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# DETERMINATION OF THE $^{93}$Zr AND $^{93}$Mo ISOTOPE CONTENTS IN NPP-PRODUCED RADIOACTIVE MATERIALS

*A photoactivation method for determining the produced activities of $^{93}$Zr and $^{93}$Mo isotopes has been developed. The method consists of irradiating the metals and sorbents of radioactive materials produced at the Zaporizhzhya NPP with bremsstrahlung $\gamma$-quanta with an end-point energy of 18.5 MeV. From the measured $\gamma$-spectra and using the yield ratios for $^{99}$Mo, $^{58}$Co, and $^{89}$Zr isotopes, the $^{92}$Mo/$^{59}$Co and $^{92}$Zr/$^{59}$Co concentration ratios were determined. From the obtained data and the measured produced activity of $^{60}$Co isotopes in the studied specimens, the overall activities of $^{93}$Zr and $^{93}$Mo isotopes are calculated.*

*K e y w o r d s*: flux-weighted average yields, photoactivation method, gamma spectrometry, zirconium, molybdenum, cobalt.

## 1. Introduction

During the entire exploitation period of a nuclear reactor, a huge amount of structural materials is exposed to ionizing radiation of various types, which leads to the appearance of the induced activity in all objects located around the active zone of the reactor [1]. The main source of the induced activity is the flux of thermal neutrons. Under their influence, neutron activation reactions take place in the structural materials. The most common among them is the reaction of neutron capture followed by the emission of a gamma quantum, the $(n, \gamma)$-reaction. As a result of such reactions, stable nuclei can be transformed into long-lived radionuclides [1].

During the dismantling of the reactor, these radionuclides provide a high radioactive background from hundreds of tons of structural materials, which differ strongly by their composition and, therefore, by the activity level and the radiation character [1]. For the further disposal or burial of such radioactive waste, it is necessary to evaluate the isotopic composition of all those materials in order to take all necessary measures to prevent the radiation pollution of the environment.

One of the challenging tasks associated with the exploitation of nuclear power plants (NPPs) is the evaluation of the activities of long-lived radionuclides, which decay without emitting gamma quanta [1]. One of those radionuclides is $^{93}$Mo nucleus. $^{93}$Mo nuclei are formed in the (n, $\gamma$)-reaction on $^{92}$Mo nuclei. When the fuel elements in the reactor are activated, the formation of $^{93}$Zr, which decays into $^{93m}$Nb, is also possible. The decay of all those ra-

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dionuclides is accompanied by the emission of electrons and characteristic radiation.

Radiochemical methods that are standard for determining the activity of such radionuclides cannot be used when dealing with hundreds of tons of structural materials because of their complexity and costs. In comparison with radiochemical methods, the photoactivation method [2] allows specimens of larger masses to be studied and requires lower resource costs. It makes it possible to determine the activity of an isotope in a specimen by analyzing the activity of a daughter isotope, which is formed, when the specimen is irradiated with a beam of bremsstrahlung radiation obtained from an electron accelerator as a result of the $(\gamma, x)$-reaction. The activity of the daughter radionuclide is determined using the gamma spectrometry method. Then the activity of the examined nuclide is calculated on the basis of the activity of a reference isotope with characteristic gamma transitions.

Proceeding from the said above, the goal of this work is the development of a photoactivation technique aimed at determining the produced activities of $^{93}$Zr and $^{93}$Mo radionuclides by comparing them with the activity of a long-lived radionuclide that emits $\gamma$-quanta and is available in irradiated structural materials simultaneously with radionuclides that decay without emitting $\gamma$-quanta. Such a reference radionuclide is $^{60}$Co. Its advantages are both a long half-life (5.27 years [3]), which allows its activity to be registered for a long time after the reactor shutdown, and a large capture cross-section of thermal neutrons by its parent isotope $^{59}$Co (37 barn [3]).

## 2. Experimental Technique and Measurement Results

Natural cobalt consists only of $^{59}$Co isotope and is present in radioactive materials. As a result of a large capture cross-section of thermal neutron by $^{59}$Co nuclei, $^{60}$Co is generated whose activity can be easily identified in all irradiated radioactive materials via the gamma lines at 1173.2 and 1332.5 keV [3].

