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Determination of ^{135}Cs and ^{135}Cs/^{137}Cs Atomic Ratio in Environmental Samples by Combining Ammonium Molybdophosphate (AMP)-Selective Cs Adsorption and Ion-Exchange Chromatographic Separation to Triple-Quadrupole Inductively Coupled Plasma−Mass Spectrometry

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Ⓢ *Supporting Information*

ABSTRACT: Since the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in 2011, the activity ratio of ^{134}Cs/^{137}Cs has been widely used as a tracer for contamination source identification. However, because of the short half-life of ^{134}Cs (2.06 y), this tracer will become unavailable in the near future. This article presents an analytical method for the determination of the long-lived ^{135}Cs ($t_{2/1} = 2 \times 10^6$ y) and the atomic ratio of ^{135}Cs/^{137}Cs, as a promising geochemical tracer, in environmental samples. The analytical method involves ammonium molybdophosphate (AMP)-selective adsorption of Cs and subsequent two-stage ion-exchange chromatographic separation, followed by detection of isolated radiocesium isotopes via triple-quadrupole inductively coupled plasma−mass spectrometry (ICP-MS/MS). The AMP-selective adsorption of Cs and the chromatographic separation system showed high decontamination factors (10^4–10^5) for interfering elements, such as Ba, Mo, Sb, and Sn. Using ICP-MS/MS, only selected ions enter the collision/reaction cell to react with N_2O, reducing the isobaric interferences (^{135}Ba$^+$ and ^{137}Ba$^+$) and polyatomic interferences (^{95}Mo^{40}Ar$^+$, ^{97}Mo^{40}Ar$^+$, ^{119}Sn^{16}O$^+$, and ^{121}Sb^{16}O$^+$) produced by sample matrix ions. The high abundance sensitivity (10^{-9} for the ^{135}Cs/^{133}Cs ratio) provided by ICP-MS/MS allowed reliable analysis of ^{135}Cs and ^{137}Cs isotopes with the lowest detection limits ever reported by mass counting methods (0.01 pg mL^{-1} and 0.006 pg mL^{-1}, respectively). The developed analytical method was successfully applied to the determination of ^{135}Cs and ^{137}Cs isotopes in environmental samples (soil, litter, and lichen) collected after the FDNPP accident for contamination source identification.
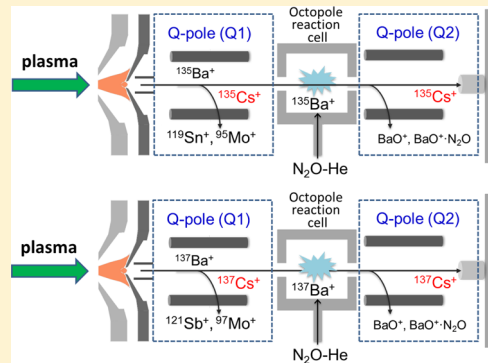
Radioactive Cs isotopes are high yield fission products (up to 6.535% and 6.236% for ^{135}Cs and ^{137}Cs, respectively) from thermal neutron fission of ^{235}U.[1] They can be released into the environment in nuclear events such as the detonation of a nuclear weapon or nuclear reactor accident, as in, for example, the Chernobyl and Fukushima Daiichi Nuclear Power Plant (FDNPP) accidents.[2−4] In the fission chains for ^{135}Cs and ^{137}Cs, a shielding of ^{135}Cs occurs due to neutron capture of its precursor, ^{135}Xe, to form ^{136}Xe, whereas production of ^{137}Cs is unaffected.[5] Thus, the ratio of ^{135}Cs/^{137}Cs will be characteristic of the reactor operation and shutdown conditions. The atomic ratio of ^{135}Cs/^{137}Cs is very important in many radioecological studies, including source identification of radioactive contamination, dispersion modeling of fission products in the environment after a nuclear accident, long-term estimation of environmental behavior of radiocesium, and development of accurate sediment geochronology.[6−8] In the context of the

Chernobyl accident in 1986, three cesium isotopes—^{134}Cs ($T_{1/2} = 2.06$ y), ^{135}Cs ($T_{1/2} = 2 \times 10^6$ y), and ^{137}Cs ($T_{1/2} = 30.2$ y)—were monitored, and a value of 0.5 for the ^{135}Cs/^{137}Cs atomic ratio was reported.[9]

Regarding the FDNPP accident, large amounts of radioactivity, including radiocesium were released into the environment similar to the Chernobyl accident. As the major radiation dose contributor, the released amounts of radiocesium, ^{134}Cs and ^{137}Cs have been estimated, and the ^{134}Cs/^{137}Cs activity ratio was immediately used to identify radioactive contamination in the environment.[10−16] However, considering the short half-life of ^{134}Cs, the ^{134}Cs/^{137}Cs activity ratio will

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become unavailable in the near future for identification of FDNPP contamination and for long-term estimation of the environmental mobility of the FDNPP accident-related fission products. Therefore, there is a strong scientific need to study the release of ^{135}Cs and to obtain the isotopic fingerprint of ^{135}Cs/^{137}Cs for the FDNPP accident.

