

# DIFFUSION OF STRONTIUM THROUGH A PAPER IN SUPERCRITICAL CARBON DIOXIDE MEDIUM

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*Fundamental possibility of using supercritical and liquid carbon dioxide (SC-CO<sub>2</sub> and L-CO<sub>2</sub>, respectively) for treating mail for purpose of detection of radioactive substance to prevent terrorist acts was shown. Diffusion of <sup>90</sup>Sr through layers of writing paper in the form of adducts of strontium di-2-ethylhexyl phosphates, di-octylfluoroamyl phosphates and perflorovalerianates with dicyclohexyl-18 crown-6 (DCH18C6) and polyethylene glycol 600 under the conditions of absence of ligand excess was studied. Coefficients of diffusion of <sup>90</sup>Sr complexes under study were calculated. Coefficient of diffusion of strontium di-2-ethylhexyl phosphate through layers of a writing paper in medium of SC CO<sub>2</sub> was found to be equal to 7.7\*10<sup>-4</sup> mm<sup>2</sup>/min. For adducts of <sup>90</sup>Sr perflorovalerianate and Sr<sup>90</sup> di-2-ethylhexyl phosphate with DCH18C6 coefficients of diffusion amounted to 3.3\*10<sup>-2</sup> mm<sup>2</sup>/min, and 2.43\*10<sup>-2</sup> mm<sup>2</sup>/min, respectively.*

## Introduction

The objective of the research complex, within the bounds of which this work was performed, is development of technology and demonstration of equipment for integrated decontamination of a mail (detection and removal of toxic chemical compounds of the radionuclides, pathogenic organisms and spores).

Now in connection with a threat of international terrorism development of such technology is urgent, because terrorists used already anthrax spores and explosive materials placing them in parcels. They threaten constantly to apply “dirty” bomb to heighten tension in human society.

Extraction of complexes of organic compounds with metals into supercritical or liquid carbon dioxide (SC-CO<sub>2</sub> and L-CO<sub>2</sub>, respectively) is well known as environmentally safe method of extraction of the radioactive metals adsorbed on solids, and such investigations are actively performed in France [12], Korea [3,4], Japan [5,6], Netherlands [7,8], United States [9], and in Russia [10- 13]. Analysis of literary data shows that a number of complexons may be used for effective extraction of the actinides, lanthanides and rare-earth elements (REE). They are di-2-ethylhexyl phosphoric acid (D2EHPA) and its mixtures with polyesters and tributyl phosphate [15- 19], mixtures of perfluorocarbonic acids with crown-ethers [20-22], a number of β-diketones in a mixture with amines [23- 26] as well as mixtures of crown-ethers with polyethylene glycols [27-28].

The above complexons and their mixtures were considered as start material for the study of kinetic regularities of the process of extraction of various radionuclides from a surface of writing paper into SC-CO<sub>2</sub> and L-CO<sub>2</sub>.

The process of radionuclide extraction may include several basic stages: diffusion of complexing agents from liquefied carbon dioxide to a surface of contaminated material, diffusion of complexing compounds within the material to the extracting radionuclide, formation of the complex, diffusion of the complex obtained to a surface of the material and further into the solution of liquefied carbon dioxide. Diffusion of compounds in the materials should be considered separately because this process may be limiting stage of the given process.

## Experimental

Diffusion of the radionuclides was studied in this work by the example of diffusion of <sup>90</sup>Sr through layers of a writing paper in supercritical (P=30 MPa, T=60°C) and liquid (P=7,5 MPa,

T=25<sup>0</sup>C) CO<sub>2</sub> in the form of adducts of strontium di-2-ethylhexyl phosphates, di-octylfluoroamyl phosphates and perfluorovalerianates with dicyclohexyl-18 crown-6 (DCH18C6) and polyethylene glycol 600 under the conditions of absence of ligand excess.

β-activity of <sup>90</sup>Sr was measured using radiometer UMF-2000 determining β- and α-emitting radionuclides within energy ranges of β- and α-radiation from 50 to 3500 keV and from 3500 to 8000 keV, respectively. The ranges of measured activity for β- and α-radiation were 0.1÷3×10<sup>3</sup> Bq and 0.01÷10<sup>3</sup> Bq, respectively.

White sheet paper for office equipment (Russia, Standard 5438-016-00253497-2001, 80 g/m<sup>2</sup>) was chosen as a paper carrier because such paper is typical for parcels of state organizations and private persons.

