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**EXPRESS DETERMINATION OF Sr-90 CONTENT IN ENVIRONMENTAL
SAMPLES WITH DICYCLOHEXYL-18-CROWN-6 (DCH18C6)**

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Abstract

A method is presented for Sr-90 determination in objects of different origin, especially in agricultural production and food. The principle of the method is based on chromatographic extraction of strontium from nitrate solutions followed by radiometric determination of Sr-90 activity. The method, based on „crown ether”, was modernized and extended to different organic sample types (vegetables, meat, etc.). The sample preparation was carried out by wet ashing. A new resistant styrene-divinyl benzene copolymer was tested and used as column substrate. Sr-90 or Sr-90+Y-90 activity was determined by liquid scintillation counting.

Introduction

Sr-90 is one of the most detrimental components of radioactive fallout. It is produced essentially by the U-235 and Pu-239 fission reaction, which has occurred during previous atmospheric nuclear tests and nuclear reactor accidents. The isotope is deposited in bones

with a high risk of development of chronic illness. Sr-90 has long physical and biological half-lives.

The Chernobyl nuclear reactor accident revealed the need for a rapid Sr-90 analytical method. In the last few years it has become common to use macrocyclic polyethers (the so-called crown ethers). Crown ethers were discovered by Pedersen in 1960. They are useful as complexing agents that help polar inorganic salts dissolve in nonpolar organic solvents. The properties of crown ethers are described in detail in (1). In this work dicyclohexyl-18-crown-6 (DCH18C6) was used that complexes with alkaline and alkaline-earth metal ions.

The scientific base of a method of determination of the Sr-90 contents in environmental objects was developed in Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences (Moscow) under the direction of B.F. Myasoedov soon after the accident at the Chernobyl NPP (2,3). This method was later adapted in Institute of Physics at National Academy of Sciences of Belarus. It is meant for Sr-90 determination in soil, water, and milk. It is described in detail in (4).

Now at the Institute of Physics at National Academy of Sciences of Belarus in association with the Institute of Environmental Physics, University of Bremen the method of express determination of Sr-90 has been adapted to objects of organic origin (cereals, leguminous plants, meat and milk production, food, etc).

Experimental

The key point of the method is Sr-90 extraction from the investigated sample by the high-selective sorbent of dicyclohexyl-18-crown-6. It makes possible to exclude other background radioactive isotopes almost completely. The principle of the method is based on chromatographic extraction of strontium from nitrate solutions followed by radiometric determination of Sr-90 activity. A highly porous matrix of styrene-divinyl benzene copolymer in the form of beads 0.2-0.5 mm in diameter is used as a substrate to support the extractant, dicyclohexyl-18-crown-6 (DCH18C6) in tetrachloroethane, which is in the liquid state deep in

the pores of the matrix. Dicyclohexyl-18-crown-6 has the ability to bind strontium with high selectivity. Furthermore, Sr-90 is extracted with 92-97 % efficiency. Figure 1 illustrates dicyclohexyl-18-crown-6 ion complex with strontium.

The method of Sr-90 determination on the basis of selective sorbent in the above objects includes the following main stages:

1. Sample preparation.

At this stage the method of wet ashing is used. Wet ashing is based on combustion of air-dry organic samples by concentrated nitric acid in the presence of perchloric acid (70 %). Reacting with organic substance, nitric acid decays to water, nitrogen dioxide and oxygen. Oxygen in free state has a huge reactivity and oxidizes hydrogen of organic substances to water. The presence of perchloric acid considerably accelerates the combustion. All samples are dried to a constant weight at 105 °C and pulverized. An aliquot of up to 10 g of dry organic sample is transported into an appropriate sized beaker. Next 10 ml of concentrated nitric acid per 1 g sample is added into the beaker. The beaker is covered with a watch glass and placed on a low temperature hotplate stirring as necessary to break up the foam. After the foam separation is finished the sample removed from the hotplate. Further of the perchloric acid to equal one-third the volume of nitric acid is added. The sample solution is heated on hotplate and keeps boiling for 5-7 hours. The wet ashing can be finished when the liquid has become translucent and almost colorless. After ashing, several aliquots can be combined to provide the desired sample size.

Thereafter the sample from the hotplate is removed and cooled to room temperature. Finally, distilled water to transform sample into 2 M nitric acid solution is added. The received solution must filter dropwise. After a filtration the solution should be transparent. Then the sample solution is ready to be extracted.

