STRONTIUM SEPARATION BY CHROMATOGRAPHIC EXTRACTION PROCESS FOR ^{90}Sr ASSESSMENT

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Abstract

The most sensitive and widely used technique for ^{90}Sr quantification is liquid scintillation counting, which relies on the efficient radiochemical separation of the interest nuclide from other beta-emitting radionuclides. ^{90}Sr separation technique is based on development of the analytical methods applicable to Sr^{2+} species. Strontium separation was developed by using the Eichrom® Sr Resin, based on an extraction system that presents selectivity for strontium. Two methods for Sr separation were carried out: a single chromatographic extraction process, and a double chromatographic extraction, respectively. The results revealed that the double chromatographic extraction process represents an interferences free strontium separation method, obtaining very good decontamination efficiencies values. Therefore, this selective and quantitative separation method can be performed prior to ^{90}Sr activity assessment. The average value of chemical recovery yield, for each of the performed separation procedures, exceeded 96 %; therefore these methods can be easily applied to samples with small activities of ^{90}Sr.

Keywords: *^{90}Sr separation, Sr Resin, extraction chromatography*

Introduction

^{90}Sr radioactive isotope is not a naturally occurring radionuclide being generated by human activities. Due to ^{90}Sr behaviour in various media such as the atmosphere, soil, water, plants and human body, it could be a potential hazard to the people and the environment if the waste containing this radionuclide is not properly disposed of [1].

Strontium typically exists in a soluble form, therefore it is less chemically bound on soil than many other radionuclides and it is readily transported deep into soils by precipitation and groundwater. This means that Sr is available for root uptake, which represents the main route by which it gets into the food chain [1].

^{90}Sr is readily absorbed in the human body by inhalation and ingestion, and it is firmly fixed in the skeleton due to the chemical similarity with Calcium. The main entry routes of ^{90}Sr into the human body are through both contaminated food (mainly agricultural crops) and milk from animals that are fed with contaminated plants [1].

^{90}Sr radioisotope is a difficult to measure radionuclide because it is a β energy emitter with no emission of gamma-rays [1]. Therefore, ^{90}Sr in various kinds of samples can be detected by using liquid scintillation counting (LSC) technique [2-4], which relies on the efficient radiochemical separation of the interest nuclide from other beta-emitting radionuclides.

The radiochemical separation and purification technique of ^{90}Sr is based on development and testing of the analytical methods applicable to natural isotopes in the form of Sr^{2+} species. There are various methods for Sr separation based on classical and instrumental analytical methods, such as: precipitation/co-precipitation, liquid-liquid extraction, ion-exchange chromatography, extraction chromatography. Extraction chromatographic method presents a series of advantages compared to the solvent extraction and ion-exchange: fewer reagents and chemicals, less hazardous waste, a better effective separation, a good contact of the reagents and fast exchange kinetics [5].

Present work carried out two methodologies for Strontium separation by extraction chromatography, namely: (1) a single Sr-selective resin column - single separation, and (2) two consecutive Sr-selective resin columns - double separation. The data presented in this study reveal the conditions under which the interferences free Strontium separation can be achieved.

Experimental set-up

Eichrom® Sr Resin [6, 7] is mainly used for Sr^{2+} separation and purification on the base of an extraction system with selectivity for strontium. The extractant is a crown-ether [4,4(5')-di-t-butylcyclohexano-18-crown-6], whose macrocyclical structure delimits intramolecular cavities in which Sr^{2+} ions are retained (see Fig. 1), forming complexes with a high stability constant.