Individual polyethylene glycol (PEG-600) as well as all inorganic chemicals were received from the firm “Vekton” (Russia). Dioctafluoroamylphosphoric acid (DOFAPA) as well as di-2-ethylhexyl phosphoric acid (D2EHPA) and perfluorovalerianic acid (PFVA) were synthesized by the workers of the St. Petersburg State University (Russia). Salts of strontium labeled by <sup>90</sup>Sr isotope (obtained from PA "Isotope", Russia) with PFVA, D2EHPA and DOFAPA as well as adducts of these salts with PEG-600 and DCH18C6 were synthesized according to the standard methods [29]. Metal concentrations and activities of the compounds obtained were within the limits of 0.03±0.01 mM and 2×10<sup>3</sup>±0,5×10<sup>4</sup> Bq/mL, respectively.

## Results and discussion

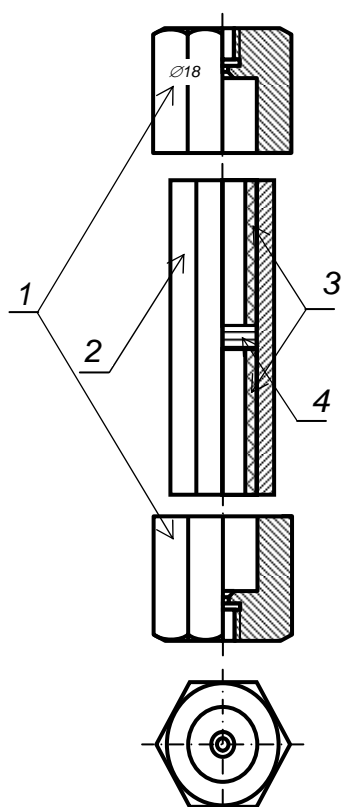


Fig. 1. Cell for the study of radionuclides diffusion in media of L-CO<sub>2</sub> and SC-CO<sub>2</sub> through a paper

In order to extract strontium salts of organic acids from a paper surface, 0.01-mL aliquot of the sample under study was applied onto a paper disk (Ø=14 mm) which was dried under IR-lamp. Then 3 pure paper disks were placed from each side of “contaminated” paper disk, and this “dense bundle of paper” (Fig.1, point 4) was gripped with Teflon tubes of equal length (3) in a body of the extraction cell (2).

The Teflon tubes and paper disks have internal diameter that is equal to inside diameter of the cell, and total height of the disks and tubes was equal to a length of the cell. Therefore the dense bundle of paper can not move along the cell after its assembling. Further the cell was assembled as set-up for supercritical extraction described in detail in [30]. After 30-min static extraction at constant rate of about 0.7 mL/min there was performed 15-min dynamic extraction. Extract was collected through restrictor into methanol. After that the system was ventilated, disassembled, and β-activities of the paper disks and aliquot of receiving solution were determined.

The results of these experiments are presented in Tables 1 and 2.

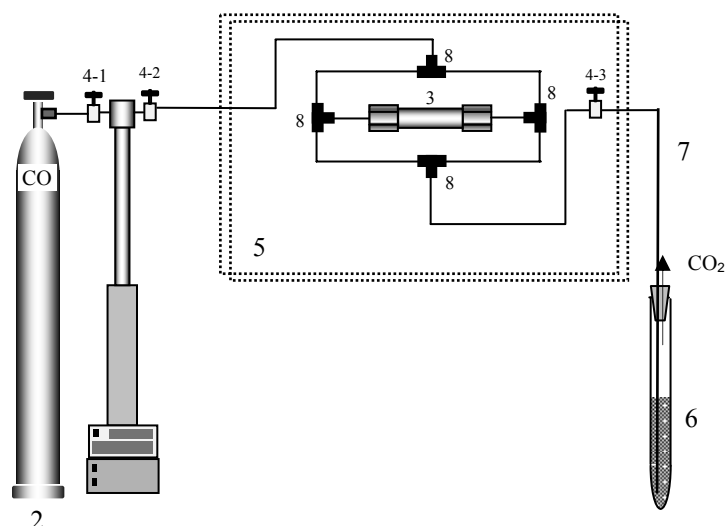
**Table 1.** Extraction of strontium salts of various organic acids by liquid CO<sub>2</sub> (7,5 MPa, 25<sup>0</sup>C)