To calculate the activities in the radioactive materials produced at nuclear power plants, the following formula is used, as a rule [4]:

$$A = N_A \sigma \varphi \left[1 - \exp(-\lambda t_{\text{irr}})\right] \exp(-\lambda t_{\text{cool}}). \qquad (1)$$

Here, $N_A$ is the number of corresponding atoms in the radioactive materials of the nuclear power plant, $\sigma$ is the activation cross-section by thermal neutrons, $\varphi$ is the average flux density of thermal neutrons that irradiates structural materials, $t_{\text{irr}}$ is the total duration of irradiation, and $t_{\text{cool}}$ is the duration of the time break between the irradiation and measurement time intervals. As the time $t_{\text{irr}}$, the values of the work duration in effective-day units are used, which are determined according to the known values of energy generation $E$ (in MW $\times$ day units). As the time $t_{\text{cool}}$, the values of the total reactor downtimes registered according to the existing block load schedules and averaged over a year are used. The flux density $\varphi$ is measured, in general, in the main irradiation nodes; however, it is obvious that due to neutron rescattering, substantial variations of flux values are possible.

The situation with the masses of irradiated materials is even more complicated. In particular, for cobalt, the calculations are often limited by assuming that its mass should not exceed 0.5% of the total mass. There are also substantial difficulties when estimating the cross-sections of reactions with thermal neutrons. In the reactor, there are "thermal" neutrons of the working reactor, and their energy is much higher than the energy of thermal neutrons for which the $(n, \gamma)$-cross-sections were measured. The energies of thermal neutrons vary from 0.025 to 0.5 eV, whereas, in the reactor, these energies are about 2 eV (see work [5] and references therein).

All this leads us to the fact that the activities calculated according to formula (1) differ from the corresponding experimental values by 1–2 orders of magnitude. To solve this problem, we have developed a method for determining the activity of a researched nuclide with respect to the produced activity of $^{60}$Co. Knowing the produced activity of $^{60}$Co and the ratios of the studied materials to cobalt impurities, it is possible to calculate their activities that were produced in the $(n, \gamma)$-reaction. To determine the content ratios between various elements in structural materials, we propose to apply the photoactivation technique [2].

When developing this technique, we studied the specimens taken at the Zaporizhzhya NPP. With the help of photoactivation technique, the content of cobalt admixture was measured in comparison with the molybdenum and zirconium contents. For this purpose, metal and sorbent specimens were irradiated with a beam of bremsstrahlung $\gamma$-quanta with an end-point energy of 18.5 MeV on the M-30 accelera-

tor at the Institute of Electron Physics of the National Academy of Sciences of Ukraine (Uzhhorod) [6].

The gamma spectrum of a typical irradiated metal specimen is shown in Fig. 1. To determine the molybdenum/cobalt and zirconium/cobalt mass ratios, we measured the intensity ratios between the $\gamma$-lines with energies of 739.5 keV ($^{99}$Mo, the half-life $T_{1/2}$ = = 65.9 h), 810.8 keV ($^{58}$Co, $T_{1/2}$ = 70.8 days), and 909.1 keV ($^{89}$Zr, $T_{1/2}$ = 78.4 h) [3]. $^{99}$Mo is formed in the reaction $^{100}\mathrm{Mo}(\gamma,n)^{99}\mathrm{Mo}$, and $^{58}$Co in the $(\gamma,n)$-reaction at $^{59}$Co monoisotope. At the same time, the $^{90}\mathrm{Zr}(\gamma,n)^{89}\mathrm{Zr}$ reaction is used to identify $^{89}$Zr.

The known formulas of activation analysis bring about the following expressions for the ratios between the numbers of $^{100}$Mo and $^{59}$Co atoms and between the numbers of $^{90}$Zr and $^{59}$Co atoms:

