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Pre-concentration and determination of ^{90}Sr in radioactive wastes using solid phase extraction techniques

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Abstract This paper describes the use of IBC′s AnaLig®Sr-01 molecular recognition technology product to effectively and selectively pre-concentrate, separate and recover strontium from radioactive waste samples. The use and effectiveness of AnaLig®Sr-01 gel was successfully validated by analysis of International Atomic Energy Agency (IAEA 375) reference soil and National Physical Laboratory (NPL)–High Alpha–Beta (2003) liquid sample. The second part of this paper focuses on analysis of radioactive waste samples from nuclear power plant A1 Jaslovske Bohunice in Slovak Republic (NPP A1).

Keywords Strontium separation · AnaLig®Sr-01 · Extraction chromatography

Introduction

One of the most difficult tasks in radiochemistry is determination of pure beta radionuclides such as ^{90}Sr in large volume soil or water samples due to very low concentrations of target nuclides and high levels of interfering matrix elements. To achieve low detection limits, efficient pre-concentration steps are essential. Metals can be concentrated from solution by solid-phase extraction (SPE). SPE usually involves passing the solution through a column, cartridge, or disk containing a solid material that more or less specifically binds the metal ions present in solution [1]. For the pre-concentration of Sr from liquid sample or sample digest AnaLig®Sr-01 gel was used. AnaLig®Sr-01 is based on using the designed specificity of host–guest recognition called molecular recognition technology [2]. AnaLig®Sr-01 gel consists of organic molecules bonded on a silica support. The exact composition is proprietary to IBC Advanced Technologies, Inc. Sr Rad Disk from 3M company contains the same organic extraction molecules as AnaLig®Sr-01 gel [3].

Cerenkov radiation effect of ^{90}Y (progeny of ^{90}Sr) was used for counting of samples for ^{90}Sr determination. The main advantage of Cerenkov counting is the simple sample preparation and a threshold character of the event, that makes counting insensitive for low energy beta emitting radionuclides (<500 keV) [4].

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Experimental

Reagents and materials

AnaLig®Sr-01 gel (60–100 mesh) was supplied by IBC Advanced Technologies, Inc. All other chemicals used were commonly available analytical grade acids and chemicals.

Overview of methods and sample preparation

For validation of method, a reference soil sample IAEA 375 was taken.

Digestion in an autoclave: 20 g IAEA 375 soil sample was digested in a mixture of 50 mL 8 M HNO_3 + 2.0 mL of 30% H_2O_2 (added to each sample for oxidation of the remaining organics in the sample) at 150 °C for 8 h. Digest was cooled and centrifuged. The supernatant was transferred to a beaker and digestion in an autoclave was

repeated twice. All supernatants were collected in a flask and taken for further analysis.

A liquid test sample from National Physical Laboratory NPL–High Alpha–Beta (2003) with certified ^{90}Sr activity was taken.

One hundred microliters of NPL High Alpha–Beta 2003 sample was pipetted into a beaker and another 20 mL of 2.5 M HNO_3 was added and than loaded on AnaLig®Sr01 column.

The tested method was applied for analysis of contaminated water and sludge from NPP A1. NPP A1 (after a second serious accident in 1978 with huge contamination of primary and secondary circuit) was shut down and is still in decommissioning.

Contaminated water sample

One liter of sample was filtered though a 0.45 μm membrane filter, acidified with concentrated nitric acid to pH < 2, and aliquots of 50 mL were taken for analysis.

Contaminated radioactive sludge from NPP A1

51.1 g of sludge was weighed into a beaker and digested in 75 mL 8 M HNO_3 + 1 mL H_2O_2 on a hot plate at 150 °C for about 8 h. The solid and liquid phases were cooled and centrifuged. Leaching was repeated twice. All supernatants were collected and adjusted to the volume of 250 mL in a volumetric flask. An aliquot of 50 mL of the digest was taken for analysis.

