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Abstract

The $^{135}Cs/^{137}Cs$ isotopic ratio is a powerful tool for tracing the origin of radioactive contamination. Since the Fukushima accident, this ratio has been measured by mass spectrometry in several highly contaminated environmental matrices mainly collected near nuclear accident exclusion zones and former nuclear test areas. However, few data were reported at ^{137}Cs environmental levels (< 1 $kBq.kg^{-1}$). This is explained by the occurrence of analytical challenges related to the very low radiocesium content at environmental level with the large presence of mass interferences, making ^{135}Cs and ^{137}Cs measurements difficult. To overcome these difficulties, a highly selective procedure for Cs extraction/separation combined with an efficient mass spectrometry measurement must be applied on a quantity of ca. 100 g of soil. In the current research, an innovative ICP-MS/MS method has been developed for the $^{135}Cs/^{137}Cs$ ratio measurement in low activity environmental samples. The use of ICP-MS/MS led to a powerful suppression of ^{135}Cs and ^{137}Cs interferences by introducing N_2O, He and, for the first time, NH_3, into the collision-reaction cell. By adjusting the flow rates of these gases, the best compromise between a maximum signal in Cs and an effective interference elimination was achieved allowing a high Cs sensitivity of more than 1.10^5 $cps/(ng.g^{-1})$ and low background levels at m/z 135 and 137 lower than 0.6 cps. The accuracy of the developed method was successfully verified by analyzing two certified reference materials (IAEA-330 and IAEA-375) commonly used in the literature as validation samples and three sediment samples collected in the Niida River catchment (Japan) impacted by the Fukushima fallout.

Introduction

Since the 1950s, radiocesium isotopes have been introduced into the environment by Nuclear Weapons Tests (thereafter NWT) (^{135}Cs and ^{137}Cs), accidents of Nuclear Power Plants (thereafter NPP) and waste reprocessing facilities (^{134}Cs, ^{135}Cs and ^{137}Cs, for these last two sources)[1–4]. The ^{134}Cs/^{137}Cs isotopic signature has long been used as a fingerprint to identify the source of environmental contamination[5–8]. Unfortunately, the short half-life of ^{134}Cs ($t_{1/2}$ = 2.1 y) limits the temporal validity of this forensic analysis to about ten years after a release[9–11]. To retrace the origin of older contamination events, ^{135}Cs ($t_{1/2}$ = 2.3.10^6 y) is the ideal substituent of ^{134}Cs[12–17]. The ^{135}Cs/^{137}Cs ratio also allows for the identification and the calculation of the respective contributions of the releases in a single analysis. Some environmental studies recently showed that the ^{135}Cs/^{137}Cs ratio is of crucial importance for the study of the fate and the transfer of ^{137}Cs in the environment. Unlike the ^{134}Cs/^{137}Cs ratio which depends only on the fission yields, the ^{135}Cs/^{137}Cs ratio also varies according to the neutron field of the reactor (flux and exposure time)[18–21].

