A rapid separation of Cs, Sr and Ba using gas pressurized extraction chromatography with inductively coupled plasma-mass spectrometry

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(Received March 20, 2024; Accepted March 25, 2024)

Abstract: We present a rapid method for the determination of Cs, Sr, and Ba, heat generators found in highly active liquid wastes, by gas-pressurized extraction chromatography (GPEC) using a column containing a cation-exchange resin. GPEC is a microscale column chromatographic technique that uses a constant flow rate of solvent (0.07 mL/min) with pressurized nitrogen gas supplied through a valve. In particular, because this method uses a small sample volume (a few hundred microliters), it produces less chemical waste and allows for faster separation compared to traditional column chromatography. In this study, we evaluated the separation of Cs, Sr, and Ba using GPEC. The eluate from the column (GPEC or conventional column chromatography) was quantitatively analyzed using inductively coupled plasma-mass spectrometry to measure the column recovery and precision. The column reproducibility of the proposed GPEC system (RSDs of recoveries) ranged from 2.7 to 4.1 %, and the column recoveries for the three elements ranged from 72 to 98 % when aqueous HCl was used as the eluent. The GPEC results are slightly different in efficiency and separation resolution compared to those of conventional column chromatography because of the differences in the eluent flow rate as well as the internal diameter and length of the column. However, the two methods had similar recoveries for Cs and Sr, and the precision of GPEC was improved by two-fold. Remarkably, the solvent volume required for GPEC analysis was five times lower than that of the conventional method, and the total analysis time was 11 times shorter.

Key words: gas-pressurized extraction chromatography, column chromatography, inductively coupled plasma-mass spectrometry, separation, reducing waste, cesium, strontium, barium

1. Introduction

Cesium and strontium, known as heat generators, are found in highly active liquid wastes (HLWs) separated from uranium and plutonium during the reprocessing of spent nuclear fuel in nuclear power plants.[1,2] As radioisotopes, both Cs-137 and Sr-90 have half-lives of approximately 30 years. Their selective separation from the HLWs is crucial for nuclear waste management and environmental remediation.[3,4]

The separation of Sr and Cs present in HLWs is achieved using various methods, including solvent extraction, ion exchange, and precipitation.[2] Further, column chromatography has been investigated for a long time for the quantification of radioactive elements,[5] and inductively coupled plasma-mass spectrometry (ICP-MS) is known to facilitate highly accurate quantification of Cs-137.[6] However, due to the isobaric interference of Ba-137, the quantitative analysis of Cs-137 requires the separation and removal of Ba-137 from the radioactive waste using column chromatography. Additionally, being a group II element, Ba has similar chemical properties to those of Sr. Consequently, the separation of Sr and Ba from their mixtures is highly challenging.[7]

Recently, a gas-pressurized extraction chromatography (GPEC) system was developed to significantly decrease the column volume to minimize the analysis time and reduce chemical waste by utilizing a small volume of the analytical sample.[8-10] This technique offers the advantage of very high precision compared to conventional column chromatography, which relies solely on gravity. The high pressure required for solvent elution due to the small column size of the GPEC can be consistently applied using pressurized nitrogen. In this study, we optimized the eluents for the rapid separation and analysis of Cs, Sr, and Ba using a GPEC column loaded with a cation-exchange resin. The eluate from the column was quantitatively analyzed using ICP-MS. The precisions and recoveries of the column were also evaluated by comparing conventional column chromatography with GPEC to explain the performance of GPEC. In a preliminary study, we used the natural isotopes of three elements, namely Cs-133, Sr-88, and Ba-138, instead of the radioactive isotopes, specifically Cs-137, Sr-90, and Ba-137, to decrease the amounts of unnecessary radioactive waste generated in the experiments.

2. Experimental

2.1. Reagents and materials

The cation-exchange resin used in this study, AG 50W-X12, was purchased from Bio-Rad Laboratories (200−400 mesh, hydrogen form, Richmond, CA, USA). Strontium ICP standard and ultrapure-grade hydrochloric acid were obtained from Merck (St. Louis, MO, USA). Cesium (ICP-12N-0.01X-1) and Barium (ICP-04N-1) were purchased from AccuStandard (New Haven, CT, USA). Ultrapure nitric acid was obtained from Merck (Suprapur 65 %, St. Louis, MO, USA). Deionized water (18 MΩ·cm) was produced using a New Human Power I system (Human Corporation, Seoul, Korea).

