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Short communication

SHORT COMMUNICATION

Desorption of ^{137}Cs from *Cetraria islandica* (L.) Ach. using solutions of acids and their salts mixtures

ANA A. ČUČULOVIĆ[1*#], DRAGAN S. VESELINOVIĆ[2#] and ŠĆEPAN S. MILJANIĆ[2]

[1]INEP – Institute for the Application of Nuclear Energy, Banatska 31b, 11080 Zemun
and [2]University of Belgrade, Faculty of Physical Chemistry,
11001 Belgrade, P.O. Box 137, Serbia

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Abstract: The desorption of ^{137}Cs from *Cetraria islandica* (L.) Ach. lichen was investigated using the solutions: A) H_2SO_4–HNO_3–K_2SO_4, B) H_2SO_4–HNO_3–Na_2SO_4 and C) H_2SO_4–HNO_3–$(NH_4)_2SO_4$–$(NH)_4NO_3$ at pH 2.00, 2.58, 2.87, 3.28 and 3.75, similar to acid rain. After five consecutive desorptions using solutions A, B and C, from 44.0 % (solution B, pH 3.75) to 68.8 % (solution C, pH 3.28) of ^{137}Cs had been desorbed from the lichen. In all cases, the most successful ^{137}Cs desorption was the first one. In the presence of K^+ (solution A) the total amount of desorbed ^{137}Cs did not depend on the pH of the solution and this was confirmed by the analogous reactions of Cs^+ and K^+, due to their similar ionic radii. The dependencies of the non-desorbed content of ^{137}Cs on the number of desorptions gave curves indicating that at least two types of sorption occur. One of them can be dominant if suitable desorbants are used. The results indicate lichens as secondary sources of environment pollution with ^{137}Cs.

Keywords: *C. islandica* (L.) Ach. lichen; acid solutions; desorption; ^{137}Cs; radioisotope.

INTRODUCTION

In a previous study,[1] the extraction of ^{137}Cs from *Cetraria islandica* (L.) Ach. was investigated using solutions of HNO_3, H_2SO_4 and mixtures of these two acids, as well as a solution containing $(NH_4)_2SO_4$, *i.e.*, solutions with pH values similar to that of acid rain. H^+ and NH_4^+ were the dominant in these solutions. However, real rainfall also contains other ions originating from substances of different origin, such as sea spray, solid aerosols, *etc.*[2–4] Normal rain contains on average 2.0 mg Na^+, 0.30 mg K^+, 0.10 mg $Cl^–$, 0.60 mg SO_4^{2-}, about

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* Corresponding author. E-mail: anas@inep.co.rs
[#] Serbian Chemical Society member.

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0.12 mg HCO_3^- and a series of other elements per 1 kg.[5] Their presence in rain is mostly due to natural processes.

In living organisms, the Cs^+ behaves as a chemical and biochemical homologue of potassium and follows its metabolism.[6,7] For this reason, an investigation of the influence of Na^+ and K^+ from atmospheric water on the desorption of Cs^+ from lichen is of interest, as cations of alkaline elements are similar to the Cs^+ and they can influence its desoprtion based on ion exchange, without other reactions. From this, the possible influence of these cations on the desorption of Cs^+ from lichen follows.

The purpose of this work was to investigate the influence of Na^+, K^+ and NH_4^+ on the desorption of ^{137}Cs from lichen, using solutions similar to acid rain, that thus become a secondary source of pollution with the ^{137}Cs.

EXPERIMENTAL

The apparatus, samples, and sample preparations were the same as in previous studies.[1,8]

Chemicals

H_2SO_4 p.a. and NH_4NO_3 p.a., Merck, Germany; HNO_3 p.a., Alkaloid, FYROM; $(NH_4)_2SO_4$ p.a., Euro Hemija, Serbia; Na_2SO_4, p.a. and K_2SO_4, p.a., Superlaboratory, Serbia; buffer solutions, pH 4.00 and 7.00, Carlo Erba, Germany, were used. The solutions were made in distilled water. Standard filter paper, Merck, was used for filtration.

The measurement error is given as the standard deviation of all the individual measurements of the same type (pH value) independent of the solution type.

