Determination of Pu Isotopes in Seawater by an On-Line Sequential Injection Technique with Sector Field Inductively Coupled Plasma Mass Spectrometry

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An on-line sequential injection (SI) system combined with sector field inductively coupled plasma mass spectrometry was developed for the determination of ultratrace level ^{239}Pu and ^{240}Pu in seawater. The potential of this method is the substantial reduction of a sample volume and rapidity in the determination of Pu isotopes. A chemical purification and preconcentration of Pu isotopes were accomplished by the on-line SI system with two micro-columns of solid-phase extraction resins, Sr-Spec and TEVA-Spec. The MCN-6000 microconcentric nebulizer was used as a sample introduction system because of low interference effect and good sample utilization. With this method, it was possible to analyze ultratrace levels of Pu isotopes in only 5 L of surface seawater with an analysis speed of 4 h/sample. The precision of the measurement for the ^{239}Pu and ^{240}Pu was less than 3.4 ($n = 7$) and 5% ($n = 7$) for 5 L of seawater. The detection limits for ^{239}Pu and ^{240}Pu were 0.64 (1.5 μBq/mL) and 0.19 fg/mL (1.6 μBq/mL), respectively. The accuracy of this method was verified by using the reference seawater (IAEA-381) as well as by the comparison with the α-spectrometry.

From the viewpoint of toxicity and radiation effect to the human being, Pu is one of the most important transuranic elements that have been released into the environment. Although lots of Pu is released into the environment due to nuclear weapon tests and a few nuclear accidents, the concentration of Pu in seawater is very low at a level of femtograms per milliliter compared to other types of environmental samples.[1,2] Accordingly, large-volume sampling and labor-intensive pretreatment are necessary to get credible results for Pu in seawater. Conventional α-spectrometry, which is the most widely used to measure the radioactivity of Pu, generally requires at least more than 60 L of seawater and a long counting time of a couple of days. Moreover, it is almost impossible to measure the ^{239}Pu and ^{240}Pu isotopes independently unless a very sophisticated high-resolution α-spectrometry is used owing to the small difference in their α-radiation energy.

Recently, inductively coupled plasma-mass spectrometry (ICPMS) has been applied widely to the measurement of Pu isotopes.[3−5] This technique overcomes the demerits of the radiometric method with the rapid development of advanced ICPMS technologies. Especially, sector field ICPMS (SF-ICPMS) can detect Pu at the femtogram per milliliter level with very low detection limit and an improved sample introduction system.[6−8] However, even SF-ICPMS requires more than several tens of liters of sample to obtain quantitative Pu data in seawater. In addition, Pu in the sample must be sufficiently purified from other interference elements such as U and Pb and bulk elements that exist in seawater to avoid polyatomic (^{238}UH/^{239}Pu, ^{204}Pb^{35}Cl/^{239}Pu, ^{204}Pb^{36}Ar/^{240}Pu, ^{207}Pb^{35}Cl/^{242}Pu) and spectral (^{238}U/^{239}Pu) interferences encountered in the measurement of Pu isotopes.[9−11] Unless sufficient chemical purification is performed, the interferences may induce severe error in the quantification of Pu isotopes in seawater. Solid-phase extraction chromatography using actinide-specific resins has been successfully utilized in the separation of Pu from interfering elements.[12−15] To shorten the analysis time

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and automate the chemical separation, diverse on-line sequential injection (SI) techniques have been recently developed for the analysis of actinides.[16,17] However, most methods developed have been focused either on the analysis of highly radioactive samples such as nuclear waste and reactor samples or on the analysis of other environmental samples contaminated with Pu. Accordingly, an on-line SI method for the analysis of Pu in seawater is important in the aspect of lightening the burden of sampling and labor-intensive analysis work.

In our previous studies,[18] an on-line SI system associated with SF-ICPMS was successfully applied for the determination of [239]Pu and [240]Pu concentrations and its atomic ratio in soil samples at a global fallout level. With this method, it was possible to determine ultratrace levels of Pu in only 1 g of soil or sediment with an analytical throughput of a single sample per 5 h. Our method drastically reduced the required sample amounts and the analysis time in the environmental Pu analysis. The sequential separation adapted in an on-line system was excellent in the elimination of U, which is the most potential interference element in measurement, as well as concentrating the Pu directly through the secondary microcolumn. For seawater, however, the level of Pu and the matrix system is totally different from that of the soil. Accordingly, a new method suitable for the seawater sample should be designed for the loading of sample preparation and on-line purification process.

The aim of the present study was to develop a rapid determination method for Pu in seawater using an on-line SI-SF-ICPMS system. Although this system was based on the previous technique, several parts of the system were modified through this work. Moreover, the precision and reproducibility of this method were carefully examined with a reference material and some test samples. Finally, this method was applied to the determination of Pu in the surface seawater.

EXPERIMENTAL SECTION

Instrumentation. All measurements were performed on a PlasmaTrace2 sector field inductively coupled plasma mass spectrometry (Micromass, Manchester, U.K.). A microconcentric nebulizer (MCN-6000, Cetac Technologies) coupled with the perfluoralkoxy (PFA) nebulizer-100 was used as a sample introduction system. The T1 nebulizer in MCN-6000 was replaced with PFA nebulizer-100 (CPI International) that is better in precision and robust for long-term use. The microautosampler (ASX-100, Cetac Technologies) has played the role of transporting the final elution from the on-line purification system to the MCN-6000.