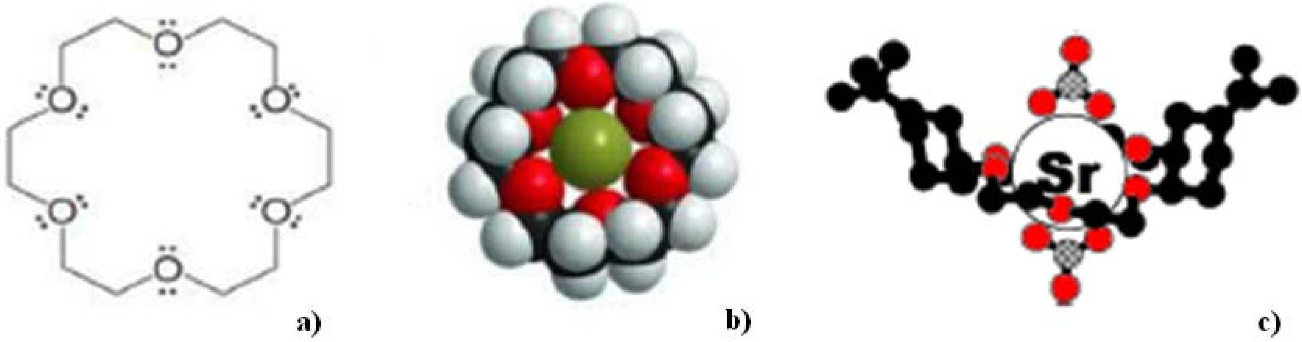

Fig. 1. Schematic structure of the extractant (a); formation of complex with a metallic cation (b); schematic structure of the Sr(NO3)2-crown ether adsorbed onto the resin (c), in which carbon atoms are shown in black, oxygen atoms are shown in red, and nitrogen atoms are shown in white with crosshatching

Strontium affinity for the resin increases with the nitric acid concentration, reaching a maximum value for a concentration of 8 M HNO_3. Therefore, high decontamination factors of interfering elements are achieved by loading the sample in 8M HNO_3 [6].

The carrier Strontium content has a great influence on the chemical yield of Strontium. When the Strontium amount in the sample is greater than 8 mg Sr/mL resin, the chemical recovery of Strontium decreases [6].

The experimental tests were carried out using a synthetic solution prepared with salts of ions corresponding to the following elements: Sr^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} to give a concentration of 10 mg mL^{-1} for each element. These elements were chosen to be relevant for typical radionuclides present with ^{90}Sr in radioactive waste.

Four aliquots of 0.25 mL from 10 mg mL^{-1} stock solution were transferred to centrifuge tubes:

- two aliquots (marked as P1 and P2) for Strontium single separation method,
- two aliquots (marked as P3 and P4) for Strontium double separation method.

10 mL of 8M HNO_3 solution was added into each of the four aliquots. The chemical procedure for both single and double separation method is schematically shown in Fig. 2.

Sr-selective resin columns were conditioned with 10 mL of 8 M HNO_3 solution and the samples were loaded on the columns and let flow by gravity. Ten mL of 8 M HNO_3 solution were used for washing resin columns to remove the matrix interferences (Ni^{2+}, Co^{2+} and Mn^{2+}). Sr^{2+} ions were eluted with 10 mL of 0.05 M HNO_3 solution.

The inductively coupled plasma-optical emission spectrometric (ICP-OES) method (using the iCAP 6000 spectrometer series) was applied for mass concentration assessment of elements (Sr, Ni, Co, Mn) in both initial samples (P1, P2, P3 and P4) and effluents resulted by using the two separation methods (*Ef1* and *Ef2* – single separation; *Ef3.1* and *Ef4.1* – double separation) on the base of the calibration curves for these elements.

The spectral analysed solutions (*Ef1.d* and *Ef2.d*) and (*Ef3.1.d* and *Ef4.1.d*) were prepared by dilution of *Ef1* and *Ef2* effluents, and *Ef3.1* and *Ef4.1* effluents, respectively, with a dilution factor of 25/0.5.

The calibration curves were obtained based on four solutions prepared from the standard reference material (single element standard solution of 1000 mg L^{-1} in 2% HNO_3 ultrapure solution) by accurately diluting a measured amount of known concentration stock solution (10 mg mL^{-1}) that contains the elements of interest (Sr^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+}) to have element mass concentrations spanning [0-5] mg L^{-1}. The 2% HNO_3 ultrapure solution was used to prepare the calibration solutions to ensure that they are free of contaminants that could cause spectral interferences.

A very good correlation between concentration and signal emitted by ICP-OES was obtained, with the following values of correlation coefficients:

Sr	*0,9999*	Co	*0,9997*
Ni	*0,9999*	Mn	*0,9998*

Analysis principle of the inductively coupled Argon plasma optical emission spectrometer

The liquid homogeneous sample is withdrawn from the sample vial by using a peristaltic pump, and then is sent to the nebuliser and transformed into an aerosol of liquid droplets that are swept into the plasma with a constant flow of Argon carrier gas. The solvent is evaporated and the residual sample undergoes atomisation and ionisation as a result of high temperature plasma source. Emission in the form of photons of light occurs because of excitation and relaxation of atoms in the plasma. Each element emits photons at specific wavelengths. The wavelength intensity is proportional to the concentration of the interest element and this is determined on the base of a calibration curve obtained with standards solutions selected to cover the concentration range of the samples. The results are generated live on screen, allowing instant access for the analyst [8, 9].