If the expected sample activity is low-level then the required amount of air-dry sample is high (more than 100 g). In that case the wet-ashing method is acid - and time-consuming.

Therefore, those samples are incinerated at 400-500 °C in an incineration furnace for about 5-6 hours to eliminate organic interference before dissolution (dry-ashing method). Next, the dissolution of samples is made with 7.5 M HNO₃. (4) At such way of sample preparation, small losses of strontium (less than 10%) are possible (4). The loss can be determined by addition of Sr-85 as tracer agent prior to ashing.

2. Selective sorbent preparation.

100 g matrix of styrene-divinyl benzene copolymer was covered with 250-300 ml 5 % solution of DCH18C6 in tetrachloroethane. The compound is heated under reflux for about 2 hour at 92-95 °C.

The obtained sorbent is loaded in to the chromatographic column. Height of sorbent is 200 mm and its diameter 5 mm. Thereafter the column is washed with 10 ml of 1.5 M nitric acid for full removal of solution residues between sorbent grains. Then the chromatographic column is ready. Chemicals consumption per chromatographic column is: styrene-divinyl benzene copolymer 7-8 g, crown ether (DCH18C6) 1 g, tetrachloroethane 12 g.

3. Extract elution with the chromatographic column.

The nitrate extract of the sample is passed through the chromatographic column (the time of completion of the sample passage is taken for the moment of separation of Y-90 and Sr-90). Then the chromatographic column is washed with 20-25 ml 1.5 M nitric acid. This has the effect of disposal of nearly all interfering radionuclides and eventual macro- and microcomponents (3). The loss of radiostrontium due to washing with nitric acid is within the limits of experimental error (less than 1-2 %). Next the column is heated to 80 °C by a thermostat, hot water is poured, and strontium desorption from the chromatographic column is carried out.

4. Activity determination

For registration of Sr-90 in the liquid phase a Liquid Scintillation Analyzer Tri-Carb-2800TR (Perkin Elmer) is used. The Sr-90 activity is determined with allowance for the

scintillating cell background, Sr-90 detection efficiency and correction for eventual Y-90 ingrowth. For registration Sr-90 in the given work scintillator cocktail Ultima Gold AB was used.

Figure 2 depicts the short-scheme of the method.

Results and discussion

To determine strontium losses and a chemical yield, tests were made using the radionuclide Sr-85 as a tracer. Sr-85 was registered by gamma spectroscopy, using an HPGe detector (Canberra Eurisys) of 50% relative efficiency and having resolution of 2.4keV at 1.33MeV.

The strontium losses at various stages were measured. The air-dry organic samples were contaminated by Sr-85. Thereafter, they were ashed by wet ashing. The measurement data on Sr-85 activity in samples prior to ashing and in the obtained extract are given in Table 1. For the all samples the Sr-85 yield is consistently near 96 %.

These solutions obtained above were passed through chromatographic column. Thereafter, strontium was desorbed by hot water at 80 °C and analyzed with gamma spectrometer. The measurement data on Sr-85 activity before and after chromatographic extraction are given in Table 2. For the all samples the Sr-85 yield is consistently near 95 %. Accordingly, of the strontium overall losses are less then 10 %

A standardized test 2 M nitric acid solution was contaminated with Sr-85 of predetermined activity. This solution obtained above was passed through the column prepared as described above. Thereafter strontium was desorbed by hot water at various temperatures. Obtained strontium eluate solutions were analyzed by gamma spectroscopy and the optimal desorption temperature of strontium was determined. Experimental results are given in Table 3. Consistent recovery of 96-97 % can be obtained at water temperatures of 70-80 °C.

Next, the optimal elution volume was determined. The eluate by parts (3 ml) was accumulated and activity was measured with gamma spectrometer. Total elution volume was 30 ml. The results of experiment are represented in Table 4. Figure 3 displays the experimentally determined elution profiles.

As may be inferred from Figure 3 the elution profiles are very similar. Indicating that the chromatographic column in this temperature range has almost constant properties. Notice that almost all strontium was extracted by 20-25 ml hot water.

