

DETERMINATION OF ^{137}Cs IN SOIL

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Abstract—The method is based on the final precipitation of ^{137}Cs as caesiumtriphenylcyanoborate. Sodiumtriphenylcyanoborate has not been used before as a reagent for determination of radioactive caesium, at least not in the samples of biosphere. Conditions of optimal leaching of ^{137}Cs from various types of soil were found. A 256-channel analyzer was used for sample counting. Conditions of optimal precipitation of caesium were determined.

INTRODUCTION

Most papers on ^{137}Cs in soil deal with the problem of ^{137}Cs fixation⁽¹⁻⁵⁾ or uptake by different plant material⁽⁶⁻¹⁰⁾ and the evaluation of all possible influences on both.⁽¹¹⁻¹³⁾ Few data are available on chemical methods for the determination of ^{137}Cs in soil.⁽¹⁴⁻¹⁶⁾ Even less data are published on separation of ^{137}Cs from large soil samples as it appears to be necessary in the determination of very low activities due to fall-out. The same applies to the variation of soil types, removal of ^{137}Cs from large amounts of nonradioactive ions obtained by leaching of bulky soil samples, contamination by natural radioactivity and possibility of interference from non-radioactive ions during separation. Starting from the above mentioned papers and published results a method with the following features has been developed:

1. Leaching of ^{137}Cs from soil.
2. Separation from large quantities of non-radioactive ions.
3. Easy to operate for less equipped laboratories.

EXPERIMENTAL

Apparatus and Reagents

Glassware and reagents commonly used in laboratory.

Cesinost: 7% aqueous sodium triphenylcyanoborate solution filtered through a SS 589³ filter-paper.

^{137}Cs -tracer as CsCl (from the Radiochemical Centre Amersham).

All reagents were of analytical grade.

Gamma-ray spectrometer with NaI crystal and multichannel analyzer.

The Samples

Five soil samples with widely differing characteristics were used for this study. Represented were an acidic, neutral, saline-alkaline and a calcareous soil. Each sample consisted of 10 borings 2 in. deep. All samples were taken from an undisturbed area or from a herbage sampling site. Each sample weighing about 3–4 kg, was air-dried, ground to pass a 2 mm sieve and dried at 110°C.

Method A

Before starting with a large-scale experiment the method has been tested on 5 g samples of soil. Each sample was artificially contaminated after drying at 105°C with 1000 pCi of ^{137}Cs . After ignition at 450°C 10 mg of Cs-carrier and 10 ml of a leaching solution (1:1 HCl) were added to each sample, and stirred for 30 min. After digestion over night, the leachate was separated by centrifugation, and the washings (at least 3) joined to the leachate. The leachate was evaporated to dryness and after silica dehydration the hydroxides were precipitated by addition of ammonia (1:1) and carbonates by a saturated solution of Na_2CO_3 . The pH of the solution was adjusted to 3 by means of 1N H_2SO_4 , the solution boiled to expel the excess CO_2 , cooled to room temperature, and 5 ml of 7% solution of $\text{Na}[(\text{C}_6\text{H}_5)_3\text{B}(\text{CN})]$

were added. The resulting solution was left for 15 min, filtered, the filtrate was discarded, and the precipitate containing $\text{Cs}[(\text{C}_6\text{H}_5)_3\text{B}(\text{CN})]$ was dried for 30 min at 105°C and weighed. The ^{137}Cs content was measured by gamma spectrometry.⁽¹⁷⁾

Method B

To an aliquot of 250 g of each soil sample ^{137}Cs tracer was added prior to further treatment.

1. Take 250 g of soil, ignite in a muffle furnace for 2 hr at 450°C (see Note 1).

2. Cool, add 100 mg of Cs-carrier, 500 ml of HCl (1:1) stir for 30 min, allow to stand overnight.

3. Filter through a Buchner funnel (Filter-paper SS 5891)* wash the residue thoroughly with water to neutral reaction.

4. Repeat the leaching twice with 500 ml HCl (2:1) and combine all filtrates.

5. Evaporate the whole solution, when nearly dry transfer to a porcelain dish and when completely dry heat for 1 hr.

6. Dissolve the residue in hot 10% HCl and wash the precipitate with hot diluted HCl .

7. Heat the filtrate after silica separation, precipitate the hydroxides by means of a hot fresh 20% NaOH solution.^(18, 19) Boil for 2–3 min under gentle stirring, let settle, filter, wash the precipitate with 5% NaOH (containing some Na_2SO_4) (see Note 2).

8. After the separation of the hydroxides, precipitate the carbonates by adding a saturated solution of Na_2CO_3 and heat just below the boiling point. Digest with occasional stirring (see Note 3). Filter after 4 hr.

9. Acidify the filtrate after the separation of the carbonates with 1N H_2SO_4 , evaporate to about 200 ml, cool to room temperature, adjust pH to 3 with H_2SO_4 , add 50 ml of a 7% Cesignost solution. Filter after 15 min, wash the precipitate with a 1% Cesignost solution, and discard the filtrate.

10. Dissolve the precipitate in a mixture of acetone and water (1:1), evaporate the acetone by heating, add 50 ml of water and adjust the pH to 3 with H_2SO_4 . Repeat step 9.

11. Dry $\text{Cs}[(\text{C}_6\text{H}_5)_3\text{B}(\text{CN})]$ at 105°C for 30 min, weigh and measure by gamma-spectrometry.