2.2. GPEC System and operation

The GPEC system, shown in *Fig.* 1, has been described previously.[11] It consists of three valves, a sample loop, an analytical column, an elution line, and a peristaltic pump. The sample loop and analytical column were made of Teflon tubing (1/16" OD × 0.03" ID, VICI, Houston, TX, USA). A pre-determined volume (270 μL) of the analytical sample was loaded with a peristaltic pump for each sample fraction. The analytical column (25 cm length, 1/16" OD × 0.03" ID) was packed with approximately 0.5 mg of the AG 50W-X12 resin using a syringe. After the preparation of the analytical column, a washing solvent was loaded into the sample loop, and then nitrogen gas was supplied through a valve at a flow rate of 0.07 mL/min. Thereafter, the washing solvent was eluted out of the analytical column. This process, involving the loading and elution of the solvent from the GPEC
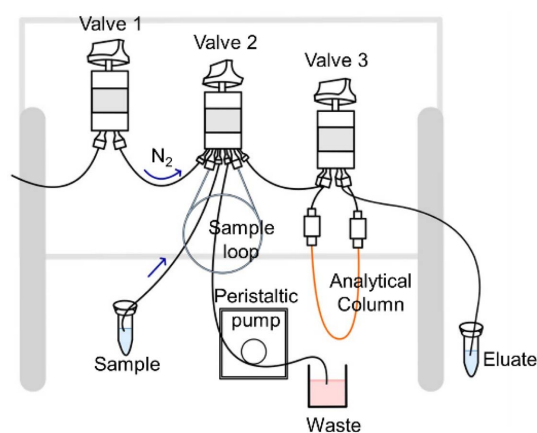

Fig. 1. GPEC system

system, is defined as one cycle or one fraction. Using the same procedure, the column was preconditioned by rinsing three times with 0.5 M HCl or 0.5 M HNO_3. Then, a sample mixture of Sr, Cs, and Ba in 0.5 M HCl or 0.5 M HNO_3 was loaded once, followed by eluents (0.5 M - 6.0 M HCl or 0.5 M - 6.0 M HNO_3). The eluents were successively injected and collected (repeated 20 times with 270 mL per cycle or fraction) from the elution line.

2.3. Conventional column chromatography

A conventional column was prepared by packing a cylindrical glass tube (length: 8 cm, ID: 4 mm) with the AG 50W-X12 resin. One fraction of the conventional column is equal to 1 mL. The analytical procedure was optimized using 1 mL of a sample volume, 5 fractions of 2.5 M HCl, and 15 fractions of 6 M HCl.

2.4. ICP-MS

The fractions collected from the GPEC system were injected into an ICP-MS instrument (SPECTRO MS, Kleve, Germany) for further quantification. The ICP-MS was equipped with a cyclonic spray chamber (Labkings, Hilversum, Netherlands) and seaspray U-series nebulizer (Labkings, Hilversum, Netherlands). The sample solutions for ICP-MS were prepared by diluting the samples collected from the GPEC system to a volume of 5 mL using a 1 % HNO_3 solution. Calibration solutions (concentration range: 1 to 20 ng/mL) were prepared using 1000 μg/mL single-element standards. The operating conditions for ICP-MS are listed in *Table* 1.

Table 1. Operating conditions for ICP-MS

Plasma power	1400 W
Peristaltic pump speed	20 rpm
Coolant Ar gas flow rate	12.0 L/min
Auxiliary Ar gas flow rate	2.3 L/min
Nebulizer Ar gas flow rate	0.93 L/min
Skimmer cone	Ni
Sample cone	Ni
Base interval/Integration time	20 ms/30 s
Measure elements	^{88}Sr, ^{133}Cs, ^{138}Ba
Software	Mass Analyzer Vision

3. Results and Discussion

3.1. Separation mechanism and optimization of the cation exchange resin for the separation of Cs, Sr, and Ba using the GPEC system