Figure 1 is a schematic diagram of the SI system, which consists of two liquid handing systems of PrepLab (Fison, Machester, U.K.) and subsidiary Rheodyne model 5041 two-way, six-port valves (Rheodyne, Cotati, CA). PepLab is composed of two six-way valves having six ports, two two-way isolation valves, and two peristaltic pumps. All the actuation mode and working time of each part in PrepLab were programmed using Gilson language in the SF-ICPMS main operating program (Prestige). The switching and working time of the Rheodyne two-way, six-
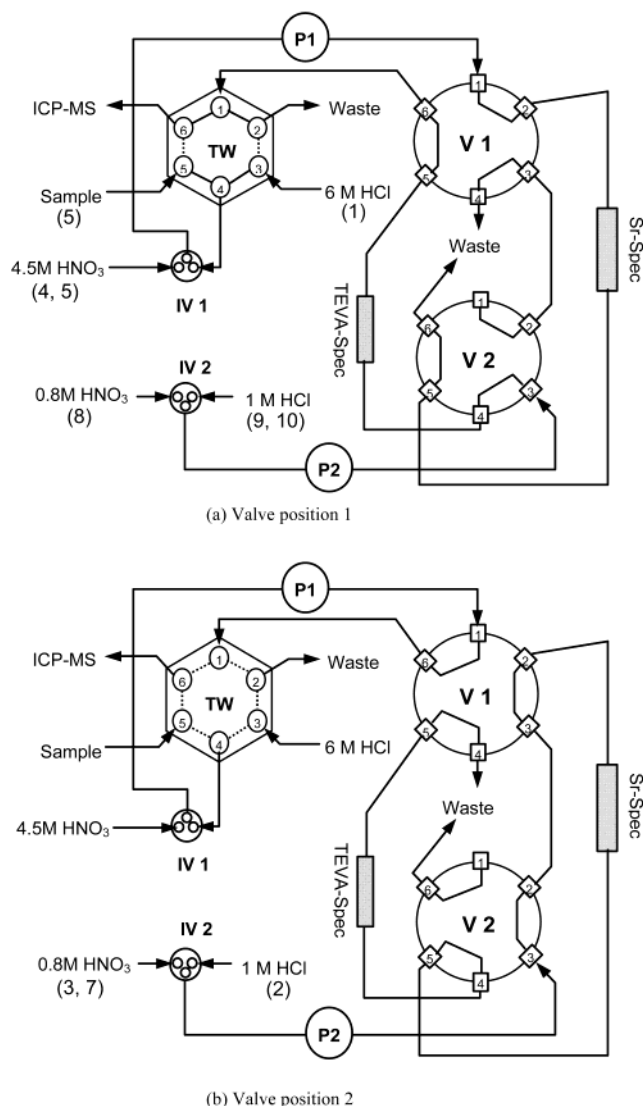
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Figure 1. Schematic diagram of the on-line SI system showing the tubing arrangement and specific resin positions: P1 and P2, peristaltic pumps; V 1 and V 2, six-way valves; TW, two-way valves; IV 1 and IV 2, isolation valve. The circled number means the procedure order described in Table 1.

port valves was also programmed by a laboratory-made control system according to the operation of PrepLab. Peristaltic pumps 1 and 2 of PrepLab were initially set at 1.6 and 0.83 mL/min by the peristaltic pump speed controller, respectively.

Two columns, a 6.6 mm i.d. × 25 mm long borosilicate column (Omnifit, Cambridge, England) and a 1.8 mm i.d. × 20 mm long PEEK column (modified/laboratory-made) were sequentially combined between the two systems. The first large column was packed with Sr-Spec resin, and the secondary minicolumn was packed with TEVA-Spec resin (Elchrom Industries, Inc., Darien, IL). The free column volumes (FCV) of the two columns were approximately 750 and 50 μL, respectively. All transport and reagent lines used to construct the manifold were made of 0.8-mm-i.d. polytetrafluoroethylene (PTFE) tubing (Upchurch Scientific, Oak Harbor, WA), except the peristaltic pump tubing (0.95-mm i.d., Tygon), which was directly connected to the barb fitting of the isolation valve. For the purpose of comparison with this

work, radiometric measurement of Pu was also performed using 440-mm² Canberra passive implanted planar silicon detectors in α-spectrometry (OASIS, Oxford Inc., Oak Ridge, TN) equipped with Oxford electronics and data acquisition system. The electrodeposited samples were counted at the position of 3 mm below detector and the counting efficiency was ∼27% at the position.

Instrumental conditions in MCN-6000 were set to guarantee high sensitivity and good precision under the optimum ICPMS acquisition conditions. The measurement was carried out by quantitative acquisition mode in the instrument operating software Prestige version 1.21.

Reagents and Materials. High-purity water (18 MΩ/cm) prepared by a Milli-Q Plus System (Millipore, Bedford, MA) was used for all reagent dilutions. Superpure HNO_3 and HCl (AA-100, Tama Chemicals) were used as a rinsing solution and an eluent in SI system. Electronic grade concentrated HNO_3 and HCl (Dongwoo Pure Chemicals, Iksan, Korea) were also used in the acid extraction of Pu and preconditioning of the Sr-Spec resin. The Sr-Spec and TEVA-Spec resins were purchased from the Eichrom Inc., in powder form, and then it was swelled at least for 7 days with 1 M high-purity HNO_3 before packing it into the column. Sodium nitrite (Aldrich, Milwaukee, WI), a reducing agent, was 99.99%, and ammonium hydroxide (Junsei, Tokyo, Japan) was GR grade. Fe carrier (25 mg/mL) was purified by Dowex-anion resin in order to remove the Pb in the solution. Lead and uranium standard solutions were prepared from 1000 μg/mL plasma grade standards (SPEX Industries, Edison, NJ) by dilution with 2% high-purity HNO_3. ^{242}Pu standard solution (SRM 4334D) used as a spike was purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD). Working ^{242}Pu standard solutions at picogram per milliliter levels were made by serial dilution of SRM 4334D solution. PVDF syringe filter (0.45 μm) (Whatman, Rockland, MA) was employed in the filtration of final dissolved iron precipitate. A reference material of seawater matrix, IAEA-381, was purchased from the International Atomic Energy Agency (IAEA, Vienna, Austria) to examine the accuracy of the proposed method.