Although ^{137}Cs can be easily measured by gamma spectrometry, the determination of ^{135}Cs by radiometric methods is very difficult and quite insensitive, because of its long half-life and low-energy β-decay (76 keV).[17,18] Neutron activation analysis (NAA), accelerator mass spectrometry (AMS), and thermal ionization mass spectrometer (TIMS) have been investigated for ^{135}Cs activity and ^{135}Cs/^{137}Cs isotope ratio analysis in environmental samples;[3,5−8,19] however, instruments for these techniques are quite expensive and not widely available. In recent years, the analytical potential of ICP-MS for determining ^{135}Cs and ^{137}Cs activities and ^{135}Cs/^{137}Cs atomic ratio has been studied;[9,20−23] however, the analysis of environmental samples remains as a great challenge. For the determination of ^{135}Cs and ^{137}Cs isotopes using ICP-MS, the most troublesome interferences are the isobaric interferences from Ba isotopes. Because of the high concentration of Ba in the environment (for example, 550 mg kg^{-1} in soil[24]), ^{135}Ba (abundance = 6.59%) and ^{137}Ba (abundance = 11.2%) could cause an extremely high background signal at m/z 135 and 137, deteriorating the limit of detection for ^{135}Cs and ^{137}Cs. Furthermore, Mo in the environmental samples (ca. 2 mg/kg in soil) could result in polyatomic interferences, ^{95}Mo^{40}Ar$^+$ and ^{97}Mo^{40}Ar$^+$. Minor polyatomic interferences are ^{119}Sn^{16}O$^+$ and ^{121}Sb^{16}O$^+$ (ca. 3 mg kg^{-1} Sn and 2 mg kg^{-1} Sb in soil) on ^{135}Cs and ^{137}Cs measurements, respectively. In addition, the high concentration of stable Cs (^{133}Cs) in environmental samples will also interfere with ^{135}Cs analysis, because of the peak tailing effect. For the global fallout source ^{135}Cs in environmental samples, the ^{133}Cs/^{135}Cs ratio is higher than 10^9; therefore, an analytical method with high abundance sensitivity is required.[8] Very recently, a triple-quadrupole ICP-MS (ICP-MS/MS) system developed by Agilent Technologies has shown great potential for the determination of radionuclides. Tanimizu et al.[25] demonstrated the determination of ultralow ^{236}U/^{238}U isotope ratios by ICP-MS/MS. Ohno and Muramatsu[4] reported a new method using triple-quadrupole ICP-MS for the determination of radioactive cesium isotope ratios in rainwater samples following the FDNPP accident. They demonstrated that radioactive cesium in rainwater can be directly measured by introducing reaction gas to suppress Ba isobaric interferences without any prior chemical separation of the Ba. However, because of the high concentration of Ba and Mo in environmental samples, such as soils, sediments, and plants, an effective chemical separation is an unavoidable requirement for reliable determination of radiocesium isotopes.

In this work, we report a new analytical method for determination of radiocesium and the ^{135}Cs/^{137}Cs atomic ratio in soil and plant samples. We developed a chemical separation method with high decontamination factors to separate radiocesium isotopes from the major interferences (Ba and Mo) and minor interferences (Sb and Sn) which involved AMP-selective adsorption of Cs and ion-exchange chromatography for Cs−Ba−Mo−Sb−Sn separation. With the ICP-MS/MS, we optimized the N$_2$O reaction with Ba to achieve an elimination of isobaric Ba interferences and

polyatomic interferences of MoAr$^+$, and suppression of the formation of SnO$^+$ and SbO$^+$ interferences. In addition, we also examined the high abundance sensitivity required for reliable radiocesium isotopes analysis. Finally, the established method was validated by the analysis of IAEA soil reference material and applied to environmental samples collected in Japan following the FDNPP accident.

■ EXPERIMENTAL SECTION

Instrumentation. To determine radiocesium isotopes in environmental samples, we used a triple-quadrupole ICP-MS/MS device (Agilent, Model 8800), which features an additional quadrupole mass filter, situated in front of the octopole collision/reaction cell and quadrupole mass filters (see Figure 1). N$_2$O gas, mixed with He gas, was introduced into the
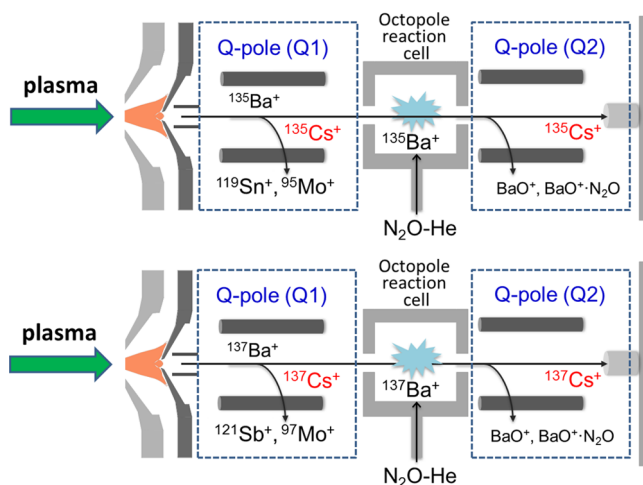

Figure 1. Schematic of ICP-MS/MS and ion−molecule reactions for ^{135}Cs and ^{137}Cs measurements. Target ions are separated from matrix ions by Q1 set at m/z 135 and 137, respectively, and they enter the collision/reaction cell, where they react with N$_2$O to separate Cs/Ba, eliminate MoAr$^+$ polyatomic interference, and suppress the formation of SbO$^+$ and SnO$^+$. Finally, Q2 is set to measure the desired ^{135}Cs and ^{137}Cs.

octopole collision/reaction cell to eliminate polyatomic and isobaric interferences, such as ^{95}Mo^{40}Ar$^+$, ^{97}Mo^{40}Ar$^+$, ^{135}Ba$^+$, and ^{137}Ba$^+$, and suppress the formation of ^{119}Sn^{16}O$^+$ and ^{121}Sb^{16}O$^+$ oxides. Sample solution was introduced into the ICP-MS/MS using a conical concentric nebulizer with a sample uptake rate of 0.3 mL/min. Optimized instrument conditions for the determination of radiocesium isotopes are listed in Table S1 of the Supporting Information. Typical measurement sensitivity for ^{133}Cs$^+$ was 5 × 10^4 cps for 1 ng mL^{-1} Cs. A sector-field ICP-MS (SF-ICP-MS, Element 2, Thermo Fisher Scientific) system was used to measure Cs, Ba, Mo, Sb, and Sn during development of the chemical separation procedure to separate radiocesium isotopes from the environmental sample matrix and the interfering elements. Activity of ^{137}Cs in the environmental samples was determined using a Ge detection system (Seiko EG&G) at the peak of 661.6 keV for 3600 s for most cases. A mixed gamma standard solution (Amersham, Model QCY-46) was used for an efficiency correction. Details of the ^{137}Cs analysis were described elsewhere.[13]

