

Dicyclohexyl-24-crown-8과 Tetraphenylborate에 의한 원자로 냉각수로부터 세슘 핵종의 이온쌍 용매추출

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Ion-Pair Extraction of Cs Radionuclides by Dicyclohexyl-24-crown-8 and Tetraphenylborate for Their Determination in Reactor Coolant

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요 약. 가압형 경수로의 일차 냉각수로부터 세슘 핵종을 선택적으로 분리하여 그 방사능을 결정하기 위한 Scheme이 연구되었다. 세슘의 분리는 dicyclohexyl-24-crown-8과 sodium tetraphenylborate에 의한 이온쌍 용매추출에 의해서 이루어졌으며 추출에 미치는 수소, 세슘, 나트륨 및 borate 이온의 영향이 연구되었다. 요오드와 크세논 핵종의 방해 현상은 각각 티오황산나트륨에 의한 요오드의 환원과 1 N 염산수용액에 의한 역추출에 의해서 제거될 수 있었다.

ABSTRACT. A study has been carried out for a scheme of the selective extraction and determination of cesium nuclides by the ion association with dicyclohexyl-24-crown-8 and sodium tetraphenylborate from primary coolant of a pressurized water reactor. For that purpose, the effects of hydrogen, cesium, sodium and borate ions on the extraction have been investigated. Interferences of iodine and xenon nuclides were found but could be removed by reducing with sodium thiosulfate and back extraction with 1 N hydrochloric acid solution, respectively.

INTRODUCTION

The primary coolant of a pressurized water reactor such as Kori unit 1 contains various radionuclides as fission products. The activities of fission products are routinely determined for their contents in the coolant because their variations are closely connected with the degree of defects of fuel rods under normal operation.

But, since the activities of ^{134}Cs and ^{137}Cs among those fission products are relatively small compared to Compton interference of some other fission products, the exact determination of them is almost impossible without chemical treatment or control of decay time. Therefore, the simple separation and determination of cesium nuclides are highly desirable for the coolant containing boric acid and lithium hydroxide which are

added for the control of neutron flux and pH, respectively.

Many crown reagents, macrocyclic polyether such as DC24C8(dicyclohexyl-24-crown-8) and DC18C6(dicyclohexyl-18-crown-6), have been synthesized, recently, because of their unique ability to form organic soluble cationic complexes with alkali and alkaline earth cations¹. Although various studies for complexation properties of the compounds have been carried out, the use of these reagents in the specific separation for the analysis of the elements has been lacking^{2,3}. Cesium ion can be predictable to make an organic soluble complex more effectively with DC24C8 by considering ionic and cavity sizes of various cations and crown ethers⁴, respectively.

In this work, a selective extraction of cesium radionuclides has been tried for their determination in primary coolant of pressurized water reactor using DC24C8 as a complexing agent. For the ion-pair formation with Cs-DC24C8 cation, tetraphenylborate ion has been used as the corresponding anion. The formed ion-pair has been extracted into chloroform, which is adopted by previous authors³.

EXPERIMENTAL

Reagents. Dicyclohexyl-24-crown-8 was obtained from the Parish Chemical Company and used without further purification. An accurately weighed amount of the reagent was dissolved in a volume of chloroform which has been previously equilibrated with aqueous phases of appropriate pH, diluted to $1 \times 10^{-2}M$ using the chloroform and used as organic phases. The tracer of ¹³⁴Cs was prepared by irradiating an appropriate amount of cesium chloride at the rotary specimen rack of TRIGA mark III and by diluting with distilled water. Sodium tetraphenylborate and other chemicals were reagent

grade.

Apparatus. The gamma-ray spectrometry was made with a 8100 channel analyzer which was connected to a Ge(Li) detector and a computer system(CANBERRA PdP 11/04). A well type NaI(Tl) scintillation counter(BAIRD Model 810s) was also used for activity measurement. The hydrogen ion concentration was measured with an Orion Model 510 pH meter.

Extraction of Cs⁺ vs. pH. To measure the extraction of cesium ion as a function of pH, aqueous solutions of various pH were prepared as follows.

