

NOTE

Extraction of ^{137}Cs from *Cetraria islandica* lichen with water

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Abstract: Extraction of ^{137}Cs sorbed in samples of *C. islandica* using distilled water was investigated. An equation describing the reduction of the ^{137}Cs content in a dry lichen sample by the number of water volumes used for successive extractions was defined. The possibilities of the existence of two different types of ^{137}Cs sorption in the lichen was established.

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

INTRODUCTION

Lichen, non-vascular plants with large absorbing surfaces, are good sensors (bioindicators)^{1–4} of atmospheric pollution with radionuclides, pesticides and heavy metals and quantitative indicators of pollution (biomonitors) resulting from their morpho-physiological characteristic.^{5–9}

Before the Chernobyl accident in 1981, the levels of ^{137}Cs activity were measured in lichen growing in hunting grounds on the territory of Bosnia and Herzegovina, found to lie between 297 and 854 Bq/kg of dry lichen, and in 1985 they were between 397 and 696 Bq/kg.¹⁰ After the accident, the average levels of ^{137}Cs activity in lichen on the territory of SFRY were significantly higher in *Evernia prunastri* and *Cetraria islandica* lichen, and in 1987 they were 16870 and 10407 Bq/kg and in 1988 7833 Bq/kg and 7442 Bq/kg.^{11,12}

Lichen are applied after their collection and drying, so they can be considered a non-alive system of biological origin which can be used as raw material of starting material for applications in medicine, the food industry, etc.^{13–15} In addition, the remains of lichen in the natural environment, after dying, can be secondary sources of pollution with cesium isotopes, due to the extraction of this element with water from rainfall (rain, snow), their transfer into the environment and also their breaking-up and distribution. Corresponding data were not found in literature.

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The purpose of this work was to establish the role of water as the basic extractant in ^{137}Cs extraction from dry lichen, in the natural environment and in application. Therefore the dried lichen – distilled water system was investigated.

EXPERIMENTAL

Apparatus

In this work the following instruments were used: a) an ORTEC-AMETEK gamma spectrometer with 8192 channels, a resolution of 1.65 keV and an efficiency of 34 % at 1.33 MeV ^{60}Co , with a measurement error below 5.0 % and b) a METLER analytical balance with a precision of 0.1 mg.

Chemicals

Distilled water and standard filter paper were used.

Lichen

Bushy lichen *Cetraria islandica* collected on the Sinjajevina Mountain in 1994, destined for production, were air – dried and preserved in porous paper bags.

Sample preparation

Lichen were cleaned from any visually noticeable impurities, mechanically chopped into small pieces with scissors, and air – dried until a constant mass was achieved.

Extraction procedure

Each sample was extracted 5 times, successively, using the following procedure: distilled water (200 cm³) at room temperature (22 °C) was poured over 10.0 g of dry sample after measurement of its activity, and left for a certain extraction time with occasional mixing. After filtration, the sample was air – dried until a constant mass was achieved. Its activity, as well as the mass, were measured and the next extraction was performed using the same procedure. The extraction times amounted to 1, 3, 5, 7, 17 and 24 h.

For each sample, the extraction procedure was repeated twice, *i.e.*, 70 extractions were made. Extraction at elevated temperature was performed using a) distilled water heated to 100 °C before extraction and b) distilled water heated to 100 °C and maintained at this temperature during the extraction. In case a), the extraction times were 10 and 20 minutes with two successive extractions, while for b) only one extraction lasting for 10 minutes was carried out. Due to denaturation of sample, subsequent extractions could not be performed.

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 cm³. The activities of ^{137}Cs were measured under the same geometric conditions for 1 h and they were used to calculate the specific activities (Bq/kg) of every sample.

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 ^{137}Cs content in each sample was expressed as a percentage of the remaining cesium in the sample after each extraction in relation to its content in the starting sample. It was obtained by expressing the sample activity after each extraction as a percentage of the activity of the starting sample. The results of measurements are given in Tables I and II as mean values with a standard measurement

error of 1.77 % for the samples extracted at room temperature and at 100 °C, respectively.

TABLE I. Activity* of ¹³⁷Cs (Bq/kg) in the *C. islandica* lichen before extraction and the percentage of the remaining ¹³⁷Cs after each of five consecutive water extractions (in relation to the starting content). Temperature ≈ 22 °C. Measurement error 1.77 %

Extraction time h	Starting activity of ¹³⁷ Cs in the lichen before extraction Bq/kg	Total extracted ¹³⁷ Cs from the lichen %	Percentage of remaining ¹³⁷ Cs in the lichen after each extraction in relation to the starting content				
			Extraction				
			I	II	III	IV	V
1	1875	55.8	69.6	62.1	57.0	51.5	44.2
3	2479	57.4	70.3	57.9	49.1	49.0	42.6
5	2497	50.5	68.7	58.2	53.9	49.7	49.5
7	2562	49.0	69.6	56.1	55.4	53.5	51.0
17	2771	50.5	72.2	55.2	55.1	54.8	49.5
19	2438	51.2	72.2	57.2	53.9	53.7	48.8
24	2596	59.6	54.4	45.2	45.1	44.3	40.4