Standards, Reagents, and Samples. All reagents used in the experiment, including nitric acid (HNO$_3$), hydrochloric acid (HCl), ammonium hydroxide (NH$_4$OH), and hydrogen

Table 1. Analytical Results of Activities of ^{135}Cs and ^{137}Cs and Atomic Ratios of $^{135}Cs/^{137}Cs$ and $^{135}Cs/^{133}Cs$ in Environmental Samples after the FDNPP Accident[a]

sample code	sample description and location	sampling date	^{137}Cs activity (mBq g^{-1})	^{135}Cs activity (mBq g^{-1})	^{135}Cs concentration (pg g^{-1})	$^{135}Cs/^{137}Cs$ atomic ratio	$^{135}Cs/^{133}Cs$ ratio ($\times 10^{-7}$)
S1	litter, Kasurao, 25 km WNW	May 20, 2011	148000 ± 1400	0.647 ± 0.015	15.2 ± 0.4	0.333 ± 0.007	1890 ± 30
S2	litter, Namie, 26 km NW	May 20, 2011	1416000 ± 4300	6.32 ± 0.031	148 ± 1	0.340 ± 0.001	1390 ± 60
S3	litter, Iitate, 32 km NW	May 20, 2011	4649000 ± 9100	20.8 ± 0.1	488 ± 3	0.341 ± 0.002	10800 ± 200
S4	lichen, Iitate, 40 km NW	May 24, 2013	659000 ± 3000	2.96 ± 0.17	69.4 ± 4.1	0.342 ± 0.020	410 ± 13
S5	litter, Oguni, 50 km NW	Oct. 14, 2012	119000 ± 300	0.536 ± 0.014	12.6 ± 0.3	0.343 ± 0.009	302 ± 8
S6	surface soil, J-Village, 20 km S	April 20, 2011	11500 ± 500	0.057 ± 0.004	1.33 ± 0.10	0.375 ± 0.024	4.32 ± 0.24
S7	litter, Tsukuba, 140 km SW	May 8, 2011	9580 ± 500	0.043 ± 0.003	1.01 ± 0.07	0.341 ± 0.016	30.7 ± 1.6
S8	surface soil, Kamagaya, 230 km SW	Aug. 7, 2011	11400 ± 90	0.053 ± 0.003	1.25 ± 0.07	0.355 ± 0.020	5.47 ± 0.28
IAEA 375 (2 g)	Chernobyl soil reference material	July 1990	3187	0.025 ± 0.002	0.58 ± 0.05	0.589 ± 0.056	6.12 ± 0.34
IAEA 375 (5 g)			3187	0.022 ± 0.001	0.52 ± 0.02	0.525 ± 0.016	5.67 ± 0.04
IAEA 375 (10 g)			3187	0.023 ± 0.002	0.54 ± 0.04	0.551 ± 0.045	6.39 ± 0.20
IAEA-375 (ref 9)			4500 (in 2008)			0.50 ± 0.05 (in 2008)	

[a]The activity of ^{137}Cs was measured using gamma spectrometry and decay corrected to March 11, 2011.

peroxide (H_2O_2), were of analytical reagent grade. Ultrapure grade HNO_3 obtained from Tama Chemicals (Tokyo, Japan) was used for preparation of the final sample solution and standard solutions for ICP-MS measurement. The water used was Milli-Q purified water (18.2 MΩ cm). Single-element standard solutions (1000 ppm) of Ba, Cs, Sb, Mo, and Sn were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Nitrous oxide gas (as 20% N_2O mixed with 80% He) was obtained from Sumitomo Seika Chemicals Co., Ltd. (Tokyo, Japan). Helium and argon gases were purchased from Taiyo Nippon Sanso Corp. (Tokyo, Japan). Soil reference material (IAEA-375) was obtained from the International Atomic Energy Agency (IAEA). Ammonium molybdophosphate (AMP) used for selective adsorption of Cs was provided by Kishida Chemical Co., Ltd. (Osaka, Japan). Anion-exchange resin (AG MP 1M, 100−200 mesh, Cl$^-$ form) and cation-exchange resin (AG 50WX8, 100−200 mesh, H$^+$ form) were purchased from Bio-Rad.

Environmental samples, including litter (samples S1−S3, S5, S7), lichen (sample S4), and surface soil (samples S6 and S8), were collected in the Fukushima, Ibaraki, and Chiba Prefectures after the FDNPP accident and were used in this work for measurement of radiocesium isotopes. Detailed sampling methods for plant and soil were described in our previous work,[26] and information on the sampling date and sampling locations are summarized in Table 1.

Autoradiography Experiment for Litter Samples. Dried leaf litter samples were enclosed in polypropylene bags and exposed to an imaging plate (BAS-IP MS2040, Fuji Film, Japan) for 1 day in darkness at room temperature. As negative control, a fallen leaf, which was collected at NIRS on Dec. 3, 2013, was used. The radioactive signals were detected using a Model FLA-5100 imaging system (Fuji Film, Tokyo, Japan).