Appropriately concentrated solutions of sodium tetraphenylborate were mixed with constant volumes of cesium chloride (tagged with ¹³⁴Cs) and boric acid solutions of given concentration. The mixed solutions were diluted to near volume in volumetric flasks of 25ml capacities with distilled water. Referring to that the hydrogen ion concentration of these solutions gave pH 5, small amounts of hydrochloric acid were added to the solutions to obtain the final hydrogen ion concentration below pH 5. For the hydrogen ion concentration above pH 5, an appropriate volume of 0.1M lithium hydroxide solution was added to adjust pH. The solutions were finally diluted to the volume by adding distilled water and used as an aqueous phase of various pH. The concentrations of cesium ion, boric acid and tetraphenylborate in the solutions were $2 \times 10^{-4}M$, $5 \times 10^{-2}M$ and $1 \times 10^{-2}M$, respectively.

A 5ml volume of the aqueous phase of given pH was mixed with the equal volume of the organic phase of the same pH in a bottle of 30ml capacity. This solution has been equilibrated in a thermostat of $25 \pm 1^\circ C$ by shaking for 15 min on a wrist-action shaker which was obtained from the Griffin and George Co. Two phases were separated after standing for about 2 hours. A 2ml volume of each phase was ta-

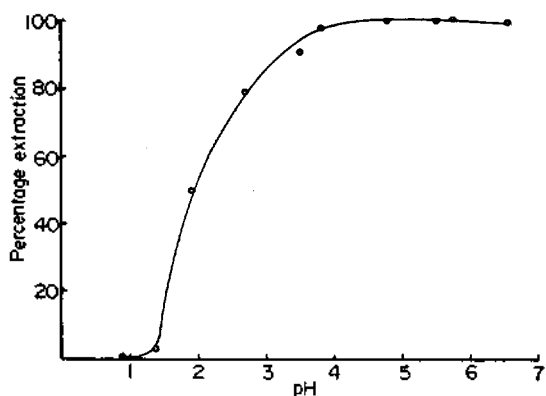


Fig. 1. Percentage Extraction as a Function of pH

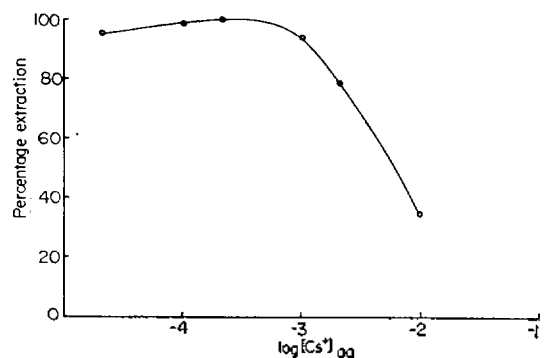


Fig. 2. Percentage Extraction of Cs^+ vs. its Concentration.

ken into a test tube and counted for the gamma-rays of ^{134}Cs by the well type scintillation counter. The activity ratios were calculated and averaged for plotting a curve of percentage extraction as a function of pH as shown in Fig. 1.

Extraction of Cs^+ vs. Its Concentration. A 5ml volume of each phase, which contain various concentrations ($1 \times 10^{-5} \sim 1 \times 10^{-2} M$) of cesium ion tagged with ^{134}Cs but constant concentrations of hydrogen ion (pH 6.5), and boric acid ($5 \times 10^{-2} M$) and tetraphenylborate ($1 \times 10^{-2} M$), was treated with an equal volume of organic phase as described above. The activity ratios were determined for plotting a curve of percentage extraction as a function of Cs^+ concentration as shown in Fig. 2.

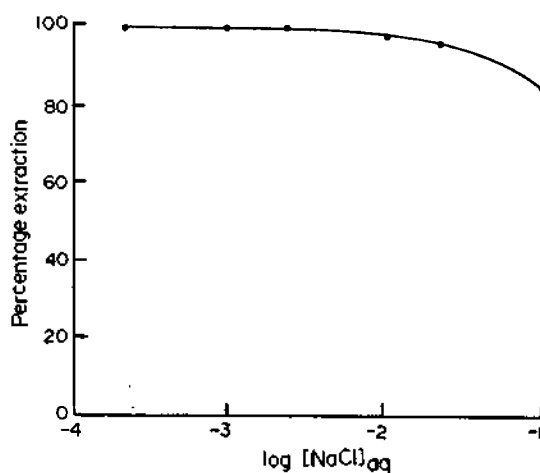


Fig. 3. Percentage Extraction of Cs^+ as a Function of Total Sodium Ion Concentration.