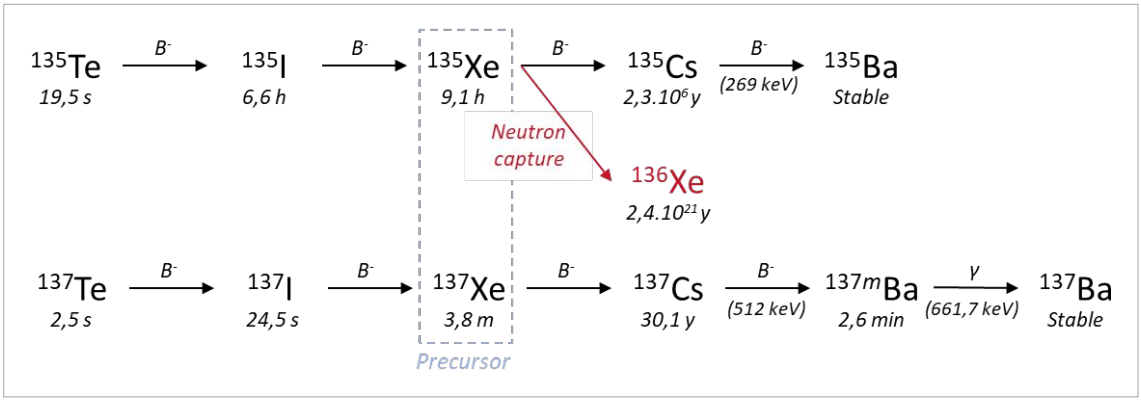

Figure 1 – Decay chain of ^{135}Cs and ^{137}Cs with their precursor

The variation in the ^{135}Cs/^{137}Cs ratios between different release events can be explained by the competition between two nuclear reactions involving ^{135}Xe (namely the precursor of ^{135}Cs) leading to *(1)* the formation of ^{135}Cs by β-decay or *(2)* the production of ^{136}Xe by neutron capture (Figure 1) [9,11,16]. This competition is mainly governed by the exposure time and the energy of the neutron flux. The higher these parameters are, the more the production of ^{136}Xe from ^{135}Xe is favored, inducing the depletion of ^{135}Cs and, consequently, the decrease of the ^{135}Cs/^{137}Cs ratio. Low ^{135}Cs/^{137}Cs atomic ratios of 0.52 ± 0.02 and 0.35 ± 0.02 (decay-corrected to March 11th, 2011) have been reported for Chernobyl and Fukushima fallout, respectively[9,11,22–24]. Conversely, for short neutron exposure times, such as those that occurred during the atmospheric testing of nuclear weapons, the characteristic ^{135}Cs/^{137}Cs ratio is much higher (2.62 ± 0.48, decay-corrected to March

11th, 2011)[12,21,22,25,26]. The $^{135}Cs/^{137}Cs$ ratio is therefore a particularly powerful indicator of the ^{137}Cs source and it can provide a long-lived fingerprint of nuclear releases. This high potential is nevertheless limited by the fact that its measurement in environmental samples is associated with several analytical challenges[10,17,19,23].

While the quantification of ^{137}Cs by gamma spectrometry is very efficient and allows to reach very low detection limits (down to 0.1 $Bq.kg^{-1}$)[27,28], the radiometric measurement of ^{135}Cs is difficult due to its low-energy beta emission (β^-, E_{max} 268.9 keV)[13,29]. Theoretically, ^{135}Cs (pure beta emitter) can be quantified by radiometric methods but the five-fold higher activity of ^{137}Cs, which is also a β-emitter, renders the analysis of ^{135}Cs difficult[30,31]. During the last two decades, the quantification of radiocesium (^{135}Cs and ^{137}Cs) has become possible thanks to the development of advanced mass spectrometry (MS) techniques[32]. The two main MS techniques used to determine the $^{135}Cs/^{137}Cs$ ratio in environmental samples are the triple-quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS)[10,11,13,14,22] and the thermal ionization mass spectrometry (TIMS)[6,16,18,33,34]. A major advantage of these MS techniques is their very low abundance sensitivity ($<10^{-9}$), which is required to limit the effect of stable cesium (^{133}Cs) peak tailing on the ^{135}Cs measurement[19,31,35]. The measurement of ^{135}Cs and ^{137}Cs by mass spectrometry raises other significant metrological difficulties due to the low amount of radiocesium atoms at low levels of contamination and to the presence of many interferences in the mass range of interest (^{135}Ba, ^{137}Ba, $^{95}Mo^{40}Ar$, $^{97}Mo^{40}Ar$, $^{119}Sn^{16}O$, $^{121}Sb^{16}O$)[36]. A specific radiochemical procedure is therefore needed to isolate the radiocesium from the sample matrix and to purify it from all other elements generating mass interferences. Usually, Cs is separated from the matrix using highly selective molecules such as ammonium molybdophosphate (AMP) and then interferents by combining the properties of anion and cation exchange resins[10,11,17,23]. In addition, due to the low radiocesium concentration in the environmental samples (i.e. collected outside of exclusion zones and former nuclear testing areas), large quantities of samples must be processed to detect ^{135}Cs[14,37].

Recently, we have thus developed a new radiochemical method allowing to analyze, for the first time to our knowledge, very large quantities of samples (up to 100 g of soil or sediment ashes) to measure accurately the $^{135}Cs/^{137}Cs$ ratio by ICP-MS/MS at environmental levels (*i.e.,* when $^{137}Cs < 1$ $kBq.kg^{-1}$ (either when $^{137}Cs < 0.3$ $pg.g^{-1}$))[38]. This procedure involves the sample acid digestion followed by a preconcentration of the Cs using AMP powder. The Cs is then separated from the analytical interferents by a sequence of two ion exchange resins. The high recovery yields

(> 80%) and the purity of the final fraction are promising and comparable to those obtained from very active gram-size samples[38].