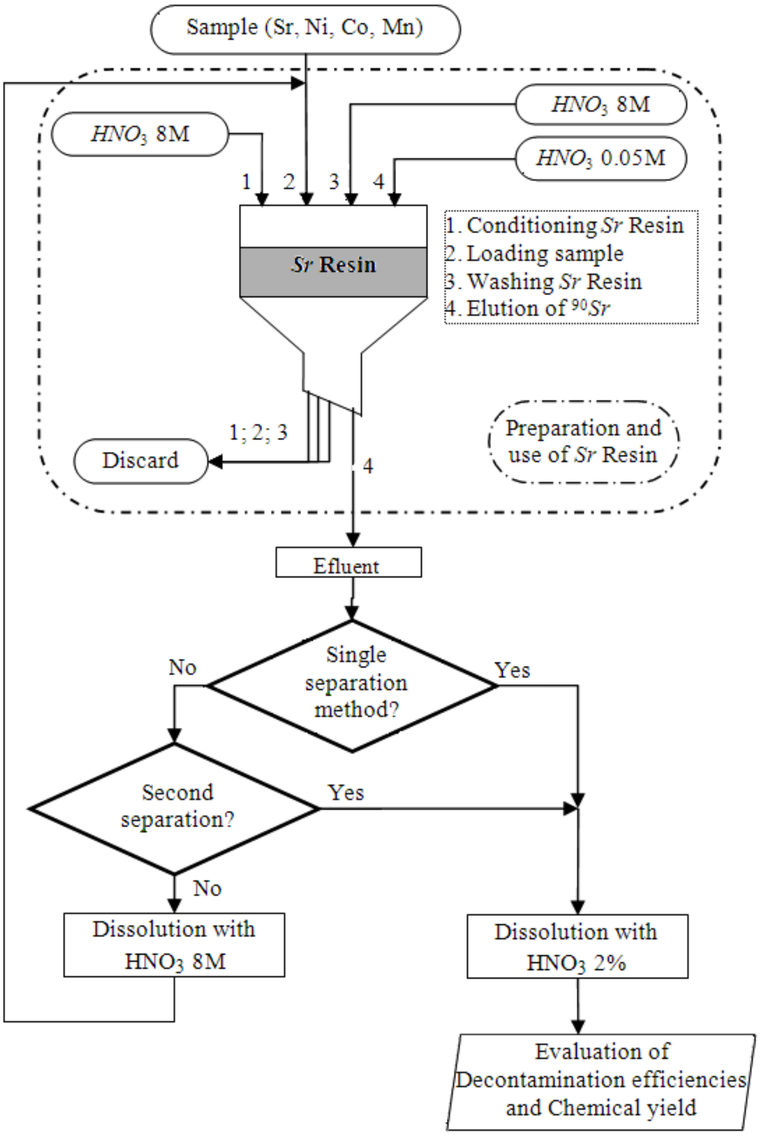

Fig. 2. Flow chart for strontium single separation and strontium double separation

Results and discussion

In Table 1 the values obtained by using the inductively coupled plasma-optical emission spectrometric method for mass concentration of elements in the (P1, P2, P3 and P4) initial samples are presented.

Tables 2 and 3 show the values obtained by using the ICP-OES method for mass concentration of elements in the *Ef1*, *Ef2* effluents (resulted by using single extraction chromatography) and *Ef3.1* and *Ef4.1* effluents (resulted by using double chromatographic extraction), respectively.

Table 1. Results obtained by spectrometric analyses of elements in the (P1, P2, P3 and P4) samples

Element	***Concentration [mg/L]***	***Std. deviation [mg/L]***	***RSD [%]***
Sr	1.998	0.0025	0.1251
Ni	1.989	0.0081	0.4072
Mn	1.991	0.0082	0.4119
Co	1.997	0.0052	0.2604

Table 2. Results obtained by spectrometric analyses of elements in the *Ef1* and *Ef2* effluents

Element	***Ef1.d***			***Ef2.d***		
	Concentration [mg/L]	***Std. deviation [mg/L]***	***RSD [%]***	***Concentration [mg/L]***	***Std. deviation [mg/L]***	***RSD [%]***
Sr	1.9780	0.0052	0.2629	1.9830	0.0051	0.2675
Ni	0.0741	0.00077	1.0391	0.0682	0.00065	0.9562
Mn	0.0411	0.00026	0.6326	0.0382	0.000298	0.7801
Co	0.0210	0.00019	0.9041	0.0230	0.00015	0.6529

Table 3. Results obtained by double spectrometric analyses of elements in the *Ef3.1* and *Ef4.1* effluents

Element	***Ef3.1.d***			***Ef4.1.d***		
	Concentration [mg/L]	***Std. deviation [mg/L]***	***RSD [%]***	***Concentration [mg/L]***	***Std. deviation [mg/L]***	***RSD [%]***
Sr	1.9180	0.0073	0.3754	1.9320	0.0054	0.2675
Ni	<DL	0.00087	0.9969	<DL	0.00081	0.8462
Mn	<DL	0.00012	1.7910	<DL	0.00015	2.4590
Co	<DL	0.00032	3.404	<DL	0.00015	1.5469

Performance parameters of Strontium separation process

The performance parameters of the Sr separation process were assessed by determining two parameters, namely the decontamination efficiency and the recovery yield.

