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EFFECT OF RETARDATION OF THE TRANSFER OF Sr-89 TO THE BODY OF RATS DRINKING WATER FILTERED THROUGH COARSELY DIVIDED NATURALLY OCCURRING MINERAL FLINT

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Data of experimental studies of the influence of flint water on the processes of accumulation and elimination of Sr-89 from the body of white rats and results of theoretical investigations aimed at substantiating an increase in the bond energy of flint water molecules with strontium ions are presented.

The large-scale tests of nuclear weapons carried out in the 1950–1960s and accidents at operating nuclear-power plants have forced scientists to direct their attention to the development of preparations which remove radionuclides from the human body.

Of the entire range of created preparations, complexons are of special importance in combining with radionuclides. Complexons are multidentated chelate-forming compounds representing cyclic structures. Analysis of the chemical formulas of these compounds points to the fact that free valences of oxygen and nitrogen which combine with radionuclides are formed in complexons.

However, a number of limitations on the use of complexons exist. The fact is that for any mechanism of delivery of radioactive substances to a body there is a primary depot of radioactivity: the lungs and digestive tract in the inhalation mechanism of delivery, the gastrointestinal tract in the case of peroral contamination, and contaminated tissues of wounds in the case of injuries.

In the process of use of complexons for removal of radioactive substances from primary applications, the resorption of radioactive isotopes from the primary depots can increase to a considerable extent. Therefore, according to [1], one cannot take complexons perorally before the radiators are removed from the gastrointestinal tract. There are also other limitations on the use of preparations of this kind.

At the same time, our investigations of many years on the properties of flint water have shown that when this water is drunk a significant effect of removal of radioactive cesium and strontium without occurrence of negative side phenomena in the vital functions of a body is possible, although the effect of combining itself will rank below that of complexons. To prove this proposition we carried out investigations combining two different trends.

In the first trend, we studied the action of flint water and ordinary water on accumulation and removal of strontium-89 from the body of rats. In the second trend, we evaluated the bond energy of the molecules of flint water and ordinary water with the cesium and strontium ions and determined the migration parameters of these ions in bone and muscular tissues in filtration of both kinds of water.

Experimental investigations were performed on 120 not thoroughbred white male rats with an initial weight of 180–190 g bred at the vivarium of the N. N. Aleksandrov Scientific-Research Institute of Oncology and Medicinal Radiology.

According to the action of "flint" water and ordinary water, the animals were subdivided into four groups 30 rats in each:

(1) monitoring with drinking of ordinary water from a 200-liter vessel with the Sr 89 added to it in a dose of 100 μCi;

(2) drinking of "flint" water from the analogous vessel with addition of the same dose of radioactive isotopes; 1 rat received 0.01 μCi of strontium-89 a day (on a 20 ml water per day basis);

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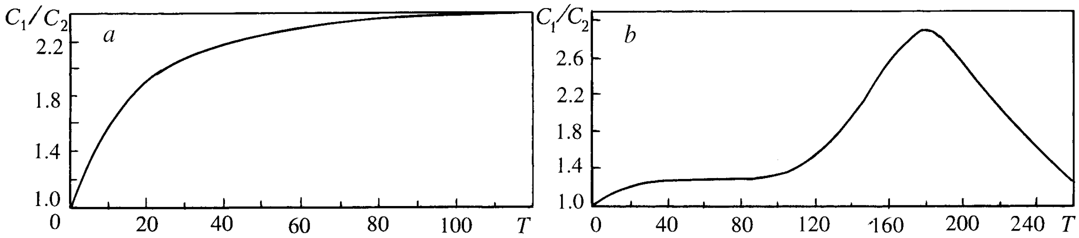

Fig. 1. Ratio of the content of Sr-89 in the skeleton of rats drinking ordinary water to the content of Sr-89 in the skeleton of rats drinking flint water in the case of dissolution of 0.5 μCi/liter strontium (a) and in the case of intravenous injection of Sr-89 in a dose of 1 μCi per kg of body weight (b) vs. duration of the experiment. C_1, concentration of Sr-89 in the body of rats drinking ordinary water; C_2, the same in the body of rats drinking flint water, T, duration of the experiment, days.