The current research builds upon our last study, proposing a Cs purification protocol, and has two major objectives. The first goal is to develop an innovative ICP-MS/MS method to quantify the $^{135}Cs/^{137}Cs$ ratio in low-level contaminated soils or sediments. The interference traces still present in solution after the radiochemical method will be eliminated by adding gas into the collision-reaction cell of the ICP-MS/MS. The optimal gas conditions (flow, nature) will be defined from the study of different gas mixtures based on nitrous oxide (the only reaction gas used so far in radiocesium analysis). The developed method will have to meet several performance criteria such as a high Cs detection sensitivity and an efficient removal of the last traces of interfering elements. To obtain accurate atomic ratios, the mass bias correction will be investigated using a ^{135}Cs and ^{137}Cs solution with an isotopic ratio previously quantified by TIMS[34]. The second objective of the current work consists in validating the analytical method. Due to the lack of certified reference materials for ^{135}Cs, the accuracy of the developed method will be evaluated by comparing the $^{135}Cs/^{137}Cs$ ratios of some environmental samples impacted by Chernobyl or Fukushima fallout with those reported in the literature for these sources.

Experimental section

Samples

ICP-MS/MS measurement method development. Three types of samples were used to design the ICP-MS/MS measurement method:

(i) A soil sample with a low ^{137}Cs activity ($^{137}Cs < 6$ Bq.kg^{-1} ash) was selected to estimate the interferent composition of the measurement fraction. Its initial activity was previously characterized by gamma spectrometry at LMRE (Laboratoire de Métrologie de la Radioactivité dans l'Environnement, France).

(ii) Synthetic samples were prepared from 0.5M HNO_3 and standard solutions of Cs, Ba, Mo, Sb and Sn (supplied by Carlo Erba) to define the optimal measurement conditions.

(iii) Due to the lack of certified solutions with a known $^{135}Cs/^{137}Cs$ ratio, the mass bias effect (usually observed by ICP-MS/MS) was assessed by measuring a fraction of Cs purified from uranium pellets irradiated in nuclear reactors with a method previously reported by Isnard et al. (2009)[34].

In summary, the Cs fraction was purified from the sample matrix by a two-step liquid chromatography procedure. First, the fission product fraction containing Cs is separated from U and Pu by anion-exchange resin. After evaporation, Cs fraction is then purified from other fission products and specially barium (isobaric interference with Cs) by high performance liquid chromatography. This Cs fraction was qualified by TIMS using a method described in the instrumentation section.

Validation of the developed method. For the evaluation of the accuracy of the protocol, two types of environmental samples were employed. Two ^{137}Cs certified reference materials (CRM) from the International Atomic Energy Agency (IAEA) were analyzed. Both CRMs, IAEA-330 and IAEA-375, were selected as they are often used in the literature to validate ^{135}Cs/^{137}Cs analytical protocols[11,12,14–16,25,39,40]. They correspond respectively to spinach and soil samples collected in Ukraine and Russia in 1990, respectively, and show a ^{135}Cs/^{137}Cs ratio characteristic of the Chernobyl fallout. The compatibility of the measured and published ^{135}Cs/^{137}Cs ratios was monitored by calculating the E_n score (E_n), given by equation (1).

$$En\ score = \frac{|IR_{measured} - IR_{published}|}{\sqrt{U^2_{IR_{measured}} + U^2_{IR_{published}}}} \#(1)$$

Where $IR_{measured}$ and $IR_{published}$ corresponding respectively to ^{135}Cs/^{137}Cs isotopic ratios measured with our method and those published in the literature and U_{IR} corresponding to their uncertainty at k = 2.

It was also chosen to verify the reliability of the measured ratios by analyzing sediment samples impacted by the Fukushima fallout. Due to the lack of easily available CRM for this radiocesium source, three sediment samples collected in 2012, 2015 and 2020 from the Niida river catchment draining a part of the main radioactive plume of the Fukushima Prefecture[41] were used. The ^{137}Cs activities of these sediments were quantified by gamma spectrometry at LSCE (Laboratoire des Sciences du Climat et de l'Environnement, France) and were 172, 38 and 4 kBq.kg^{-1} (53, 12 and 1.2 pg.g^{-1}) respectively at the sampling date.