$$\begin{aligned}\frac{m(\mathrm{Mo})}{m(\mathrm{Co})}&=\frac{N(\mathrm{Mo})(1-e^{-\lambda(\mathrm{Co})t_{\mathrm{irr}}})(1-e^{-\lambda(\mathrm{Co})t_{\mathrm{meas}}})e^{-\lambda(\mathrm{Co})t_{\mathrm{cool}}}Y(\mathrm{Co})\lambda(\mathrm{Mo})}{N(\mathrm{Co})(1-e^{-\lambda(\mathrm{Mo})t_{\mathrm{irr}}})(1-e^{-\lambda(\mathrm{Mo})t_{\mathrm{meas}}})e^{-\lambda(\mathrm{Mo})t_{\mathrm{cool}}}Y(\mathrm{Mo})\lambda(\mathrm{Co})},\\ \frac{m(\mathrm{Zr})}{m(\mathrm{Co})}&=\frac{N(\mathrm{Zr})(1-e^{-\lambda(\mathrm{Co})t_{\mathrm{irr}}})(1-e^{-\lambda(\mathrm{Co})t_{\mathrm{meas}}})e^{-\lambda(\mathrm{Co})t_{\mathrm{cool}}}Y(\mathrm{Co})\lambda(Zr)}{N(\mathrm{Co})(1-e^{-\lambda(\mathrm{Zr})t_{\mathrm{irr}}})(1-e^{-\lambda(\mathrm{Zr})t_{\mathrm{meas}}})e^{-\lambda(\mathrm{Zr})t_{\mathrm{cool}}}Y(\mathrm{Zr})\lambda(\mathrm{Co})}.\end{aligned} \tag{2}$$

Here, $m$(Mo), $m$(Co), and $m$(Zr) are the numbers of $^{100}$Mo, $^{59}$Co, and $^{90}$Zr atoms, respectively; $\lambda$(Co), $\lambda$(Mo), and $\lambda$(Zr) are the radioactive decay constants for $^{58}$Co, $^{99}$Mo, and $^{89}$ Zr, respectively, s$^{-1}$; $Y$(Mo), $Y$(Co), and $Y$(Zr) are the weighted average yields of $^{99}$Mo, $^{58}$Co, and $^{89}$Zr, respectively; $N$(Mo), $N$(Co), and $N$(Zr) are the numbers of $^{99}$Mo, $^{58}$Co, and $^{89}$Zr radioactive nuclei, respectively; and $t_{\mathrm{irr}}$, $t_{\mathrm{cool}}$, and $t_{\mathrm{meas}}$ are the durations of the irradiation, cooling, and measurement operations, respectively.

The half-life times $T_{1/2}$ of $^{99}$Mo, $^{58}$Co, and $^{89}$Zr are equal to 65.9 h, 70.8 days, and 78.4 h, respectively [3]. The specimens were irradiated for $t_{\mathrm{irr}}$ = 2÷3 h. Thus, for the produced nuclides, $T_{1/2} \gg t_{\mathrm{irr}}$, and the expressions with $t_{\mathrm{irr}}$ can be expanded in Taylor series, thus obtaining that $1-e^{-\lambda(\mathrm{Co})t_{\mathrm{irr}}} \approx$ $\approx \lambda(\mathrm{Co})t_{\mathrm{irr}}$, $1-e^{-\lambda(\mathrm{Mo})t_{\mathrm{irr}}} \approx \lambda(\mathrm{Mo})t_{\mathrm{irr}}$, and $1-$ $-e^{-\lambda(\mathrm{Zn})t_{\mathrm{irr}}} \approx \lambda(\mathrm{Zn})t_{\mathrm{irr}}$. Since the measurement time $t_{\mathrm{meas}}$ was 2 days, a similar approximation with $t_{\mathrm{meas}}$ is valid only for $^{58}$Co: $1-e^{-\lambda(\mathrm{Co})t_{\mathrm{meas}}} \approx \lambda(\mathrm{Co})t_{\mathrm{meas}}$. Substituting those approximations into expressions (2), we obtain

$$\begin{aligned}\frac{m(\mathrm{Mo})}{m(\mathrm{Co})}&=\frac{N(\mathrm{Mo})\lambda(\mathrm{Co})t_{\mathrm{meas}}e^{-\lambda(\mathrm{Co})t_{\mathrm{cool}}}Y(\mathrm{Co})}{N(\mathrm{Co})(1-e^{-\lambda(\mathrm{Mo})t_{\mathrm{meas}}})e^{-\lambda(\mathrm{Mo})t_{\mathrm{cool}}}Y(\mathrm{Mo})},\\ \frac{m(\mathrm{Zr})}{m(\mathrm{Co})}&=\frac{N(\mathrm{Zr})\lambda(\mathrm{Co})t_{\mathrm{meas}}e^{-\lambda(\mathrm{Co})t_{\mathrm{cool}}}Y(\mathrm{Co})}{N(\mathrm{Co})(1-e^{-\lambda(\mathrm{Zr})t_{\mathrm{meas}}})e^{-\lambda(\mathrm{Zr})t_{\mathrm{cool}}}Y(\mathrm{Zr})}.\end{aligned} \tag{3}$$

