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Application of Titanium Dioxide for Zirconium Ions Adsorption and Separation from a Multicomponent Mixture

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This work studies the adsorption of zirconium ions by the mesoporous titanium dioxide and by sodium-modified mesoporous titanium dioxide. Experimental maximal adsorption values of zirconium ions by H-TiO₂ and Na-TiO₂ were found to be 64 mg/g and 109.5 mg/g respectively. This process depends on the interaction time, the equilibrium concentration of zirconium ions, and the acidity of the solution. Adsorption kinetics fit well into the diffusion kinetic model and indicate several stages of zirconium ions adsorption. Equilibrium adsorption of zirconium ions is well described by Langmuir's adsorption theory for both adsorbents. The results obtained by inductively coupled plasma mass spectrometry showed that the investigated adsorbent selectively adsorb zirconium ions from the mixture with strontium and yttrium ions in the range of solution pH = 0 - 1. The percentage of maximum extraction of zirconium ions is 86.61 % for H-TiO₂ and 94.11 % for Na-TiO₂. This fact is extremely valuable for nuclear forensics or the determination of ⁹⁰Sr in low activity background samples.

Keywords: mesoporous TiO₂, zirconium ions, adsorption, separation, ICP-MS.

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Introduction

The relevance of studies of the adsorption of zirconium ions from aqueous solutions and its selective separation from strontium and yttrium can be explained by multiple factors. One of them is the determination of the low activity of ⁹⁰Sr in environmental samples. Radioactive ⁹⁰Sr is a very harmful beta-emitter that accumulates in bones or fish scales [1] and may, significantly harm living organisms in which it accumulates due to the long half-life. Therefore, the maximum allowable levels of ⁹⁰Sr in the environment are extremely low [2], and their analysis is very difficult to perform. ⁹⁰Sr is a pure beta-emitter. Gamma spectrometry is unable to determine the amount of ⁹⁰Sr because it does not produce gamma lines. Its daughter nuclide ⁹⁰Y also does not emit gamma rays. ⁹⁰Y β- particles have higher maximum energy than β- particles of ⁹⁰Sr (2.281 MeV versus 0.546 MeV, respectively) and completely shield strontium. The amount of ⁹⁰Sr can be approximately determined based on Vavilov-Cherenkov radiation generated by yttrium β- particles [3]. Another technique of environmental ⁹⁰Sr measurement is the separation of ⁹⁰Sr from yttrium by the oxalate precipitation and subsequent determination of ⁹⁰Sr amount based on the freshly formed daughter ⁹⁰Y. This technique is used in the determination of the amount of ⁹⁰Sr in aquatic ecosystems of the Chornobyl Exclusion Zone [1]. However, the accuracy of the oxalate technique is not very high and does not allow determining ⁹⁰Sr in low-level environmental samples. In this case, inductively coupled plasma mass spectrometry (ICP-MS) may be the only method of ⁹⁰Sr analysis. Several leading laboratories worldwide [4-6] use this method to analyze ⁹⁰Sr in the environment. The effectiveness of the ICP-MS method compared to other highly sensitive modern methods is presented in fig. 1.

This method of analysis is very sensitive (Fig. 1), but it diagnoses ⁹⁰Sr, ⁹⁰Y, and ⁹⁰Zr as a single peak at the mass
of 90amu. The isotopes of $^{90}$Sr, $^{90}$Y, and $^{90}$Zr

I.

Experimental Techniques

1.1. Synthesis of H-TiO$_2$ and Na-TiO$_2$ adsorbents

Experimental samples of anatase modification titanium dioxide with protonated and sodium-modified surface were obtained by sol-gel method, using a solution of titanium aqua complex [Ti(OH)$_3$]$^{3+}$∙3Cl$^{-}$ as a precursor [12]. The 0.1M solution of titanium precursor was heated at 60 °C for 60 minutes to prepare titanium dioxide with a protonated surface (H-TiO$_2$). Globular particles of TiO$_2$ with a diameter of 4 - 5 nm were formed in the reaction medium, due to the hydrolysis of the precursor, and condensation of the molecules Ti(OH)$_3$∙2H$_2$O. The 10 % NaOH solution was added dropwise to the dispersion to deoxidize the resulting product. At pH ~ 5.3 the dispersion thickened rapidly because of gel formation. The hydrogel with a pH of ~ 7.0 was washed with distilled water from the absorbed impurities of Na$^+$, Cl$^-$ ions. Then, it was dried for 4 hours, at a temperature of 140°C.