Sample Preparation. All samples were oven-dried at 80 °C overnight. The dried soil samples were passed through a 2-mm-mesh sieve to remove large stones. Organic matter in soil samples was decomposed by heating in a muffle oven at 450 °C

for 2 h. For ^{135}Cs and $^{135}Cs/^{137}Cs$ atomic ratio analysis, a sample (∼2−5 g; for IAEA-375 soil reference material, up to 10 g was used) was weighed out and put in a lidded PTFE vessel (120 mL). After adding 20 mL of concentrated HNO_3, the lid of the PTFE vessel was tightened and heated on a hot plate (160 °C) for 2 h, and then the lid was removed. The samples were heated continuously at the same temperature. During the acid digestion process, for litter and lichen samples, 4 mL of H_2O_2 was added to destroy the organic matter. When the digested sample solution had been heated to near dryness, the residual was dissolved in 20 mL concentrated HNO_3. Then, the sample solution was filtered through an Advantec filter into a beaker (250 mL). From the filtered sample solution 0.1 mL was taken out and diluted to 10 mL with 4% HNO_3, prepared for the analysis of stable Cs to be used as yield monitor. The rest of the sample solution was adjusted to 1.6 M HNO_3 by adding Milli-Q water.

AMP Adsorption of Cs. After the sample solution was adjusted to 1.6 M HNO_3, 35 mg of AMP was added for the adsorption of Cs. The mixture was stirred for 1 h and then passed through a 0.45-μm syringe filter (Sartorius Stedim Biotech, Goettingen, Germany) to retain the Cs-adsorbed AMP. AMP was dissolved from the filter into 5 mL of 1.5 M NH_4OH, and was then ready for loading onto the AG MP-1 M resin column.

Separation of Interfering Elements (Mo, Sb, and Sn) from Cs and Ba Using AG MP-1 M Resin. After preconditioning the AG MP-1 resin column (2 mL, 6.5−8.5 mm × 58 mm, i.d.) with 10 mL 1.5 M NH_4OH, the sample solution (in 5 mL 1.5 M NH_4OH) was loaded to remove Mo, Sb, and Sn. Another 3 mL of 1.5 M NH_4OH was used for the elution of Cs and Ba. The effluent during sample loading and the eluent were collected together in a 30-mL PTFE vessel. Then, the sample solution was evaporated to dryness and dissolved in 5 mL 0.15 M NH_4OH, ready for loading onto the AG 50 WX8 resin column.

Separation of Cs from Ba Using AG 50 WX8 Resin. The 2-mL AG 50 WX8 resin column (6.5−8.5 mm × 58 mm, i.d.) was preconditioned with 10 mL of 1.5 M HCl, 10 mL of H_2O, and 10 mL of 0.15 M NH_4OH. After sample loading, the column was washed with 10 mL of 0.15 M NH_4OH and 10 mL of H_2O. Cs was eluted from the AG 50 WX8 resin with 30 mL of 1.5 M HCl, while Ba was retained on the column. The solution was evaporated to near dryness and dissolved in 4 mL of 4% HNO_3, in preparation for ICP-MS/MS analysis.

■ RESULTS AND DISCUSSION

Comparison of Different Ion-Exchange Sorbents for Adsorption of Cs and Interfering Elements (Ba, Mo, Sb, and Sn). AMP is characterized by its highly selective Cs sorption in acid solution, and has been widely used for ^{137}Cs analysis in environmental samples.[27] In our previous work,[28] we investigated the content of stable Cs (^{133}Cs) as an impurity in the powdered AMP from different makers and found that AMP (from Kishida Chemical Co., Ltd.) had the lowest ^{133}Cs impurity among the AMP from five makers. In this work, we further examined the adsorption efficiency of Kishida's powdered AMP and two other sorbents (AMP-PAN and KNiFC-PAN, from Eichrom Technology) for Cs and interfering elements (Ba, Mo, Sb, and Sn). By binding the inorganic ion-exchanger (AMP and KNiFC) on an organic polymer (polyacrylonitrile, PAN), granulometric properties of the powdered AMP and KNiFC are improved.[27] We performed a batch experiment to test the adsorption efficiency of the three sorbents. Weighed amounts of powdered AMP (35 mg), AMP-PAN (100 mg), and KNiFC-PAN (100 mg) were placed into 100 mL of 1.6 M HNO_3, which contained Cs, Ba, Mo, Sb, and Sn in a concentration of 5 ng mL^{-1}. The mixture was stirred for 1 h and then passed through a 0.45-μm syringe filter to retain the Cs-adsorbed AMP, AMP-PAN, and KNiFC-PAN. Concentrations of Cs, Ba, Mo, Sb, and Sn in the filtrate were measured to evaluate the adsorption efficiency. As summarized in Table S2 in the Supporting Information, all three ion-exchange sorbents showed extremely high selectivity for Cs sorption (98.7%−100%). For the adsorption of interfering elements, the powdered AMP showed the lowest adsorption efficiency: 12% for Ba, 16.7% for Sn, and no adsorption of Sb. The adsorption of Ba and Sn on KNiFC-PAN was found to be significant: 21.1% for Ba and 60% for Sn. Thus, AMP was the best material to separate Cs from interfering elements. Based on these results, we selected the powdered AMP for the adsorption of Cs after the acid digestion of environmental samples.

Chromatographic Separation of Interfering Elements (Ba, Mo, Sb, and Sn). Cesium affinity to AMP is very high, resulting in difficulties for the quantitative desorption of Cs. Thus, in this work, we use ammonium hydroxide (NH_4OH) for the decomposition of AMP to achieve the quantitative recovery of cesium. In the presence of alkaline solution, the interfering elements of Mo, Sb, and Sn are present in negatively charged ions, for example, molybdate ion (MoO_4^{2-}), stannite and stannate ions ($HSnO_2^-$ and SnO_3^{2-}), and antimonite and antimonate ions (SbO_2^- and SbO_3^-);[29] therefore, we conducted an anion-exchange chromatographic separation using AG MP-1 M resin to separate the interfering elements of Mo, Sb, and Sn from the positively charged Cs$^+$ and Ba^{2+}. We found that, with a feed solution of 1.5 M NH_4OH, Cs$^+$ and Ba^{2+} passed through the AG MP-1 M column, while MoO_4^{2-}, $HSnO_2^-$, SnO_3^{2-}, SbO_2^-, and SbO_3^- were retained on the column. Because of the high Mo content in AMP ion exchange

sorbent, the decomposition of AMP introduced additional Mo into the sample solution; thus, particular attention was paid to the separation of Mo from the Cs fraction. Figure S1 in the Supporting Information shows the mass spectra of removal of Mo by AG MP-1 M anion-exchange chromatography. Clearly, the effective separation of Mo from the Cs fraction was achieved.