Desorption solutions

Tree types of solutions were used: A) H_2SO_4–HNO_3–K_2SO_4; B) H_2SO_4–HNO_3–Na_2SO_4 and C) H_2SO_4–HNO_3–$(NH_4)_2SO_4$–NH_4NO_3. Solutions of H_2SO_4 (a) and HNO_3 (b) had pH values of 2.00, 2.58, 2.87, 3.28 and 3.75 (solutions 1 to 5). The H_2SO_4–HNO_3 solutions were obtained by mixing equivalent volume of solutions a and b, with the same pH values. Solutions A and B were obtained by adding 1.0 g of K_2SO_4 or Na_2SO_4 into H_2SO_4–HNO_3 solution. Solutions C were obtained by adding 0.50 g of $(NH_4)_2SO_4$ or NH_4NO_3 into 100 cm^3 of the H_2SO_4–HNO_3 solution.

Desorption procedure

After measuring the activity of the sample, 200 cm^3 of each solution was poured over 10.0 g of dried sample. The desorptions were performed at room temperature (≈ 22 °C) and lasted 24 h with occasional stirring. After this time, the solution was decanted, the sample dried and its activity remeasured.

Measurement of the ^{137}Cs activity in the sample

Before the first extraction and after every subsequent extraction, the filtrated and dried lichen sample was placed into a plastic vessel with a diameter of 7.5 mm and a volume of 150 cm^3. The activities of ^{137}Cs in every sample were measured under the same geometric conditions for 1 h using an HP Ge spectrometer (Ortec-Ametek), with 8193 channels, an energy resolution of 1.65 keV and a relative efficiency of 34 % at 1332.5 keV ^{60}Co. The activity values were used to calculate the specific activities (Bq/kg). The mass of the sample was reduced after extraction by 0.6 % (average value), *i.e.*, less than the error of the measurement.

RESULTS AND DISCUSSION

The content of ^{137}Cs in each sample was expressed as the percentage of the remaining radiocesium in the sample after each of the five consecutive desorptions, as related to its content in the original sample. All desorptions were repeated twice and the mean values are given in Tables I–III.

TABLE I. Activity[a] of ^{137}Cs (Bq/kg) in *C. islandica* lichen before desorption, totaly desorbed ^{137}Cs from lichen (%) and percentage of remaining ^{137}Cs in lichen after each desorption using the solution H_2SO_4–HNO_3–K_2SO_4 (A) (in relation to the starting content in lichen, 100 %). Room temperature (≈ 22 °C). Desorption time: 24 h. Mean measurement error: 1.64 %

pH value of solution A	Starting activity of ^{137}Cs in lichen before desorption, Bq/kg	Total desorbed ^{137}Cs from lichen %	Remaining ^{137}Cs in lichen after each desorption in relation to the starting content, %				
			Desorption				
			I	II	III	IV	V
2.00	2726	65.7	37.3	35.3	34.8	34.8	34.3
2.58	2938	67.0	40.3	35.5	33.7	33.2	33.0
2.87	2445	64.2	42.8	38.1	37.5	36.8	35.8
3.28	2435	64.5	38.8	37.5	36.7	36.2	35.5
3.75	2552	64.3	42.6	37.1	36.5	35.9	35.7

[a]Mean value from two measurements

TABLE II. Activity[a] of ^{137}Cs (Bq/kg) in *C. islandica* lichen before desorption, total desorbed ^{137}Cs from lichen (%) and percentage of remaining ^{137}Cs in lichen after each desorption using the solution H_2SO_4–HNO_3–Na_2SO_4 (B) (in relation to the starting content in lichen, 100 %). Room temperature (≈ 22 °C). Desorption time: 24 h. Mean measurement error: 1.64 %

pH value of solution B	Starting activity of ^{137}Cs in lichen before desorption, Bq/kg	Total desorbed ^{137}Cs from lichen %	Remaining ^{137}Cs in lichen after each desorption in relation to the starting content, %				
			Desorption				
			I	II	III	IV	V
2.00	2193	59.8	57.7	48.1	43.8	42.1	40.2
2.58	2266	61.0	53.4	47.9	46.1	40.5	39.0
2.87	2343	53.6	63.7	50.5	50.0	46.8	46.4
3.28	2140	52.9	63.8	51.7	49.8	47.2	47.1
3.75	2394	44.0	68.1	61.1	59.3	59.2	56.0

[a]Mean value from two measurements

According to the data in these Tables, high starting activity levels of ^{137}Cs (between 2140 and 3265 Bq/kg) were measured in all *C. islandica* samples. After five consecutive desorptions using solutions A, B and C, between 44.0 % (solution B, pH 3.75) and 68.8 % (solution C, pH 3.28) ^{137}Cs had been desorbed, leading to the conclusion that ^{137}Cs cannot be completely desorbed from lichen by this procedure. The solution pH influences ^{137}Cs desorption from lichen when the desorption was performed using solution B and to a lesser degree using solution C, which indicates an indirect or direct influence of H^+ in the desorption processes, besides the presence of Na^+ and NH_4^+ (Fig. 1).

