

Separation of Radiostrontium from Environmental Sample Using Strontium Selective Chromatographic Resin(Sr. SpecTM)

Kwang-Hee Hong, Chang-woo Lee, Yong-Ho Choi, Myung-Ho Lee

Korea Atomic Energy Research Institute

KAERI, Head office, P.O.Box 7 Daeduk-danji, Taejeon, Korea 305-606

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스트론튬 선택적이온교환수지(Sr.SpecTM)를 이용한 환경시료중의 방사성 스트론튬의 분리

홍광희 · 이창우 · 최용호 · 이명호

한국원자력연구소

Abstract - Strontium selective chromatographic material (Sr-SpecTM) was investigated for separation of radiostrontium from environmental soil and water sample. This chromatographic material has great capacity of binding of strontium ion in nitric acid media, and has selectivity to permit the separation of strontium from bulk amount of calcium. But the extraction of strontium was reduced by the other interfering ions such as K and Ba. So, in order to apply this material to the soil sample, prior removal treatment of K and Ba was needed. But the Sr-Spec material could provides simple and effective methods for the separation and removal of radiostrontium from liquid sample.

Key words : radiostrontium, crown ether, ion selective resin, environmental sample

요약 - 스트론튬선택성을 갖는 크로마토그래피용 수지인 Sr-SpecTM을 이용한 환경시료중 토양 시료와 물시료에 대한 방사성 스트론튬 분리를 고찰하였다. 이 수지는 질산수용액에서 스트론튬과 큰 결합능력을 가졌으며, 다량의 칼슘원소의 존재에서도 스트론튬분리를 할 수 있는 선택성을 가졌다. 그러나 K 나 Ba와 같은 방해원소에 의해서는 스트론튬 추출능력이 감소하였고, 때문에 토양 시료중의 스트론튬 분석시에는 이러한 방해원소의 제거단계가 필요하였다. 그러나 물시료중 스트론튬분석에서는 이 수지를 사용함으로써 간편하고 효율높게 분리할 수 있었다.

Key words : 방사성스트론튬, crown ether, 이온선택성수지, 환경시료

INTRODUCTION

Radiostrontium (⁸⁹Sr and ⁹⁰Sr) is among the most hazardous isotopes generated in nuclear operations. Long-lived nuclides ²³⁹⁺²⁴⁰Pu, ²³⁸Pu, ²⁴¹Am, ⁹⁰Sr, and ¹³⁷Cs were deposited on the soil surface in the sixties as a result of the global fallout from nuclear weapons testing[1, 2] and again in 1986 after the reactor accident at Chernobyl[3] ⁹⁰Sr is

the long-lived beta emitter(about 28 year), and have no gamma-ray emissions and therefore had to be radiochemically separated and measured by means of their beta emissions. Because of their chemical similarity to calcium, radiostrontium can replace calcium in the biosphere and reaches man via the food-chain. These isotopes, if ingested, are readily incorporated within bone tissue, where they may be retained for a considera-

ble length of time (biological half-life is about 50 year[4]). Due to the long residence time in the human body and the high radiotoxicity of radiostrontium, the separation and measurement of radiostrontium and its activity in environmental samples have important meanings. In recent years, numerous methods have been made in separation of strontium. There are a number of different radiochemical procedures available in the literature which based upon precipitation[5], liquid-liquid extraction[6], ion-exchange[7], and chromatography[8]. All of these procedures, however, suffer from various limitations. For example, precipitation method must contain tedious and time-consuming treatment which must often be repeated several times to obtain adequate recovery of strontium. Furthermore, this method involves the use of fuming nitric acid which is extremely hazardous. Liquid-liquid extraction is too cumbersome for use with large number of samples and usually requires the use of toxic solvent such as tri-butyl phosphate or dichloroethane. Ion-exchange procedures typically require careful pH control, because satisfactory separations from calcium are archived only within a narrow pH range. Moreover, this pH range is affected by the amount of calcium present [9]. Horowitz and coworkers have shown that strontium may be efficiently extracted from aqueous solutions containing high concentrations of nitric acid by solution of various crown ethers dissolved in any of a number of aliphatic alcohols and ketons[10, 11]. He demonstrated that extraction chromatography, using a solution of 4,4'(5')-bis(tert-butylcyclohexano)-18-crown-6 (DtBuCH18C6) (Fig. 1) in 1-octanol sorbed on an inert substrate (Amberchrome or Amberlite), provides a simple and effective method for the preconcentration and separation of strontium from nitric acid media[12]. Such a work has recently become commercially available under the trade name Sr.Spec (EiChroM Industries, Inc.) By considering the possibility that Sr.SpecTM could be successfully applied to the