Extraction of Cs^+ vs sodium ion Concentration. Aqueous phases were made as wide variable in concentrations of, total sodium ion as $2 \times 10^{-2} \sim 1 \times 10^{-1} M$, but constant in other concentrations, *i. e.*, $1 \times 10^{-2} M$, $2 \times 10^{-4} M$ and pH 6.5 in sodium tetraphenylborate, in cesium ion tagged with ^{134}Cs and in hydrogen ion, respectively. A 5ml volume of the aqueous phase was equilibrated with an equal volume of organic phase as described above for plotting a curve of percentage extraction against total sodium ion concentration as shown in Fig. 3.

Interference of Borate Ion and Sodium Thiosulfate. Aqueous phases were made as variable in concentrations of borate ion as $4.9 \times 10^{-2} \sim 5.2 \times 10^{-1} M$ which is added as boirc acid form, but constant in the other ion concentrations, *i. e.*, $1 \times 10^{-2} M$, $2 \times 10^{-4} M$ and pH 6.5 in sodium tetraphenylborate, in cesium ion tagged with ^{134}Cs and in hydrogen ion concentration, respectively. An aliquot of aqueous phase was treated similarly as described above. The activities of each phase were estimated for the percentage extraction and the results are given

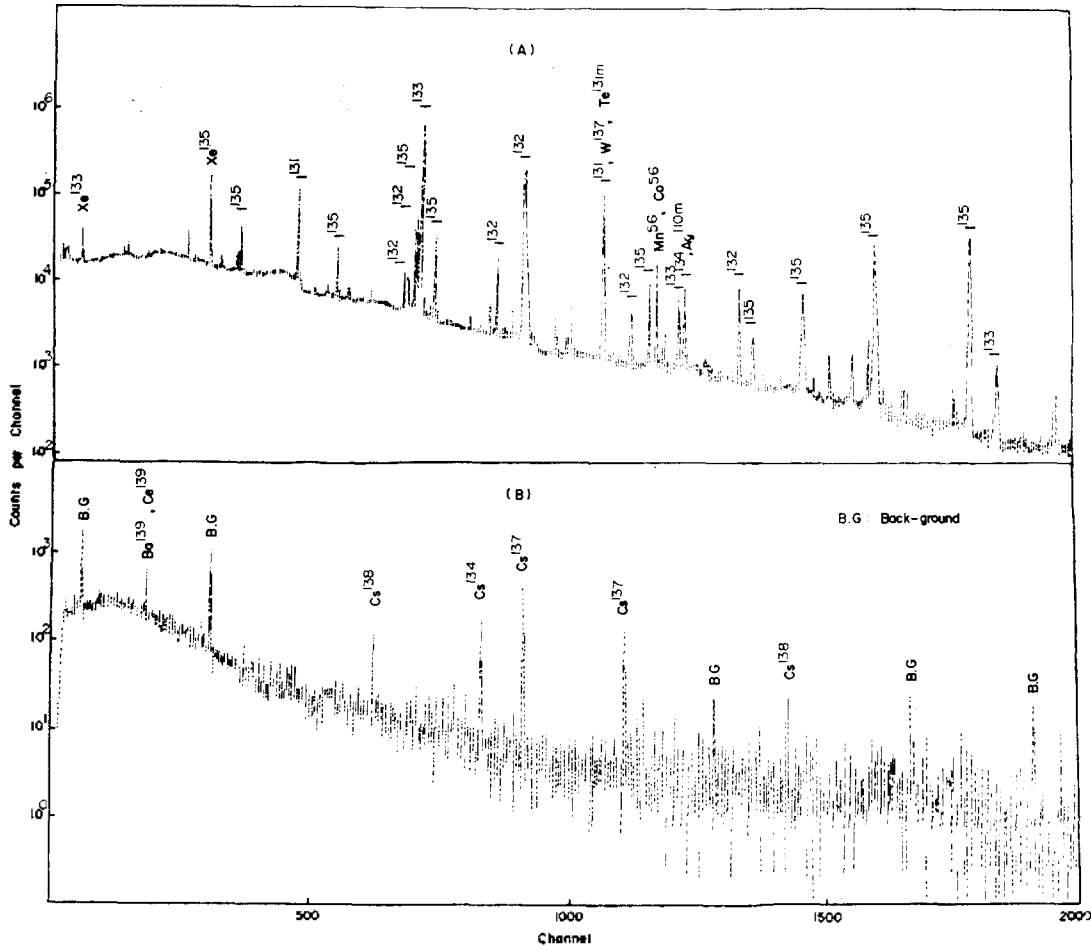


Fig. 4. Typical Gamma-ray Spectrum: (A) Gamma-ray Spectrum obtained without Separation, (B) Gamma-ray Spectrum obtained after Separation.

Table 1. Effect of borate ion concentration on the extraction of Cs-DC24C8-tetraphenylborate.

Molarity of borate ion	Activity of aq. phase (counts/10 min.)	Activity of org. phase (cpm)	Percentage extraction
4.9×10^{-2}	340	7595	99.6
8.6×10^{-2}	352	7653	99.6
1.7×10^{-1}	343	7529	99.5
2.6×10^{-1}	291	7620	99.6
3.4×10^{-1}	420	7612	99.4
4.3×10^{-1}	394	7592	99.5
5.2×10^{-1}	462	7601	99.4

Table 2. Effect of $\text{Na}_2\text{S}_2\text{O}_3$ concentration on the extraction of carrier free ^{131}I (activity of $^{131}\text{I} : 4 \times 10^{-1} \mu\text{Ci/ml}$).

Molarity of $\text{Na}_2\text{S}_2\text{O}_3$	Activity of aq. phase (cpm)	Activity of org. phase (cpm)	Distribution ratio