Thus, for NPPs operating in the normal mode, the expressions for producing the activities of $^{99}$Mo and $^{89}$Zr isotopes taking the quantum yields for the relevant gamma lines into account–12.1% for the 739.5-keV line ($^{99}$Mo), 100% for the 909.1-keV line ($^{89}$Zr), and 99.45% for the 810.8-keV line ($^{58}$Co)–become substantially simplified and look like

$$\begin{aligned}&\frac{m(\mathrm{Mo})}{m(\mathrm{Co})}=\\ &=8{,}22\frac{N_\gamma(739{,}5)\lambda(\mathrm{Co})t_{\mathrm{meas}}e^{-\lambda(\mathrm{Co})t_{\mathrm{cool}}}Y(\mathrm{Co})}{N_\gamma(810{,}8)(1-e^{-\lambda(\mathrm{Mo})t_{\mathrm{meas}}})e^{-\lambda(\mathrm{Mo})t_{\mathrm{cool}}}Y(\mathrm{Mo})},\\ &\frac{m(\mathrm{Zr})}{m(\mathrm{Co})}=\\ &=\frac{N_\gamma(909{,}1)\lambda(\mathrm{Co})t_{\mathrm{meas}}e^{-\lambda(\mathrm{Co})t_{\mathrm{cool}}}Y(\mathrm{Co})}{N_\gamma(810{,}8)(1-e^{-\lambda(\mathrm{Zr})t_{\mathrm{meas}}})e^{-\lambda(\mathrm{Zr})t_{\mathrm{cool}}}Y(\mathrm{Zr})},\end{aligned} \tag{4}$$

Here, the coefficients 8.22 and 1 are the quantum yield ratios between the gamma lines at 810.8 and

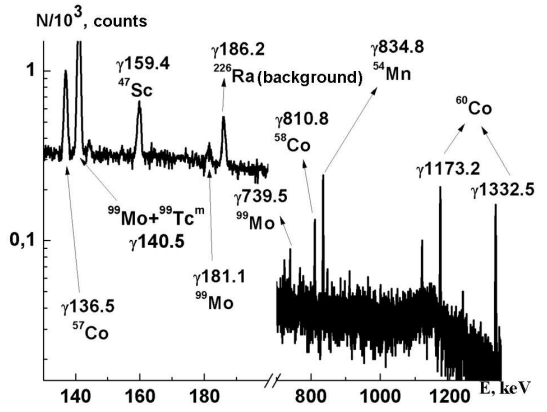


***Fig. 1.*** Fragment of the $\gamma$-spectrum of an activated metal target 2 g in mass. The duration of stay in the NPP operating zone was 1 year