Note 1. No losses of ^{137}Cs were observed.

Note 2. If necessary insert between steps 7 and 8 the following separation: Evaporate the filtrate almost to dryness, add 50 mg of Ba-carrier, adjust pH to 5.5 with HCl ,^(20, 21) add 5 ml of 6 M acetic acid and 10 ml of 6 M ammonium acetate, heat to boiling point, add 5 ml of a 10% Na_2CrO_4 solution, digest under stirring for 15 min, heat until the precipitate starts to settle, cool and centrifuge if possible (dependent on the total volume) or allow to stand for 2 hr. Discard the precipitate.⁽¹⁹⁾

Note 3. Control the completeness of the precipitation by adding a few drops of Na_2CO_3 solution before filtration.

RESULTS

To control the efficiency of the method the following steps were checked by gamma-spectrometry:

1. Spectrum of soil samples contaminated with ^{137}Cs before chemical treatment and after ignition (for eventual losses due to heating).

2. The residues after leaching.

3. The combined precipitates following each chemical separation for other nuclides that might be present.

The results of these controls are listed in Table 1.

The results show a marked difference in leaching efficiency between large samples, such as are necessary for fall-out determination, and samples used for the development of the method (Table 2). This implies the impossibility of transferring the method from small scale to large scale by simply calculating the amount of necessary solutions. The ratio of count rate versus volume of solution to count rate versus gram of soil is not constant. The results in Table 3 for ^{137}Cs gravimetric and gamma-spectrometric yield in 250 g samples agree within the probable error of the determination.

DISCUSSION

Experiments on 5 g soil samples were made to try the method on samples where no significant natural radioactivity or fall-out radioactivity interfered with the separation. No inter-

* Schleicher & Schuell A. G., Feldmeilen, Switzerland.

Table 1. Percentage of ^{137}Cs Tracer Extracted from 5 g Soil Samples

Sample	Removal per leach 1:1 HCl	Cesignost $\text{Cs}[(\text{C}_6\text{H}_5)_3\text{B}(\text{CN})]$ chem. yield
1. Podzol	95.0 ± 0.9	91.0 ± 0.6
2. Rendzina	86.0 ± 1.6	84.0 ± 0.9
3. Alluvial solonetz	80.0 ± 2.3	76.0 ± 1.4
4. Terra Rossa	87.0 ± 1.1	84.0 ± 0.9
5. Mineral carbonate	86.0 ± 1.3	79.0 ± 1.5

The results are an average of 3 values.

ference was found, since all radioactivity present was just under the detection limit of the measuring instrument.

Prior to the chemical analysis all the samples were leached three times. No additional leachings were required, inasmuch as no significant removal of unextracted ^{137}Cs was observed from further treatment of the residue.

The lower leaching efficiency arises from the difficulty of dealing with a large volume of solution and macro amounts of SiO_2 , Al_2O_3 and CaCO_3 present in samples.

Instead of 9N H_2SO_4 or 8N HNO_3 as proposed by other authors the HCl leaching was adopted according to results published by Shvedov and Zhilkina.⁽²³⁾ To shorten the time for silica elimination attempts have been made to hasten the precipitation by adding 5 g of gelatine in a strongly acidic solution. It proved impossible to obtain the necessary acidity, as no precipitate was formed even after prolonged boiling.

For the hydroxide precipitation, which proved to be satisfactory with ammonia on 5 g soil

samples, when dealing with 250 g of soil NaOH had to be used instead of ammonia, since large amounts of ammonia interfere with the Cesignost precipitation. Chromate precipitation has been applied for ^{140}Ba elimination in the case when this happened to be necessary. Cesignost is a less known reagent belonging to the tetraphenylborate group. Until now only Havar studied properties of Cesignost on stable Cs-salt solutions. Cesignost proved to be selective for Cs, forming less soluble salts with cesium than with other alkaline metals. Working with up to 10 mg of ammonia Havar got no precipitate with Cesignost.

There are no interferences in Cs precipitation in the presence of 2–3-valent cations. For that reason NaOH can be applied as a precipitant for hydroxides. Under some circumstances the elimination of ammonia by evaporation can prove to be impractical.

The precipitation of Cs with Cesignost sodium (triphenylcyanoborate) must be performed in sulphuric acid media at temperatures not higher

Table 2. Percentage of ^{137}Cs Tracer Extracted from 250 g Soil Samples

Sample	1. leaching HCl : H_2O (1 : 1)	2. leaching HCl : H_2O (2 : 1)	3. leaching HCl : H_2O (2 : 1)
1. Podzol	65.5	78.2	87.0
2. Rendzina	32.2	56.2	67.4
3. Alluvial solonetz	12.0	32.0	40.0
4. Terra Rossa	53.0	61.7	67.4
5. Mineral carbonate	49.0	54.4	64.6

Table 3. Yield of ^{137}Cs in 250 g Soil Samples

Sample	% chem. yield	% gamma by spectrometry
1. Podzol	66.0	66.0
2. Rendzina	61.0	62.0
3. Alluvial solonetz	45.0	38.0
4. Terra Rossa	64.0	59.0
5. Mineral carbonate	62.0	61.0

than 25°C. At higher temperatures the precipitate partly dissolves. Upon longer standing (several hours) part of potassium present in the solution might coprecipitate with caesium.

Part of the losses in chemical yield may be attributed to sample transfer between beakers.

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