Radiocesium purification procedure for environmental solid samples

Radiocesium is extracted from solid environmental matrices and purified using the method described in our previous work[38]. For each sample, the mass to be analyzed was defined based on their ^{137}Cs activity, previously measured by gamma spectrometry. In this study, the mass ranged

from 15 to 100 grams of ash sample. Cesium was extracted from the solid matrix by four successive acid leaching steps of 8 hours on a hot plate set at 180 °C in presence of hydrogen peroxide. The first leaching step was conducted using concentrated nitric acid. *Aqua regia* (HNO_3/HCl mixture) was used for the following ones. After each leaching, the solid residue was separated from the supernatant by centrifugation and the supernatants were combined, evaporated near to dryness, and then diluted in ultra-pure milli-Q water (with resistivity 18.2 $M\Omega.cm^{-1}$, Merck Millipore). Then, 120 mg of ammonium molybdophosphate (AMP) powder (provided by Alfa Aesar) were added to the solution to selectively concentrate the cesium. The solution was stirred for 30 minutes at room temperature and centrifuged. After removal of the supernatant, the precipitate containing the cesium was filtered on a polyvinylidene fluoride membrane filter (PVDF, 0.45 µm pore size, Merck Millipore). The Cs was released from the precipitate by adding 24 mL of 2M NH_4OH onto the filter. Two ion exchange resins provided by Biorad Technologies were used to separate the Cs from its interferents. First, to remove polyatomic interferents such as Mo, Sb and Sn, the sample was loaded onto a column containing 3 mL of AG®MP-1M anion exchange resin (100 – 200 mesh, Cl^- form) conditioned with 1.5M NH_4OH. Cesium ions were not adsorbed on the resin and were collected in the loading and rinsing fractions (2 x 3 mL of 1.5M NH_4OH), whereas polyatomic interferents remained on it. Then, Cs was separated from its isobaric interferent (Ba) using a column containing 8 mL of AG®50W-X8 cationic resin (100 – 200 mesh, H^+ form) conditioned with 20 mL of milli-Q H_2O followed by 20 mL of 1.5M NH_4OH. The sample was loaded, and the resin was rinsed with 50 mL of 1.5M NH_4OH and converted by 20 mL of milli-Q water followed by 20 mL of ultra-pure 1.5M HNO_3. Cs was eluted with 50 mL of ultra-pure 1.5M HNO_3 while Ba remained fixed on the AG®50W-X8 resin. After measurement by gamma spectrometry to determine the chemical yield, the eluate was evaporated and redissolved in 5 mL of ultra-pure 0.5M HNO_3 to be measured by ICP-MS.

Development strategy of the $^{135}Cs/^{137}Cs$ measurement method by ICP-MS/MS

The measurement method for ^{135}Cs and ^{137}Cs by ICP-MS/MS was developed in three steps. The first one aims at estimating the interferent concentrations in the purified fraction during the analysis of 100 grams of soil samples and reagent blanks. Then, the reaction gas conditions in the reaction/collision cell were optimized to obtain the best compromise between a total interference suppression (at m/z 135 and 137) and a good Cs signal sensitivity by monitoring ^{133}Cs. Finally, the corrections applied on the $^{135}Cs/^{137}Cs$ atomic ratio were well constrained to provide accurate ratio.

Instrumentation

Triple-quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS/MS). Concentration and isotopic ratio measurements were performed with the Agilent 8900#100 triple-quadrupole ICP-MS coupled with the SPS4 auto-sampler and controlled by the MassHunter 4.6 software. All measured solutions (blanks, standards and samples) were prepared in 0.5M ultra-pure nitric acid and introduced into the ICP-MS by a MicroMist nebulizer with a peristaltic pump at a rate of 0.35 $mL.min^{-1}$. When analyzing environmental samples with low ^{137}Cs contamination, an Apex Ω desolvating system (Elemental Scientific Inc.) was used to maximize the sensitivity by improving the sample introduction efficiency. The formed aerosol was transferred to a hot plasma and then the ions were extracted and focused with a Ni skimmer cone and a x-lens block. The instrument is equipped with an octopole reaction-collision cell (CRC) between two quadrupole mass filters (Q1 and Q2) allowing an efficient removal of interferences. Q1 filtered the target ions subsequently led into the CRC. For radiocesium analysis, the CRC aimed to promote the collision or reaction of interferents with a specific gas mixture. Finally, the analyte ions were again filtered by Q2 to be measured in on-mass mode. All the experimental conditions are listed in Table S1.

The interferent (Ba, Mo, Sb, Sn) contents were measured in single quadrupole mode without reaction gas and evaluated by an external calibration method. The standards were prepared from ultra-pure milli-Q water and certified mono-elemental solutions provided by Carlo Erba.