* Average value

TABLE II. Activity* of ¹³⁷Cs (Bq/kg) in the *C. islandica* lichen before extraction and percentage of remaining ¹³⁷Cs after extraction with water a) previously heated to 100 °C and b) maintained at 100 °C

Heating method	Extraction time min	Starting ¹³⁷ Cs activity before extraction Bq/kg	Percentage of remaining ¹³⁷ Cs in the lichen in relation to the starting content	
			Extraction	
			a)	b)
a)	10	1897	44.6	9.6
a)	20	2365	42.0	11.1
b)	10	2243	26.4	–

* Average value

The changes of the ¹³⁷Cs content in the sample with the number of extractions for experiments performed at room temperature and extraction times of 1, 3, 7 and 24 h are shown in Fig. 1. The forms of the curves for all other employed extraction times are of the same type.

The curves obtained using the Origin 7.0 software indicate an exponential dependence of the remaining amount of ¹³⁷Cs, as well as of the amount extracted on the number of successive extractions. This can be explained by the fact that in a 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 ¹³⁷Cs is a desorption process.

For the lichen–extractant system, the ratio between the amount of substance in the solid (C_s) and liquid (C_l) phase are determined by a distribution coefficient D :

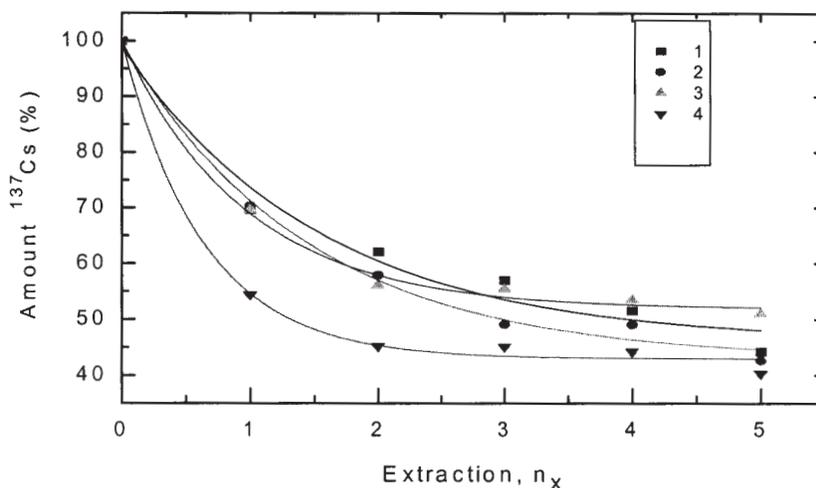


Fig. 1. ^{137}Cs content in the lichen/%, in relation to the starting content in dependence on the consecutive extraction number, n_x , for extraction times of 1–1 h, 2–3 h, 3–7 h, 4–24 h.

$$D = C_s/C_1 \quad (1)$$

If a series of consecutive extractions of a substance sorbed in the solid phase is performed, the amount of sorbed substance is reduced. For successive extractions with equal volumes of extractant, the change of the sorbed substance in dependence on the number of extractions is given by:

$$-dC_x/dn_x = kVC_x \quad (2)$$

where dC_x is the change in the amount of sorbed substance, dn_x is the change in the number of successive volumes of the extractant, k a constant, V is the extractant volume and C_x is the amount of the sorbed substance in the solid phase. Under given experimental conditions using the same basic volume of extractant, $kV = a = \text{const}$. After integration in the limits of C_0 to C_x and 0 to n_x , the following expression is obtained:

$$C_x = C_0 \exp[-an_x] \quad (3)$$

i.e., in the logarithmic form:

$$\ln C_x = \ln C_0 - an_x \quad (4)$$

From the above equation, 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 used during the extraction. This conclusion can be applied to a real system only if one type of sorption exists, or if one type is dominant and hence the other types can be ignored. Otherwise there will be deviations from the straight line. These deviations show that the sorbed substance can simultaneously be bound to the sorbent by various types of sorption. According to Equation (4), the value C_0 represents the amount of sorbed substance before the onset of extrac-

tion and can be obtained by extrapolation of the straight line representing Equation (4) to $n_x = 0$. In the case when only one type of sorption exists, this straight line is identical to the total content of sorbed substance. If other types of sorption exist, the value obtained by extrapolation of the straight line according to Equation (4) gives a part of the total amount of sorbed substance. Simultaneously, this reduced value of C_0 obtained by extrapolation indicates that different types of sorption of the observed substance exist.