Loading Sample Preparation. Prior to chemical pretreatment, 3−10 L of seawater samples were filtered with the cellulose nitrate membrane filter (0.45 μm). After adding a known amount of ^{242}Pu spike and 25 mg of ferric ion carrier into the seawater, the sample was stirred for 30 min for homogenization. After the pH of the sample was adjusted to above 8.0 with ammonium hydroxide, the Pu in seawater was coprecipitated with iron hydroxide. The precipitate was filtered with a GF/C glass filter (Whatman) in a bell jar, and then the filtrate was dissolved with 8 M HCl in a 150-mL tall beaker. The solution was heated on the gas burner until it was boiled. After being adjusted to pH 8.0, the solution was recoprecipitated with iron hydroxide. The iron hydroxide precipitate was recovered in a 50-mL centrifuge tube using a high-speed centrifuge and then was dissolved with 2 mL of 9 M HNO_3. Once the precipitate was completely dissolved, the solution was filtered with a 0.45-μm syringe filter and then the centrifuge tube and the filter were washed with 5 mL of 4.5 M HNO_3. The resulting solution was transferred to a precleaned 20-mL Teflon vial. Prior to loading the sample to the SI system, 20 mg of sodium nitrite was added to the solution to reduce the Pu.

About 100 mL of the reference seawater, IAEA-381, was pretreated by the same method used in seawater except that the first coprecipitation step was omitted. A total of 60 L of seawaters for α-spectrometry were purified by an anionic exchange column, and then the purified Pu was electrodeposited on a stainless steel disk in $(NH_4)_2SO_4$ solution.

Sequential Injection System. The whole purification process of Pu in the SI system was designed with a total of 10 steps from the rinsing step to the collection of the final elution in the microautosampler. Detailed operation conditions of on-line SI system and a description of each step are given in Table 1. In the preconditioning of Sr-Spec, 4.5 M HNO_3 was loaded with a speed of 2.3 mL/min in the fast pump mode.

Operation of the two-way valve system was programmed in an independent control system to match each operation of PrepLab. The delicate actuation of PrepLab was programmed by Gilson language in method editor mode of the ICPMS operation program. The entire on-line SI procedure was automatically controlled. In the final step, step 10, the purified Pu on TEVA-Spec was eluted with 1 M HCl in a 2-mL conical vial for the microautosampler and then was injected into the plasma through MCN-6000. It took ∼36 min to treat one sample with the SI system.

Data Acquisition. The operation conditions of SF-ICPMS are summarized in Table 2. The dwell times for Pu isotopes and other elements were set to consume the entire sample solutions in the microautosampler. The dwell time for ^{240}Pu was 2.5 times longer than that of ^{239}Pu, because of the low concentration. Pb and U were measured for a short time, 20 ms, to check the degree of interference effect resulting from these elements. Peak widths were selected as narrow as possible to cover the acquisition spectrum. Although the peak area counts for ^{239}Pu and ^{240}Pu were not sufficiently large, the individual mass range was scanned three times to obtain a statistically significant result. Argon gas flow rates in auxiliary, nebulizer, and sweep gas in ICPMS were calibrated to give a high sensitivity and stable signal prior to the start of the SI analysis. About 6 min was required to measure the Pu isotopes, Pb, and U per sample.

Calculation of Pu and Detection Limit. Mass spectral data were acquired with an instrument operating software, Prestige. The integrated net chromatographic peak areas were obtained by subtraction from the blank. After integration of the total area count for ^{239}Pu, ^{240}Pu, and ^{242}Pu, the concentrations of these isotopes and chemical yield were calculated on a spreadsheet program. The concentration of ^{239}Pu and ^{240}Pu were calculated using the isotope dilution method applied in the previous work.[18] The measured isotope ratios had to be further corrected for mass bias of ICPMS. For this purpose, mass bias was checked for several times using a standard solution of Pu. The mass bias observed was ∼0.4%/amu in the area of Pu isotopes. The effect caused by this mass bias was very negligible in the calculation of concentration compared to the deviation of the total count of Pu isotopes in the sample. Thus, the mass bias correction can be ignored in the calculation of Pu concentration.

The relative detection limits for the individual plutonium isotopes were calculated at a concentration equivalent to three times the standard deviation of the blank solution (3σ, $n = 3$). In the calculation of absolute detection limit (ADL), the following

Table 1. PrepLab Program and Description of Program Steps

step	pumped medium	valve position six-way	valve position two-way	flow rate, mL/min pump1	flow rate, mL/min pump2	isolation valve 1	isolation valve 2	time, s
1	6 M HCl	1	1	2.3	0	right		480
2	1 M HCl	2	1	0	0.83		right	180
3	0.8 M HNO$_3$	2	1	0	0.83		left	240
4	4.5 M HNO$_3$	1	1	2.3	0	left		180
5	4.5 MHNO$_3$	1	2	1.6	0	right		360
6	4.5 M HNO$_3$	1	2	1.6	0	left		240
7	0.8 M HNO$_3$	2	2	0	0.83		left	360
8	0.8 M HNO$_3$	1	1	0	0.83		left	60
9	1 M HCl	1	1	0	0.83		right	20
10	1 M HCl	1	2	0	0.83		right	47

step	description of step
1	6 M HCl is pumped through Sr-Spec to rinse residual Pb
2	1 M HCl is pumped through Sr-Spec and TEVA-Spec to rinse residual elements
3	0.8 M HNO$_3$ is pumped through Sr-Spec and TEVA-Spec to rinse Sr-Spec and to pretreat TEVA-Spec
4	Sr-Spec is pretreated with 4.5 M HNO$_3$ at 2.3 mL/min
5	sample is loaded to Sr-Spec at 1.6 mL/min
6	4.5 M HNO$_3$ is pumped through the same pathway of step 5 to rinse residual sample and interference materials
7	0.8 M HNO$_3$ is pumped through Sr-Spec and TEVA-Spec to elute Pu from Sr-Spec and then to load continuously the Pu to TEVA-Spec
8	0.8 M HNO$_3$ is pumped through TEVA-Spec to rinse interference material and clean the injection tube
9	1 M HCl is pumped through TEVA-Spec to elute Pu at 0.8 mL/min for 20 s until 1 M HCl reaches the two-way valve
10	~650 μL 1 M HCl is pumped to elute Pu on TEVA-Spec