Salt-forming acid	Taken, Bq	Found in the receiving solution, Bq	Extraction efficiency, %
PFVA	255	10	4
D2EHPA	260	18	7
DOFAPA	223	96	43

**Table 2.** Extraction of strontium salts of PFVA and D2EHPA as well as extraction of adducts of these salts with DCH18C6 and PEG-600 by supercritical CO<sub>2</sub> (30 MPa, 60<sup>o</sup>C)

Compound	Taken, Bq	Found in receiving solution, Bq	Extraction efficiency, %
Sr salt of PFVA	200	0	0
Adduct of Sr salt of PFVA with DCH18C6	217	122	56
Sr salt of D2EHPA	250	150	60
Adduct of Sr salt of D2EHPA with PEG -600	241	24	10
Adduct Sr salt of D2EHPA with DCH18C6	244	73	30

The experiments on the study of kinetics of distribution of strontium salt of D2EHPA in layers of a paper as a function of duration of the experiment in medium of SC-CO<sub>2</sub> differed by



*Fig. 2. Setting scheme for the study of radionuclides diffusion in media of L-CO<sub>2</sub> and SC-CO<sub>2</sub> through a paper against time.*

the fact that strontium salt of D2EHPA was applied onto 5 discs of writing paper with diameter of 14 mm, and 40 pure paper disks were then placed from each side of these contaminated disks. The “dense bundle of paper” obtained was also pressed with Teflon rings and placed in the extraction cell.

As shown in Fig. 2, the cell is situated horizontally and it is assembled in the system so that inlet into the system and outlet occurred from two sides simultaneously. Similarly to the first part of the work at closed stopcock 4-3 CO<sub>2</sub> was pumped into the system from the balloon 2 by high-pressure pump up to required pressure at established temperature. After that the system

was kept under given conditions for 30, 60 and 120 min. Then inlet cock 4-2 was closed, stopcock 4-3 was opened, and the system was ventilated through restrictor 7 into receiving solution 6. Further the cell was disassembled, and extracted dense bundle of paper was divided by a pincette in layers each of which contained 5 sheets (layers 1-8). The 9-th layer contained 5 sheets of paper contaminated by strontium salt. The following 40 disks of pure paper were also divided in 5-sheet bundles (10<sup>th</sup>–17<sup>th</sup> layers). Thus altogether there were obtained 17 layers. Activity of each layer was measured, and on the basis of the data obtained diagrams were drawn (see Figs. 3- 5).

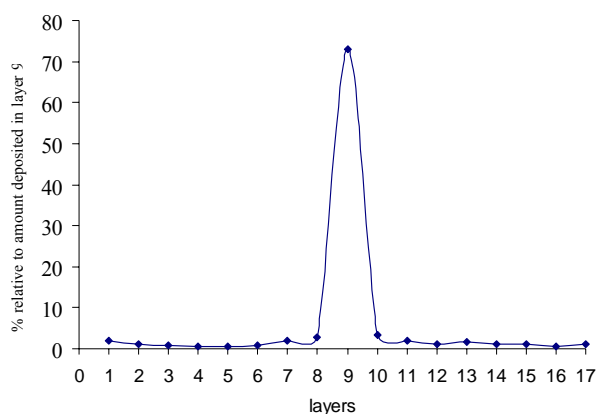


Fig. 3. Diffusion of strontium salt of D2EHPA through writing paper in medium of SC CO<sub>2</sub>. (30 MPa, 60 °C. Duration of the experiment - 30 min.

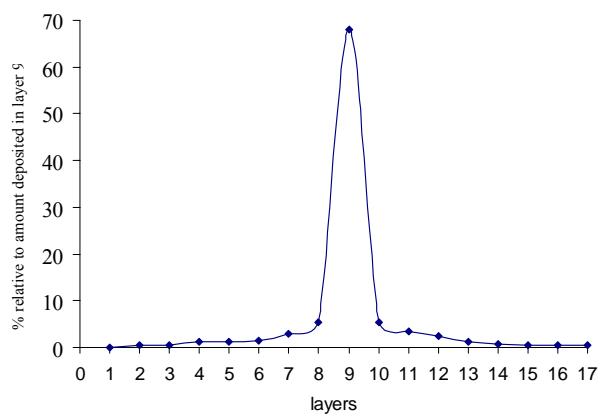


Fig. 4. Diffusion of strontium salt of D2EHPA through writing paper in medium of SC CO<sub>2</sub>. (30 MPa, 60 °C. Duration of the experiment - 60 min.