Titanium dioxide with a sodium surface was obtained by contacting globular TiO$_2$ particles with 10 % NaOH solution. The TiO$_2$ dispersion was kept in an alkali medium (pH ~ 12) for 3 hours at room temperature, then the dispersion was washed with distilled water. Washing and decantation of the dispersion were repeated at least 5 times, and after establishing the pH ~ 7, it was dried at a temperature of 140°C. The main textural characteristics of the adsorbents are shown in Table 1.

1.2. Batch adsorption studies

Recommendations for the separation of elements can be made after studying the general patterns of the process of adsorption of the studied elements. Studies of the adsorption capacity of H-TiO$_2$ and Na-TiO$_2$ toward zirconium cations were performed under batch conditions. The weight of the adsorbent was 50 mg, and the volume of the ZrOCl$_2$ aqueous solution was 5 ml. The influence of time interaction, the equilibrium concentration of the zirconium ions, and the acidity of the solution was investigated. Initial and residual concentrations of

| Sample  | $S_{\text{BET}}$ (m$^2$g$^{-1}$) | $S_{\text{micro}}$ (m$^2$g$^{-1}$) | $S_{\text{meso}}$ (m$^2$g$^{-1}$) | $V_p$ (cm$^3$g$^{-1}$) | $V_{\text{micro}}$ (cm$^3$g$^{-1}$) | $V_{\text{meso}}$ (cm$^3$g$^{-1}$) | pH $_{\text{pzc}}$ |
|---------|------------------|-----------------|-----------------|----------------|----------------|----------------|----------------|
| H-TiO$_2$ | 349              | 129             | 230             | 0.191         | 0.061          | 0.130          | 5.35           |
| Na-TiO$_2$ | 239              | 100             | 139             | 0.152         | 0.054          | 0.098          | 9.42           |
zirconium ions were determined using direct complexometric titration in a strongly acidic medium with Xylenol Orange as an indicator [16]. Adsorption values were calculated using (eq.1) as follows:

\[ q_e = \frac{\left(C_0 - C_e\right)V}{m}, \]

where \( q_e \) – is the amount of adsorbate uptake, mg/g; \( C_0 \) and \( C_e \) – are initial and residual concentrations of adsorbate, mg/L; \( V \) – is solution volume, L; \( m \) - mass of adsorbent, g [17].

The influence of solution acidity on zirconium cations adsorption by investigated adsorbents was studied under the same conditions, however, the volume of the solution was 10 ml (5 ml of ZrOCl\(_2\) solution and 5 ml of the medium) and the mass of the adsorbent remained unchanged.

The most common adsorption kinetic models were applied to experimental data: kinetic models based on pseudo-first, pseudo-second-order equations; Elovich and diffusion kinetic models. However, special attention was paid to the Elovich model (\( q = f \left(\ln t\right)\)) and the diffusion kinetic model (\( q = f \left(t^{0.5}\right)\)), as they allow predicting the mechanism of adsorption: mainly physical (diffusion model), or chemisorption (Elovich model) [18-23].

Langmuir and Freundlich’s adsorption theories were used to analyze the equilibrium adsorption. The equations of these theories (2) and (3) are given below:

\[ q_e = \frac{A_{\text{max}}K_Ce}{1+K_Ce}, \]

\[ q_e = K_f \times C_e^n, \]

where, \( A_{\text{max}} \) (mg/g) – maximum adsorption value, which corresponds of fill in the whole adsorption centers; \( K_L \) (L/mg) – Langmuir constant; \( C_e \) (mg/L) – adsorbate equilibrium concentration; \( q_e \) (mg/g) – quantities of adsorbate uptake at equilibrium; \( K_f \) – Freundlich constant, \( mg/g \cdot L^{n} \); \( n \) - Freundlich intensity parameter.