(3) monitoring with a single intravenous injection of Sr-89 in a dose of 1 μCi per kg of body weight; subsequently the rats drank ordinary water in unlimited quantities;

(4) single intravenous injection of Sr-89 in a dose of 1 μCi per kg of body weight; subsequently the rats drank flint water in unlimited quantities.

As the Sr-89 source we used the preparation metastrone of the Nycomed Amersham Company (England) widely used worldwide for treatment of oncologic patients with metastases of malignant tumors in the backbone. The half-life is 50.5 days and the mode of decay is that of a β particle with an energy of 1.463 MeV.

The rats were kept in a specially equipped room of area 36 m^2 with natural lighting (alternate light day and night (1:1)) at a temperature of 16–18^{o}C and a humidity of 60–70%. The animals received standardized briquetted mixed fodder, meat, chalk, root-crops, sunflower oil, and curds daily. The food was given at a certain time of the day; ordinary or flint water was given in unlimited quantities.

Every 14 days we determined the levels of accumulation and elimination of Sr-89 in each animal using an automatic spectrometer (NK-350, Hungary) designed for the purpose of nuclear measurements. Prior to measurement the rats were brought into the state of neuroleptanalgesia (0.25% solution of droperidol + 0.005% solution of phentanyl in the proportion 2:1; 0.3 ml per 100 g of animal mass intramuscularly) and alternately immersed into the well of an ND-302E scintillation sensor connected to the spectrometer.

The measurement results were cleared from the natural background of radiation by a background-substation unit built into the device.

Figure 1 presents the results of the experimental investigations.

As follows from Fig. 1a, the accumulation of Sr-89 in the body of the rats drinking flint water with an initial level of contamination of 0.5 μCi/liter is less intense that in the rats drinking ordinary water. Thus, on the 30th day after the beginning of the experiment it decreased 2.2 to 2.3 times.

As follows from Fig. 1b, we have significant differences in the process of removal of Sr-89 from the body of the rats injected intravenously with this radionuclide on the 100th day after the beginning of the experiment, i.e., from this time the removal of Sr-89 is more intense in the rats drinking flint water than in the rats drinking ordinary water.

The maximum of the relative intensity of removal of Sr-89 falls on the 175th day from the beginning of the experiment; then it decreases but on the 260th day we detect a substantial increase in the relative intensity of removal of Sr-89 in the rats drinking flint water. Thus, over a period of more than 160 days, the body of rats drinking flint water experiences a lighter load from radioactive irradiation than the body of rats drinking ordinary water. This fact cannot but have an effect on the occurrence of a number of biochemical processes in the organs of the animals. It has been found in the experiments that in the rats drinking flint water the loss in body mass is smaller than in the rats drinking ordinary water (Table 1).

To answer the question why the accumulation of Sr-89 is less intense and its removal is more intense in the animals drinking flint water we performed investigations aimed at determining the coefficients of diffusion and distribution of strontium ions, dissolved in ordinary water and flint water, in bone flour as well as at calculating the bond energy of these ions with the molecules of ordinary water and flint water.