Table 2. Operating Conditions of the ICPMS and MCN-6000

	ICP and interface
rf power, W	1350
coolant gas flow, L/min	14
auxiliary gas flow, L/min	2.1
carrier gas flow, L/min	1.10
load coil to aperture, mm	7
aperture diameter, mm	1
expansion chamber pressure, mbar	1.6
	MCN-6000
sweeping gas flow. L/min	1.85
spray chamber temp., °C	70
membrane desolvator temp., °C	160
sample uptake rate, mL/min	0.10
type of nebulizer	PFA −100

	date acquisition [208]Pb	date acquisition [238]U	date acquisition [239]Pu	date acquisition [240]Pu	date acquisition [242]Pu
mass range, amu	207.8−208.6	237.8−238.6	238.5−239.6	239.4−240.5	241.4−242.6
dwell time, ms	20	20	200	500	50
width points	100	100	100	100	100
peak widths	1.3	1.3	1.5	1.5	1.5
runs	3	3	3	3	3
resolving power			450		
total analysis time, s/sample	7.8	7.8	90	225	22.5

equation was used, which includes the chemical yield and final injection volume.

$$\text{ADL} = \frac{3\sqrt{(\text{BKG})\,T}\,CV}{(A - \text{BKG})\,TY}$$

where A and BKG are count rates (counts/s) for a known concentration (*C*) of Pu isotopes standard solution and 2% high-

purity nitric acid, respectively, and *T* is integration time (second) for measurement by SF-ICPMS. *Y* and *V* are the chemical recovery of Pu and volume of final eluate (mL), respectively.

RESULTS AND DISCUSSION

Interference due to [238]U and Pb Isotopes. Since the concentrations of U and Pb in surface seawater would be in excess by at least 10^7−10^9 over that of Pu (i.e., U ≅ 3 μg/L; Pb ≅ 0.03
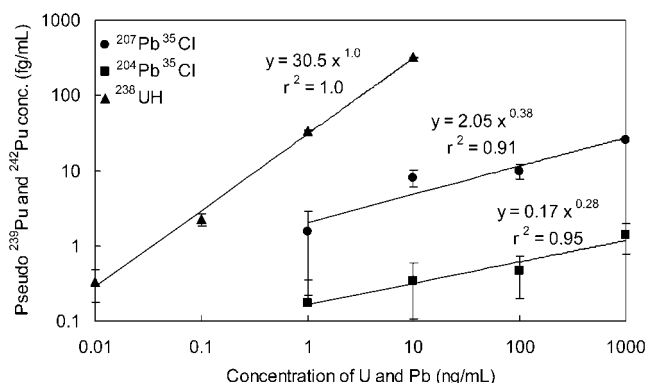
Figure 2. Interference of Pb and U at 239 and 242 *m/z* with Pb and U concentration. Error bars on individual analysis are ±1σ of triplicate measurements.

μg/L; Pu ≅ 3 fg/L),[2,19] the polyatomic molecules, $^{238}UH^+$, ^{204}Pb-$^{35}Cl^+$, and $^{207}Pb^{35}Cl^+$, resulting from ^{238}U, ^{204}Pb (abundance, 1.4%), and ^{207}Pb (abundance, 22.1%) can cause severe problems at 239 and 242 *m/z* as shown in Figure 2. Generally, several measurement conditions such as sample introduction system, gas flow rate, and distance of torch from cone have been known to affect the formation of uranium hydride ions on plasma.[10,20,21] Among above conditions, the sample introduction system was realized to be a very important factor that can affect the hydride generation. In our previous work, the influence of the interference effect of ^{238}U at 239 *m/z* with various sample introduction systems was investigated. The MCN-6000 microconcentric nebulizer coupled with the membrane desolvation system showed the lowest hydride formation among several sample introduction systems with 1.4 × 10^{-5} of the UH^+/U^+ ratio.[18] Meanwhile, even if the concentration of Pb in seawater is not as much as that of soil, the interference effect resulting from Pb could be serious in the ultratrace level of ^{239}Pu, due to the Pb from reagents such as Fe carrier, ammonium hydroxide, acidic solution, and sodium nitrite. As shown in Figure 2, a PbCl interference found at *m/z* 240 was very weak compared to that at *m/z* 239 (from $^{204}Pb^{35}Cl$), and the total interference effect resulting from PbCl was much less than $^{238}UH^+$ at the same concentration of U and Pb. The interference of $^{207}Pb^{35}Cl$ at 242 *m/z* was negligible since sufficient ^{242}Pu was added to compensate the error resulting from $^{207}Pb^{35}Cl$. The average activity of $^{239+240}Pu$ found by Kim et al.[2] in open surface seawater collected around the Korean peninsula is ~8 μBq/L, which corresponds to 2.1 fg/L ^{239}Pu and 0.38 fg/L ^{240}Pu under the assumption that the $^{240}Pu/^{239}Pu$ atom ratio is 0.18 of the global fallout value reported by Kelly et al.[22] Assuming that the sample volume of seawater is 5 L, and the chemical recovery is 70%, the ^{239}Pu and ^{240}Pu concentrations in the final solution (~0.7 mL) could be approximately 10.5 and 1.9 fg/mL, and U and Pb concentrations would be approximately 15 and 1 μg/mL, respectively. However, almost all of the Pb resulted from the reagents used in the purification process of Pu, whose contents was ~50 μg. Taking

into account the decontamination factors of U and Pb (as described in Table 7) found in the on-line SI system, U and Pb concentrations in the final eluate would be approximately 13 pg/mL and 2.5 ng/mL, respectively. As shown in Figure 2, the total concentration of pseudo-^{239}Pu originating from above U and Pb is ~0.5 fg/mL, which corresponds less than 5% to the total ^{239}Pu concentration in the final eluent.