Separation factor \( a_{Sr, Zr} \) of strontium and zirconium was calculated according to [7]:

\[ a_{Sr, Zr} = \frac{\text{Intensity [cps] }^{88-Sr}}{\text{Intensity [cps] }^{90-Zr}}, \]

where Intensity in [count per second] was experimentally measured value by ICP-MS of corresponding isotopes after adsorption.

Nonlinear approximation of experimental results was processed in the “Solver add-in” to Microsoft Office Excel. The chi-squared test is highly recommended for the nonlinear method to confirm the best fitting isotherm for a given adsorption system. High \( \chi^2 \) indicates high divergence between the experiment and the model. The chi-square value \( \chi^2 \) and coefficient of determination \( R^2 \) were calculated using equations (5) and (6). In general, the recommendations from the publication [20] were used in the analysis of experimental adsorption results.

\[ R^2 = 1 - \frac{\sum(\text{qexp}-\text{qcalc})^2}{\sum(\text{qexp}-\text{qmean})^2}, \]

\[ \chi^2 = \sum \frac{(\text{qexp}-\text{qcalc})^2}{\text{qcalc}}. \]

### 1.3. ICP-MS analysis of separation of investigated cations

The study of the possibility of strontium, yttrium, and zirconium ions separation using the investigated adsorbents was performed under batch conditions. The \(^{88}\text{Sr}, ^{89}\text{Y}, ^{90,91}\text{Zr}\) isotopes were analyzed by the inductively coupled plasma mass spectrometer (ICP-MS) [4-6] ‘Element 2’ with argon plasma, located in the Nuclear Forensics laboratory of KINR, Kyiv. The study was performed with a mixture of the high purity standards solutions (High Purity Standards, USA) of the corresponding elements.

The results were measured in the number of [CPS] pulses "count per second" relative to m/x.

As has been said above, \(^{90}\text{Y}\) does not play a significant role in determining the date of fabrication of a \(^{90}\text{Sr} \cdot ^{90}\text{Y}\) radioactive source. This is due to the fact, that the half-life of \(^{90}\text{Y}\) is much shorter (64 hours) than the half-life of \(^{90}\text{Sr}\) (28.8 years) and its amount throughout the life of \(^{90}\text{Sr}\) remains constant. This statement can be illustrated by formulas (7) - (9):

\[ \lambda_2 - \lambda_1 \cong \lambda_2, \]

Where \( \lambda_2 \) – Decay constant of \(^{90}\text{Y}\); \( \lambda_1 \) – decay constant of \(^{90}\text{Sr}\).

The number of daughter nuclei is related to the number of parent nuclei by the equation (7):

\[ N_Y = \frac{\lambda_1}{\lambda_2 - \lambda_1} \times N_{Sr} \left( e^{-\lambda_2 t} - e^{-\lambda_1 t} \right) \cong \frac{\lambda_1}{\lambda_2} N_{Sr} \left( 1 - e^{-\lambda_2 t} \right) \]

\[ N_Y = \frac{\lambda_1}{\lambda_2} \left( N_{Sr} \right), \text{ or } N_Y = \frac{N_{Sr}}{\left( t_{1/2} \right)^2} = \frac{N_{Sr}}{\left( T_{1/2} \right)^2} \]

\[ \lambda_2 \left( T_{1/2} \right)^2 \rightarrow \text{Half-life of } ^{90}\text{Y}; \]

\[ \lambda_1, \left( T_{1/2} \right)^{-1} \sim \text{Half-life of } ^{90}\text{Sr}. \]