AG 50W-X12 is a styrene-divinylbenzene-sulfonic acid resin with sulfonic acid (-SO_3H) functional groups. The proton on the -SO_3H group is exchanged with other cations in the sample solution.[12] According to a previous study by Strelow, the separation factors for Sr and Ba in AG 50W-X12 and AG 50W-X16 were 2.6 and 2.9, respectively.[7] However, when a resin with higher cross-linkage was used, band spreading and tailing occurred due to the considerably slow ion-exchange rates, resulting in increased analysis time. Therefore, we chose the AG 50W-X12 resin, considering its appropriate separation factor for the targeted cations and reasonable analysis time. In ion exchange chromatography, the degree of cation separation on the column depends on the distribution coefficient (K_d). The higher the distribution coefficient, the stronger the adsorption of the cation to the resin. Conversely, the lower the distribution coefficient, the greater the amount of cation remaining in the mobile phase. Strelow calculated the distribution coefficients of Sr and Ba upon the AG 50W-X12 resin using aqueous HCl and HNO_3 solutions as eluents, and the results are shown in *Table* 2.[7]

A greater separation between Sr and Ba using an ion-exchange resin requires a greater difference in the distribution coefficients of Sr and Ba depending on the acid concentration in the eluent. Based on the

Table 2. Distribution Coefficients Sr and Ba upon using the AG50W-X12 resin and acid solutions (HCl and HNO_3)[7]

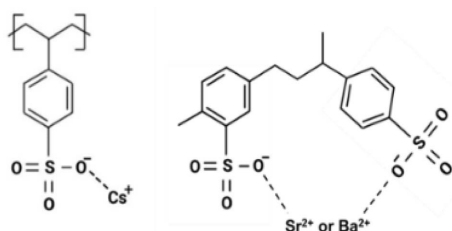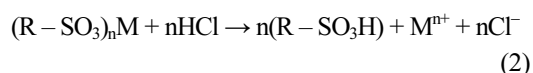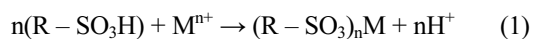| Eluent	HCl		HNO_3	
Normality	Sr	Ba	Sr	Ba
0.1	3040	8900	2940	6300
0.2	960	2960	968	2450
0.5	208	550	221	489
1.0	69	175	66	127
2.0	22	58	16.2	28.6
3.0	12	29.8	7.1	7.5
4.0	8.1	19.9	4.2	3.8

Fig. 2. Interaction mechanism between the cation-exchange resin and three metal cations.

results in *Table* 2, it was determined that the HCl solution was more effective than HNO$_3$ in separating Sr and Ba. We compared the separation of Cs, Sr, and Ba on the GPEC system using 0.5–6.0 M aqueous HCl and HNO$_3$ solutions as eluents. The separation mechanism of the three metal cations (M^{n+}) using the AG 50 W-X12 resin with sulfonic acid groups and HCl solutions is as follows: the protons in the sulfonic groups (R–SO$_3$H) of the resin are exchanged with the metal cations in the solution. As the solution containing metal species passes through the column, the metal ions are exchanged for hydrogen ions on the resin, as represented by Eqs. (1) and (2).[13] The interactions between the resin and each of the three cations are shown in *Fig.* 2.

$$n(R - SO_3H) + M^{n+} \rightarrow (R - SO_3)_nM + nH^+ \qquad (1)$$

$$(R - SO_3)_nM + nHCl \rightarrow n(R - SO_3H) + M^{n+} + nCl^- \qquad (2)$$

First, we used aqueous HNO$_3$ as the eluent and varied its concentration in each section to separate the three cations. The column was eluted with 2.5–6.0 M HNO$_3$ solutions, resulting in the separation of Cs and Sr. However, Sr and Ba were only partially coeluted and they did not separate completely (see *Fig.* 3). Further, as shown in *Fig.* 4, Cs and Sr could be separated using HCl solution as the eluent as well. We expected that Sr and Ba would also separate under this condition. Therefore, we optimized the HCl concentration in the eluent to successfully separate all three cations (Cs, Sr, and Ba), and the results are shown in *Fig.* 5. Eventually, using 2.5 and 6.0 M HCl solutions as eluents for a defined section, the analysis time was shortened, and the complete separation of
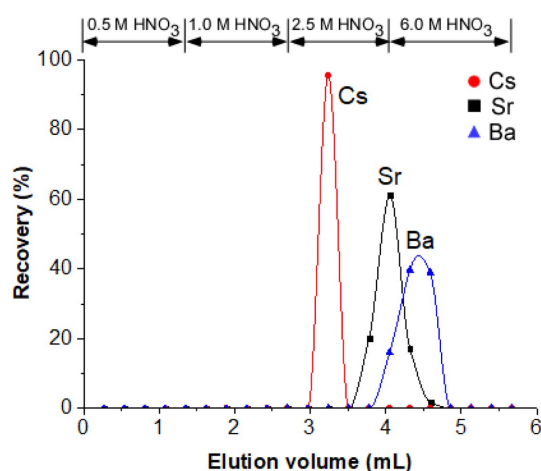