TABLE 1. Change in the Body Weight in Rats in the Groups of Investigations

Groups of rats	Type of action	Initial weight of the rats (aged three months), g	30th day		60th day		90th day		120th day		150th day		180th day	
			weight, g	change in weight, %	weight, g	change in weight, %	weight, g	change in weight, %	weight, g	change in weight, %	weight, g	change in weight, %	weight, g	change in weight, %
	Normal weight (prior to the action)	184.8	223.2	+21	244.8	+32	258.4	+40	268.0	+45	279.7	+51	280.9	+52
1	Animals drinking ordinary water with a concentration of 0.5 μCi/liter	183.4 ±4.1	193.2 ±4.7	+5	194.5 ±4.6	+6	203.2 ±4.6	+11	230.3 ±4.9	+26	285.2 ±5.6	+56	309.3 ±6	+67
2	Animals drinking flint water with a concentration of 0.5 μCi/liter	190.1 ±4.5	215.2 ±5.1	+13	220.3 ±4.5	+16	221.0 ±6.2	+16	253.4 ±5.0	+33	304.1 ±5.4	+60	327.4 ±7.3	+72
3	Animals drinking ordinary water after intraveneous injection of Sr-89 in a dose of 1 μCi per kg of body weight	189.4 ±0.9	205.9 ±1.2	+9	194.2 ±1.3	+3	204.0 ±1.6	+8	228.5 ±1.8	+21	279.3 ±5.5	+44	294.0 ±6.1	+55
4	Animals drinking flint water after intraveneous injection of Sr-89 in a dose of 1 μCi per kg of body weight	188.2 ±1.4	211.2 ±1.9	+12	197.3 ±2.0	+5	211.4 ±1.8	+13	299.8 ±1.9	+27	275.0 ±6.2	+46	319 ±7.5	+67

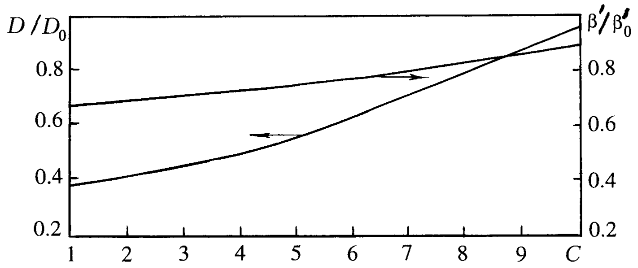

Fig. 2. Relative values of the coefficients of diffusion D/D_0 and distribution β'/β'_0 of strontium ions vs. concentration of the filtering solution.

The diffusion coefficient of strontium was determined in the experiments in the "dynamic" regime. The bone flour was placed in glass columns 20 mm in diameter and 30 cm in length. The thickness of the flour layer was 1.25–2.5 cm. Prior to the experiment, the samples were washed with distilled water and then a strontium solution was allowed to pass. In the course of the experiment, the filtrate was collected in small portions (10 mg) at the outlet of the column both at the initial instant of the filtration cycle and in the subsequent cycles in certain time intervals. The solutions produced were filtered and analyzed for the content of strontium in them.

In the experiments, we determined the filtration time and the concentration of ions in the filtrates and calculated

$$\bar{C} = \frac{C}{C_0}, \tag{1}$$

$$\Sigma = \sqrt{t \operatorname{arcerfc}(1 - 2\bar{c})} = \frac{x}{2\sqrt{D/n}} - \frac{V_f n t}{2\sqrt{D/n}}. \tag{2}$$

The diffusion and distribution coefficients were found for concentrations of 10, 7, 5, 3, and 2 mg/liter of the filtering solutions prepared with ordinary water and flint water. Figure 2 shows the dependences of the relative values of the diffusion and distribution coefficients of the strontium ions on the concentration of the filtering solutions. These dependences are expressed by the following empirical formulas:

$$\frac{D}{D_0} = A \exp(aC) = 0.352 \exp(0.1015C), \tag{3}$$

$$\frac{\beta'}{\beta'_0} = B \exp(kC) = 0.632 \exp(0.0354C), \tag{4}$$

where D and D_0 are, respectively, the diffusion coefficients of the strontium ions, dissolved in flint water and in ordinary water, in bone flour, β' and β'_0 are the distribution coefficients in flint water and ordinary water, and A, B, a, and k are the empirical coefficients.