TABLE III. Activity[a] of ^{137}Cs (Bq/kg) in *C. islandica* lichen before desorption, total desorbed ^{137}Cs from lichen (%) and percentage of remaining ^{137}Cs in lichen after each desorption using the solution H_2SO_4–HNO_3–$(NH_4)_2SO_4$–NH_4NO_3 (C) (in relation to the starting content in lichen, 100 %). Room temperature (≈ 22 °C). Desorption time: 24 h. Mean measurement error: 1.64 %

pH value of solution C	Starting activity of ^{137}Cs in lichen before desorption, Bq/kg	Total desorbed ^{137}Cs from lichen %	Remaining ^{137}Cs in lichen after each desorption in relation to the starting content, %				
			Desorption				
			I	II	III	IV	V
2.00	3265	62.7	47.3	38.9	38.5	37.9	37.3
2.58	2910	65.3	48.3	41.0	40.0	36.6	34.7
2.87	2902	65.4	47.4	41.9	39.7	39.0	34.6
3.28	2895	68.8	46.7	39.7	36.2	33.4	31.2
3.75	2863	63.3	51.6	43.8	41.8	40.1	36.7

[a] Mean value from two measurements

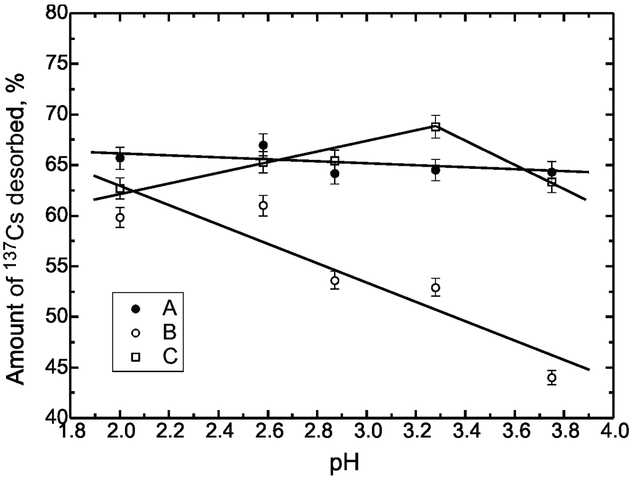

Fig. 1. Changes in the total amount of desorbed ^{137}Cs with the pH value of the desorption solutions A, B and C.

However, in the presence of K^+ (solution A), there were practically no changes in the amount of extracted ^{137}Cs with changing pH, indicating the specific and dominant influence of K^+ as compared to the influence of H^+ on ^{137}Cs desorption. This is in accordance with data obtained from the literature,[6,7] that Cs^+ in living organisms is the chemical and biochemical homologue of potassium, not HN_4^+. Also, the value of the ionic radius[9,10] (crystal) of Cs^+ (167 pm) is more similar to the ionic radius of K^+ (133 pm) than to the ionic radius of Na^+ (97 pm), from which it differs significantly.

In all cases, the highest percentage of desorbed ^{137}Cs was achieved during the first desorption.

Consecutive desorptions with identical desorbent volumes led to changes in the amount of sorbed substance (c_x) with the number of desorptions (n_x). In order to analyze this dependence, the following equation was applied:

$$c_x = c_0 e^{-an} \tag{1}$$

where c_0 is the concentration of the sorbed substance (^{137}Cs) before desorption.[8]

Graphical representations using Origin 7.0 software[11] to the data given in Tables I–III gave curves showing an exponential dependence of the remaining amount of ^{137}Cs, *i.e.*, the desorbed amount, on the number of successive desorptions, regardless of the solution pH.