The chromatographic column loaded with DCH18C6 was tested in view of reusability. The experimental results show that the extraction agent loaded into the column can be used several times. As may be inferred from the Figure 4 6-fold use is possible. Based on the results, the re-use of the chromatographic column can be recommended only if it is known that the expected activities of all samples in the series are comparable, as a slight contamination from previous extraction cannot be excluded.

Also a maximal volume of extract was determined by experiment. The maximal volume of sample solution can be 250-300 ml. In this case of strontium losses are less than 5 %.

A modified method is presented for fast Sr-90 determination in objects of different origin, especially in agricultural production and food. The present method provides considerable reduction of time needed for measurement of a sample (8-10 hours) in comparison to traditional radiochemical method (up to 2 weeks). The method may be applied to determine the Sr-90 contamination of objects and territories, which were exposed to accidents at nuclear facilities, buffer areas of NPP, and possible use of so called «dirty» bombs.

Conclusion

The stepwise investigation of the overall method showed that significant strontium losses occur only in acid ashing of the prepared samples and in desorption from the chromatographic column. Losses are considerably reduced by use of the wet combustion method. Detection limits depend both on the chemical steps and the quality of the radiometer. The present modernized method permits determination Sr-90 activities in objects of different origin down to 0,1 Bq per sample.

Now in the modified method are:

- The method was extended to any organic sample types (vegetables, meat, food, etc.).
- The samples preparation was carried out by wet ashing that permits decrease of strontium losses at this stage.
- A now resistant porous matrix of styrene-divinyl benzene copolymer as a substrate to support the extractant was tested and used that permits multiple use.
- To carry out the direct measurement of Sr-90 activity by liquid scintillation counting without relying on Y-90 accumulation.

The present method was adapted for real environmental samples and is completely ready for the further use.

References

1. Hiraoka, M.: Crown Compounds. Their Characteristics and Applications, Elsevier Inc., New York 1992.
2. Kremlyakova, N.Yu., Novikov, A.P., Myasoedov, B.F.: Extraction Chromatographic Separation of Radionuclides of Sr, Cs, and Ba with the Use of Tvex-DCH18C6, Nucl. Chem. Letters, **145/1**, 23 (1990).

3. Kremlyakova, N.Yu.: The Determination of Radiostrontium in Environmental Objects by Extraction Chromatography Using TVEX-DCH18C6, J.Radional. Nucl Chem. Articles, **170**, 186-194 (1993).
4. Zablotsky, S., Rudak, E., Stopolyanskaya, L. and Wiley, J.: Improvements in the Method of Strontium-90 Extraction from Environmental Samples with Dicyclohexyl-18-crown-6, Kerntechnik, **60**, 262-264 (1995).

Table 1. Sr-85 activity before and after sample preparation.

Sample #	1	2	3	4	5
Sample activity, Bq	109	134	117	105	103
Extract activity, Bq	104	129	111	101	100
Yield, %	95	96	95	96	97

Table 2. Sr-85 activity before and after chromatographic extraction.

Sample #	1	2	3	4	5
Extract activity, Bq	104	129	111	101	100
Eluate activity, Bq	99	124	104	96	95
Yield, %	95	96	96	95	95

Table 3. Determination of the optimal desorption temperature

Desorption temperature, °C	30	40	50	60	70	80	90
Yield, %	63	67	70	92	96	97	92

Table 4. Determination of the optimal elution volume.

Desorption temperature, °C	Extract activity, Bq	Eluate activity, Bq	Yield, %									
			1	2	3	4	5	6	7	8	9	10
60	1023	916	2.0	18.9	57.4	7.0	2.1	1.5	1.1	1.0	0.8	0.5
70	1056	1016	1.6	27.8	51.7	6.6	2.8	1.9	1.3	1.1	1.0	0.4
80	1002	972	1.7	19.0	61.7	7.5	3.0	1.8	1.0	0.8	0.6	0.2
90	1025	945	1.9	10.9	64.9	7.1	2.4	1.3	1.2	1.0	0.7	0.6