It should be noted that the distribution coefficient is

$$\beta' = \frac{C_0}{N_0}, \tag{5}$$

where C_0 and N_0 are the corresponding limiting equilibrium concentrations of the ions in the solution and on the sorbent.

As follows from formulas (3) and (4), $D/D_0 = 0.352$ and $\beta'/\beta'_0 = 0.632$ for $C \to 0$, i.e., when flint water is used the diffusion of strontium in the bone tissue decreases 3 times while the concentration of strontium in the solution decreases 1.6 times.

Thus, in the case of use of flint water radioactive strontium is concentrated primarily on the surface of bone tissue and penetrates into this tissue with a lower (nearly threefold) intensity.

Simultaneously with the process of retardation of the transfer of Sr-89 to the bone tissue a more intense removal of the radionuclide from the body of rats drinking flint water occurs. The established experimental fact can be explained by the increase in the bond energy of a strontium ion with a molecule of flint water. To prove this proposition we performed experiments and calculations. New ideas of the method for calculating the bond energy of ions with a water molecule which takes into account the features of the structure of flint water have been presented in [2]. To determine the energy of interaction between two atoms belonging to one or several systems we use the theory of chemical capture developed in [3]. Chemical capture is a phenomenon caused by interatomic matrix interaction elements. The chemical-capture energy is determined by the contributions of noncentral (nonvalence) forces, and the formula to calculate this energy can be represented as follows:

$$E_{\text{capture}} = \frac{2W_2^4}{|2W_3|^3} \sum_{\gamma>\beta} \cos^2 \theta_{\gamma\beta} \, , \tag{6}$$

$$W_2 = \eta_{ijk} \, \hbar^2/(md^2) \, , \tag{7}$$

$$W_3 = \varepsilon_s^{\mathrm{c}} - \varepsilon_p^{\mathrm{a}} \, , \tag{8}$$

where γ and β are the numbers of vectors, m is the electron mass, and n_{ijk} is the parameter that takes on four universal constant values corresponding to matrix elements of the type $ss\delta$, $sp\delta$, $pp\delta$, and $pp\pi$ (s, p, δ, and π are the names of orbitals in the atom). The quantities $\theta_{\gamma\beta}$ are the angles between the vectors formed by the central ions and neighboring atoms. In our work, we consider two systems for which

$$\sum_{\gamma>\beta} \cos^2 \theta_{\gamma\beta} = 1 \, .$$

To determine the bond energy of the strontium ion with the water molecule we must know the energy level (term) of the oxygen atom in this molecule and the hydrated radius of the ion.

To evaluate the energy level of the oxygen atom in the water molecule we apply the concept given by W. Harrison in [3], according to which it is established (with account taken of the conditional orthonormality of the wave functions of atomic states) that the wave functions of hybridized states are orthonormalized. These orbitals are not eigenfunctions corresponding to the states with prescribed energy. The expected value of the energy turns out to be average and is called the hybridized state:

$$\varepsilon = (\varepsilon_s + 3\varepsilon_p) \; 0.25 \, . \tag{9}$$

Measurement of the energy of an electron in the state described by a hybridized wave function shows that 25% of the time the electron has the energy ε_s and 75% of the time it has the energy ε_p; the hybridized orbitals are oriented toward the nearest neighbors and can be constructed for each sort of atoms that form a molecule, a crystal, and a cluster.

To determine the energy level $\varepsilon_p^{\mathrm{a}}$ of the oxygen atom in the water molecule we use the data of the "Generalized Periodic System of Elements" [2] and the values of the energy level of the hydrogen atom in H_2O:

$$\varepsilon^{\mathrm{a}}_{p\,(\text{oxygen in } \mathrm{H_2O})} = [3\,(3\varepsilon^{\mathrm{a}}_{p(\mathrm{O})} + \varepsilon^{\mathrm{c}}_{s(\mathrm{H})}) \cdot 0.25 + \varepsilon^{\mathrm{c}}_{s(\mathrm{H})}] \cdot 0.25 \;\; \mathrm{eV} \, , \tag{10}$$

where $\varepsilon^{\mathrm{a}}_{p(0)} = 14.13$ eV is the energy level of the p-state of the oxygen atom in the isolated state and $\varepsilon^{\mathrm{c}}_{s(\mathrm{H})}$ is the energy level of the hydrogen atom in H_2O.