Since a certain amount of Ba remained in the Cs fraction after the anion-exchange chromatographic separation (Figure S1 in the Supporting Information), a cation-exchange chromatographic separation (AG 50WX8 resin) was introduced to achieve further separation of Cs from the Ba that remained. Figure 2 shows the elution profiles of Cs and Ba in IAEA-375
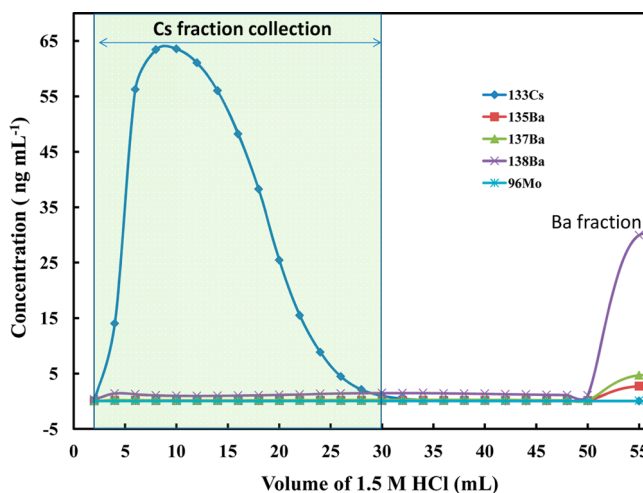

Figure 2. Elution profiles of Cs and Ba in IAEA-375 soil reference material obtained by cation-exchange chromatographic separation (AG 50WX8 resin).

soil reference material. It can be seen that Cs was eluted with 30 mL 1.5 M HCl, while Ba remained on the column during Cs elution, thus a complete separation between Cs and Ba was achieved. Figure S2 in the Supporting Information shows the entire chemical separation procedure that we established for environmental samples. This is a rapid procedure, and all operations can be completed within 1 day. By the analysis of stable ^{133}Cs in the sample solution after the acid digestion and in the final Cs fraction after the chromatographic separations, we found the recovery of Cs was higher than 95%. In addition, because of the combination of AMP-selective adsorption of Cs and anion- and cation-exchange chromatographic separations, high decontamination factors were obtained for Ba (1.8×10^4), Mo (4.1×10^5), Sb (2.6×10^4), and Sn (6.7×10^4). Thus, in the final Cs fraction prior to ICP-MS measurement, only traces of interfering elements remained. For the soil and plant samples that we investigated, we found that Ba and Mo were present at a level of <5 ng mL^{-1}, and Sb and Sn are present at a level of <1 ng mL^{-1} in the final Cs fraction.

Optimization of the Nitrous Oxygen Flow Rate for Cs/Ba Separation. Although <5 ng mL^{-1} Ba remained in the final Cs fraction prior to ICP-MS, that amount still causes significant isobaric interferences for reliable ^{135}Cs and ^{137}Cs isotope measurement. To reduce the $^{135}Ba^+$ and $^{137}Ba^+$ isobaric interferences in ICP-MS measurement, the use of ion−molecule reactions to shift Ba to higher m/z has been proposed in the literature.[9,20,30,31] Granet et al.[30] demonstrated that the addition of N_2O gas in a hexapole reaction cell led to

antagonistic behavior of Cs^+ and Ba^+, since the latter reacted with the gas to form BaO^+ and $BaOH^+$ products while Cs^+ remained unreactive. Here, we investigated the possibility of separation of Cs/Ba in an octopole collision/reaction cell of the ICP-MS/MS system (Agilent, Model 8800) using N_2O (20%) reaction gas with He buffer gas (Figure 1). The N_2O flow rate was optimized while aspirating a test solution (10 ng mL^{-1} for Cs and Ba) to suppress the $^{137}Ba^+$ signal and maximize the
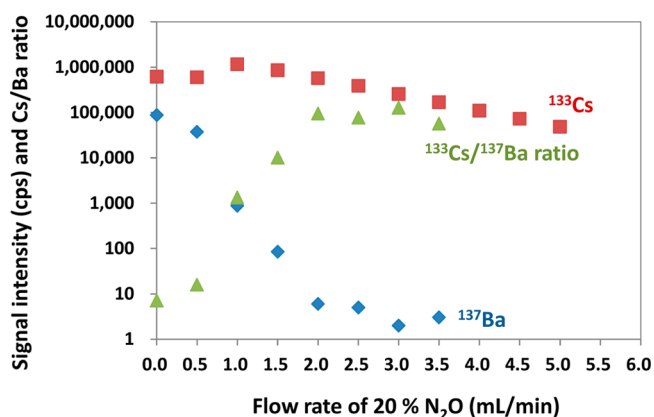
Figure 3. Effect of nitrous oxide flow rate on ^{133}Cs intensity, ^{137}Ba intensity and $^{133}Cs/^{137}Ba$ ratio for a solution of 10 ng mL^{-1} Cs and Ba. N_2O was introduced into the collision/reaction cell via the third cell gas line, and He was introduced at a constant flow rate of 1 mL min^{-1} via the second cell gas line of the ICP-MS/MS.

