CESIUM EXTRACTION BY SOLUTIONS OF FLUORINE-CONTAINING PHOSPHORIC ACIDS IN LIQUID CARBON DIOXIDE

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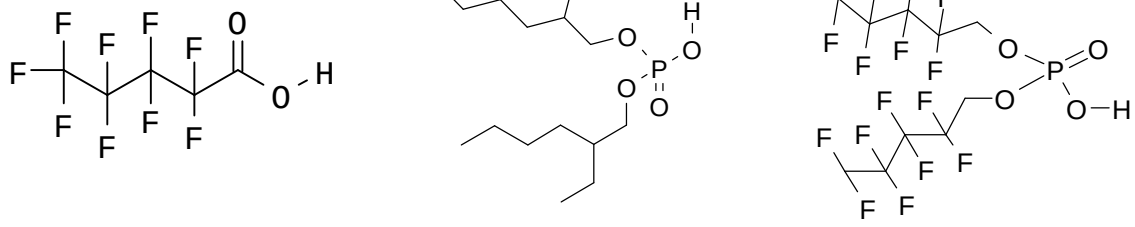
INTRODUCTION

The problem on decontamination of overalls and small articles, as a rule, is not limited only to removal of uranium and transuranium elements. One further element to be removed from solid surfaces is such ecologically hazardous radionuclide as cesium. It is known that cesium can be extracted from aqueous solutions or from solids by solutions of fluorocarboxylic acids and D2EHPA in SC-CO_2 [1,2]. However, the cesium removal efficiency by these complexones is not sufficiently high. For increasing the extraction efficiency crown-ethers or polyethylene glycols should be introduced into the system. Solutions of fluorocarboxylic acids and polyethers efficiently remove cesium from surfaces of stainless steel and other non-sorbing surfaces. At the same time, penetration of polyethers on fabric causes its impregnation with polyethers and sharply decreases the cesium recovery degree. The objective of this work is to select the acids capable of recovering cesium without any addition of polyethers.

I- MATERIALS AND METHODS

The following materials were used: polyethylene glycol-600, octyl alcohol (OctOH) and di-2-ethylhexylphosphoric acid (D2EHPA) received from "Vekton" Ltd (Russia), and laboratory samples of perfluorovaleric (PFVA) and dioctafluoroamylphosphoric (DOFAPA) acids synthesized at St.-Petersburg University (Russia). Structural formulas of the investigated acids are given on Fig. 1. According to data of gas-liquid chromatography, the compounds contained more than 98 % of main substance and were used without any additional purification. Cs^{137} isotope produced by "Isotop" Co (Russia) was also used .



Perfluorovaleric acid (PFVA)

Di-2-ethylhexylphosphoric acid (D2EHPA)

Dioctafluoroamylphosphoric acid (DOFAPA)

Fig. 1. Structural formulas of acids under investigation

Cotton samples contaminated by cesium nitrate were prepared by applying an aliquot of solution on sample surface with subsequent drying at 120°C.

A complex of laboratory equipment consisting of high-pressure syringe pump with cooled head (Grant-Instrument, Russia) and extraction cell made of stainless steel covered by pyrolytic chrome (3,5 ml, Keystone, USA). Cotton samples, as well as aliquots of acids and water, were placed into extraction cell. In some experiments an aliquot of PEG-600 was additionally introduced into extraction cell. Thereafter, CO_2 was forced into cell up to pressure of 70 atm, thermostatically controlled at 25° C and then was kept for 40 min up to equilibrium (static extraction); CO_2 was passed through the cell under the same pressure and temperature during 40 min (dynamic extraction). Extract was collected into methanol through capillary restrictor. Extracted and residual quantities were determined by radiometry with the use of gamma-spectrometer Canberra InSpector 1270.

II- RESULTS AND DISCUSSION

It is known that PEG should be introduced into the system for efficient recovery of cesium by acid solutions [2]. In the course of preliminary studies it was found that the cesium recovery efficiency depends on applying site of PEG addition Table 1).

Table 1. Removal of cesium nitrate from cotton surface by acid solutions in CO_2 in the presence of PEG (60 atm, 25°C, 100 μg $CsNO_3$, 10 μl octanol, 10 μl H_2O, PEG-600, 20 min)

Acid	Cs recovery, %			
	1 mg of PEG-600 is added		60 mg of PEG-600 are added	
	on fabrics	on cell wall	on fabrics	on cell wall
PFVA, 10 μl	< 0,1	55 ± 9	< 0,1	66 ± 3
D2EHPA, 10 μl	4 ± 2	12 ± 6	6 ± 2	6 ± 4
DOFAPA, 10 μl	52 ± 8	50 ± 9	27 ± 6	55 ± 9

The conducted investigations have shown that the efficient extraction of cesium nitrate in the presence of PEG-600 is observed on introducing PEG on a cell wall for PFVA and DOFAPA solutions. Because of the high cesium content on fabric surface (100 μg) the cesium extraction by D2EHPA solutions was not efficient in both cases. Direct penetration of PEG-600 on a fabric being processed results in lesser removal of cesium by all acids, and only DOFAPA solutions in liquid carbon dioxide permit to recover cesium even in the case of PEG penetration on fabric being processed. Since it is rather difficult in decontamination practice to prevent PEG penetration on fabric, further studies were directed to searching for PEG-free systems which efficiently extract cesium. The possibility of replacing PEG with octyl alcohol was investigated as well.

The results obtained (Table2) have revealed that the solutions of both perfluorovaleric and dioctafluoroamylphosphoric acids in liquid carbon dioxide can be used for cesium removal from cotton surface. Comparison of data presented in Tables 1 and 2 shows that the cesium extraction degree by PFVA and DOFAPA solutions in liquid carbon dioxide is considerably less in the absence of PEG (by a factor of 2), but the introduction of octyl alcohol into the system increases the cesium recovery up to a value feasible for arrangement of decontamination process in continuous operating conditions.

Table 2. Removal of cesium nitrate from cotton surface by acid solutions in CO_2 (60 atm, 25°C, 100 μg $CsNO_3$)

Acid	H_2O, μl	OctOH, μl	Recovery, %
PFVA, 10 μl	10	---	$25_{\pm 15}$
	10	10	$35_{\pm 9}$
D2EHPA, 10 μl	10	---	$11_{\pm 5}$
	10	10	$12_{\pm 4}$
DOFAPA, 10 μl	10	---	$25_{\pm 3}$
	10	10	$38_{\pm 8}$

Hence, the conducted investigations have made it possible to determine the conditions for cesium extraction by solutions of fluorine-containing acids in liquid carbon dioxide without introduction of polyethers into the system. Three successive operations of cotton treatment by liquid carbon dioxide containing DOFAPA and OctOH enable to remove cesium by 85 and 99 %, respectively.

CONCLUSION

It is shown that the solutions of dioctafluoroamylphosphoric acid and polyethylene glycol-600 make it possible to extract cesium from cotton surface even in the case of direct penetration of PEG on fabric. It is found that the solutions of perfluorovaleric and dioctafluoroamylphosphoric acids in liquid carbon dioxide in the presence of octyl alcohol enable to remove 30-40 % Cs from cotton surface in one operation. It is established that the threefold treatment of cotton with these solutions allows to attain the needed decontamination factor of 50-100.

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