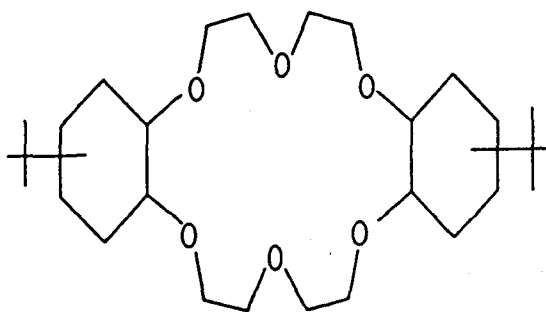


Fig. 1. Structural formular of 4,4'(5')-bis(tert-butylcyclohexano)-18-crown-6.

analysis of radiostrontium, we applied this chromatographic material for separation of strontium from environmental sample, and examined the fact that Sr.SpecTM has selectivity to permit the separation of strontium from samples containing various interfering radionuclides and large amount of calcium. We examined its applicability to determination of radiostrontium about environmental radiation monitoring programs also.

EXPERIMENTAL

Materials The chromatographic material (Sr.SpecTM) was obtained from EiChroM industries, II.USA. The characteristics and properties of this material are described in table 1, and was used without any purification. The tracer ⁸⁵Sr, ⁵⁴Mn, ⁶⁰Co, ¹³⁷Cs were obtained from Isotope Product Laboratory (Burbank, California, U.S.A.) as aqueous solutions of the nitrate. All other reagents were ACS grae and were used as purchased.

Apparatus Gamma counting were performed on a high purity Ge(Li) low - background detector. (EG&G Ortec, Inc., TN) Gamma spectra were evaluated with MAESTRO (Ortec) software and IBM PC-AT personal computer for multichannel analyzer emulation.

Procedures Distribution ratio (D_M) measurement; The distribution ratio of strontium from 3 M HNO₃ solution by the resin was measured by mixing of ⁸⁵Sr spiked solution of

Table 1. Characteristics of Sp.Spec™ chromatographic material and packed column.

Sp.Spec™ Material	
Stationary Phase	1.0M DtBuCH18C6 in 1-octanol (d=0.912g/ml)
Support	Amberchrom™ CG-71 or Amberlite™ XAD-7
Particle Size(diam.)	50-100 μm
Extractant Loading	40 weight percent
Average Density of Extractant-loaded Beads	1.12g/ml
Packed Column	
Vs ml/ml of Bed	0.146 ± 0.004
Bed Density(g/ml)	0.33
Vm(F.C.V.) ml/ml of Bed	0.71 ± 0.01
Capacity(mg/ml of Bedh)	10.6

various concentration with DtBuCH18C6. Equal volumes(1 ml) of a ⁸⁵Sr tracer in 3 M nitric acid and various concentration of DtBuCH18C6 dissolved in an n-octyl alcohol, were pipetted into a 15-ml glass-stoppered tube and stirred for nearly 60 min. at room temperature. After settling for about 60 min. aliquots from aqueous phase were withdrawn for radioassay. The distribution ratio(D_M) of the ions defined as the ratio of concentration of the ion in the organic phase and in the aqueous phase, was calculated by described below.

$$D_M = \frac{A_b - A_a}{A_a} \frac{V_{aq}}{V_s}$$

where A_b and A_a are the activity of the aqueous solution before and after equilibration with constant nitric acid concentration solution. V_{aq} is total aqueous phase volume and V_s is aqueous phase volume needed for radiometric determination.

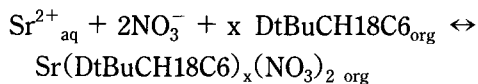
Preparation of soil sample; Woodland undisturbed surface soil were taken to a depth of 2 cm. A sample of 2 kg was then weighed,