Optimization of the On-Line SI System. (a) Configuration of Specific Resin Columns. Recently, various analytical methods using actinide-specific resin such as TEVA-Spec, TRU-Spec, and UTEVA-Spec were developed for the analysis of Pu in various samples.[23-25] Those methods help to shorten the analysis time and to simplify the complicated chemical procedure in Pu purification. However, it is not easy to eliminate U to the level of subpicograms per milliliter by just one column step. In the previous study,[18] we recognized that Sr-Spec and TEVA-Spec resins are very effective to reduce the U concentration in the final solution to subpicograms per milliliter, because they have the capability to separate Pu from U and Pb due to the huge difference in affinity, which depends on the acid concentration and the kinds of acid. Therefore, Sr-Spec (the first column) and TEVA-Spec (the second column) were sequentially connected in the on-line SI system. Contrary to the previous study, the first column (750 μL) was a little enlarged to eliminate a large amount of Pb recovered from 5 L of seawater and to treat many samples. Comparing with that used in the previous study, the second column (50 μL) was cut down by a factor of 3 in dead volume to obtain the narrow and sharp elution profile. Table 3 presents that relationship between the final eluate volume and the precision of measurement result. The relative standard deviation (RSD) for each column was calculated by combing the standard deviations for the sample and background measurement since the dwell time for each column was different. For the 50-μL column, the precision and absolute detection limit were improved more than 30 and 15%, respectively. The relative detection limit for ^{239}Pu and ^{240}Pu were 0.64 (1.5 μBq/mL) and 0.19 fg/mL (1.6 μBq/mL), respectively, which corresponds to an absolute detection limit of 1.33 and 0.25 fg in the 0.65-mL final eluent as shown in Table 3. These low-level detection limits for ^{239}Pu and ^{240}Pu were achieved by the small amount of final eluate and an efficient sample introduction system. Compared with other methods, the relative detection limits were similar to that reported by Chiappini et al.[20] and a little higher that reported by Becker and Dietze.[26] Moreover, the total measurement time was shortened about 2.3 and 3.2 times, respectively, compared to the other two columns. By the reduction of the second column volume, the chemical recovery was decreased about 2-4% compared to a large size column. To make up for the loss of chemical recovery, the loading and rinsing solutions for the first column was substituted to 4.5 M HNO_3, which was estimated to be the optimum concentration to show the highest capacity factor (K) for Pu in the Sr-Spec resin.[27]

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Table 3. RSD and Detection Limit According to the Different Second Column Volumes

second column vol, μL	eluate vol, mL	dwell time, s		RSD,[a] %		absolute detection limit,[b] fg	
		^{239}Pu	^{240}Pu	^{239}Pu	^{240}Pu	^{239}Pu	^{240}Pu
50	0.65	0.20	0.50	3.1	4.6	1.33	0.25
100	1.5	0.46	1.15	4.8	7.9	1.43	0.36
180	2.1	0.64	1.6	6.4	6.9	1.59	0.35

[a] The RSD was calculated from four replicate determinations of a Pu isotope standard solution, in which the total amounts of ^{239}Pu and ^{240}Pu were 22.8 and 5.5 fg, respectively. [b] Absolute detection limits were calculated on the basis of a final eluate volume and chemical recovery.
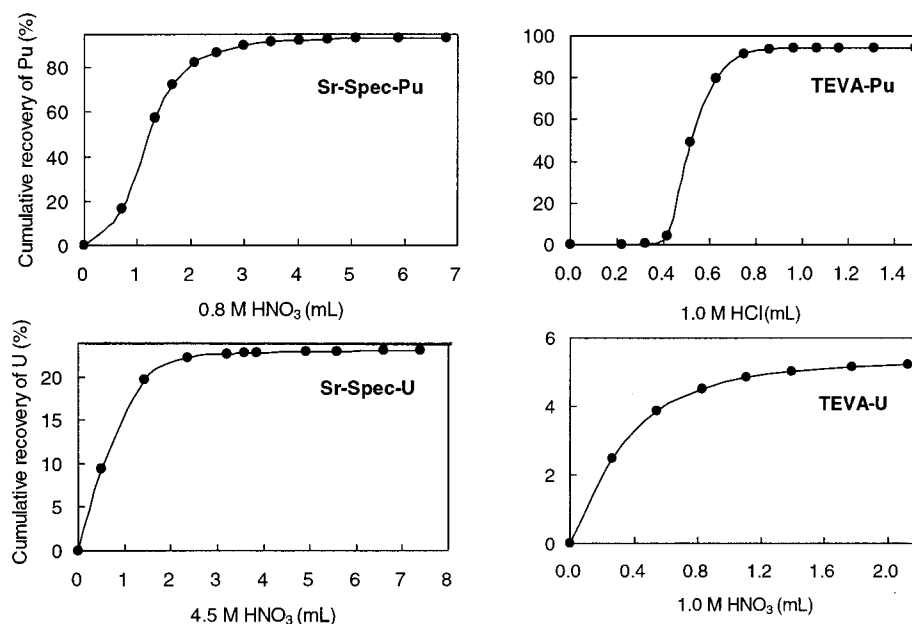

Figure 3. Cumulative recovery profiles of U and Pu in Sr-Spec resin (first column) and TEVA-Spec resin (second column).