The $^{135}Cs/^{137}Cs$ isotopic ratios were obtained in triple quadrupole mode by setting Q1 and Q2 to the 135 and 137 m/z and adding one or a mixture of reaction gases in the collision-reaction cell. To effectively remove the last traces of interferences, several N_2O-based gas mixtures (99.998% purity, Messer) were investigated: N_2O with He (99.9992% purity, Air product), and N_2O with NH_3/He mixture (10/90 m/m, 99.98% purity, Air product).

The sensitivity and oxide rate settings were optimized using a multi-element solution concentrated to 2.5 $ng.g^{-1}$ in Cs, Ce and Ba prepared from certified solutions (Carlo Erba). Each measurement was corrected with an acid blank and the matrix effect was monitored using an internal standard of indium (concentrated to 3 $ng.g^{-1}$).

Isotopic ratios were corrected for mass bias by the sample standard bracketing approach consisting in framing the sample measurement with that of a solution with a known $^{135}Cs/^{137}Cs$ ratio and delivered by the Laboratory of Analytical development for Nuclear Isotopic and Elemental

analysis (LANIE, CEA). The acquisition parameters of the $^{135}Cs/^{137}Cs$ isotopic ratios are reported in Table 1.

Table 1 – ICP-MS/MS acquisition parameters for $^{135}Cs/^{137}Cs$ isotopic ratio measurements.

Parameter	Setting
Integration time	1 s for m/z = 115 and 138 5 s for m/z 135 and 137
Replicates	5
Sweeps/replicate	1 000
Q2 peak pattern	3 points

Thermal Ionization Mass Spectrometry (TIMS). Thermal ionization mass spectrometry measurements were carried out on an Isoprobe-T (IsotopX, Manchester, UK), which have been already described in Mialle et al. 2012[42]. This instrument is surrounded by a glovebox to handle radioactive materials.

An outgassed rhenium mono filament configuration is used. Deposits with graphite are performed onto the filament:

(i) A droplet of H_3PO_4 0.25N is firstly deposited and evaporated near to dryness by applying a 0.5 A current.

(ii) A 1µL droplet of colloidal graphite (Aquadag) into water/ethanol solution is then deposited and evaporated at the same current near to dryness.

(iii) A 1µL droplet containing 25 ng of Cs is deposited on this graphite layer and evaporated at the same current near to dryness.

This method of deposition is applied to ensure a stable emission of cesium[34].

Cesium isotope ratio measurements are performed on multistatic detection mode. Each Cs isotopes is collected on different Faraday cup and $^{138}Ba^+$ ion beam is also monitored (Table 2) to control the absence of interference at masses 137 and 135. Intercalibration gains between Faraday cups are daily measured and the fluctuation of the electronic gains are lower than 20 ppm/day. The used method is so-called sequential[34,43]: the filament is heated at different temperatures in order to reach different values of $^{133}Cs^+$ signal (respectively 30 mV, 200 mV, 500 mV, 1 V and 3 V). For each heating

step, 6 blocks of 10 measurement cycles are performed with an integration time of 5 s. For each cycle, half-masses are measured and applied. Only the data obtained at the 3 V-step are used for the calculation. This progressive evaporation allows to control the isotopic fractionation[34] and to "burn" the eventual traces of barium, which can be present in the sample. To validate cesium measurements with this method, several operating parameters should be systematically verified:

(i) the current applied to the filament should increase continuously between the different steps,

(ii) the ion beam should not decrease more than 20 % in the stability zone (*i.e.,* 3 V-step),

(iii) the standard deviation should be < 0.1 % for the last 60 measurements (*i.e.*, for the 3 V step) of the major isotope ratios.

Table 2 – TIMS experimental parameters.

Collectors	**L1**	**Ax**	**H1**	**H2**	**H3**	**Integration time**	**Cycles**	**Blocs**
Isotopes	**^{133}Cs**	**^{134}Cs**	**^{135}Cs**	**^{137}Cs**	**^{138}Ba**			
Low half-masses	132.5	133.5	134.5	136.5	137.5	5 s	10	6
High half-masses	133.5	134.5	135.5	137.5	138.5			

Results and discussion

Optimization of the ICP-MS/MS measurement method to determine the ^{135}Cs/^{137}Cs ratio in low-level radioactive samples.