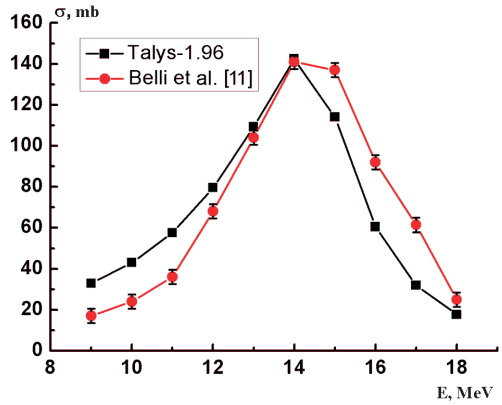


***Fig. 2.*** Simulated and experimental excitation functions of the reaction $^{100}$Mo$(\gamma, n)^{99}$Mo

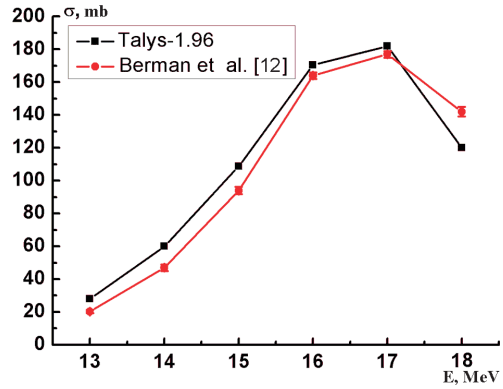


***Fig. 3.*** Simulated and experimental excitation functions of the reaction $^{90}$Zr$(\gamma, n)^{89}$Zr

**Weighted average yields of researched reactions**

| Element | $^{100}$Mo (Talys) | $^{100}$Mo [11] | $^{59}$Co (Talys) | $^{59}$Co [13] | $^{90}$Zr) (Talys) | $^{90}$Zr [12] |
|---|---|---|---|---|---|---|
| $(Y\gamma, n)$, mb | 59.3(42) | 54.3(54) | 20.8(15) | 20.3(20) | 73.9(52) | 67.9(55) |

739.5 keV and between the gamma lines at 810.8 and 909.1 keV, respectively; $N_\gamma$(739.5 keV) is the number of counts in the 739.5-keV peak with regard for the efficiency of spectrometer registration (in this case, 5.6%); $N_\gamma$(810.8 keV) is the number of counts in the total absorption peak at an energy of 810.8 keV considering the efficiency of the spectrometer registration (in this case, 5.2%); and $N_\gamma$(909.1 keV) is the number of counts in the 909.1-keV peak accounting for the efficiency of spectrometer registration (in this case, 4.6%). Since the target was three-dimensional, the self-absorption of $\gamma$-quanta was calculated using the MCNP-4c code [7] and accounted in formulas (4).

In studies of this kind, the yields of corresponding reactions are critical. The weighted average yields of the reactions $^{100}$Mo$(\gamma$,n$)^{99}$Mo, $^{90}$Zr$(\gamma, n)^{89}$Zr, and $^{59}$Co$(\gamma, n)^{58}$Co$^{\text{tot}}$ were determined as a result of the convolution with a step of 1 MeV using the formula

$$Y = \frac{\sum\limits_{i=1}^{N} \sigma_i \varphi_i}{\sum\limits_{i=1}^{N} \varphi_i}, \qquad (5)$$

where $\sigma_i$ are the tabular values of the cross-sections of the indicated reactions for monochromatic $\gamma$-quanta, and $\varphi_i$ are the relative flow magnitudes of the spectrum of braking $\gamma$-quanta simulated in Geant4 [8] for various numbers of events and reduced to the threshold energy values for those reactions.

To calculate the weighted average yields, the reaction cross-section values were taken from two sources: the tabulated experimental data and the data calculated using the Talys-1.96 software program [9]. In the case of discrepancies between them that exceeded the experimental error limits, the experimental data were used. In particular, the obtaining of the yield for the reaction $^{59}$Co$(\gamma, n)^{58}$Co$^{\text{tot}}$ was described in detail in work [10] for $E_{gr} = 37$ MeV. In our case, the number of convolution steps decreases at $E_{\text{gr}} = 18.5$ MeV, and, therefore, the weighted average yield also becomes somewhat lower (see Table).

To calculate the weighted average yields of the reactions $^{100}$Mo$(\gamma, n)^{99}$Mo and $^{90}$Zr$(\gamma, n)^{89}$Zr (see Figs. 2 and 3), we used experimental data from works [11] and [12], respectively. The obtained reaction yield values are also quoted in Table. As one can see from this table, the difference between the experimental and theoretical yields does not exceed the required accuracy of the method for all reactions. In our calculations, we used the experimental data of other authors.