Stable \(^{90}\text{Y}\), in contrast to \(^{90}\text{Y}\), plays a significant role, because it was very often used as a carrier for radioactive \(^{90}\text{Sr}\) and \(^{90}\text{Y}\). This was because, the separation of \(^{90}\text{Sr}\) from a mixture of fission radionuclides, during fabrication of \(^{90}\text{Sr} \cdot ^{90}\text{Y}\) radioactive source, was carried out by the reaction of precipitation of strontium and yttrium with oxalates [1]. Stable \(^{90}\text{Y}\) in the resultant \(^{90}\text{Sr} \cdot ^{90}\text{Y}\) source may be at a high concentration. It can affect the selective adsorption of \(^{88}\text{Sr} \cdot ^{89}\text{Zr} \cdot ^{91}\text{Zr}\) and \(^{90}\text{Y}\) are also adsorbed on the surface of titanium dioxide. Therefore, a mixture of isotopes of \(^{88}\text{Sr}, ^{90}\text{Zr}, ^{91}\text{Zr}, \text{ and } ^{90}\text{Y}\) was subjected to the analysis by ICP-MS. A great advantage of ICP-MS is its multi-element capability, which allows multiple elements to be measured simultaneously in a single analysis. However, interferences need to be controlled. Internal standardization is usually employed to
correct for changes in instrument operating conditions and sample-specific matrix effects. According to recommendations, which were given in publication [5], the internal standard will have a similar mass and ionization potential to the analyte ($^{88}\text{Sr}$, $^{89}\text{Y}$, $^{90}\text{Zr}$, $^{91}\text{Zr}$). Therefore, $^{103}\text{Rh}$ was chosen, as an internal standard. External calibration of the ICP-MS was performed using calibration Standard A, containing known concentrations of the elements. The error due to the formation of polyatomic ions $^{89}\text{Y}^{1}\text{H}$ in plasma was determined using Standard 1. Standard 1 is a mixture of about 10 ng $^{88}\text{Sr}$ and $^{89}\text{Y}$. Standard solution 2 (Standard 2) was a mixture of $^{88}\text{Sr}$, $^{89}\text{Y}$, $^{90}\text{Zr}$, $^{91}\text{Zr}$, which was divided into 5 equal parts, four of them were mixed with adsorbents, and the fifth was left as a control solution. In addition, Standard 3 was pure 2 % HNO$_3$ ‘Optima’.

Adsorption and separation of strontium, yttrium, and zirconium ions were performed in batch conditions for an hour. Mass of adsorbents was 100 mg, volume of solutions – 10 ml. After adsorption, the adsorbents were separated from the solution by filtration. The slow-filtering paper with dense narrow pores for finest deposits was selected for this purpose. Selective adsorption of zirconium and the possibility of separation of zirconium from strontium and yttrium were evaluated by analyzing the isotopes $^{88}\text{Sr}$, $^{89}\text{Y}$, $^{90}\text{Zr}$, $^{91}\text{Zr}$, and $^{103}\text{Rh}$ by ICP-MS at least three times.

II. Results and Discussion

2.1. Adsorption of zirconium ions by H-TiO$_2$ and Na-TiO$_2$

The results of the dependence of the zirconium adsorption values by H-TiO$_2$ and Na-TiO$_2$ on agitation time are shown in Fig. 2.

![Fig. 2. Dependence of the adsorption values of zirconium ions by H-TiO$_2$ and Na-TiO$_2$ on the agitation time.](image)

The results, which are shown in Fig. 3 and Table 2, indicate that the diffusion model best describes the process of adsorption of zirconium ions by the investigated adsorbents. According to the results of the analysis, the zirconium ions adsorption by H-TiO$_2$ and Na-TiO$_2$ occurs in several stages: diffusion from solution to the surface of the adsorbents (Step 1 ‘bulk transport’); diffusion on the adsorbent’s surface (Step 2 ‘film diffusion’) and diffusion deep into the pores of the adsorbent (Step 3 ‘intraparticle diffusion’). The highest diffusion coefficients ($k_{ipd}$) were