(b) Elution Profile of Pu in Sr-Spec and TEVA-Spec Columns. To obtain optimum conditions for the rinsing and elution processes in two columns, a cumulative recovery curve and elution profile for U and Pu were obtained as shown in Figure 3. Before loading the standard test solution to the on-line SI system, sodium nitrite was added to reduce Pu as previously proved in other reports.[14,16] Although, U was mostly eliminated in the loading step on both the first (Sr-Spec resin) and 2nd columns (TEVA-Spec resin), an additional 4 mL of 4.5 M HNO$_3$ in the first column and 1.2 mL of 0.8 M HNO$_3$ in the second column are necessary to remove the residual U in the rinsing step of two columns as can be seen in Figure 3. For the elution step of the first column, at least 3.8 mL (5 FCV) of eluent (0.8 M HNO$_3$) should be pumped through Sr-Spec resin to recover ~99% Pu in total accumulated recovery. From above optimum separation conditions, 5.0 mL of 0.8 M HNO$_3$ was necessary as a rinsing and eluent solution in step 7 as described in Table 1. Meanwhile, for the second column, Pu recovery was decreased to nearly 0% after pumping ~0.95 mL of 1 M HCl. However, a small dead volume (~0.30 mL) was seen at the beginning stage of the elution profile before 1.0 M HCl leaving from the isolation valve reached the second column. To discard the dead volume, therefore, the pathway of 1.0 M HCl coming from the second column was connected for 20 s to a waste line through the two-way, six-port valve. Finally, the final eluate volume was decreased to 0.65 mL

(13 FCV) by deduction of the dead volume, which was lessened by a factor of nearly 4 compared to the previous condition (2.4 mL).[18] A preconcentration factor as high as 7.6×10^3 can be achieved if 5 L of seawater was treated in this system.

(c) Elimination of Pb. As described by Horwitz,[27] Pb showed strong affinity to the Sr-Spec resin in strong nitric acid media; accordingly, most of the Pb in the sample was attached in the Sr-Spec resin when the sample was loaded. Table 4 showed the behavior of Pb in Sr-Spec and TEVA-Spec columns with a separation step. The concentration of Pb in the final eluent could be lowered sufficiently by rinsing the TEVA-Spec column with small amounts of nitric acid prior to the final elution step. However, Pb was strongly retained during all separation steps in the Sr-Sepc resin, showing at most ~4% recovery in total. The remaining Pb in the Sr-Spec column lowered the capacity of the Sr-Spec resin to attach Pu. Consequently, this will cause the gradual decrease of the chemical recovery when the next sample passes through the column. To successively reuse the column for the next samples, the Pb accumulated in Sr-Spec resin should be removed before running the new sample. The concentrated hydrochloric acid was more effective than other acids among those tested to rinse the Pb on the Sr-Spec resin, which agreed with the previous studies in Pb-Spec resin (a modified version of the Sr-Spec resin).[28] However, to use highly concentrated acid in a cleanroom is difficult to handle, because of the hazardous fume gas. Therefore,

Table 4. Behavior of Pb in Sr-Spec and TEVA-Spec Resin

separation step	Sr-Spec[a]		TEVA-Spec[a]	
	amt, FCV	rec,[b] %	amt, FCV	rec, %
loading[c]	6.1	2.0	7.0	65.9
rinsing-1[c]	0−6.8	1.2	0−2.6	21.9
rinsing-2	6.8−12.5	0.3	2.6−5.5	7.0
rinsing-3	12.5−19.2	0.2	5.5−8.6	2.9
rinsing-4	19.2−25	0.3	8.6−11.5	1.1
rinsing-5	25−31	0.3	11.5−14.6	0.8
elution[d]	6.0	0.1	5.9	0.7

[a] Free column volume of Sr-Spec column and TEVA-Spec column were 750 and 350 μL, respectively. [b] Recovery means the fraction ratio of Pb recovered to total Pb loaded. [c] Loading and rinsing solution for Sr-Spec and TEVA-Spec were 4.5 and 0.8 M HNO_3, respectively. [d] Eluent for Sr-Spec and TEVA-Spec were 0.8 M HNO_3 and 1.0 M HCl, respectively.

6 M HCl was selected as a rinsing solution for Pb on the Sr-Spec resin column. About 95% residual Pb in the Sr-Spec resin column was cleaned with 18.6 mL (25 FCV) of 6 M HCl as illustrated in the elution profile. The two-way, six-port valve was used to load alternatively the 6 M HCl and 4.5 M HNO_3 according to the programmed step.

Meanwhile, when the eluent of the Sr-Spec column was loaded on the TEVA-Spec column, a small amount of Pb was moved to the TEVA-Spec column from the Sr-Spec column. Accordingly, it was necessary to rinse the TEVA-Spec column with 0.8 M HNO_3 for ~60 s, prior to the final elution step. The rinsing solution was supplied through two-way, six-port valve directly to the TEVA-Spec column and transported to the waste line. This rinsing step was also helpful to reduce the U content in the TEVA-Spec column as depicted in Figure 3.

(d) Memory Effect and Recycling. To reuse the specific columns multiple times in the on-line SI system, it was necessary to check the memory effect from Pu after one-cycle sample analysis. Memory effects are caused typically by the previous analytes remaining in the extraction resin, sample introduction system, and instrument. The memory effect originating from the on-line SI system can be quantitatively measured by using a blank test. The blank experiments were performed once every five samples running with blank samples composed of only 4.5 M nitric acid. The average carryovers for ^{239}Pu, ^{240}Pu, and ^{242}Pu in the blank test were approximately 0.6, 0.3, and 1.0%, respectively; these results were similar in both the first and the second blank samples. Considering ~8% of the counting error observed in the measurement of Pu isotopes in seawater above the carryover was not serious. Although Pu is not a memory-prone element, the large surface area associated with desolvation membrane in the MCN-6000 and long time measurement (~6 min) might increase the background count rate. However, any remarkable change in the background count was not observed when sufficient washing time (~60 s) was set between the serial measurements. Furthermore, after running 10 samples in the on-line SI system, there was no considerable memory effect or visible degradation in chemical recovery found. Therefore, the same columns could be use up to 10 samples.

(28) Horwitz, E. P.; Dietz, M. L.; Rhoads, S.; Felinto, C.; Gale, N. H.; Houghton, J. *J. Anal. Chim. Acta* **1994**, *292*, 263−273.