AnaLig®Sr-01 procedure

The soil digest, NPL sample, contaminated water or sludge digest from NPP A1 were traced with ^{85}Sr or 6 mg of stable strontium carrier. The acidity of each sample was adjusted (if necessary) with concentrated nitric acid to >1 M. Sample was than loaded on 1 g of AnaLig®Sr-01 column. Each column was washed with 2 × 20 mL of 1 M HNO_3 and 2 mL of deionized water. Sr was eluted from the column with 20 mL of 0.05 M Na_4EDTA [5]. Flow rates were 1–2 mL/min. It is very important to use Na_4EDTA solution of pH > 9. Elution of Sr with the neutral solution of Na_2H_2EDTA is not possible due to low stability constant of the Sr–EDTA complex.

Measurement

Final eluted fractions were measured either on a high purity germanium detector (HPGE) for ^{85}Sr recoveries at 514 keV line or by inductively coupled plasma mass spectrometry (ICP-MS) when stable Sr was used as tracer. Samples were counted repeatedly by Cerenkov counting over a 2 week period to monitor the ingrowth of ^{90}Y on TRI CARB 2900 TR (PerkinElmer). The instrument was calibrated in low level counting mode by using certified ^{90}Sr solution from Czech Metrology Institute. The 1–25 keV energy window was chosen for activity measurement. As a color quenching agent (chemical quench doesn't exist at Cerenkov counting) was used saturated $FeCl_3$ solution (0–500 mg) added to each ^{90}Sr standard. As the quench parameter we used SIS (spectral index of sample). The typical counting efficiency was between 50 and 60%. We counted eluted Sr fractions for 90 min 4–5 times during 2 weeks after Sr separation.

Results and discussion

Samples were processed and analyzed as described above in the experimental part of this paper.

IAEA 375 soil sample

^{90}Sr activity in IAEA 375 reference soil sample is 108 Bq kg^{-1} (95% confidence interval 101–114 Bq kg^{-1}) at reference date 31st December 1991.

The high recovery as well as good selectivity of a single stage Sr AnaLig® gel separation was a surprise because we expected contamination from the decay products of lead and radium (according to Smith et al. [6]). The contribution from lead and radium was not so significant and little strontium was lost. We performed another four strontium separations by using AnaLig®Sr-01. The results shown in Table 1 are in good agreement with the reference value. We had almost 90–100% strontium recovery (ICP-MS) and results within 95% confidence interval for the IAEA sample. We think that there is no need for further separation or purification after elution from AnaLig®Sr-01, which makes the method faster, simpler and less time consuming.

Measuring of Sr recovery by ICP-MS was more convenient because used ^{85}Sr tracer solution contained ^{89}Sr (E_{max} = 1200 keV) impurity interfering by Cerenkov counting and increasing background counts in ^{90}Y counting window.

NPL High Alpha–Beta 2003 sample

^{90}Sr activity in NPL High Alpha–Beta is 9.631 Bq g^{-1} at reference date 1st March 2004.

In Table 2 are the results of three analyses of this sample. All results are in good agreement with the reference value and chemical recovery of almost 90% and higher. The AnaLig®Sr-01 procedure is a quick and very effective separation method with high flow rates through the column (>2 mL/min) and high recoveries as well.

Table 1 Activity concentrations in Bq kg^{-1} for ^{90}Sr—IAEA 375 reference sample (2 U is combined uncertainty)

Experiment no.	Recovery (%)	A_t-measured ± 2 U (Bq kg^{-1})	A_0 at 31st December 1991 (Bq kg^{-1})	Reference value (Bq kg^{-1})
1	100.0	64.0 ± 8.3	101.1	108
2	97.4	65.7 ± 8.4	103.7	108
3	92.4	70.5 ± 8.9	111.3	108
4	96.4	67.7 ± 8.8	106.8	108
5	69.8	69.7 ± 8.4	110.1	108
Average	91.2	67.5 ± 8.7	106.6	