air dried and placed in an oven at 100°C for 24 hour, and sieved to remove stones and pebbles, and crushed to pass through a 2-mm mesh sieve. The dry sample was carefully ashed at 550°C over night. If the ash was not free of organic carbon, the residue was moistened with concentrated nitric acid, fumed off to dryness, and ashed again at 550°C over night. To a 50 g of pretreated sample into a 3 liter beaker, 200 mg of Ca carrier, 50 mg of Sr carrier and 0.1 ml of ⁸⁵Sr tracer were added. The sample was dissolved with 500 ml of conc. HCl by heating on a hot plate about 2 hour. The sample filtered and washed the residue with hot water and preserved the filtrate. The residue was redissolved with conc.HCl with stirring, followed by filtering and washing with hot water and transferred the filtrate and washing to the first of filtrate. The filtrate was evaporated to 400 ml and added 1 liter of conc.HNO₃ and evaporated to 100-200 ml. Allowed to cool and diluted to approximately 1500 ml with water. And added 50g of oxalic acid with stirring until the powder was completely dissolved, and adjusted the pH of solution to 5.5-6.0 with 1:1 ammonia water. If the brown color of ferric hydroxide persists, add more oxalic acid and readjust the pH. After several hours the solution was cooled and filtered and the precipitate washed with distilled water. The precipitates and filtering paper were transferred to an appropriate size platinum dish and dried overnight at 100°C and ignited the oxalate precipitate in a muffle furnace at 400-500°C. Continuous heating with slow raising the temperature about to 700°C for 2 hours performed complete ignition of precipitates. After cooled to room temperature the remaining precipitate was dissolved by heating with 20 ml portions of 1:1 HNO₃, and evaporated to completely dryness and the final residue was dissolved with 10 to 20 ml of 3 M HNO₃. In order to perform the chromatographic separations of strontium from soil samples, prepare the Sr.Spec™ column and add 15 ml of 3M HNO₃ to the column and

add 15 ml of M HNO₃ to the column and let it drain out of the column by 1 ml/min. flow rate. Transfer the sample solution using a plastic transfer pipette to the reservoir of the column. Add half and let it drain before adding the rest. Rinse the sample beaker with 3 ml of 3M HNO₃ and add it to the column reservoir after the feed has passed through. Rinse the column three times with 6 ml portion of 3M HNO₃. Let one solution pass completely through the reservoir before adding the next. Rinse the column reservoir with each addition. Record the end time of the last rinse to the nearest 15 minutes as the start of yttrium ingrowth. Elute the strontium with 20 ml of 0.05M HNO₃ into a plastic beaker. Weigh the counting planchet accurate to the nearest tenth of a milligram. Evaporate the strontium eluate onto the planchet under a infrared heat lamp by adding small portions to the planchet and allowing each portion to evaporate to near dryness between additions. Cool the dish and reweigh after all of the solution has evaporated. Calculate the residue weight and the chemical recovery of strontium. Dissolve the precipitate with a small portion of 3M HNO₃ and diluted to 500 ml of plastic container with water. Count the gamma activity of ⁸⁵Sr and calculate the recovery of ⁸⁵Sr and compare the chemical yield of strontium by gravimetric and radiometric method. In order to test the existing of non-retained strontium through the step of loading of sample solution and washing, eluates of each step were collected using with-fractional collector (ISCO retriever 500™) and counted ⁸⁵Sr gamma activity each portions.

RESULTS AND DISCUSSION

To examine the nature of the species extracted, the dependence of distribution ratio (D_M) on the extractant concentration was investigated for Sr, keeping the [HNO₃] constant at 3M. In terms of chemical equilibria, the extraction of these cations by crown ether is described by



The equilibrium constant, K_n , is given by

$$K_n = \frac{D_M}{[\text{DtBuCH18C6}]_{\text{org}}^x [\text{NO}_3^-]_{\text{aq}}^2} \quad (1)$$

with

$$D_M = \frac{[\text{Sr}(\text{DtBuCH18C6})_x(\text{NO}_3)_2]_{\text{org}}}{[\text{Sr}^{2+}]_{\text{aq}}}$$

and it follows

$$\log D_M = \log K_n + 2 \log [\text{NO}_3^-]_{\text{aq}} + x \log [\text{DtBuCH18C6}]_{\text{org}} \quad (2)$$

As seen from equation(2), a plot of $\log D_M$ to $\log [\text{DtBuCH18C6}]_{\text{org}}$ at constant [HNO₃] should be a straight line with a slope equal to the number x of extractant molecules binded to the strontium ions in the crown ether in organic phase [13]. For strontium the slope is near unit (1.15) which indicates the formation of 1 : 1 complexes (Fig. 2). Log K_n values for strontium with crown ether are 1.88, which shows the relatively high extractability of strontium. These facts supports the conclusion that the diameter of the hole in

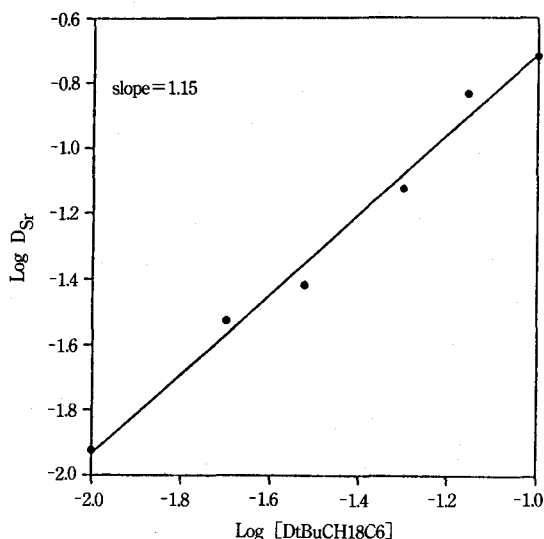


Fig. 2. Log-log plot of the distribution ratio of Sr, D_{Sr} vs crown ether concentration in n-octanol.