In [2], we have presented the theory of calculation of $\varepsilon^{\mathrm{c}}_{s(\mathrm{H})}$ and obtained a formula to determine $\varepsilon^{\mathrm{c}}_{s(\mathrm{H})}$ for different values of the valence angle in H_2O:

$$\varepsilon^{\mathrm{c}}_{s(\mathrm{H})} = \left\{\exp\left[-0.0331\,(\alpha - 90)^{0.6641}\right]\right\}^2 \cdot 13.6 \ \ \mathrm{eV}\,, \tag{11}$$

where α is the valence angle in H_2O in degrees.

According to [3, 4] and other works, the potential E_{c} (potential energy) of interaction between the ion and the dipole in a medium with permittivity ε_0' is determined as follows:

$$E_{\mathrm{c}} = -\frac{Ze\overline{m}}{\varepsilon_0'\varepsilon_0''d^2}\,, \tag{12}$$

in vacuum, it is determined as

$$E_{\mathrm{c}} = -\frac{Ze\overline{m}}{\varepsilon_0''d^2}\,. \tag{13}$$

Then

$$\Delta E_{\mathrm{c}} = \frac{Ze\overline{m}}{\varepsilon_0''d^2}\left(1 - \frac{1}{\varepsilon_0'}\right), \tag{14}$$

$$d = \sqrt{\frac{Ze\overline{m}}{\varepsilon_0''\Delta E_{\mathrm{c}}}\left(1 - \frac{1}{\varepsilon_0'}\right)}\,. \tag{15}$$

In formula (15), we know all the parameters except for ΔE_{c} and $\overline{m}$.

To determine ΔE_{c} we used the method of NMR spectroscopy which is based on measurements of the longitudinal relaxation times of protons in the aqueous solutions of salts. In this work, we have investigated the aqueous solutions of $SrCl_2$ with a concentration of 0.002, 0.004, 0.006, 0.008, and 0.01 N. prepared with flint bidistillate and ordinary bidistillate.

From the data of NMR spectroscopy the quantity ΔE_{c} is determined as follows:

$$\Delta E_{\mathrm{c}} = \Sigma\,\Delta U C_{\mathrm{c}}\,, \tag{16}$$

where C_{c} is the number of water molecules per cation in the solution of calculated concentration and $\Sigma\Delta U$ is the change in the potential energy of vibrations of the water molecules due to the change in the valence angle and the valence-bond length (it is determined by analysis of the relative values of the longitudinal relaxation times; the calculation method is presented in [6]).

For flint bidistillate $\Sigma\Delta U = 0.2073$ kcal/mole in the range of concentrations 0.002–0.01 N, while for ordinary bidistillate $\Sigma\Delta U = 0.1100$ kcal/mole in the same range of concentrations.

According to [7], the dipole moment of the water molecule can be determined as follows:

$$\overline{m} = 2\,\mathrm{erf}_0\left(\frac{r}{r_0}\right)^6 \cos\frac{\alpha}{2} - 4\left[1 + f_0\left(\frac{r}{r_0}\right)^6\right] e\,\frac{\sqrt{-\cos\alpha}}{1 - \cos\alpha} \times$$

$$\times \cos\frac{\alpha}{2}\left(a' - r_0 + \frac{r}{2}\right) + \frac{4e\sqrt{-\cos\alpha}}{\cos^2\dfrac{\alpha}{2} - \cos\alpha}\cos\frac{\alpha}{2}\left(\overline{X}' + \frac{r - r_0}{2}\right), \tag{17}$$