For the weighted average yields, calculated according to the data of the Talys-1.96 code, the error included the error of the braking spectrum simulation in the Geant 4 code, which fell within 7%. If the experimental data were used, the total error was slightly larger because, besides the simulation error, the experimental cross-section error was also taken into account. For each cross-section, the error was

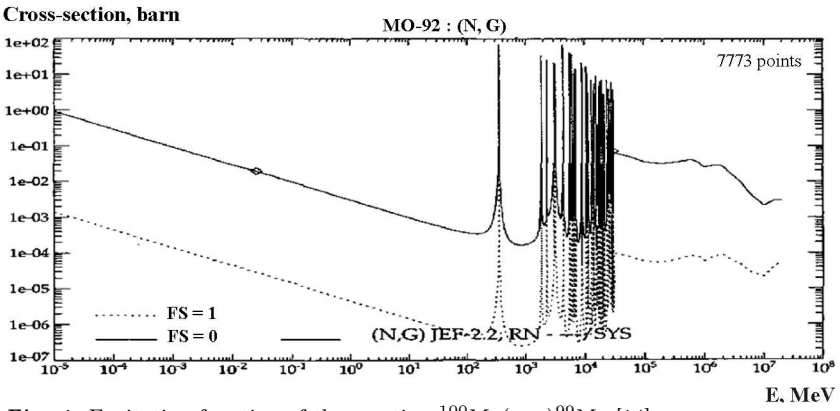


***Fig. 4.*** Excitation function of the reaction $^{100}\mathrm{Mo}(\gamma, n)^{99}\mathrm{Mo}$ [14]

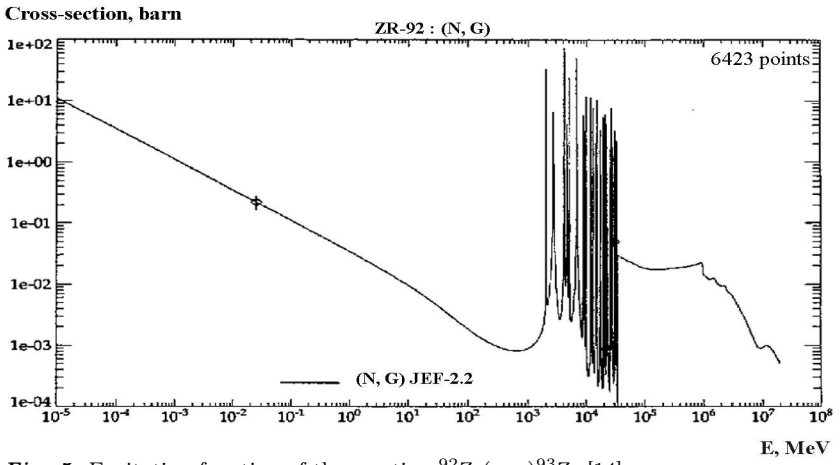


***Fig. 5.*** Excitation function of the reaction $^{92}\mathrm{Zr}(n, \gamma)^{93}\mathrm{Zr}$ [14]

taken with its weighting factor, i.e., the weighted average error was calculated, which was also equal to 5–7%. Therefore, the total determination error of the weighted average yields used in our calculations was within the limits of 8–10%.

The errors of weighted average yields dominated while calculating ratios (4). In our case, the determination errors of quantum yields were less than 1%, because we used the most intensive $\gamma$-lines. The total error of the registration efficiency was within 2–3%, because we performed relative measurements and used high-energy $\gamma$-quanta with close energies. This error consisted of the intensity errors and the errors of the quantum yields of the $\gamma$-lines emitted by the calibration source. This error also included the error of the smoothing polynomials, if the energy of the required $\gamma$-quantum was between the peaks of calibration $\gamma$-lines. Therefore, the total calculation error of ratios (4) was within 9–11%. The excitation functions obtained when producing the activities of $^{93}$Mo and $^{93}$Zr isotopes during the reactor operation are shown in Figs. 4 and 5, respectively. At the bottom of the figures, the libraries used to calculate the excitation functions are indicated. The number of points used in the calculations is indicated in the upper right corner. The experimental measurements were carried out at energies of 0.0253 and 30 keV.