Table 5. Analytical Results of $^{239+240}$Pu and ^{240}Pu/^{239}Pu Atom Ratios in the Standard Reference Material (IAEA-381) Using On-Line SI-ICPMS

sample	chem rec, %	U, pg/mL	Pb, ng/mL	$^{239+240}$Pu,[a] mBq/kg	^{240}Pu/^{239}Pu atom ratio
1	68	0.74	0.39	13.4 ± 0.39[b]	0.243 ± 0.013
2	73	0.57	2.91	14.1 ± 0.46	0.248 ± 0.017
3	59	0.33	0.93	13.8 ± 0.25	0.245 ± 0.009
4	74	0.47	0.82	14.4 ± 0.16	0.236 ± 0.005
5	65	0.40	0.87	15.0 ± 0.34	0.242 ± 0.011
6	74	0.24	0.44	14.4 ± 0.36	0.241 ± 0.012
7	72	0.21	0.69	14.2 ± 0.30	0.230 ± 0.010
8	71	0.29	0.66	14.3 ± 0.22	0.234 ± 0.007
9	65	0.31	0.59	14.6 ± 0.53	0.238 ± 0.002
10	58	0.14	0.43	14.4 ± 0.39	0.241 ± 0.014
mean	68	0.37	0.87	14.3 ± 0.44	0.240 ± 0.005
RSD, %				3.1	2.1

[a] The half-lives for ^{239}Pu and ^{240}Pu used in the conversion of mass results to α-activities are 24 119 and 6564 y, respectively. [b] Standard deviation (±1σ).

Accuracy and Precision. (a) Accuracy of On-Line SI-SF-ICPMS. Ten samples of reference seawater, IAEA-381, were analyzed in order to verify the accuracy of the on-line SI-SF-ICPMS for the determination of Pu isotopes in seawater. Each sample was independently analyzed by the same on-line SI method. The concentration of Pu in the reference seawater was much higher than the normal low-level surface seawater. Therefore, 100 mL of sample was used for the validation test, whose results are described in Table 5. All results for $^{239+240}$Pu activity were within the confidence interval,[29] 12.1−14.5 mBq/kg, recommended by IAEA, except for the fifth sample. Although the result of the fifth sample deviated a little from the certified value, the difference was not large. The concentrations of U and Pb ranged from 0.14 to 0.74 pg/mL and 0.39 to 2.9 ng/mL, and the chemical yield ranged from 58 to 74%. Meanwhile, the mean value of ^{240}Pu/^{239}Pu atom ratio was 0.24 with a good precision of 2% RSD, which agreed well with the reported value (0.242 ± 0.004) by MEL laboratory.[30] The reference seawater was analyzed mostly by a radiometric method, so the exact individual concentration of ^{239}Pu and ^{240}Pu was unknown. Nevertheless, the accuracy of the present method was well proved by virtue of fair agreement in both $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio. Furthermore, the steady chemical recovery above 58% and credible results for 10 multiple analyses of IAEA-381 in one system without replacement of resins guaranteed the possibility of recycle use of the present specific resins in the on-line SI system. Although, the same reference samples were treated with the same procedure, however, a small difference in the amounts of reagents used in the pretreatment in the preparation of loading sample and sample amount around 100 mL of reference seawater could differentiate the U and Pb content in the sample.

(b) Comparison of Present Method with α-Spectrometry. With conventional α-spectrometry, ~60 L of seawater is required when the anion resin purification method is used. Finally, Pu

(29) *29. Report on the Intercomparison Run IAEA-381*; IAEA/AL/118, IAEA: Vienna, 1999.

(30) Lee, S. H.; Gastaud, J.; La Rosa, J. J.; Liong, L.; Kwong, W.; Povince, P. P.; Wyse, E.; Fifield, L. K.; Hausladen, P. A.; Di Tada, L. M.; Santos, G. M. *J. Radioanal. Nucl. Chem.* **2001**, *248*, 757−764.

Table 6. Comparison of $^{239+240}$Pu Concentration Measured by SI-SF-ICPMS and α-Spectrometry in Surface Seawater Collected around the Korean Peninsula

sample	α-spectrometry, μBq/kg	SI-SF-ICPMS, μBq/kg	SI-SF-ICPMS/ α-spectrometry
1	7.61 ± 0.84	8.15 ± 0.65	1.07
2	5.38 ± 0.75	5.90 ± 0.12	1.10
3	5.99 ± 0.30	6.09 ± 0.24	1.02
4	5.90 ± 0.41	6.32 ± 0.51	1.07
5	6.68 ± 1.07	6.34 ± 0.44	0.95
6	6.92 ± 0.35	6.44 ± 0.13	0.93
7	5.84 ± 0.41	5.67 ± 0.34	0.97
mean			1.02 ± 0.07

Figure 4. Variations of precision and accuracy for ^{239}Pu (a) and ^{240}Pu (b) with the sample volume. The mean value and two standard deviations are illustrated by solid and dashed horizontal lines, respectively. Error bars on individual analysis are $\pm 1\sigma$ of the mean value.

electrodeposited on stainless plate is measured by α-spectrometry for at least 12 days to obtain a statistically significant count. Despite large sample amounts and long measurement time, the total peak area for $^{239+240}$Pu in α-spectrometry was not over 100 counts, whereas the counting number for ^{239}Pu and ^{240}Pu obtained in the present SI-SF-ICPMS was over 140 and 75, respectively. The $^{239+240}$Pu concentrations obtained by SI-SF-ICPMS and α-spectrometry are presented in Table 6. The average standard deviation for SI-ICPMS was calculated from triplicate measurement results for three independent seawaters, whereas the standard deviation for α-spectrometry was obtained through triplicate measurements for one sample. The mean value of standard deviations for SI-SF-ICPMS and α-spectrometry were 5.3 and 9.3%, respectively.