![Fig. 3. Application of kinetic models to experimental results of zirconium ions adsorption by H-TiO$_2$ and Na- TiO$_2$: (a) Pseudo-second; (b) Elovich; (c) Pseudo-first; (d) Intra-particle diffusion kinetic models.](image)
observed during the diffusion of zirconium ions along the surface of H-TiO₂ and Na-TiO₂. The values of the constant C mg/g in the equations of the diffusion model are related to the thickness of the boundary layer [20]. The larger value of C means the greater effect of the thickness of the boundary layer on the adsorption of zirconium ions. When zirconium ions diffuse along the Na-TiO₂ surface, the boundary layer does not affect the adsorption. In all other cases, the values of C are significant, so the thickness of the boundary layer of the adsorbent surface affects the process of adsorption of zirconium ions from the neutral medium. For the adsorbent H-TiO₂, the value of C increases in the series Step 1-Step 2-Step 3 and has a value of 19 mg/g; 20.7 mg/g, and 52 mg/g, respectively.

### 2.2. Equilibrium adsorption of zirconium ions by H-TiO₂ and Na-TiO₂ and influence of solution acidity on the adsorption process

The results of equilibrium studies of zirconium ions adsorption by H-TiO₂ and Na-TiO₂ are shown in Fig. 4 and Fig. 5. The application of the Langmuir and Freundlich theories to the experimental results is given in Table 3.

The experimental isotherms of zirconium ions adsorption by the studied adsorbents are better described by Langmuir's theory than by Freundlich's theory for both adsorbents. However, the divergence between the experimental results and calculated by Langmuir theory (χ²) for Na-TiO₂ are higher. The main differences between the experimental values and the theoretically calculated ones for zirconium ions adsorption by the Na-TiO₂ are in the region of low equilibrium concentrations of the adsorbate. This can be explained by the very active surface of the adsorbent. In our opinion, this is the reason for rather high values of χ². The values of the maximum adsorption of zirconium ions calculated according to Langmuir theory are in good agreement with the experimentally determined ones (Table 3) and are lower than the values of adsorption of strontium ions by the H-TiO₂ and Na-TiO₂ [12]. The maximum adsorption values

| Model          | Adsorbent      | Equation                        | Parameters       | R²   |
|----------------|----------------|---------------------------------|------------------|------|
| Pseudo-first   | H-TiO₂         | log(qe-q₀) = -0.035t+2.035      | k₁ = 0.035       | 0.8952 |
|                | Na-TiO₂        | log(qe-q₀) = -0.035t+1.98       | k₁ = 0.035       | 0.9365 |
| Pseudo-second  | H-TiO₂         | χ = 0.019t +0.49                | k₂ = 0.019       | 0.8664 |
|                | Na-TiO₂        | χ = 0.012t +0.27                | k₂ = 0.0128      | 0.9511 |
| Elovich        | H-TiO₂         | χ = 19.33 ln t -29             | α = 4.32; β = 0.0517 | 0.9155 |
|                | Na-TiO₂        | χ = 18.17 ln t -29             | α = 6.82; β = 0.055 | 0.902  |
| Diffusion      | Step 1         | qₜ = 5.14 t₀.₅ +20.7            | kₚ = 2.52; C = 19 | 0.999  |
|                |                |                               | kₚ = 2.78; C = 9.4 | 0.999  |
|                | Step 2         | qₜ = 5.14 t₀.₅ +20.7            | kₚ = 5.14; C = 20.7 | 0.9723 |
|                |                |                               | kₚ = 7.79 C = 7.79 | 0.9446 |
|                | Step 3         | qₜ = 0.768 t₀.₅ +52            | kₚ = 0.768; C = 52 | 0.999  |
|                |                |                               | kₚ = 0.072; C = 50 | 0.999  |

Table 2

Fig. 4. Isotherm of zirconium ions adsorption by H-TiO₂; nonlinear approximation by Langmuir and Freundlich theories.