TABLE 2. Basic Calculated Parameters of the Molecules of Ordinary Water and Flint Water and the Bond Energies of the Strontium Ion with These Molecules

Type of water	Valence-bond length r, Å	Valence angle α, deg	Hydrated radius of the ion d, Å	Energy level in H_2O, eV		Bond energy of the strontium ion with H_2O, kcal/mole
				of hydrogen ε_s^c	of oxygen ε_p^a	
Ordinary	0.96	104.5	1.7435	9.1338	11.9441	4.045
Flint	0.965	107.2	1.3315	8.6960	11.7526	47.674

where r is the length of the valence bond in the molecule of H_2O for the valence angle equal to α, r_0 is the same for a valence angle of 104.5^o ($r_0 = 0.96$ Å), f_0 is the charge of the O–H bond at $\alpha = 104.5^o$ ($f_0 = 0.133$), and a' and $\overline{X}'$ are the quantities determined from the coordinates of point charges in the molecule of H_2O according to [8] ($a' = 0.583$ Å and $\overline{X}' = 0.179$ Å). For flint bidistillate $\overline{m} = 1.9706$D, while for ordinary bidistillate $\overline{m} = 1.8866$D.

The basic calculated parameters required for determination of the bond energy of the strontium ion with the flint water molecule are presented in Table 2. As follows from the table, the bond energy of the strontium ion with the flint water molecule is 12 times higher than the energy of its bond with the molecule of ordinary water. The role of flint water in intensification of the process of removal of radioactive strontium from the body of rats becomes clear.

Thus, we have established in the work that flint water combines with radioactive strontium intensely and removes it from a biological object.

Analogous results were obtained in studying the processes of migration of a cesium ion in muscular tissue.

At the same time, we assume that in the case of drinking flint water the removal of selenium, whose shortage in the body causes numerous diseases, is less intense. These data necessitate a separate publication.

NOTATION

V_f, filtration rate of the solution; x, filtration path length; n, porosity; $\overline{C}$, relative concentration of ions in the filtrate; t, filtration time; C, running concentration of ions in the filtrate; ε_s^c, atomic energy level of cations of the s-state; ε_p^a, atomic energy level of anions of the p-state; ΔE_c, change in the potential energy of interaction between the ion and the dipole; z, charge (valence) of the ion; e, electron charge; $\overline{m}$, dipole moment of a molecule; ε_0'', electric constant equal to $8.85 \cdot 10^{-12}$ F/m; d, distance between the nuclei (hydrated radius of the ion); ε_0', static permittivity of the liquid. Subscripts and superscripts: f, filtration; c, cation; s and p, electronic states.

REFERENCES

1. Yu. F. Koval', *Acceleration of Elimination of Radioactive Isotopes from the Body* [in Russian], Moscow (1972).
2. P. P. Olodovskii and O. V. Karpel', *Inzh.-Fiz. Zh.*, **74**, No. 2, 141–147 (2001).
3. W. A. Harrison, *Electronic Structure and the Properties of Solids* [Russian translation], Vol. 1, Moscow (1983).
4. E. Anis, *Influence of Solvent on the Rate and Mechanism of Chemical Reactions* [Russian translation], Moscow (1968).
5. K. P. Mishchenko and G. M. Poltoratskii, *Thermodynamics and Structure of Aqueous and Non-Aqueous Solutions of Electrolytes* [in Russian], Moscow (1968).
6. P. P. Olodovskii and I. L. Berestova, *Inzh.-Fiz. Zh.*, **62**, No. 6, 853–858 (1992).
7. P. P. Olodovskii, *Inzh.-Fiz. Zh.*, **67**, Nos. 5–6, 437–445 (1994).
8. E. A. Moelwyn-Hughes, *Physical Chemistry* [Russian translation], Vol. 1, Moscow (1962).