Interference quantification in the measurement fraction. A major analytical challenge in measuring the ^{135}Cs/^{137}Cs ratio at environmental levels arises from the presence of many interference sources and this particularly valid when the sample quantities were significantly increased. Three types of interferences can be distinguished: the ^{133}Cs peak tailing effect, the occurrence of isobaric interferences as those generated by Ba and polyatomic species such as Sb and Sn oxides or Ar-Mo recombination[36]. In this work, the ^{133}Cs peak tailing contribution on the ^{135}Cs measurement was effectively reduced thanks to the low abundance sensitivity achieved by the triple quadrupole ICP-MS. For isobaric and polyatomic interferences, a significant amount of Ba, Sb, Sn and Mo was removed by the radiochemical treatment of the sample (see experimental section). Nevertheless, traces of these elements were still present in the measured fraction and could interfere with the ^{135}Cs and ^{137}Cs measurements. To eliminate them, one gas or a mixture of collision-reaction gases

were introduced into the ICP-MS/MS reaction-collision cell where their flow rates are conditioned by the purity of the measurement fraction. Indeed, the higher the interference level, the higher is the gas flow rates to be added into the CRC resulting in a significant decrease of the Cs signal. It is therefore essential to obtain the purest possible sample but also to know the interference contents to adapt the gas mixture. Interferent element concentrations in the measurement solution were estimated based on the analysis of reagent blank and 100 g of purified sediment. The results provided in Table 3 showed that the interference levels were close for both sediment and blank samples. The concentrations of Ba, Mo and Sb were comparable with those reported in the literature for lower sample masses. For Sn, significant levels were observed in both blanks and sediments. This contamination was due to the use of peristaltic pump tubing releasing Sn during radiochemical treatment and sample introduction into the ICP-MS/MS. Rinsing these tubing with milli-Q water had already reduced Sn pollution by a factor of 5.

In this study, the best reaction gas conditions were also investigated by measuring a solution containing Cs and its interferents at levels overestimated by a factor of 10 compared to those given in Table 3. The objective was to obtain powerful interference removal conditions and a measurement method applicable to different matrices.

Table 3 - Analytical results in terms of purity of the measurement fraction obtained on reagent blanks (synthetic samples composed only of reagent and treated according to the described protocol) and on 100 g of sediment.

Sample type	Final fraction composition (ng.mL^{-1})			
	Mo	Sb	Sn	Ba
Reagent blank *(n=5)*	0.09 ± 0.04	0.06 ± 0.01	6.8 ± 2.7	0.31 ± 0.11
100 g of sediment *(n=4)*	0.48 ± 0.22	0.04 ± 0.01	5.7 ± 0.3	0.36 ± 0.11

Study of the optimal gas conditions in the collision-reaction cell. In the literature, the reaction gas exclusively used until now for the measurement of ^{135}Cs and ^{137}Cs without interference was nitrous oxide (N_2O)[10,11,14,22,40,44,45] with flow rates from 0.50 to 0.94 mL.min^{-1}. When introduced in the CRC, N_2O oxidized barium in a thermodynamically favorable exothermic reaction (Δ_rH= -236.8 < 0 kJ.mol^{-1}). Thus, $^{135}Ba^{16}O^+$ and $^{137}Ba^{16}O^+$ species were detectable at m/z 151 and 153, while $^{135}Cs^+$ and $^{137}Cs^+$ ions did not react (Δ_rH= 106.3 > 0 kJ.mol^{-1}) and were measured in 'on-mass' mode at m/z 135 and 137[46,47]. The impact of N_2O on Ba removal and Cs sensitivity was studied

for flow rates between 0 and 0.85 mL.min^{-1} by monitoring ^{138}Ba and ^{133}Cs. A significant reduction of the ^{138}Ba signal (up to a factor of 2.10^4) and a 7-fold attenuation of the Cs signal were observed for a N_2O flow rate of 0.85 mL.min^{-1} (Figure 2). Nevertheless, under these measurement conditions with the Agilent 8900#100 instrument (model used for the first time to our knowledge for this application), interference removal at m/z 135 and 137 was incomplete with minimum residual signals of 16 cps and 6 cps, respectively. Comparison of the measured signals with those expected for only Ba contamination revealed that the Ba natural abundance (^{135}Ba=6.59%, ^{137}Ba=11.32% and ^{138}Ba=71.66%) was no longer expected for N_2O flow rates higher than 0.20 mL.min^{-1}. Thus, other substances than Ba were causing an interference and N_2O as the reaction gas was not able to completely remove them.

