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Extraction of ^{137}Cs from *Cetraria islandica* lichen using acid solutions

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Abstract: The extraction of ^{137}Cs sorbed in samples of *C. islandica* using acid solutions was investigated. An equation describing the reduction of the ^{137}Cs content in a dry lichen sample with the number of volumes of acid solutions used for successive extractions was used. The possibility of the existence of two different types of sorption of ^{137}Cs in the lichen was confirmed. Acid rains were shown to influence the extraction of ^{137}Cs.

Keywords: ^{137}Cs sorption, extraction of ^{137}Cs from lichen, *C. islandica* lichen, acid solutions.

INTRODUCTION

Lichen react with ozone, SO_2 and ammonia which are present in air as the pollutants.[1–5] Acid rains, which contain H_2SO_4 and HNO_3, formed from SO_2 and NO_2 in air, can result in the extinction of lichen. The problems of the influence of acid rain on lichens have been reported in the literature.[6–9] In a previous study,[10] the desorption of ^{137}Cs from the lichen *Cetraria islandica* was investigated using distilled water (pH = 6.48). It was found that after five successive extractions, 49.0 % and 59.6 % of the ^{137}Cs had been extracted after equilibration time of 7 and 24 h, respectively. These results indicate lichens as secondary sources of environment pollution with ^{137}Cs.

Since there are no data in the accessible literature on the extraction of ^{137}Cs, or other metals, from lichens by acid rains, the extraction of ^{137}Cs from dried lichen using a solution having the properties of acid rain was investigated in this study.

EXPERIMENTAL

In the present experiments, the apparatus, vessels, sample, extraction procedure and the measurement of the ^{137}Cs activity in the samples were the same as reported previously.[10] The employed sulfuric acid, nitric acid and ammonium sulfate were of *p.a.* grade and were obtained from Merck, Alkaloid and Euro Hemija, respectively.

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Extraction procedure

Four types of solutions were used: A–H_2SO_4; B–HNO_3; C–H_2SO_4–HNO_3 and D–H_2SO_4–HNO_3–$(NH_4)_2SO_4$. Solutions A and B were made of 200 cm^3 of distilled water into which the required concentrated acid was added until the desired pH value were attained: 2.00; 2.87 and 3.75 (solutions A_1, A_2, A_3 and B_1, B_2, B_3). Solutions C was obtained by mixing 100 cm^3 of solution A and 100 cm^3 of solution B, with the same pH values (solutions C_1, C_2 and C_3). Solution D was obtained by adding 1 g of ammonium sulfate to 100 cm^3 of solution C and adjusting the pH value with concentrated sulfuric acid. After measuring the activity, 200 cm^3 of the required solution was poured over 10 g of dried lichen. The extractions were performed at room temperature (~22 °C) and lasted 24 h with occasional mixing. The lichen material was recovered by filtration and its activity remeasured. All extractions were repeated twice and the mean values are given in the Tables I–IV.

RESULTS AND DISCUSSION

The ^{137}Cs content in every sample is expressed as the percentage of the cesium remaining in the sample after every extraction and in relation to its content in the initial sample. The results of the measurements are given in Tables I–IV, as mean values with a standard measurement error of 2.1 (Table I) and 2.5 % (Tables II and III).

TABLE I. Activity* of ^{137}Cs (Bq/kg) in *C. islandica* lichen before extraction and the percentage of remaining ^{137}Cs after each of five consecutive extractions with solutions at pH 2.00. Room temperature (~22 °C). Mean measurement error 2.5 %.

Starting activity of ^{137}Cs in lichen before extraction A / Bq kg^{-1}	2603	2310	2295	3166
Extraction solution**	A	B	C	D
Extraction	Percentage of remaining ^{137}Cs in lichen after each extraction in relation to the starting content (100 %)			
I	61.1	60.3	51.8	46.5
II	49.6	49.9	41.7	34.9
III	45.0	45.8	39.4	34.1
IV	42.6	44.4	39.2	34.0
V	42.1	41.9	36.5	33.6
Total extracted ^{137}Cs from lichen / %	57.9	58.1	63.5	66.4

*mean values, **solution compositions are given in the Experimental

From Tables I–III, it can be seen that changes in the pH value of the solution influence the extraction of radiocesium from lichen, *i.e.*, the significant role of H^+ ion in the exchange of $^{137}Cs^+$ ion. The first extraction was the most significant for the extraction of ^{137}Cs, indicating the presence of the two types of extraction mechanism. Also, regardless of the pH value of the solution, the extractions with solution D were the most efficient, indicating the significant role of NH_4^+ ion in the exchange of Cs^+ ion. In comparison with results obtained with distilled water, it can be seen that the extraction with water was also high (pH = 6.48; total extracted 59.6 %),[10] and that the presence of other cations changed the total effect of the desorption of Cs$^+$. No influence of anions was registered, most probably because the Cs$^+$ ion, as an alkali metal ion, practically does not form complex compounds.