Fig. 3. Separation of Cs, Sr, and Ba by GPEC depending on HNO$_3$ concentration in the eluent. Other conditions as experimental section
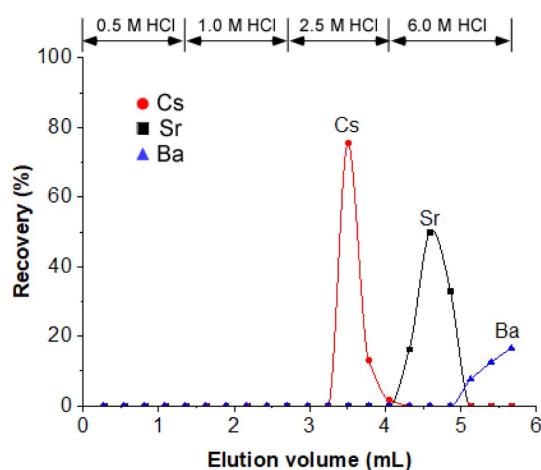

Fig. 4. Separation of Cs, Sr, and Ba by GPEC depending on the concentration of HCl. Other conditions as experimental section.

Sr and Ba was achieved. For the separation of Cs, Sr, and Ba on the GPEC system, the total volume of the eluent required is 4.3 mL, and the overall elution time, based on a flow rate of 0.07 mL/min, is approximately 60 min. When radioactive elements Cs-137 and Ba-137 are used, Cs and Ba cannot be distinguished from each other in ICP-MS. However, by using GPEC, they can be completely separated as shown in *Fig.* 3, and each eluate can be quantified and analyzed in ICP-MS.
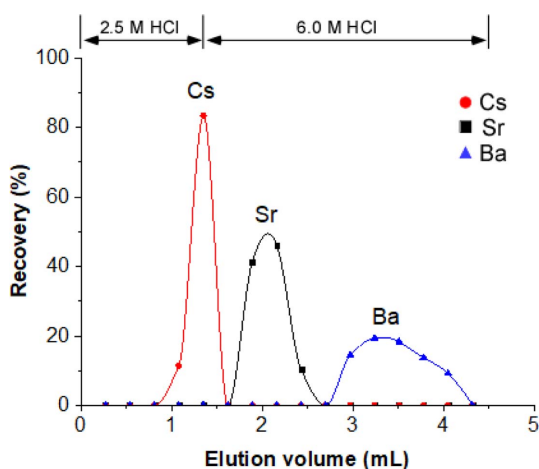
Fig. 5. Optimization of the separation of Cs, Sr, and Ba by GPEC by varying the concentration of HCl Other conditions as experimental section.

Table 3. Recovery and reproducibility of GPEC

GPEC	Sr	Cs	Ba
Column Recovery[a] (n = 4, %)	98	95	72
RSD (n = 4, %)	3.9	4.1	2.7

[a]Recovery (%) is calculated as follows: Measured analyte concentration/Original sample concentration) × 100

3.2. Column recovery and reproducibility of separation of Cs, Sr, and Ba using GPEC with ICP-MS

Having optimized the experimental conditions (*Fig.* 5), we evaluated the reproducibility (RSDs) and recovery of the column in the GPEC system. Recovery is defined as the amount of analyte eluted through the column relative to that in the original sample. Column recovery was calculated from the value obtained by the quantitative analysis of the eluates from the column using ICP-MS. *Table* 3 shows that >95 % recovery was achieved for Sr and Cs for GPEC conducted using the AG50W-X12 resin; however, the recovery of Ba was relatively low. The RSDs ranged from 2.7 % to 4.1 % (see *Table* 3).