The decontamination efficiency is defined by Eq. (1) and Table 4 presents the mass values for interfering elements in initial samples and effluents (*Ef1* and *Ef2*).

$$E.D. = 100 - [(m_{final}/m_{initial}) \cdot 100] \qquad (1)$$

where:
E.D. = decontamination efficiency [%];
m_{final} = mass of interfering elements (Ni^{2+}, Co^{2+}, Mn^{2+}) in the purified fractions obtained by application of the separation analytical methods [g];
$m_{initial}$ = mass of interfering elements in the initial samples (P1, P2, P3, P4) [g].

Table 4 Mass values for interfering elements in the initial samples and effluents (*Ef1* and *Ef2*)

Element	***m_i* [mg]**	***m_{Ef1}* [mg]**	***m_{Ef2}* [mg]**
Ni	2.486	0.093	0.085
Mn	2.496	0.026	0.029
Co	2.489	0.051	0.048

The values of decontamination efficiencies (illustrated in Fig. 3) achieved by performing the single separation method are higher than the values resulted by using the double separation method.

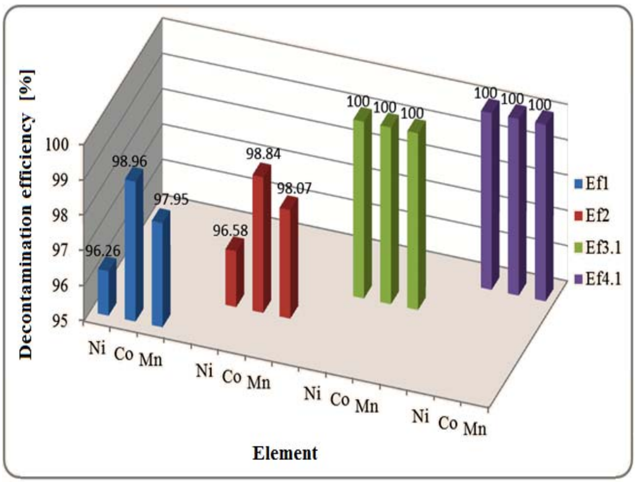

Fig. 3. Decontamination efficiency variation [%]

The recovery yield, Rec [%] for Strontium is computed using Eq. (2).

$$Rec = (m_{final}/m_{initial}) \cdot 100 \qquad (2)$$

where:
Rec = recovery yield [%];
m_{final} = mass of strontium (Sr^{2+}) in the purified fractions obtained by application of the separation analytical methods [g];
$m_{initial}$ = mass of strontium (Sr^{2+}) in the initial samples (P1, P2, P3, P4) [g].

The values of Strontium recovery yield (comparatively depicted in Fig. 4) are reproducible for each separation method, spanning from 96.00 % to 99.25 %, with the following average values:

- 99.13 % for extraction chromatography;
- 96.35 % for double chromatographic extraction.

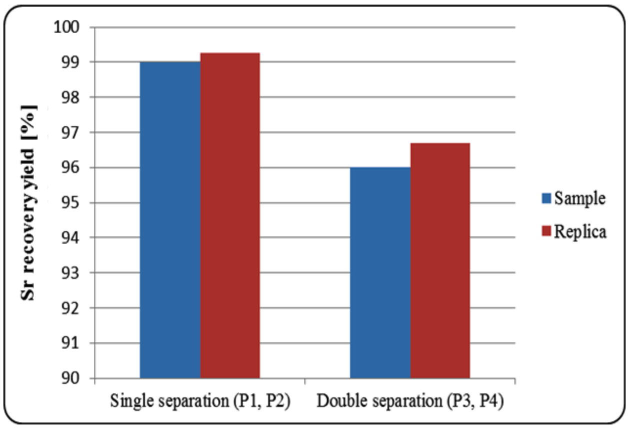

Fig. 4. Strontium recovery yields for (P1, P2, P3, P4) samples

Regeneration degree assessment of Sr Resin

The regeneration process of the Strontium Resin used in these experiments was performed by applying the same procedure as for the single separation shown in Fig. 2.