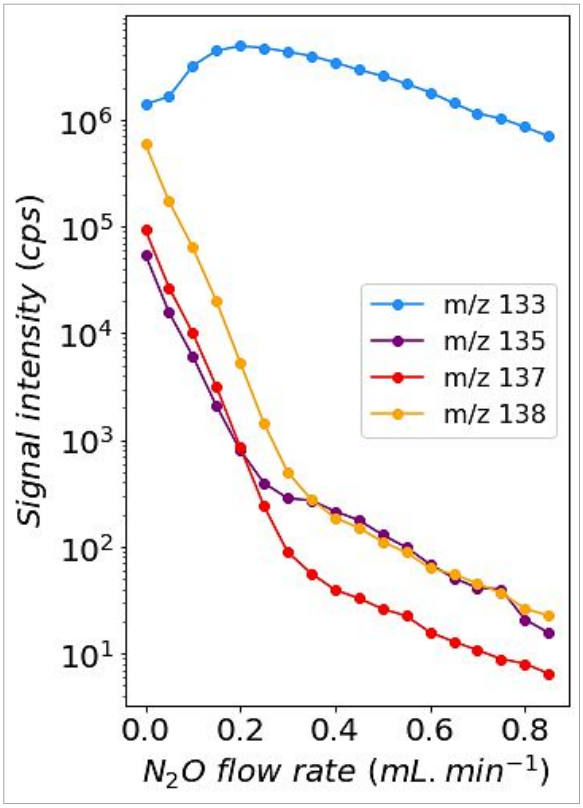

Figure 2 - Variation of signal intensities at m/z 133, 135, 137 and 138 with the addition of N_2O in the CRC (between 0 and 0.85 mL.min^{-1}) for solution containing Cs (10 ng.mL^{-1}), Mo (3 ng.mL^{-1}), Sb (0.5 ng.mL^{-1}), Sn (50 ng.mL^{-1}) and Ba (5 ng.mL^{-1}).

To identify residual species, solutions containing Cs and a single interferent (Mo, Ba, Sn or Sb) were measured. The results available in SI (Figure S1) demonstrated the presence of higher signals at m/z 135 and 137 when measuring solutions containing tin and antimony. These elements interfere with radiocesium measurement under oxide form: ^{119}Sn^{16}O and ^{121}Sb^{16}O. To dissociate the polyatomic species, the use of a low reactive collision gas (He) was studied for flow rates between

1 and 7 mL.min^{-1} in the presence of N_2O (Figure S2). The data obtained for this experiment indicated that helium did not significantly reduce the interference. However, the addition of He in the CRC with a flow rate of 1.2 mL.min^{-1} led to an improvement of the Cs signal (+38%). This phenomenon could be explained by a better focusing of the ions in the presence of helium.

Finally, an efficient elimination of interferences was obtained by combining nitrous oxide with ammonia as a complementary reaction gas. In the literature, although very few data were available regarding the thermodynamics of reactions between Sn or Sb oxides and NH_3, two hypotheses could be put forward. The first one is related to the interference removal by charge transfer and the second one by cluster formation. The flow rates of each gas were optimized by varying the ammonia (as a NH_3/He mixture) between 0 and 6 mL.min^{-1} with several fixed N_2O flow (Figure S3). With the addition of NH_3, the contributions to the 135 and 137 masses were significantly reduced (from 16 cps and 6 cps, respectively down to 0.1 cps), but the Cs sensitivity was also reduced. This attenuation of the Cs signal was accentuated with increasing gas flows (Figure S3.c). The best compromise to obtain both a maximum Cs sensitivity and a powerful interference removal was achieved by adjusting the flow of N_2O to 0.52 mL.min^{-1} (introduced via the 4th cell gas line), the NH_3/He mixture to 4.79 mL.min^{-1} (added by the 3rd cell gas line) and He to 1 mL.min^{-1} (minimum safety flow required when using the 3rd gas line). Under these conditions, the residual signals obtained at m/z 135 and 137 were lower than 0.6 cps for blank and multi-element solutions and the sensitivity was 1.10^5 cps for 1 ng.mL^{-1} of Cs. For the analysis at very low levels, this sensitivity could be improved by a factor of 3 using an Apex Ω desolvating system. It was then in the same order of magnitude as that obtained by Zheng et al. (2016)[14] and Zhu et al. (2020)[10] with the Apex-Q combined with the Agilent 8800 ICP MS/MS. Based on the method of 3σ of the procedure blank, the ^{135}Cs and ^{137}Cs detection limits were estimated to be 1.66 fg.g^{-1} and 0.67 fg.g^{-1}, respectively (or 7x10^{-5} mBq.g^{-1} for ^{135}Cs and 2 mBq.g^{-1} for ^{137}Cs). These detection limits were up to 12 times and 3 times, for ^{135}Cs and ^{137}Cs respectively, lower than those reported in the literature[10,14].