Application of the logarithmic form of Eq. (1) on the values given in Tables I–III resulted in two types of curves. A linear dependence was obtained using mixtures: A for pH 2.00 and 3.28; B for pH 2.58 and 3.75 and C for pH 2.87 and 3.28. This indicates that one sorption type is dominant in these cases. In all the other cases, curves like those given in Fig. 2 for selected examples were obtained. They are slightly different from those mentioned above and indicate the existence of at least two types of sorption, but when the corresponding desorbants were used, the desorption of ^{137}Cs was not sufficiently separated to be dominant. Desorptions performed with mixture A, pH 2.58, 2.87 and 3.75, B, pH 2.00, 2.87 and 3.28 and C pH 2.00, 2.58 and 3.75, gave this curve type. This shows the

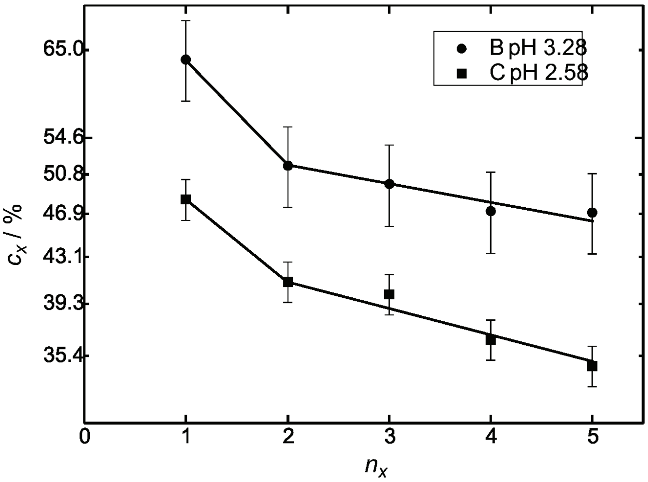

Fig. 2. Percentage of remaining ^{137}Cs content in lichen (shown on ln scale) as a function of the successive desorption number (n_x) according to Eq. (1), with solution B, pH 3.28 and solution C pH 2.58, for an equilibrium time of 24 h.

existence of the simultaneous action of H^+ and other cations that did not lead to the formation of dominant sorption, *i.e.*, a linear dependence according to Eq. (1).

The obtained results lead to the conclusion that *Cetraria islandica* lichen, *i.e.*, its remains, become sources of secondary pollution with radiocesium, not only due to the action of acid rain, *i.e.*, H^+, but also due to the action of K^+, *i.e.*, its compounds. To a lesser degree, the action of NH_4^+ is similar to that of K^+.

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ИЗВОД

ДЕСОРПЦИЈА ^{137}Cs ИЗ ЛИШАЈА *Cetraria islandica* (L.) Ach. РАСТВОРИМА СМЕША КИСЕЛИНА И ЊИХОВИХ СОЛИ

АНА ЧУЧУЛОВИЋ[1], ДРАГАН ВЕСЕЛИНОВИЋ[2] и ШЋЕПАН С. МИЉАНИЋ[2]

[1]*ИНЕП – Институт за примену нуклеарне енергије, Банатска 31б, 11080 Земун и*
[2]*Факултет за физичку хемију, Универзитет у Београду, п.пр. 137, 11001 Београд*

Испитивана је десорпција ^{137}Cs из лишаја *Cetraria islandica* (L.) Ach. растворима: A) H_2SO_4–HNO_3–K_2SO_4, B) H_2SO_4–HNO_3–Na_2SO_4 и C) H_2SO_4–HNO_3–$(NH_4)_2SO_4$–$(NH)_4NO_3$ при pH 2,00; 2,58; 2,87; 3,28 и 3,75 сличним киселим кишама. После пет узастопних десорпција растворима A, B и C из лишаја је десорбовано од 44,0 % (раствор B, pH 3,75) до 68,8 % (раствор C, pH 3,28) ^{137}Cs. Најуспешнија десорпција ^{137}Cs је при првој десорпцији у свим случајевима. У присуству K^+ (раствор A) укупна количина десорбованог ^{137}Cs не зависи од pH раствора, што потврђује аналогне реакције Cs^+ и K^+, због сличних јонских пречника. Зависности недесорбоване количине ^{137}Cs од броја десорпција даје криве које указују да постоје најмање два типа сорпције, али да при коришћењу одговарајућих десорбенаса један од њих може да буде доминантан. Резултати указују да су лишајеви извори секундарног загађивања изотопом ^{137}Cs.

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