \quad (7)$$

where \bar{x} – average value without considering the doubtful value; σ – standard deviation without considering the doubtful value; x_i – dubious value.

This parameter β_{calc} compare with the tabulated β_{table} and if the condition is met

$$\beta_{calc} \geq \beta_{table}, \quad (8)$$

this result is considered a miss.

Ten standards were chosen as samples and activities were obtained for nuclides such as ^{56}Mn , ^{192}Ir , ^{194}Ir . Then the β_{calc} coefficients for each activity value were calculated (it was assumed that each value could be a miss). The results are presented in Table 1.

Table 1 – Romanowsky criterion for ten samples

Sample	$A(^{56}\text{Mn})$	$A(^{192}\text{Ir})$	$A(^{194}\text{Ir})$	$\beta_{calc}(^{56}\text{Mn})$	$\beta_{calc}(^{192}\text{Ir})$	$\beta_{calc}(^{194}\text{Ir})$
i-11	266	1695	583	0,33	0,23	0,12
i-12	21	121	61	45,56	7,50	8,36
i-13	267	2290	792	0,33	1,52	1,44
i-14	264	1718	579	0,30	0,27	0,10
i-15	259	1664	583	0,22	0,17	0,12
i-16	265	1702	597	0,31	0,24	0,20
i-17	277	1550	595	0,48	0,05	0,19
i-18	273	1728	609	0,41	0,29	0,27
i-19	263	1586	606	0,28	0,02	0,25
i-20	268	1714	607	0,35	0,26	0,26

For ten measurements the coefficient $\beta_{table} = 2,41$. Obviously, sample i-12 stands out sharply from the selection. It is more likely due to the fact that it was irradiated insufficiently in comparison with other samples. Thus, the standard was removed and the analysis of the remaining nine samples was performed (Table 2).

Table 2 – Romanowsky criterion for nine samples

Sample	A(^{56}Mn)	A(^{192}Ir)	A(^{194}Ir)	$\beta_{calc}({}^{56}\text{Mn})$	$\beta_{calc}({}^{192}\text{Ir})$	$\beta_{calc}({}^{194}\text{Ir})$
i-11	266	1695	583	0,11	0,21	0,54
i-13	267	2290	792	0,07	9,38	16,38
i-14	264	1718	579	0,48	0,10	0,61
i-15	259	1664	583	1,87	0,37	0,54
i-16	265	1702	597	0,34	0,18	0,31
i-17	277	1550	595	3,01	0,97	0,36
i-18	273	1728	609	1,19	0,05	0,12
i-19	263	1586	606	0,84	0,77	0,17
i-20	268	1714	607	0,20	0,12	0,15

For nine measurements the coefficient $\beta_{table} = 2,34$. In this case, sample i-13 values are knocked out for both iridium, while the β_{table} value for manganese does not satisfy condition 8. This suggests that this standard is not suitable for the determination of iridium in samples but may be suitable for the identification of manganese. We did not identify "misses" when conducting a follow-up test for eight values.

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