DtBuCH18C6 is good enough to accommodate the strontium ions. In order to test the unretained strontium through elution of sample solution, we checked the gamma activity of ^{85}Sr for eluent fractions during the loading of sample solution and washing elution, and calculated with respect to the initial ^{85}Sr tracer activity of the sample vs number of free column volume(F.C.V.). The mixture of 0.1 ml mixed source, which contained the isotopes such as ^{85}Sr , ^{137}Cs , ^{54}Mn and ^{60}Co and 10 mg of Sr carrier, and bulk amounts of Ca(~ 100 mg) was loaded to Sr.Spec™ column in 3M HNO_3 and washed with 3M HNO_3 about 10 F.C.V. and stripped with distilled water for strontium ion. Elution pattern of Sr.Spec™ column chromatography was shown in Fig. 3. This figure shows that the separation of strontium usingwith Sr.Spec™ column material was achieved satisfactorily in 3M HNO_3 and distilled water. There was no strontium activity detection until 24 F.C.V. and stripping of strontium requires only a small volume of distilled water, typically 5–10 F.C.V.(radio-

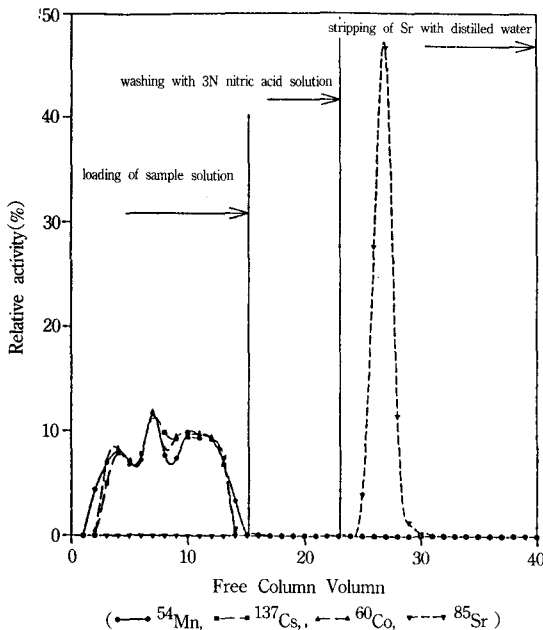


Fig. 3. Chromatographic separation of Sr from mixed-source standard solution, which did not contain interfering ions such as Ba and K.

metric yield was about 95 %) Gravimetric yield of strontium was 93 %. The good agreement of radiometric and gravimetric recovery of strontium shows that strontium was effectively separated from sample solution contains bulk amount of calcium. However, several other cations, most notably potassium and barium, also have diameters which could enable them to fit in the crown cavity. As a result, although the crown ether resin prefers strontium, in the presence of sufficiently large quantities of ions such as potassium and barium, and the extraction of strontium reduced. In order to examine the effects of competing ion upon the retention of an such an ion on a Sp.Spec™ column material, elution fraction of standard solution, which contains bulk amounts of barium, potassium ion (about 50 mg respectively) was evaluated, and calculated the tracer ^{85}Sr activity. In this case, strontium activity was detected in initial stage of elution through loading of standard solution and washing the column. Elution pattern was shown in Fig. 4. The loss of strontium from loading and washing stage was about 13 %. This means that some losses of strontium will occur during the scrubbing

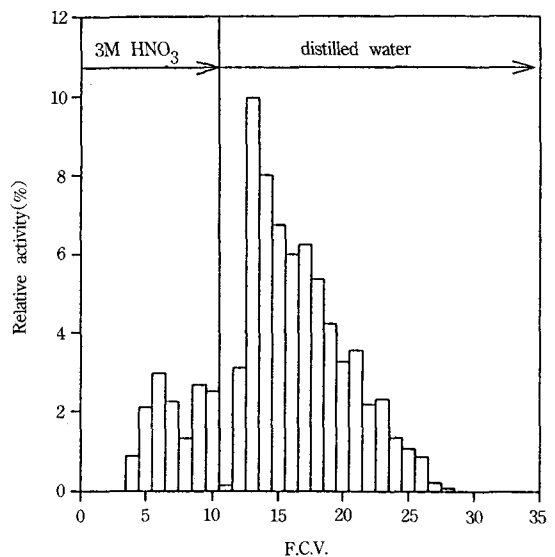


Fig. 4. Elution pattern of Sr when the bulk concentration of K and Ba were added to the solution.