Fig. 5. Isotherm of zirconium ions adsorption by Na-TiO₂; nonlinear approximation by Langmuir and Freundlich theories.
ontium ions in the neutral medium are 

\[ Zr^{4+} \] by H-TiO \(_2\) and Na-TiO \(_2\) 

| Adsorption process | Theory       | Parameters of equation of corresponding theory | Calculated \( q_{max} \) mg/g | \( R^2 \) | \( \chi^2 \) |
|-------------------|--------------|-----------------------------------------------|-------------------------------|------------|-----------|
| \( Zr^{4+} \) by H-TiO \(_2\) \( q_{exp} = 61.4 \) mg/g | Langmuir     | \( K_L = 0.00318 \) \( A_{max} = 70.46 \) | 64.23 | 0.8544 | 15.11 |
|                  | Freundlich   | \( K_f = 4.458 \) \( n = 0.338 \)             | 68.73 | 0.7747 | 26.78 |
| \( Zr^{4+} \) by Na-TiO \(_2\) \( q_{exp} = 109.5 \) mg/g | Langmuir     | \( K_L = 0.00169 \) \( A_{max} = 128.99 \) | 109.1 | 0.9166 | 16.17 |
|                  | Freundlich   | \( K_f = 3.893 \) \( n = 0.4188 \) | 114.9 | 0.8862 | 14.27 |

Values of self-diffusion coefficients of Zr (IV) and Sr (II) ions in aqueous solutions with different pH according to publication [25].

| pH    | \( Zr^{IV} \) \( D \times 10^{-5} \) cm\(^2\)/s | \( Zr^{IV} \) radius, Å | \( Sr^{II} \) \( D \times 10^{-5} \) cm\(^2\)/s |
|-------|-----------------------------------------------|--------------------------|-----------------------------------------------|
| 9M    | 0.3 ± 0.016                                   | 4.8                      | 5.58 ± 0.08                                   |
| 6M    | 0.345 ± 0.05                                 | 4.8                      | 6.0 ± 0.13                                    |
| 3M    | 0.42 ± 0.007                                  | 4.8                      | 6.23 ± 0.07                                   |
| 2M    | 0.46 ± 0.01                                  | 4.8                      |                                             |
| 1M    | 0.48 ± 0.014                                 | 4.8                      |                                             |
| 0.4 M | 0.488 ± 0.003                                | 4.8                      |                                             |
| 0.1 M | 0.351 ± 0.006                                | 7.0                      |                                             |
| pH = 2| 0.205 ± 0.011                                | 11                       | 7.75 ± 0.04                                   |
| pH = 2.8| 0.137 ± 0.004                          | 12                       |                                             |
| pH = 4.2| 0.056 ± 0.004                       | 44                       |                                             |
| pH = 7.5| 0.05 ± 0.009                       | 50                       | 7.79 ± 0.1                                   |
| pH = 8.2| 0.115 ± 0.004                       | 21                       |                                             |
| pH = 10.4| 0.106 ± 0.021                      | 23                       |                                             |
| pH = 11.5| 0.13 ± 0.012                      | 19                       | 7.58 ± 0.06                                   |

of the strontium ions in the neutral medium are 78.4 mg · g\(^{-1}\) by H-TiO \(_2\) and 208.4 mg · g\(^{-1}\) by Na-TiO \(_2\) and the maximum adsorption of zirconium ions are 61.4 mg · g\(^{-1}\) by H-TiO \(_2\) and 109.5 mg · g\(^{-1}\) by Na-TiO \(_2\). The reason for the lower adsorption of zirconium ions compared to strontium ions in aqueous solutions with a neutral pH may be the high tendency of zirconium cations to hydrolysis [24, 25].

The plot, shown in Fig. 6 indicates that the weakest adsorption of zirconium ions occurs in a neutral medium. The tendency of zirconium cations to hydrolyze [20, 21] determines the large size of hydrolyzed zirconium ions and their low mobility in solution and, accordingly, insignificant adsorption.

The results presented in Fig. 6 are in good agreement with the literature data on the mobility and size of zirconium ions in solution, shown in Table 4. For comparison, the table shows the values of the mobility of strontium cations, as well. The concentration of the corresponding ions was \( 10^{-5} \) mole/L; studies were performed using HCl, NH\(_4\)OH, and 100-fold excess of electrolyte NH\(_4\)Cl.