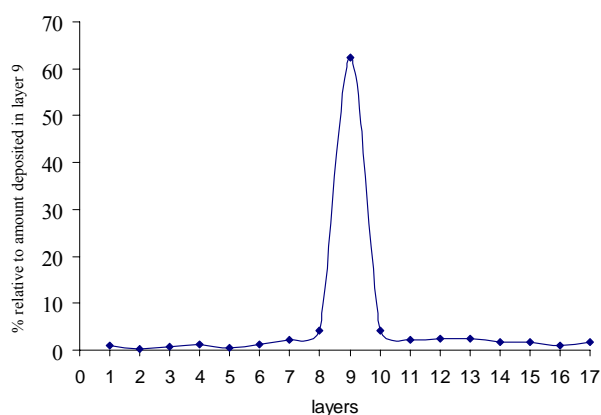


Fig. 3. Diffusion of strontium salt of D2EHPA through writing paper in medium of SC CO<sub>2</sub>. (30 MPa, 60 °C. Duration of the experiment - 120 min.

Coefficients of diffusion of strontium salt of D2EHPA through a writing paper in SC- CO<sub>2</sub> medium were calculated on the basis of the results obtained by the method of layer fragmentation proposed in [31] and described in detail in the present publication [32]. They are presented in Table 3.

Diffusion of strontium through the layers of writing paper in SC-CO<sub>2</sub> in the form of the adducts of strontium di-2-ethylhexyl phosphates and perfluorovalerianates with dicyclohexyl-18 crown-6 under the conditions of absence of ligand excess was studied in the following way. Weighed portion of stable strontium nitrate (62 mg)

was added to 0.1 mL of aqueous <sup>90</sup>Sr(NO<sub>3</sub>)<sub>2</sub> solution with specific β-activity of 1.1 MBq/mL, 34 mg of Na<sub>2</sub>CO<sub>3</sub>, and this mixture was covered with 10 mL of water. This system was twice roiled (every time during 5 min) at ambient temperature with 20-min pause before the second roiling. After centrifugation aqueous phase was discarded.

**Table 3.** Calculated values of coefficients of diffusion strontium salt of D2EHPA through a writing paper in SC- CO<sub>2</sub> medium for various times of the experiment

Time of static experiment, min	D, mm <sup>2</sup> /min	D <sub>average</sub> , mm <sup>2</sup> /min
30	1.2*10 <sup>-3</sup>	7.7*10 <sup>-4</sup>
60	7.7*10 <sup>-4</sup>	
120	3.45*10 <sup>-4</sup>	

Total mass of the prepared strontium carbonate was 36 mg. It was divided into two parts. Then 79 mg of PFVA, 57 mg of DCH18C6 (79 mg of D2EHPA, 57 mg of DCH18C6), 5 drops of water and 10 mL of acetone were added to the first (and to the second) portion of strontium carbonate (18 mg). The mixtures obtained were kept for 24 hours and periodically shaken at ambient temperature to intensify the process of formation of the respective complexes. Acetone phase containing synthesized adduct of strontium perfluorovalerianate with dicyclohexyl-18 crown-6 (of strontium di-2-ethylhexyl phosphate with dicyclohexyl-18 crown-6) was separated by centrifuging and evaporated at 40<sup>0</sup>C for 36 hours in drying box. The complex obtained was dissolved in 5 mL of benzene for subsequent applying onto the paper discs. After that, with the

exception of the fact that initial paper disc contaminated with strontium complex was placed between other 60 paper disks, diffusion experiment was carried out in the same way as the experiment described above. Thus there were situated 30 disks near each side of contaminated disk. This central disk was marked as “zero disk”. After completion of the experiment the cell was also disassembled, and dense bundle of paper was divided in layers, each of which contained three sheets of paper. All in all there were obtained 21 layers (30, each of which contained 3 disks, and one central initial disk marked as “zero”). Activity of each layer was measured, and on the basis of the data obtained diagrams were drawn (see Figs. 6 and 7).