$^{133}Cs/^{137}Ba$ ratio. Figure 3 shows the effect of N_2O flow rate on ^{133}Cs intensity, ^{137}Ba intensity, and $^{133}Cs/^{137}Ba$ ratio. N_2O was introduced into the collision/reaction cell via the third cell gas line, and He was introduced at a constant flow rate of 1 mL min^{-1} via the second cell gas line of the ICP-MS/MS. The $^{137}Ba^+$ signal intensity decreased quickly as the N_2O flow rate increased, because of the formation of BaO^+ through the reaction channel of O atom transfer and $BaO^+ \cdot N_2O$ formed via the secondary N_2O addition when He was introduced as a buffer gas.[31] When increasing the N_2O flow rate from 0 mL min^{-1} to 3 mL min^{-1}, more than 10^4-fold improvement of $^{133}Cs/^{137}Ba$ ratio was observed at the optimum flow rate (3 mL min^{-1}), and the signal intensity of 10 ng mL^{-1} Ba was reduced to close to 1 cps, indicating that, for a concentration of 10 ng mL^{-1} Ba, the Ba$^+$ isobaric interferences can be completely removed under the optimized conditions.

Elimination of Polyatomic Interferences of $^{95}Mo^{40}Ar^+$ and $^{97}Mo^{40}Ar^+$. Because of the high content of Mo in the AMP sorbent employed for selective Cs adsorption, trace Mo is present in the final solution for ICP-MS measurement. The polyatomic interferences of $^{95}Mo^{40}Ar^+$ and $^{97}Mo^{40}Ar^+$ should be removed for reliable ^{135}Cs and ^{137}Cs analysis. We used a test solution of 10 ng mL^{-1} Mo to investigate the possibility of elimination of $^{95}Mo^{40}Ar^+$ and $^{97}Mo^{40}Ar^+$ polyatomic interferences in ICP-MS/MS measurement. First, we introduced N_2O at the optimized flow rate of 3 mL min^{-1} and operated the ICP-MS/MS under the single MS mode (Q2). From the mass spectrum shown in Figure 4A, signal intensities of several tens of cps could be observed at m/z 135 and 137, representing the trace polyatomic interferences of $^{95}Mo^{40}Ar^+$ and $^{97}Mo^{40}Ar^+$. Then, by introducing N_2O gas, we operated the ICP-MS/MS under the MS/MS mode, that is, Q1 was set for m/z 135 and
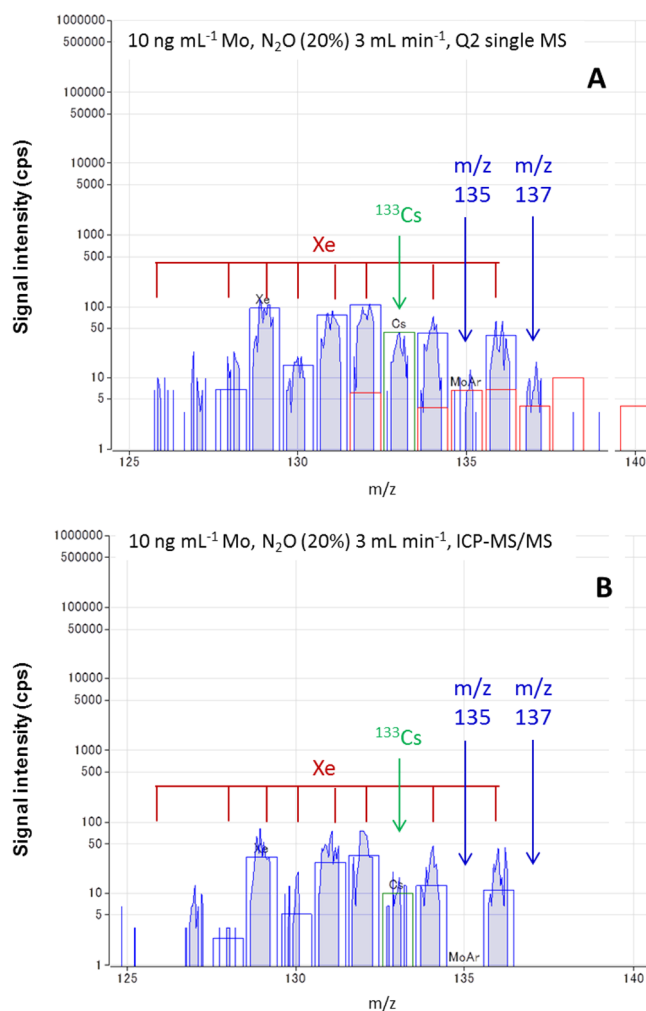

Figure 4. Mass spectra of a solution containing 10 ng mL^{-1} Mo obtained using the N_2O reaction mode with single MS mode (Q2) and MS/MS scan by set Q1 at m/z 135 and 137, respectively. The flow rate of N_2O (20%) was 3 mL min^{-1}, with a He flow rate of 1 mL min^{-1}.

137, respectively, to reject the interfering ions, such as $^{95}Mo^+$, $^{97}Mo^+$, $^{40}Ar^+$, and $^{40}ArO^+$ ions from getting into the Q1 mass filter. As shown in Figure 4B, the signal intensities at m/z 135 and 137 decreased to close to zero cps (0.00 cps with two effective digits), indicating a complete elimination of $^{95}Mo^{40}Ar^+$ and $^{97}Mo^{40}Ar^+$ polyatomic interferences when Mo was analyzed at a concentration of 10 ng mL^{-1}. This result suggested that the formation of MoAr$^+$ ions in the plasma was negligible with the corresponding Mo concentration of 10 ng mL^{-1}, because of the high extent of Mo ionization. The observed trace MoAr$^+$ ions in Figure 4A were mainly due to their formation in the octopole collision/reaction cell. Considering the fact that, after the effective chemical separation, less than several ng mL^{-1} Mo was present in the final solution prior to the ICP-MS/MS measurement, we concluded that the determination of ^{135}Cs and ^{137}Cs isotopes in our analytical system is free of $^{95}Mo^{40}Ar^+$ and $^{97}Mo^{40}Ar^+$ polyatomic interferences for environmental samples.