(c) Reproducibility of SI-SF-ICPMS. To study the variation of RSD with different sample volumes, the precision test was carried out with the surface seawaters collected around the Korean peninsula. The surface seawater sample was classified into three groups depending on sample volumes, 3, 5, and 10 L. Four samples in each group were analyzed. Each sample was measured three times to get the RSD. The mean values and standard deviations of ^{239}Pu and ^{240}Pu with sample volumes are plotted in Figure 4. For all samples, the mean values for ^{239}Pu and ^{240}Pu were 4.05 and 0.98 fg/L with 7 and 8% of RSD, respectively. Almost all results
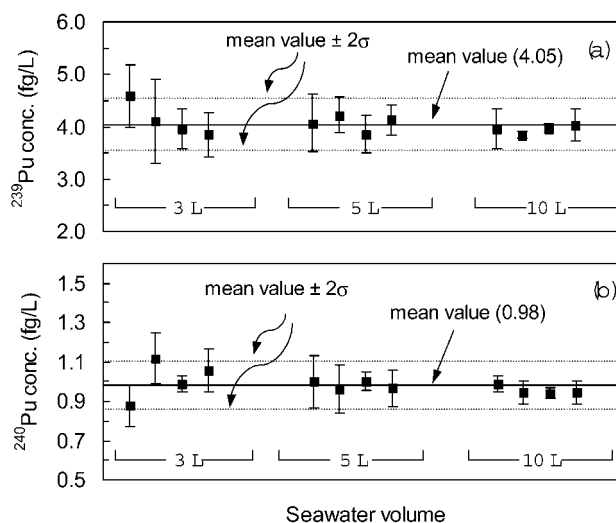
for ^{239}Pu and ^{240}Pu concentration showed good reproducibility within mean $\pm$ 2 σ. The RSD for each measurement and the average standard deviation for each group were improved with increasing the sample volume. In case of 5 L sample, the RSDs for ^{239}Pu and ^{240}Pu in each sample were 6 $\sim$ 13 and 7 $\sim$ 10%, respectively. Besides, the values of four analyses for the same sample volume group did not differ by more than 2.5%. However, 3 L group showed the large RSD (> 10%) for each sample as well as the RSD for four samples was also over 8%. Consequently, this result indicates that at least 5 L sample volume is required to obtain the results with sufficient accuracy and precision in the determination of Pu in surface seawater by SI−SF−ICPMS.

To examine the reproducibility of present method, 7 samples of 5 L surface seawater were analyzed. As shown in Table 7, the average concentrations of ^{239}Pu and ^{240}Pu were 4.1 and 1.0 fg/mL

Table 7. Precisions of ^{239}Pu and ^{240}Pu in the Replicate Measurement of Surface Seawater

sample	chem rec, %	concn in final eluate (decontamination factor)[a] U, fg/mL	Pb, pg/mL	concn, fg/mL ^{239}Pu	^{240}Pu
1	52	5.9 (1.2×10^6)	2.2 (3.3×10^4)	4.07 ± 0.96[b]	1.00 ± 0.13
2	61	4.5 (1.6×10^6)	4.5 (1.6×10^4)	4.22 ± 0.84	0.96 ± 0.17
3	58	4.9 (1.5×10^6)	2.9 (2.5×10^4)	3.86 ± 0.50	1.00 ± 0.13
4	60	3.8 (1.9×10^6)	3.9 (1.8×10^4)	4.13 ± 0.55	0.97 ± 0.14
5	83	4.2 (1.7×10^6)	1.8 (3.8×10^4)	4.29 ± 0.55	1.08 ± 0.13
6	61	3.8 (1.9×10^6)	2.0 (3.7×10^4)	3.99 ± 0.34	1.05 ± 0.12
7	78	3.0 (2.4×10^6)	2.2 (3.4×10^4)	4.06 ± 0.29	0.96 ± 0.09
mean	65	4.3 (1.7×10^6)	2.8 (2.9×10^4)	4.09 ± 0.14	1.00 ± 0.05
RSD, %				3.4	5.0

[a] Decontamination factor is defined as the total amounts of atom in the loading solution divided by total amounts of atom in the final eluate.
[b] Standard deviation ($\pm 1\sigma$).

with the RSDs of 3.4 and 5%, respectively, which are about twice lower than that in α-spectrometry. The final concentration of U and Pb were about 4.3 fg/mL and 2.8 pg/mL, therefore, the interference effect caused by U and Pb were less than 1 and 2% in final ^{239}Pu result, respectively. The ranges of decontamination factors for U and Pb in the 5 L of seawater were $1.2-2.4 \times 10^6$ and $1.6-3.8 \times 10^4$, respectively, as shown in Table 7. The decontamination factor for U was about 1 order higher than those found in other studies using a single column separation sheme.[5,31]

CONCLUSIONS

The on-line sequential injection system linked with SF-ICPMS (SI-SF-ICPMS) was successfully applied to the determination of ultratrace level Pu isotopes in the open surface seawater. This method overcame the polyatomic interferences from U and Pb isotopes and improved drastically the precision by reducing the final eluate volume and the size of the secondary column. Also, this method was capable of the determination of ultratrace level Pu with even an amount of surface seawater as small as 5 L within 4 h. By using this method, the sample amount required for the determination of Pu was reduced by about 10−20 times, and the analysis time was shortened by about 20 times compared to those of the conventional radiometric methods. The detection limits of ^{239}Pu and ^{240}Pu 0.64 (1.5 μBq/mL) and 0.19 fg/mL (1.6 μBq/mL), respectively. The RSDs for ^{239}Pu and ^{240}Pu in a real sample were less than 3.4 ($n = 7$) and 5% ($n = 7$), respectively. Consequently, the on-line SI-SF-ICPMS technique could become a powerful tool for not only the rapid determination of Pu in environmental samples but also the enhanced safeguard activities, when the sample volume and the analysis time are very much limited.

(31) Warwick. P. E.; Croudace, I. W.; Oh, J. S. *Anal. Chem.* **2001**, *73*, 4310−3416.