The researched radioactive materials were located in places, where thermal and epithermal neutrons with energies up to 10 eV dominated. As one can see from Figs. 4 and 5, when activating molybdenum, zirconium, and cobalt (see Fig. 6 [15]), just these neutrons gave the main contribution to the production of the $^{93}$Mo, $^{93}$Zr, and $^{60}$Co isotopes. The capture cross-sections of these neutrons are described by the formula $\sigma \sim \sigma(E = 0.025\ \mathrm{eV}) \times V(E = 0.025\ \mathrm{eV})/V(E)$,

where $V(E)$ is the neutrons' velocity. As one can see, when performing relative measurements, data for a neutron energy of 0.025 eV can be used. The contributions from epithermal and fast neutrons can be neglected; therefore, in our further calculations, we used tabular cross-section values for thermal neutrons. We estimated the activity ratios $^{93}$Mo/$^{60}$Co and $^{93}$Zr/$^{60}$Co by the following formulas:

$$\begin{aligned}
&\frac{A(^{93}\mathrm{Mo})}{A(^{60}\mathrm{Co})} = \\
&= \frac{(1-e^{-\lambda(^{93}\mathrm{Mo})t_{\mathrm{irr}}})e^{-\lambda(^{93}\mathrm{Mo})t_{\mathrm{cool}}}\Phi_n\sigma^n_{^{92}\mathrm{Mo}}N_{^{92}\mathrm{Mo}}}{(1-e^{-\lambda(^{60}\mathrm{Co})t_{\mathrm{irr}}})e^{-\lambda(^{60}\mathrm{Co})t_{\mathrm{cool}}}\Phi_n\sigma^n_{^{59}\mathrm{Co}}N_{^{59}\mathrm{Co}}} = \\
&= \frac{(1-e^{-\lambda(^{93}\mathrm{Mo})t_{\mathrm{irr}}})e^{-\lambda(^{93}\mathrm{Mo})t_{\mathrm{cool}}}\sigma^n_{^{92}\mathrm{Mo}}N_{^{92}\mathrm{Mo}}}{(1-e^{-\lambda(^{60}\mathrm{Co})t_{\mathrm{irr}}})e^{-\lambda(^{60}\mathrm{Co})t_{\mathrm{cool}}}\sigma^n_{^{59}\mathrm{Co}}N_{^{59}\mathrm{Co}}}, \\
&\frac{A(^{93}\mathrm{Zr})}{A(^{60}\mathrm{Co})} = \\
&= \frac{(1-e^{-\lambda(^{93}\mathrm{Zr})t_{\mathrm{irr}}})e^{-\lambda(^{93}\mathrm{Zr})t_{\mathrm{cool}}}\Phi_n\sigma^n_{^{92}\mathrm{Zr}}N_{^{92}\mathrm{Zr}}}{(1-e^{-\lambda(^{60}\mathrm{Co})t_{\mathrm{irr}}})e^{-\lambda(^{60}\mathrm{Co})t_{\mathrm{cool}}}\Phi_n\sigma^n_{^{59}\mathrm{Co}}N_{^{59}\mathrm{Co}}} = \\
&= \frac{(1-e^{-\lambda(^{93}\mathrm{Zr})t_{\mathrm{irr}}})e^{-\lambda(^{93}\mathrm{Zr})t_{\mathrm{cool}}}\sigma^n_{^{92}\mathrm{Zr}}N_{^{92}\mathrm{Zr}}}{(1-e^{-\lambda(^{60}\mathrm{Co})t_{\mathrm{irr}}})e^{-\lambda(^{60}\mathrm{Co})t_{\mathrm{cool}}}\sigma^n_{^{59}\mathrm{Co}}N_{^{59}\mathrm{Co}}},
\end{aligned} \tag{6}$$