![Fig. 6. pH dependence of zirconium ions adsorption by H-TiO\(_2\) and Na-TiO\(_2\)](Image)
2.3. Selective adsorption of zirconium ions from the mixture

Schematically, the experiment on the adsorption separation of strontium, yttrium, and zirconium ions is shown in Fig. 7.

The results presented in Tables 5 and 5 (a) indicate the selective adsorption of zirconium ions from a mixture of strontium and yttrium ions. This process is illustrated in Figs. 8 (a) and (b). The results in Table 5 (a) indicate that the amount of strontium, yttrium and internal rhodium ions was not changed after interaction with adsorbents. This fact evidences the absence of adsorption of these elements under experimental conditions. Analysis by ICP-MS showed that the error due to the formation of $^{89}$Y$^1$H polyatomic ions is 1210 counts per second at a mass of 90amu. In addition, the number of contaminants of $^{88}$Sr and $^{90}$Zr in the used solvent was recorded. If we take into account all these contributors to the mass peak of 90amu and subtract the background number of counts from $^{90}$Zr, the percentage of extracted $^{90}$Zr will be 86.61 % for H-TiO$_2$ and 94.11 % for Na-TiO$_2$.

Figures 8 (a) and (b) illustrate the selective adsorption of zirconium ions by H-TiO$_2$ and Na-TiO$_2$ from nitric acid with HF micro-impurities in the absence of adsorption of strontium and yttrium ions. The amount of strontium ions even slightly increases due to the $^{88}$Sr contaminated micro impurities (Fig. 8 (a)).

Selective zirconium ion adsorption is observed in the range of solutions acidity pH = 0 - 1. This range of solution acidities is below the pHpzc of the studied adsorbents (Table 1). The number of adsorption centers (≡ТіО$^-$) able to bind cations is slightly reduced and the surface of H-TiO$_2$ or Na-TiO$_2$ has an overall positive charge in the experimental conditions, although some areas are still able to bind cations on the adsorbent surface. The overall positive surface charge of H-TiO$_2$ or Na-TiO$_2$ becomes a Coulomb barrier for the adsorption of relatively large, positively charged ions of divalent strontium and trivalent yttrium. Therefore, strontium and yttrium ions were not adsorbed by these adsorbents in the 0.32M HNO$_3$ medium. It should be noted, that at pH values closer to a

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**Table 5**

| C initial 90-Zr (Standard 2) | Adsorbent | Intensity [cps] After adsorption | Adsorption 90-Zr | C residual, 90-Zr | Uncertainties | $\alpha$ Sr,Zr |
|-----------------------------|-----------|---------------------------------|------------------|------------------|---------------|---------------|
| Intensity [cps] | ng | | | | | |
| 1057427 | 5.094 | H-TiO$_2$ | 156695±554 | 4.3392 | 85.18 | 0.7548 | 1210 |
| 2229000 | 6.46 | Na-TiO$_2$ | 146506±768 | 6.0355 | 93.42 | 0.4245 |

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**Table 5 (a)**

| Isotop | C initial (Standard 2) | Adsorbent | Intensity [cps] After adsorption | Uncertainties $^{90}$Zr Standard 3 [cps] |
|--------|------------------------|-----------|--------------------------------|----------------------------------|
| Intensity [cps] | ng | | | $^{88}$Sr, $^{89}$Y and $^{103}$Rh before and after adsorption |
| 88-Sr | 2101905 | 9.9 | H-TiO$_2$ | 4017586 | 510471 |
| 89-Y | 2431139 | 10 | H-TiO$_2$ | 3179047 | 9245 |
| 88-Sr | 10413000 | 14.5 | Na-TiO$_2$ | 10027000 | 14588 |
| 89-Y | 5715000 | 12.5 | Na-TiO$_2$ | 4663000 | 1768.8 |
| 103-Rh | 516693 | 3 | H-TiO$_2$ (Na-TiO$_2$) | 448009 | - |