Polyatomic Interferences of $^{119}Sn^{16}O^+$ and $^{121}Sb^{16}O^+$. Studies have indicated that polyatomic interferences of $^{119}Sn^{16}O^+$ and $^{121}Sb^{16}O^+$ could be a problem for determination of ^{135}Cs and ^{137}Cs isotopes using quadrupole ICP-MS.[20] We

examined the extent of polyatomic interferences of $^{119}Sn^{16}O^+$ and $^{121}Sb^{16}O^+$ in our ICP-MS/MS system by analysis of a test solution containing Sb and Sn at a concentration of 10 ng mL^{-1}. As shown in Figure S3 in the Supporting Information, the formation of $^{119}Sn^{16}O^+$ and $^{121}Sb^{16}O^+$ resulted in a signal intensity of ~10 cps at m/z 135, and 100 cps at m/z 137, respectively, when only He gas was used at a flow rate of 1 mL min^{-1}. When N$_2$O flow rate was increased, signal intensities of $^{119}Sn^{16}O^+$ and $^{121}Sb^{16}O^+$ quickly decreased, and could be completely suppressed to close to zero cps when a higher flow rate (>5 mL min^{-1}) was applied. Figure 5 showed the

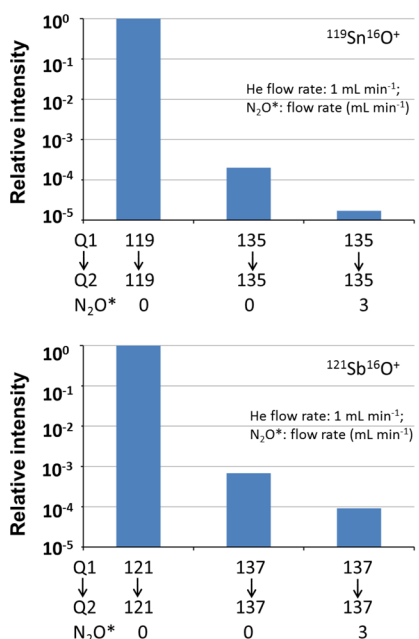**Figure 5.** Production proportion of (a) $^{119}Sn^+$ and $^{119}Sn^{16}O^+$, and (b) $^{121}Sb^+$ and $^{121}Sb^{16}O^+$ for a sample solution of 10 ng mL^{-1} Sb and Sn. Q1 and Q2 express mass numbers of ions that can enter the first and second quadrupoles, respectively.

production proportions of Sn, Sb, and their oxides under different operation conditions of the ICP-MS/MS using MS/MS mode. When only He at a flow rate of 1 mL min^{-1} was introduced into the cell, the signal intensities of $^{119}Sn^{16}O^+$ and $^{121}Sb^{16}O^+$ constituted less than 2.0×10^{-4} and 6.8×10^{-4} of the total Sn and Sb signal, respectively. When N$_2$O gas was introduced into the cell at the optimized flow rate of 3 mL min^{-1}, the signal intensities of $^{119}Sn^{16}O^+$ and $^{121}Sb^{16}O^+$ constituted less than 1.7×10^{-5} and 9.2×10^{-5} of the total Sn and Sb signal, respectively; that is, a decrease of ~1 order of magnitude in the signal intensities of $^{119}Sn^{16}O^+$ and $^{121}Sb^{16}O^+$ was observed. Because of the high decontamination factors of Sb and Sn in our chemical separation procedure, for environmental samples, <1 ng mL^{-1} of each Sb and Sn were present in the final solution for ICP-MS/MS measurement, and the polyatomic interferences of $^{119}Sn^{16}O^+$ and $^{121}Sb^{16}O^+$ were negligible for our analytical method.

Abundance Sensitivity and Limits of Detection. The ICP-MS/MS uses the tandem mass spectrometer configuration with two quadrupole mass filters (Q1 and Q2), which significantly improved the abundance sensitivity. In the MS/MS mode, both Q1 and Q2 are operated as unit mass filters, so the overall abundance sensitivity of the instrument is the

product of the Q1 abundance sensitivity × Q2 abundance sensitivity. With two high-frequency and hyperbolic quadrupoles, each operating with an abundance sensitivity of 10^{-7}, the combined abundance sensitivity of ICP-MS/MS is theoretically 10^{-14}.[32] Figure 6 shows the mass spectrum of analysis of ^{133}Cs
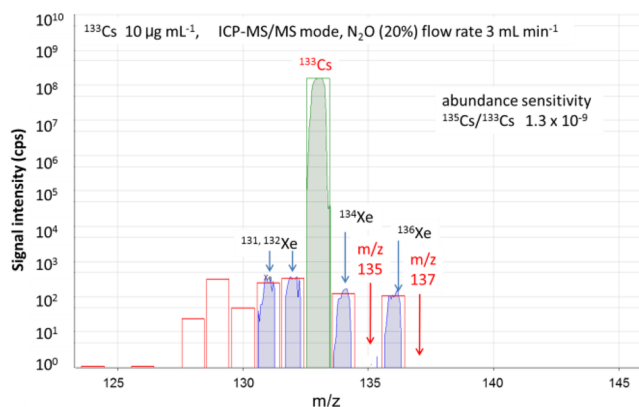

Figure 6. Abundance sensitivity of ICP-MS/MS under the MS/MS mode with N$_2$O (3 mL min^{-1}) and He (1 mL min^{-1}). For this investigation, a Cs standard solution of 10 μg mL^{-1} was measured.

standard solution at a concentration of 10 μg mL^{-1}. A high abundance sensitivity (^{135}Cs/^{133}Cs ratio) of 1.3×10^{-9} was obtained, providing sufficient abundance sensitivity for ^{135}Cs isotope measurement to eliminate the interference of stable ^{133}Cs in the environmental samples.