3.3. Comparison between conventional column chromatography and GPEC

For comparison, we also conducted conventional column chromatography to separate Cs, Sr, and Ba
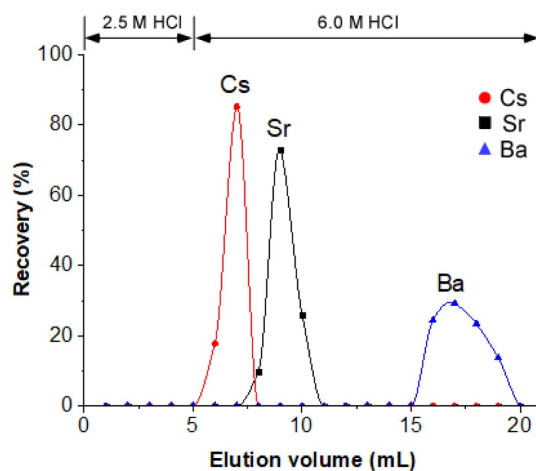

Fig. 6. Separation of Cs, Sr, and Ba by conventional column chromatogrpahy depending on HCl concentration. Other conditions as experimental section.

using a glass column of 8 cm length and 4 mm ID. In conventional column chromatography, 1 mL of the eluent was used as a one-time fraction volume. *Fig.* 6 shows the results of conventional column chromatography in the separation of the three cations. The flow rate was 0.03 mL/min, the eluent volume used for the overall analysis was 20 mL, and the total analysis time was approximately 670 min, which is more than 11 times the analysis time of GPEC. Notably, the column volume of GPEC is 2.5 times lower than that of conventional column chromatography, and it also has different lengths and inner diameters compared to conventional column chromatography. However, the pressure required for GPEC is 200 times greater than that for gravity separation. This is calculated by Eq. (3), where column pressure (*P*) is determined by the flow rate (u_x), solvent viscosity (η), column length (L), colun radius (r), particle diameter (d_p), and specific permeability (*f*).[14]

$$P = f \frac{u_x \eta L}{\pi r^2 d_p^2} \tag{3}$$

The advantage of GPEC is that a constant pressure can be applied using pressurized nitrogen gas, which enables faster analysis, potentially leading to lower RSD values compared with those of conventional column chromatography. As shown in *Table* 4, the

Table 4. Recovery and reproducibility of conventional column chromatography

Conventional method	Sr	Cs	Ba
Column Recovery (n = 4, %)	109	103	91
RSD (n = 4, %)	8.0	8.5	9.0

RSD (reproducibility) in the case of conventional column chromatography ranged from 8 % to 9 %, which is approximately twice that of GPEC. The separation conditions of the two devices are different in terms of the column length, ID, and linear flow rates. Therefore, according to the van Deemter equation, they may affect eddy diffusion and the capacity factor based on a low flow rate.[14] Therefore, conventional column chromatography exhibited 1.3–3.6 times higher efficiency and resolution (R) for Ba and Sr, resulting in an R(Sr/Ba) value of 1.8, which is superior to that achieved with the GPEC method (R = 0.9). However, the total analysis time was more than 10 times longer compared to GPEC.

4. Conclusions

Cs, Sr, and Ba were separated using GPEC by adjusting the concentration of HCl in the aqueous eluent, as specified for a discrete section. Compared with conventional column chromatography, the column recovery was similar for Cs and Sr, with the exception of Ba. Nevertheless, GPEC provided more than double the precision. In addition, the total analysis time could be shortened by 11 times, and the three elements could be analyzed using only 4 mL of the eluent, which corresponds to five times reduction in solvent usage compared with the conventional method. GPEC conducted using constant nitrogen pressure provides superior precision and accuracy compared to general methods that rely on gravity. In particular, when analyzing radioactive substances using GPEC in the future, the amount of the radioactive waste can be reduced by more than five times compared to that used in the conventional method, making it a method that would enable faster analysis. In addition, GPEC can be applied as a powerful analysis method to replace conventional column chromatography as a separation technique, or as a pretreatment technique when measuring a substance is challenging due to isobaric interferences in ICP-MS.

Acknowledgements

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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