TABLE II. Activity* of ^{137}Cs (Bq kg^{-1}) in *C. islandica* lichen before extraction and the percentage of the remaining ^{137}Cs after each extraction of five consecutive extractions at pH 2.87. Room temperature (~22 °C). Mean measurement error 2.1 %

Starting activity of ^{137}Cs in lichen before extraction A / Bq kg^{-1}	2534	2870	2689	2804
Extraction solution**	A	B	C	D
Extraction	Percentage of remaining ^{137}Cs in lichen before each extraction in relation to the starting content (100 %)			
I	60.7	65.0	70.9	39.9
II	56.4	57.6	60.1	32.6
III	54.4	51.5	58.7	32.4
IV	50.7	47.4	58.3	31.7
V	49.7	46.9	55.0	30.6
Total extracted ^{137}Cs from lichen / %	50.3	53.1	45.0	69.4

*mean values, **solution compositions are given in the Experimental

TABLE III. Activity* of ^{137}Cs (Bq/kg) *C. islandica* lichen before extraction and the percentage of the remaining ^{137}Cs after each extraction of five consecutive extractions at pH 3.75. Room temperature (~22 °C). Mean measurement error 2.1 %

Starting activity of ^{137}Cs in lichen before extraction A / Bq kg^{-1}	2595	2129	2500	2878
Extraction solution**	A	B	C	D
Extraction	Percentage of remaining ^{137}Cs in lichen before each extraction in relation to the starting content (100 %)			
I	76.6	65.3	70.0	44.5
II	65.9	59.0	62.1	41.7
III	62.2	51.3	61.6	41.2
IV	61.6	50.0	58.6	39.3
V	60.7	46.3	54.6	38.3
Total extracted ^{137}Cs from lichen / %	39.3	53.7	45.4	61.7

*mean values, **solution compositions are given in the Experimental

Using the Origin 7.0 software package, the obtained curves show an exponential dependence of the remaining amount of ^{137}Cs, *i.e.*, extracted amount from the number of successive extractions, regardless of pH value, as presented in Fig. 1 for selected examples. This can be explained by the fact that in the solid state–solution system, the amount of sorbed substance is determined by a distribution coefficient, regardless of whether the sorption–desorption mechanism is based on physical or chemical sorption or ionic exchange. According to this, the extraction process of ^{137}Cs is a process of desorption.

TABLE IV. Values of the starting activity of ^{137}Cs (C_0'), determined by extrapolation of the curves in Fig. 3, given as a percentage in relation to the experimentally determined values of C_0 (100 %)*

Extraction solution**	pH	C_0' /%	$\Delta C_0=100-C_0'$
A	2.87	68.03	31.97
B	2.87	46.53	53.47
C	3.75	63.12	36.88

*mean values, **solution compositions are given in the Experimental

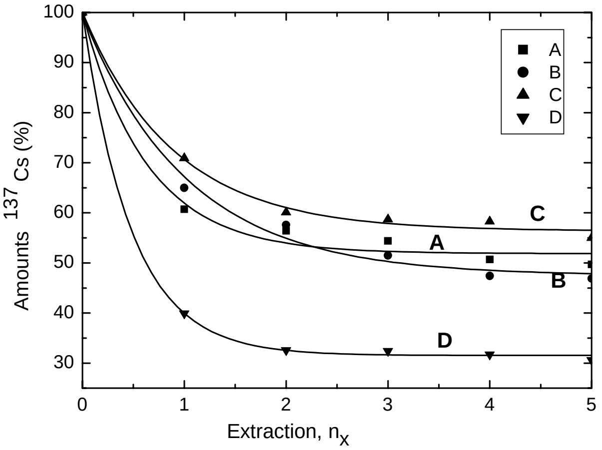

Fig. 1. ^{137}Cs content in lichen (%) in relation to the starting content in dependence on the number of successive extractions, n_x. The lichen was treated with solutions at pH 2.87 for 24 h.