Table 2 Activity concentrations in Bq g^{-1} for ^{90}Sr—NPL ABH 2003 (2 U is combined uncertainty). Reference date 1st March 2004

Experiment no.	A(^{90}Sr) ± 2 U (Bq g^{-1})	Recovery (%)	Reference value (Bq g^{-1})
1	9.9 ± 1.1	96.6	9.6
2	10.0 ± 1.1	90.9	9.6
3	9.3 ± 1.2	89.2	9.6
Average	9.7 ± 1.1	92.5	9.6

Contaminated water and sludge sample

The results for the radioactive water sample are presented in the Table 3. There were six analyses of this sample performed, all with high recoveries >85%. The average value was 383.1 Bq L^{-1} with 95% confidence interval 360.6–407.8 Bq kg^{-1}.

Radioactive sludge was analyzed twice with high recovery demonstrating good method performance for solid waste samples as well. The results are shown in the Table 4.

The laboratory time for AnaLig®Sr-01 column separation method was only 1–2 h, which makes the method simple and high effective.

Table 3 Activity concentrations in Bq L^{-1} for ^{90}Sr—contaminated water sample from NPP A1 Jaslovske Bohunice. (2 U is combined uncertainty)

Experiment no.	A(^{90}Sr) ± 2 U (Bq L^{-1})	Recovery (%)
1	378.6 ± 47.9	96.6
2	361.8 ± 45.6	99.3
3	392.0 ± 49.7	92.9
4	397.7 ± 43.9	90.4
5	380.3 ± 41.9	92.0
6	388.0 ± 43.1	85.0
Average	383.1 ± 45.3	92.7

Table 4 Activity concentrations in Bq g^{-1} for ^{90}Sr-contaminated sludge from NPP A1 Jaslovske Bohunice. (2 U is combined uncertainty)

Experiment no.	A(^{90}Sr) ± 2U (Bq kg^{-1})	Recovery (%)
1	3.2 ± 0.4	95.9
2	3.2 ± 0.4	86.9
Average	3.2 ± 0.4	91.4

Conclusion

Strontium-90 was determined by using strontium specific AnaLig®Sr-01 gel. Activity was measured using Cerenkov counting on TRI CARB 2900 TR spectrometer. For the chosen samples, the use of AnaLig®Sr-01 gel was effective for determination of ^{90}Sr in liquid and solid samples. The measured activities for the two reference samples demonstrated a good accuracy and precision for the above described method. There is no need for further purification of eluted strontium fraction after using AnaLig®Sr-01 gel. The main advantage of the AnaLig®Sr-01 method is a fast and efficient strontium-90 separation, with high chemical recoveries. Separation could be done from acid solutions of wide molarity range 1–10 M [7].

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References

1. Mitra S (ed) (2003) Sample preparation techniques in analytical chemistry. Wiley-Interscience, New Jersey
2. Izatt SR, Bruening RL, Krakowiak K, Izatt RM (2003) The selective separation of anions and cations in nuclear waste using commercially available molecular recognition technology products. In: Proceedings of WM 03 Conference, Tucson
3. Goken GL, Bruening RL, Krakowiak KE, Izatt RM (1999) Metal-ion separations using superlig or analig materials encased in empore cartriges and disks, ACS symposium series 716, American Chemical Society,Washington, 251

4. Larsen IL (2001) Surface and groundwater monitoring for Sr-90 using Cerenkov counting. Radioact Radiochem 12(1):36
5. IBC advanced technologies: analig gel data sheet strontium column series SR-01, IBC Advanced Technologies, Inc
6. Smith LL et al (1996) Application of empore strontium rad disks to the analysis of radiostrontium in environmental water samples. Radiochim Acta 73:165
7. Remenec B (2006) The selective separation of ^{90}Sr and ^{99}Tc in nuclear waste using molecular recognition technology products. Czechoslov J Phys 56:D645