where $A(^{93}\mathrm{Mo})$, $A(^{93}\mathrm{Zr})$, and $A(^{60}\mathrm{Co})$ are the produced activities of $^{93}$Mo, $^{93}$Zr, and $^{60}$Co isotopes, respectively, in Bq units; $\Phi_n$ is the neutron flux in the reactor, in neutron/s units; $\sigma^n_{^{92}\mathrm{Mo}}$, $\sigma^n_{^{92}\mathrm{Zr}}$, and $\sigma^n_{^{59}\mathrm{Co}}$ are the tabular cross-section values for the reactions $^{92}$Mo(n,$\gamma$)$^{93}$Mo, $^{92}$Zr(n,$\gamma$)$^{93}$Zr, and $^{59}$Co(n,$\gamma$)$^{60}$Co, respectively, taken from work [3], in barn units; $\lambda(^{93}\mathrm{Mo}) = 0.693/T_{1/2}(^{93}\mathrm{Mo})$, $\lambda(^{93}\mathrm{Zr}) = 0.693/T_{1/2}(^{93}\mathrm{Zr})$, and $\lambda(^{60}\mathrm{Co}) = 0.693/T_{1/2}(^{60}\mathrm{Co})$ are the radioactive-decay constants of $^{93}$Mo, $^{93}$Zr, and $^{60}$Co isotopes, respectively, in $\mathrm{s}^{-1}$ units; $T_{1/2}(^{93}\mathrm{Mo})$, $T_{1/2}(^{93}\mathrm{Zr})$, and $T_{1/2}(^{60}\mathrm{Co})$ are the half-lives of $^{93}$Mo, $^{93}$Zr, and $^{60}$Co isotopes, respectively, in s units; and $N_{^{92}\mathrm{Mo}}/N_{^{59}\mathrm{Co}}$ and $N_{^{92}\mathrm{Zr}}/N_{^{59}\mathrm{Co}}$ are the ratios between the numbers of corresponding atoms (these ratios can be calculated for a given specimen from formulas (4) for the ratios between the numbers of atoms $^{100}$Mo/$^{59}$Co and $^{90}$Zr/$^{59}$Co, respectively, after accounting for the content of $^{92}$Mo isotope in the natural mixture of molybdenum, and $^{92}$Zr in the natural mixture of zirconium).

The produced activities of $^{93}$Mo and $^{93}$Zr in metals calculated according to formulas (6) were found to equal $(100\div150)\pm(20\div30)$ mBq/g and $(6\pm2)$ nBq/g, respectively.

The total error of the activities was obtained as the square root of the sums of the squared errors of the ratios (their calculation was described above), the errors of the tabulated cross-sections of (n,$\gamma$)-reactions, and the errors of the quantum yields, registration efficiencies, and peak areas of $\gamma$-quanta that accompany the decay of $^{60}$Co nuclei. The error for the neutron flux was not taken into account, because the fluxes were reduced. The systematic error was estimated by carrying out measurements on another spectrometer. It was found to be within 1–2%. In our measurements, the errors were 20–30%, and they were mainly associated with a low statistical accuracy of $\gamma$-peaks.

## 3. Conclusions

The developed photoactivation method for determining the produced activities of $^{93}$Zr and $^{93}$Mo isotopes makes it possible to considerably simplify their identification, control, and certification in the structural materials of NPPs and radioactive waste of various types.

Nowadays, new materials for NPPs have been developed, in which the molybdenum concentration reaches a value of 7.5%. In our specimens, the content of Mo admixture was 0.2–0.3%. It is easy to estimate that, during long-term exploitation, the produced activity of $^{93}$Mo can reach values of 300–500 Bq/g even not directly in the region of large fluxes. This is already at the level of the maximum permissible concentration for metals and points to that the monitoring over the produced $^{93}$Mo activity is mandatory. Since the molybdenum content in new materials is 7.5%, the produced activity of $^{93}$Mo can reach $10^4$ Bq/g. Despite that the activity of $^{93}$Zr is very low, it should also be monitored because since Zr is used in the reactor core where its concentration reaches 100% and the neutron flux is 5–6 orders of magnitude larger than in the structural materials beyond the reactor core.

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ВИЗНАЧЕННЯ ВМІСТУ $^{93}$Zr ТА $^{93}$Mo
В РАДІОАКТИВНИХ МАТЕРІАЛАХ АЕС

Розроблено фотоактиваційний метод визначення напрацьованих активностей $^{93}$Zr та $^{93}$Mo шляхом опромінення металів та сорбентів радіоактивних матеріалів ЗАЕС гальмівними $\gamma$-квантами з граничною енергією 18,5 МеВ. Використовуючи співвідношення виходів $^{99}$Mo, $^{58}$Co та $^{89}$Zr, з виміряних $\gamma$-спектрів ми визначили співвідношення концентрацій ізотопів $^{92}$Mo та $^{92}$Zr до концентрації $^{59}$Co. З отриманих даних та виміряної напрацьованої активності $^{60}$Co в досліджуваних зразках отримано повні активності $^{93}$Zr та $^{93}$Mo.

*Ключові слова*: середньозважені виходи, фотоактиваційний метод, гамма-спектрометрія, цирконій, кобальт, молібден.