The ICP-OES method was applied for mass concentration assessment of Sr in both initial sample (Ai) and purified fractions (R1 and R2) on the base of the calibration curve for this element. The mass values of Strontium are comparatively depicted in Fig. 5.

The values of Strontium recovery yield (calculated on the base of Eq. (2)) obtained by applying the regeneration process of Sr Resin, are presented in Fig. 6, with an average value of 99.02 %.

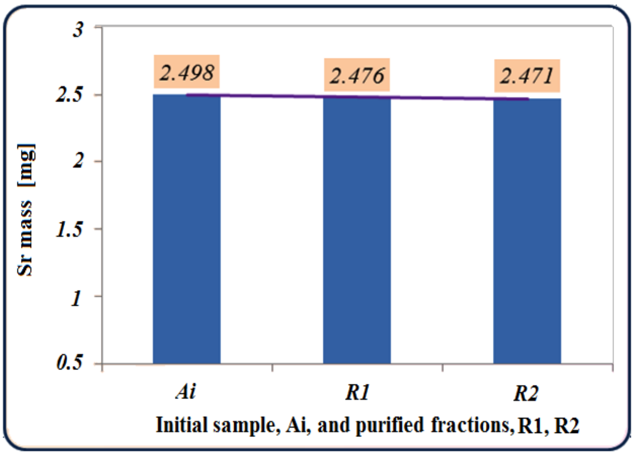

Fig. 5. Initial sample and purified fractions composition

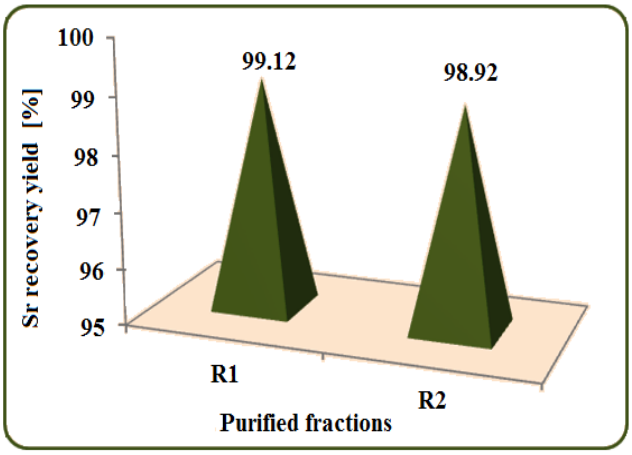

Fig. 6. Variation of Sr recovery yield in Sr Resin regeneration process

Conclusions

The results achieved by applying the two Strontium separation methods, with the aim of Sr mass concentration quantification in liquid samples, reveal that double chromatographic extraction represents an interferences free Sr separation method, obtaining very good decontamination efficiencies values (practically 100 %). For this method, the inductively coupled plasma-optical emission spectrometric measurements of purified fractions did not detect the presents of Ni, Co, Mn interfering elements.

The values of strontium (Sr^{2+}) recovery yield, for each of the considered Strontium separation procedures, exceeded 96 %; therefore these methods can be easily applied to samples with small radioactivity.

References

[1] *** Department of Energy (1996) ″Selected Radionuclides Important to Low-Level Radioactive Waste Management″, DOE/LLW-238, DOE, USA.

[2] Lee, M.H., Chung, K.H., Choi, G.K., Lee, C.W (2002) ″Measurement of ^{90}Sr in aqueous samples using liquid scintillation counting with full spectrum DPM method″, *Applied Radiation and Isotopes*, Vol. 57(2), pp. 257/263.

[3] Kessler, M.J. editor (2015) *Liquid Scintillation Analysis: Science and Technology*, Perkin Elmer Inc, USA

[4] L'Annunziata, M.F. (2003) *Handbook of Radioactivity Analysis*, Elsevier Science, USA.

[5] Vajda, N., Kim, C.K. (2010) ″Determination of Radio strontium Isotopes: a Review of Analytical Methodology″, *Applied Radiation and Isotopes*, Vol. 68(12), pp. 2306-2326, DOI:10.1016/j.apradiso.2010.05.013.

[6] *** Triskem International ″Sr Resin″, product sheet, http://www.triskem-international.com

[7] Horwitz, E.P., Chiarizia, R., Dietz, M.L. (1992) ″A novel strontium-selective extraction chromatographic resin″, Solvent Extr. Ion Exch., Vol. 10, pp.313-336.

[8] *** Thermo Electron Corporation (2005) ″ICP Emission spectrometer Technical Reference manual″, Cambridge, UK.

[9] *** Thermo Fisher Scientific (2008) ″iTEVA Software Manual, Operators Manual″, Cambridge, UK.