1.0×10^{-2}	23964	236	9.8×10^{-3}
5.0×10^{-3}	24035	156	6.4×10^{-3}
1.0×10^{-3}	23734	155	6.5×10^{-3}
5.0×10^{-4}	23695	135	5.6×10^{-3}
1.0×10^{-4}	23873	206	8.6×10^{-3}
less than 5×10^{-8}	8073	15352	1.9×10^0

in Table 1.

In the direct extraction of cesium radionuclides from coolant, iodine nuclides such as ^{131}I ,

^{132}I , ^{133}I , ^{134}I , and ^{135}I were extracted into the organic phase and gave an interference when counting subsequently. It was confirmed by tracer works that the interference of iodine could, however, be eliminated by reducing various iodines to I^- on the basis of the procedures given by Kolthoff et al⁵ as shown below. Aqueous solutions were made variable in the concentration of sodium thiosulfate but the same as given above in other concentrations. To the solutions a $100\mu\text{l}$ volume of ^{131}I tracer (about $4 \times 10^{-1} \mu\text{C}/\text{ml}$) was spiked. A 5ml volume of each aqueous solution was equilibrated with equal volume of organic phase as described above. The activities of each phase were estimated for the distribution ratios of the radionuclides. As shown in Table 2, most iodine is reduced and remained in aqueous phase by adjusting the concentration of sodium thiosulfate more than $1 \times 10^{-4} M$.

To measure the influence of sodium thiosulfate concentration on the extraction of cesium, aqueous phases were made such a variable concentrations as $5 \times 10^{-4} - 1 \times 10^{-2} M$ in sodium thiosulfate, but constant in other ion concentration, i. e., $1 \times 10^{-2} M$ and $2 \times 10^{-4} M$ in sodium tetraphenylborate and in Cs^+ tagged with ^{134}Cs ,

respectively. An aliquot of aqueous phase was treated similarly as described above. The activities of each phase were estimated for the percentage extraction and the results are given in Table 3.

RESULTS AND DISCUSSION

Cesium ion is quantitatively extracted in the pH range 4–7 as shown in Fig. 1. The pH 5.5~7 was chosen as optimum pH range for the quantitative separation of cesium in this work.