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neutral or alkaline environment, the adsorption of strontium ions by these adsorbents is extremely intense [9-14]. Ionic radius of Zr<sup>4+</sup> is smaller than the corresponding value of Sr<sup>2+</sup> or Y<sup>3+</sup> (0.84 Å compared to 1.02 Å for Y<sup>3+</sup> and 1.26 Å for Sr<sup>2+</sup> ions) [26]. Zirconium loses its hydrate shell under such acidity of the solution. This fact allows zirconium ions to neglect electrostatic repulsion and interact with residual cation-bonding adsorption cites of the adsorbents. On the other hand, the mobility of zirconium ions is much lower than the mobility of strontium ions [25]. Therefore, after approaching the surface of TiO<sub>2</sub>, zirconium generally remains in the adsorbed state.

The obtained results are promising for the separation of <sup>90</sup>Sr and <sup>90</sup>Zr isotopes. The absence of adsorption of strontium and yttrium ions under such extreme solution acidity indicates that zirconium ions can be selectively adsorbed even with an excess of cations of alkaline earth elements and elements of the YRE group. The resistance of TiO<sub>2</sub> to the acidic media allows direct one-stage separation of zirconium ions without additional procedures for the separation of alkaline earth elements and lanthanides, which can shift the initial ratio of <sup>90</sup>Sr/<sup>90</sup>Zr [27-29]. This fact is extremely valuable for nuclear forensics or the determination of <sup>90</sup>Sr in low activity background samples.

**Conclusion**

The adsorption of zirconium ions by titanium dioxide has been studied. The dependence of this process on the agitation time, the equilibrium concentration of the zirconium ions, and the acidity of the solution have been established.

The kinetics of zirconium ions adsorption by H-TiO<sub>2</sub> and Na-TiO<sub>2</sub> is stepwise and fitting well with the diffusion kinetic model.

Experimental maximum values of adsorption of zirconium ions by the studied adsorbents are 61.4 mg·g<sup>-1</sup> for H-TiO<sub>2</sub> and 109.5 mg·g<sup>-1</sup> for Na-TiO<sub>2</sub>. These values are in good agreement with the calculated values of the maximum adsorption according to Langmuir's theory.

Separation of strontium and zirconium ions was performed. The residual solution was analyzed by ICP-MS. It was shown that the investigated adsorbents selectively adsorb zirconium ions from the mixture with strontium and yttrium ions in the range of solution pH = 0 - 1. The percentage of maximum extraction of zirconium ions is 86.61 % for H-TiO<sub>2</sub> and 94.11 % for Na-TiO<sub>2</sub>. This fact is extremely valuable for nuclear forensics or the determination of <sup>90</sup>Sr in low activity background samples.

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Використання діоксиду титану для адсорбції йонів цирконію та виділення їх із багатокомпонентної суміші

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Дана робота присвячена дослідженням адсорбції йонів цирконію мезопористим діоксидом титану та діоксидом титану із натрованою поверхнею. Експериментально визначено величини максимальної адсорбції йонів цирконію складають 64 мг/г та 109,5 мг/г відповідно для адсорбентів H2TiO2 і Na-TiO2. Процес адсорбції залежить від тривалості взаємодії, рівноважної концентрації йонів цирконію та кислотності розчину. Кінетика адсорбції найкраще може бути описана дифузійною кінетичною моделью і вказує на ступінчастий характер адсорбції йонів цирконію обома адсорбентами. Рівноважну адсорбцію йонів цирконію адсорбентами H2TiO2 і Na-TiO2 найкраще описує теорія Ленгмюра. Із застосуванням мас-спектрометрії з індуктивно зв'язаною плазмою, показано, що досліджені адсорбенти селективно поглинають йони цирконію із суміші із іонами стронцію та ітрію при значенні кислотності розчину рН = 0 - 1. Відсоток вилученого цирконію із суміші складає 86,61 % для H2TiO2 і 94,11 % для Na-TiO2. Цей факт є дуже корисним для ядерної криміналістики а також при визначенні кількості 90Sr у низькофонових зразках навколишнього середовища.

Ключові слова: мезопористий TiO2, йони цирконію, адсорбція, розділення, ICP-MS.