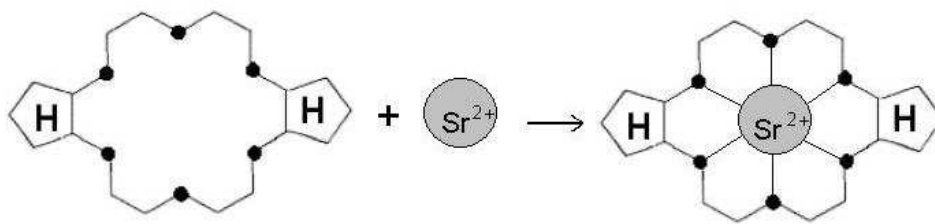


Fig. 1. Dicyclohexyl-18-crown-6 make ion complex with strontium

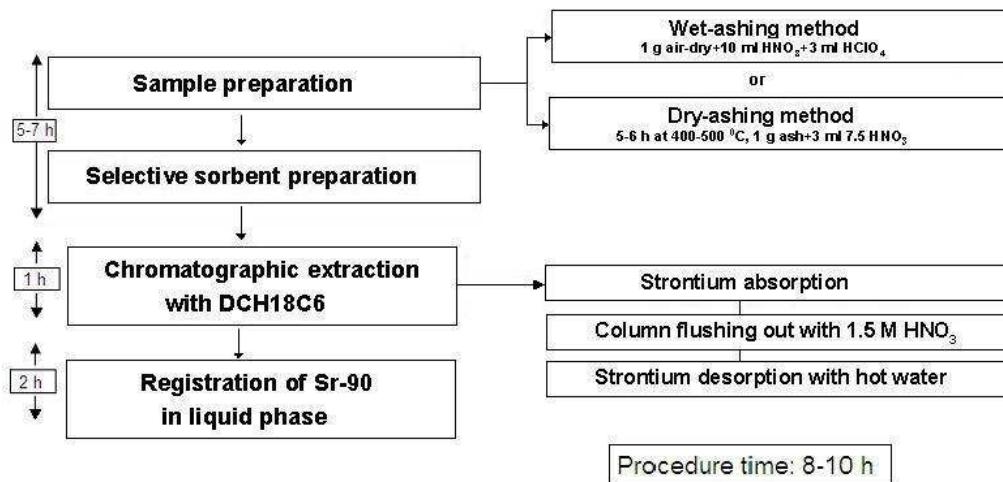


Fig. 2. Express determination of Sr-90 in environmental samples.

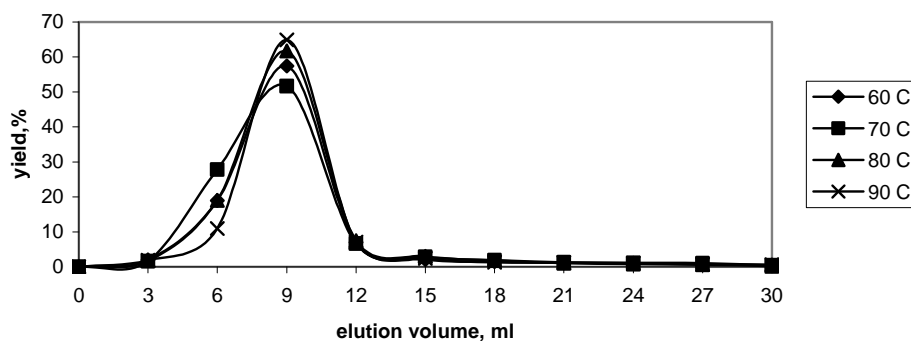


Fig. 3. Elution profiles at various temperatures

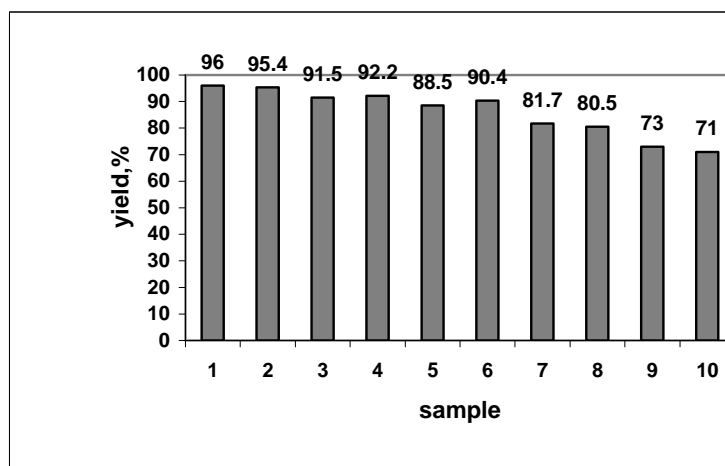


Fig 4. Multiple use of the chromatography column