Table 2. Comparison between radiometric and gravimetric recovery of strontium from environmental soil sample with prior removal of K and Ba, and water sample without prior removal of K and Ba.

No. of soil sample	radiometric yield of Sr(%)	gravimetric yield of Sr(%)	No. of water sample	radiometric yield of Sr(%)	gravimetric yield of Sr(%)
1	74.8	74.1	1	95.1	93.1
2	62.0	71.1	2	94.0	93.8
3	73.0	71.0	3	96.5	94.6
4	76.1	72.4	4	95.8	94.1

elution due to the competing role of K and Ba for the crown ether resin. The significant low value of strontium yield (65 %) indicates that the extraction of strontium was reduced due to the presence of interfering ions. Furthermore, much more volume of distilled water (20 F.C.V.) was needed for stripping of strontium than the solution without interfering ions. It follows that a reliable radio analytical separation of strontium by use of Sp. SpecTM crown ether resin requires prior removal of the other interfering ions present in the sample. Removal of the K and Ba can be easily achieved by oxalate and barium chromate precipitation. Table 2 shows the analytical recovery data of strontium from environmental soil with prior removal of the K and Ba and from environmental water without prior removal of such ions. There was good agreement between gravimetric and radiometric yield of strontium. But the total strontium yield was lower than the yield of strontium about water sample. For the water sample, good agreement of strontium yield was achieved even if the water sample was not treated for prior removal of other ions. The contents of other interfering ions in water is relatively small compare to the soil sample and it is possible to think that the role of competing ions in water is less effective than the complicate matrix of soil sample. The separation of strontium by use of Sp. SpecTM was more effectively acquired for water sample than the soil sample. Fig. 5 shows the gamma spectra of multi-nuclides standard solution before and after the passing through

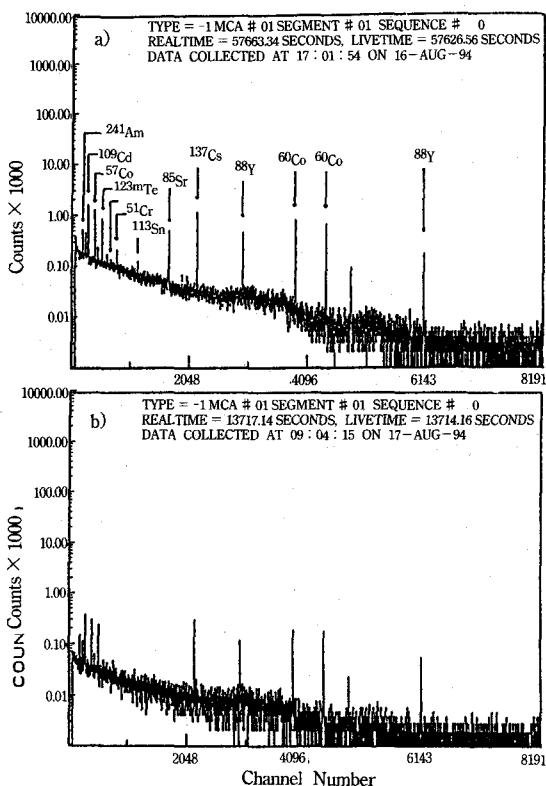


Fig. 5. Gamma spectra of multi-nuclides-mixed standard solution a) before and b) after the passing through Sp.SpecTM column.

Sp.SpecTM column. According to these gamma spectra, the Sp.SpecTM material did show high selectivity for strontium. In particular, the various elements that were present (²⁴¹Am, ^{123m}Te, ⁵¹Cr, ¹¹³Sn, ⁸⁸Y) were not retained on the column. Therefore, the Sp.SpecTM material could provide simple and effective methods for the separation and removal of radiostrontium from nuclear waste solution.

CONCLUSION

The work described here demonstrated that Sp.SpecTM chromatographic material has great capacity of selective binding of strontium ion in nitric acid media. This material has selectivity to permit the separation of strontium from bulk amount of calcium. But the extraction of strontium was reduced by the interfering ions such as K and Ba. So, in order to apply this material to the separation of strontium about environmental soil sample, prior removal treatment of K and Ba was needed. But the Sp.SpecTM material could provide simple and effective methods for the separation and removal of radiostrontium from nuclear waste solution.

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