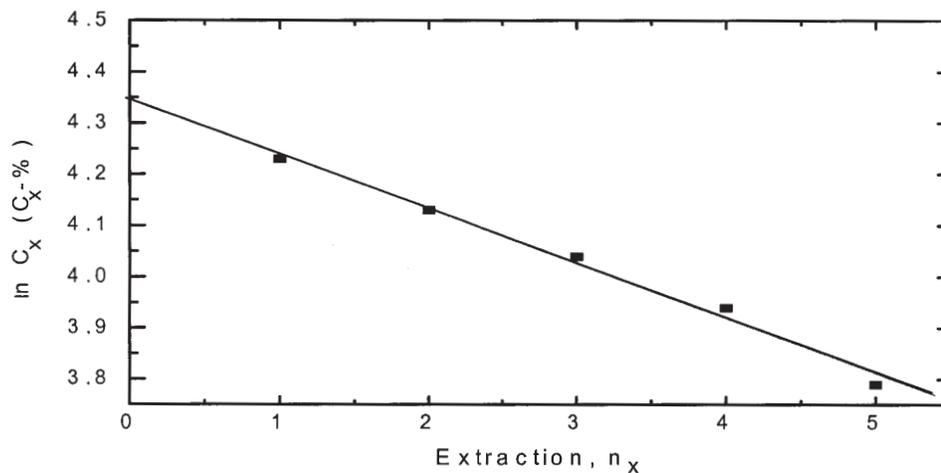


Fig. 2. ^{137}Cs content/%, in the sorbent (*C. islandica*) as a function of the number of consecutive water extractions (n_s), according to Equation (4), for an extraction time of 1h.

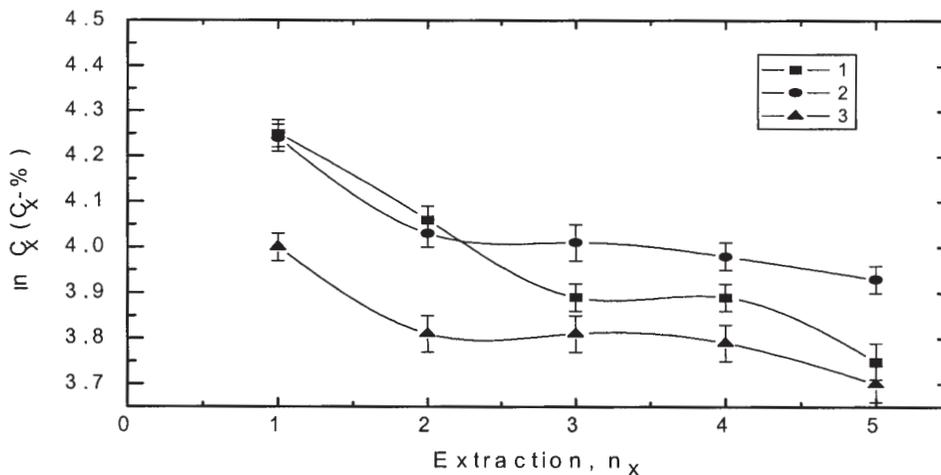


Fig. 3. ^{137}Cs content/%, in the sorbent (*C. islandica*) as a function of the number of successive water extractions (n_x), according to Equation (4), for an extraction times of 1–3 h, 2–7 h, 3–24 h.

The curves obtained using the data from Table I are shown in Figs. 2 and 3. When an extraction time of 1 h was used, the obtained change of $\ln C_x$ with n_x was

in accordance with Equation (4) (Fig. 2). In all other cases when longer extraction times were used, there are deviations from the linear dependence, as can be seen in Fig. 3, which shows representative curves for extraction times of 3, 7 and 24 h. This indicates that there are at least two types of ^{136}Cs binding in the examined lichen. The extraction process which is dominant is at the same time the fastest. As the lichen was picked 8 years after the Chernobyl accident, the possibility that the first fast extraction process involves mechanically remaining dust particles containing ^{137}Cs can be, with certainty, excluded since such particles would have been washed off by rainfall during the ensuing years. The existence of another slower process (or several of them) indicates that ^{137}Cs was sorbed in different ways in the lichen. This was confirmed by determining C_0 through extrapolation of the straight line in Fig. 2. The obtained value of C_0 was 73.4 % of the total amount of sorbed ^{137}Cs .

The obtained results indicate the possibility of using *C. islandica* in the region of its growth to obtain an indication of the contamination of the area with ^{137}Cs . However, its application for other purposes is not possible since the amounts of ^{137}Cs remaining after five 24-hour extractions were quite high (> 40 %) (Table I).

The results obtained at elevated temperatures (Table II) indicate a significant increase in the extraction, especially if the extraction took place at 100 °C. However, further experiments were not performed because structural destruction of the plant occurred. The results obtained show that a temperature increase aids the extraction of ^{137}Cs .

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ИЗВОД

ЕКСТРАКЦИЈА ^{137}Cs ИЗ ЛИШАЈА *Cetraria islandica* ВОДОМ

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Испитивана је екстракција ^{137}Cs сорбованог у узорцима лишаја *C. islandica* дестилваном водом. Постављена је једначина која даје смањење садржаја ^{137}Cs у сувом узорку лишаја са бројем коришћених запремина воде, при сукцесивним екстракцијама. Показана је могућност постојања различитих типова сорпције ^{137}Cs у лишају, и могућност да се то утврди коришћењем постављене једначине.

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