Because of the effective chemical separation and almost interference-free ICP-MS/MS measurement, the developed analytical method was characterized by extremely low detection limits. Based on the definition of 3σ of the operational blank, the detection limits for ^{133}Cs, ^{135}Cs, and ^{137}Cs were estimated to be 0.9, 0.01, and 0.006 pg mL^{-1}, respectively, or, in terms of radioactivity, 9×10^{-4} mBq g^{-1} for ^{135}Cs and 40 mBq g^{-1} for ^{137}Cs (calculated in 1 g of solid sample). These detection limits are 1 order of magnitude lower than those obtained with a dynamic reaction cell (DRC)-ICP-MS.[9]

Method Validation and Analytical Applications. To assess the accuracy and applicability of the developed analytical method for environmental samples, the IAEA-375 soil reference material was analyzed. This reference material was prepared from soils collected from the 30 km zone around Chernobyl containing ^{135}Cs released from the accident. Its ^{135}Cs/^{137}Cs atomic ratio has been reported in the literature,[9] making it a suitable material for method validation. We analyzed IAEA-375 in different sample weights (2 g, 5 g, and 10 g) to check the soil matrix effect and possible interference of stable ^{133}Cs present in soil on the determination of ^{135}Cs and ^{137}Cs. The analytical results are presented in Table 1. The ^{135}Cs/^{133}Cs atomic ratio was found to be on a level of ca. 6×10^{-7}; taking into account the abundance sensitivity of 1.3×10^{-9} of the ICP-MS/MS used, we concluded that the developed analytical method is capable of determining ^{135}Cs in soil sample, even with a sample size as large as 10 g. Among the three sample sizes, constant results were obtained for the ^{135}Cs/^{137}Cs atomic ratio, ^{135}Cs activity (calculated from the certified ^{137}Cs activity using the measured ^{135}Cs/^{137}Cs atomic ratio), and ^{135}Cs/^{133}Cs atomic ratio. The ^{135}Cs/^{137}Cs atomic ratios measured agreed very well with the value reported by an earlier study.[9]

The developed analytical method was applied to environmental samples (soil, litter, and lichen) collected in Japan after the FDNPP accident. The analytical results are summarized in Table 1. It should be noted that, for the determination of ^{137}Cs in environmental samples, gamma spectrometry has a much lower detection limit (ca. 1 mBq g^{-1}), compared to the detection limit of 40 mBq g^{-1} of the developed ICP-MS/MS method. Therefore, although a comparison of ^{137}Cs activities in environmental samples measured by the developed ICP-MS/MS and gamma spectrometry showed a good agreement (Figure S5 in the Supporting Information), ^{137}Cs activities measured by using gamma spectrometry were used for quantification of ^{135}Cs activities. The activities of ^{137}Cs varied in a wide range from ca. 10 000 mBq g^{-1} to more than 4 million mBq g^{-1}; the plant samples (litter and lichen) collected in the forests of Fukushima Prefecture (samples S1–S5) generally showed higher ^{137}Cs activities. Autoradiography measurement of litter samples (Figure S4 in the Supporting Information) indicated heavy deposition of radiocesium in a granular form, similar to that reported in bamboo and shiitake mushroom.[33] It was noted that the atomic ratios of $^{135}Cs/^{137}Cs$ in these plant samples from Fukushima Prefecture, especially samples collected in the area northwest of the nuclear power plant, showed very similar values, ranging from 0.333–0.343 (reference to March 11, 2011 for ^{137}Cs decay correction), indicating that radioactive Cs isotopes deposited on the surface of litter and lichen were mostly released from the same source in the FDNPP accident.[34] Higher ratios (0.355–0.375) were observed in soil samples (samples S6 and S8) collected in the J-Village complex, 20 km south of the FDNPP and in Kamagaya City, 230 km southwest of the FDNPP. The detected $^{135}Cs/^{137}Cs$ isotope ratios in environmental samples in this study were generally in good agreement with the values reported in plant samples from Fukushima Prefecture obtained using TIMS measurement,[3] and that in rainwater samples reported by Ohno and Muramatsu.[4] In addition, we noted that the levels of the $^{135}Cs/^{133}Cs$ ratio in plant samples from Fukushima Prefecture (10^{-3}–10^{-5}) were 2–4 orders of magnitude higher than that in soil samples (10^{-7}), because of heavier contamination in plant samples and higher ^{133}Cs concentration in soil. This result indicated that our analytical method provided sufficient abundance sensitivity for the reliable determination of ^{135}Cs and ^{137}Cs in soils for the environmental radioactivity studies related to the FDNPP contamination.

CONCLUSIONS

A novel analytical method based on the combination of AMP-selective Cs adsorption and ion-exchange chromatographic separation with ICP-MS/MS detection was developed for the determination of ^{133}Cs, ^{135}Cs, and ^{137}Cs, and the atomic ratios of $^{135}Cs/^{133}Cs$ and $^{135}Cs/^{137}Cs$ in environmental samples. The established chemical separation procedure was characterized by a high recovery of Cs isotopes (>95%) and high decontamination factors (10^4–10^5) of the interfering elements of Ba, Mo, Sb, and Sn. This chemical separation procedure is rapid, and can be completed within 1 day. By introducing N_2O–He gases into the octopole collision/reaction cell of the ICP-MS/MS and operating in the MS/MS mode, elimination of Ba isobaric interferences and MoAr$^+$ polyatomic interferences was achieved. In addition, the interferences of $^{121}Sb^{16}O^+$ and $^{119}Sn^{16}O^+$ were suppressed to negligible levels, thus, interfer-ence-free determination of ^{135}Cs and ^{137}Cs in environmental samples was realized with the lowest limit of detection ever reported for ICP-MS analysis. The developed analytical method was successfully applied to the analysis of soil and plant samples collected in Japan after the FDNPP accident and analysis results were used for source identification. Important applications to studies on the long-term environmental behavior of the released radiocesium isotopes can be expected.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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