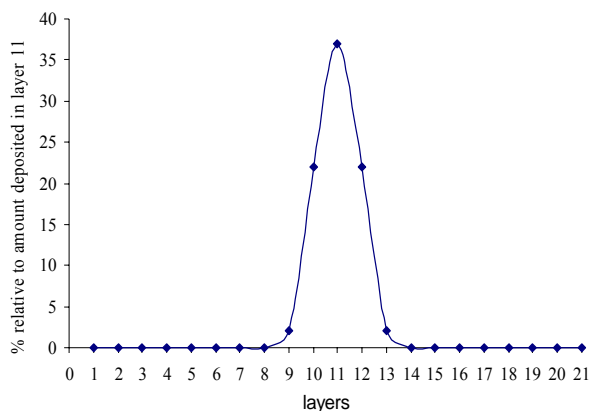


Fig. 6. Diffusion of adduct of strontium salt of **PFVA** with **DCH18C6** through dense bundle of writing paper in medium of SC CO<sub>2</sub> under static conditions (15 MPa, 60 °C, duration of the experiment-20 min,  $V_{cell(free)}=4.1\text{cm}^3$ , weight of the complex=20.5 mg,  $A_{init.}=20550$  Bq, each layer contains 3 paper disks).

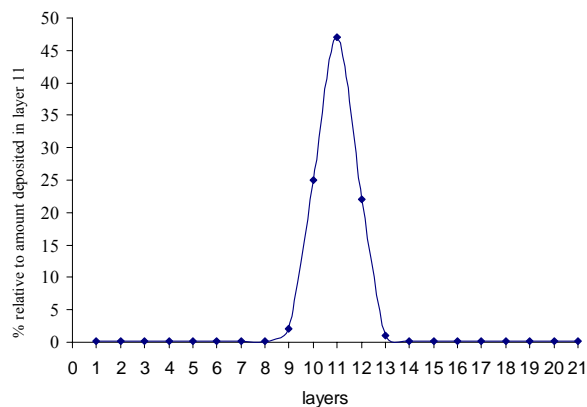


Fig. 7. Diffusion of adduct of strontium salt of **D2EHPA** with **DCH18C6** through dense bundle of writing paper in medium of SC CO<sub>2</sub> under static conditions (15 MPa, 60°C, duration of the experiment-20 min,  $V_{cell(free)}=4.1\text{cm}^3$ , weight of the complex=17.8 mg,  $A_{init.}=12595$  Bq, each layer contains 3 paper disks).

On the basis of the data obtained coefficients of diffusion of strontium complexes were calculated. Coefficient of diffusion of the adduct of strontium salt of D2EHPA with DCH18C6 was found to be equal to  $2,43 \cdot 10^{-2}$  mm<sup>2</sup>/min. Higher value of coefficient of diffusion of strontium salt in the form of its adduct compared with that of strontium salt of D2EHPA ( $7,7 \cdot 10^{-4}$  mm<sup>2</sup>/min) may be explained by its better solubility in medium of liquefied CO<sub>2</sub> as well as by larger chemical stability of the adduct owing to coordination saturation of strontium with DCH18C6.

## Conclusions

1. Possibility of the use of L- and SC-CO<sub>2</sub> for treating mail for the purpose of revealing radioactive substances was shown.
2. Diffusion of <sup>90</sup>Sr through layers of writing paper in the form of adducts of strontium di-2-ethylhexyl phosphates, dioctafluoroamyl phosphates and perfluorovalerianates with dicyclohexyl-18 crown-6 and polyethylene glycol 600 under the conditions of absence of ligand excess was studied.
3. Diffusion coefficients of <sup>90</sup>Sr complexes under study were found. Coefficient of diffusion of strontium di-2-ethylhexyl phosphate through layers of writing paper in medium of SC-CO<sub>2</sub>, was found to be equal to  $7.7 \cdot 10^{-4}$  mm<sup>2</sup>/min. For the adducts of <sup>90</sup>Sr perfluorovalerianate and di-2-ethylhexyl phosphate with dicyclohexyl-18 crown-6 amounted to  $3.3 \cdot 10^{-2}$  mm<sup>2</sup>/min and  $2.43 \cdot 10^{-2}$  mm<sup>2</sup>/min, respectively.
4. Applicability of the method of layer fragmentation for determination of kinetics of diffusion of radionuclides with organic compounds through porous materials in medium of liquefied gases was demonstrated.
5. The diffusion coefficients decrease when increasing duration of the experiments possibly owing to chemical instability of the complexes in the absence of excess of D2EHPA. почему только его, In future we are planning to study this phenomenon in more detail.

6. Now we are treating the experimental data obtained on diffusion of  $^{137}\text{Cs}$ ,  $^{152}\text{Eu}$ ,  $^{241}\text{Am}$  and  $^{239}\text{Pu}$  through a writing paper.

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