If a series of consecutive extractions of the substance sorbed in the solid phase is performed, the amount of sorbed substance is reduced. For successive extractions with an equal volume of extractant, the change of the sorbed substance with the number of extractions is presented by the following equation:

$$\ln C_x = \ln C_0 - a n_x \tag{1}$$

where C_0 is the concentration of the sorbed substance before extraction.[10]

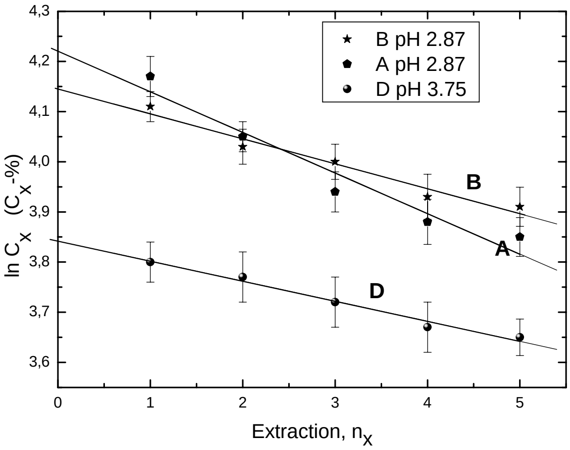

Fig. 2. ^{137}Cs content (%) in the sorbent (*C. islandica*) as a function of the number of successive extractions with solutions at pH 2.87 (A and B) and pH 3.75 (D), (n_x), according to Eq. (1), for an equilibration time of 24 h.

From Eq. (1), it follows that the dependence of the logarithm of the amount of sorbed substance in the solid state is a linear function of the number of successive volumes employed during extraction. For real systems, this is valid when only one type of sorption exists, or if one type is dominant, so that the others can be disregarded (this was the case for extraction with distilled water lasting 1 hour[10]). In other cases, deviations from a straight line occur, indicating that the sorbent can bind the sorbed substance by different types of sorption, *i.e.* different sorbent points.

Using Eq. (1), two types of curves were obtained with the results given in Tables I–III. A linear dependence was obtained when solutions A and B at pH = 2.87 and solution D at pH = 3.75 were used. Extrapolation of the curves (Fig. 2) gave values marked as C_0 given in Table IV. They are smaller than the corresponding initial values given in Tables II and III, indicating that one type of sorption is dominant in these cases, but at least one more type of sorption is present. In the remaining cases, curves were obtained, selected examples of which are given in Fig. 3, demonstrating the presence of at least two types of sorption, but the extraction of cesium when using the corresponding extractant was not differentiated enough to make one of them dominant.

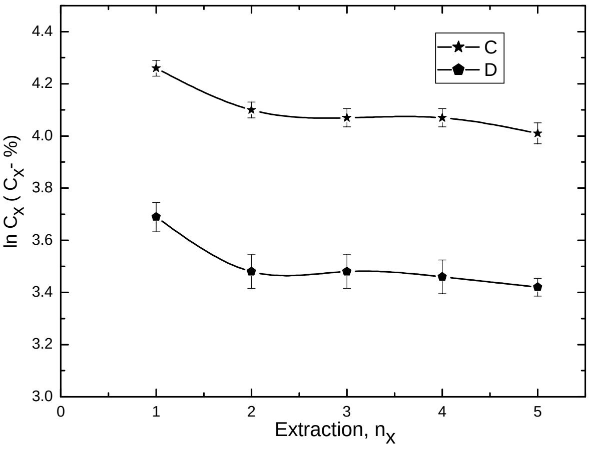

Fig. 3. ^{137}Cs content (%) in the sorbent (*C. islandica*) as a function of the number of successive extractions with solutions B and C, pH 2.87 (n_X), according to Eq. (1), for an equilibration time of 24 h.

Additionally, the obtained results also indicate that ^{137}Cs extraction, to a certain degree, depends on the acidity of rain, *i.e.* its pollution. The obtained changes of the amount of extracted ^{137}Cs range from 0.2 %, when solutions A and B, the most acidic ones (pH = 2.00), were used to 24.4 % when some of the solutions C and D with pH = 2.87 were employed, as can be seen from the data given in Tables I–III. Also, for all pH values covered by the present experiments, the highest percentage of extracted ^{137}Cs was obtained when solution D was used, indicating the role of NH_4^+ ions in the extraction process.

The results obtained show that lichen, *i.e.* its remnants, become sources of secondary pollution with ^{137}Cs, also due to the possibility of accumulation of other elements.

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ИЗВОД

ЕКСТРАКЦИЈА ^{137}Cs ИЗ ЛИШАЈА *Cetraria islandica* КИСЕЛИМ РАСТВОРИМА

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Испитивана је екстракција ^{137}Cs сорбованог у узорцима лишаја *C. islandica* киселим растворима. Коришћена је једначина која даје смањење садржаја ^{137}Cs у сувом узорку лишаја са бројем коришћених запремина киселих раствора, при сукцесивним екстракцијама. Показана је могућност постојања различитих типова сорпције ^{137}Cs у лишају, као и утицај киселих киша на екстракцију ^{137}Cs.

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