The percentage extraction of cesium ion was plotted as a function of its concentration as shown in Fig. 2, which shows quantitative extraction of Cs^+ in the range $1 \times 10^{-4} \sim 2 \times 10^{-3} M$ of its concentration. The concentration of Cs^+ , $5 \times 10^{-4} M$, was, therefore, taken as an optimum concentration and total Cs^+ content was adjusted to this value. The influence of sodium ion in the extraction was negligible when its total concentration is below $0.01 M$ as shown in Fig. 3. Boric acid is contained in a wide range of its concentration and acts as neutron flux controller. The dependence of Cs^+ extraction on the concentration of borate ion was examined and given in Table 1. The results show that the extraction is quantitative over a wide range of borate ion concentration. The coolant contains iodine radionuclides such as ^{131}I , ^{132}I , ^{133}I , ^{134}I and ^{135}I in various chemical forms. The interference of the radionuclides could be eliminated with reduction of iodine to I^- form by adjusting sodium thiosulfate concentration more than $1 \times 10^{-4} M$ in aqueous phase as shown in Table 2 and 3.

The inert radiogases such as ^{131}Xe and ^{135}Xe were contained in the coolant and could not be removed completely by boiling, which is usually applied in the practical works. Some of them were found to be extracted into organic phase and gave an interference on the subse-

Table 3. Effect on $\text{Na}_2\text{S}_2\text{O}_3$ concentration on the extraction of $\text{Cs-DC24C8-tetraphenylborate}$.

Molarity of $\text{Na}_2\text{S}_2\text{O}_3$	Activity of aq. phase (cpm)	Activity of org. phase (cpm)	Percentage extraction
1.0×10^{-2}	1001	31486	96.9
5.0×10^{-3}	678	31313	97.9
1.0×10^{-3}	226	31931	99.3
5.0×10^{-4}	140	31130	99.5
1.0×10^{-4}	101	31902	99.7

quent counting. By examining gamma-ray spectra, it was found that the interference was, however, completely eliminated by back extraction with 1 N hydrochloric acid solution in the present work. The back extraction was found to be quantitative in the collection of cesium nuclides, which is also predictable from the results in Fig. 1.

Some other alkali-metal nuclides such as ^{88}Rb and ^{89}Rb were found to be coextracted with cesium ion, but did not give any interference because of their short half lives.

As shown in Fig. 3, the influence of sodium ion in the extraction of cesium was negligible when its concentration is below than 0.01M. Considering that the radius of lithium ion is even smaller than that of sodium ion, the influence of the former can be assumed negligible. In order to check further the accuracy of the present method, a known amount of ^{134}Cs tracer was added to the 5ml volume of simulated aqueous solution of pH 6.5 which is obtained from actual coolant through the experimental procedures set up as described above. The same experimental procedures were repeated for the recovery of the added known amount of ^{134}Cs tracer into an aqueous solution. It was found that the recovery was more than $96 \pm 5\%$.

A separation scheme has been set up for the determination of Cs radionuclides in primary coolant of pressurized water reactor on the bases of above experimental results.

An extraction Scheme for the Determination of Cesium in Reactor Coolant. A 1ml volume of primary coolant, which gave such a spectrum as shown in Fig. 4 (A), was taken into a 50ml beaker and mixed with 10ml of distilled water. A 1ml volume of $5 \times 10^{-3}\text{M}$ cesium carrier solution was added and boiled for 10 min. to remove inert radiogases. The solu-

tion was transferred into a 25ml volumetric flask and 10 ml volume of $2.5 \times 10^{-2}\text{M}$ sodium tetraphenylborate and 1ml volume of $1.25 \times 10^{-2}\text{M}$ sodium thiosulfate solution. The solution was diluted to near volume and adjusted to pH 6~7 by adding dropwise 0.1M lithium hydroxide solution. The final concentrations of cesium, tetraphenylborate and thiosulfate ions in the solution were $2 \times 10^{-4}\text{M}$, $1 \times 10^{-2}\text{M}$ and $5 \times 10^{-4}\text{M}$, respectively.

A 15ml volume of the solution was taken into the separatory funnel of 50 ml capacity and equilibrated with 15ml of organic solution of pH 6.5 for about 15 min. The two phases were separated by standing for about 2 hours. The cesium radionuclides in the organic phase were back-extracted into a 10ml volume of 1N hydrochloric acid solution and counted for gamma-rays. A typical gamma-ray spectrum thus obtained is given Fig. 4(B) and show small interference from ^{139}Ba due to its formation of a complex with DC24C8 as described by previous authors². However, this interference is not significant on the determination of cesium radionuclides because of its low energy and such low activities as less than 0.5%.

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