Estimation of the correction factors

The ^{135}Cs/^{137}Cs isotopic ratio measured by ICP-MS/MS was affected by specific biases due to the used instrumentation, requiring the application of corrections. The first one was related to the blank correction corresponding to the non-zero signal given by amplifiers even if they received nothing. To estimate it, the nitric acid used to dilute the sample was measured prior to sample solution. The HNO_3 signals obtained at 135 and 137 masses were deduced from those of samples.

$$IR_{corrected} = IR_{measured\ in\ sample} \times \left(\frac{M_{^{135}Cs}}{M_{^{137}Cs}}\right)^{\beta} \quad with \quad \beta = \frac{\ln\left(\frac{IR_{certified}}{IR_{measured\ in\ certified\ solution}}\right)}{\ln\left(\frac{M_{^{135}Cs}}{M_{^{137}Cs}}\right)} \#(2)$$

The blank correction was estimated to be lower than 0.60 cps. The second correction was related to the mass bias caused by the difference in behavior of two isotopes of the same element during the measurement[48]. This correction could be estimated by the sample-standard bracketing approach. The measured $^{135}Cs/^{137}Cs$ ratio was corrected for mass bias according to Equation (2).

Where:

$IR_{measured\ in\ sample}$ = $^{135}Cs/^{137}Cs$ isotopic ratio without correction measured by ICP-MS/MS

$M_{^{135}Cs}$ and $M_{^{137}Cs}$ = atomic mass of ^{135}Cs and ^{137}Cs, respectively.

β = mass bias factor with $IR_{certified}$ corresponding to the certified $^{135}Cs/^{137}Cs$ isotopic ratio of the reference solution and $IR_{measured\ in\ certified\ solution}$ to the $^{135}Cs/^{137}Cs$ isotopic ratio measured in the reference solution by ICP-MS/MS.

Ideally, the standards used should contain the analytes. Unfortunately, no certified solution including a certified $^{135}Cs/^{137}Cs$ ratio is currently available. An alternative has been proposed in the literature in single quadrupole ICP-MS mode by measuring certified solutions near radiocesium in mass, such as antimony (m/z 121 and 123) and europium (m/z 151 and 153)[34]. Tests to correct the mass bias with a solution containing these elements were inconclusive since a complete oxidation of europium was observed in the optimized ICP-MS/MS measurement conditions. Another possibility was to use a solution with ^{135}Cs and ^{137}Cs already analyzed by a validated analytical method. This approach was investigated by measuring a Cs purified fraction from a diluted spent fuel sample which $^{135}Cs/^{137}Cs$ was quantified before by TIMS according to the method described by Isnard et al. 2009[34] and detailed in the instrumentation section. The $^{135}Cs/^{137}Cs$ reference value was evaluated by thirteen measurements performed in two analytical sessions in July and August 2022. The reference value on March 11th, 2011 ($^{135}Cs/^{137}Cs$ =0.7334 ± 0.0024) is the mean of these thirteen measurements. The expanded uncertainty with a coverage factor k=2 is U(k=2) = 0.0030. It has been assigned using the standard deviation of these 13 measurements (σ = 0.0012). The $^{135}Cs/^{137}Cs$ isotopic ratios measured for this sample by TIMS (CEA/LANIE, France) and ICP-MS/MS (IRSN/LMRE, France) are reported in Table 4. Using the ratio determined by TIMS as a reference, the average β factor observed by ICP-MS/MS was -2.98 ± 0.76.

Table 4 - $^{135}Cs/^{137}Cs$ isotopic ratio of a spent fuel sample determined with two different mass spectrometry techniques (TIMS and ICP-MS/MS).

Sample type	**Mass spectrometry technique**	**$^{135}Cs/^{137}Cs$ isotopic ratio[a]** *(at/at)*

Purified spent fuel	TIMS	0.7334 ± 0.0024 *(n=13)*
	ICP-MS/MS	0.72 ± 0.02 *(n=22, without mass bias correction)* β correction factor = -2.98 ± 0.76

[a] *Decay-corrected to March 11th, 2011. The isotopic ratios shown are the average of the replicates with uncertainty at k = 2.*

Validation of the developed analytical method.

The $^{135}Cs/^{137}Cs$ ratio of the Chernobyl (IAEA-330 and IAEA-375) or Fukushima (Niida River sediments) accident was then compared with those previously published by studies characterizing these two sources of radioactive contamination.

Analysis of commonly used IAEA standards. For both IAEA reference samples, the values reported in the literature and the analytical results obtained with the developed method are presented in Table 5. Accordingly, the $^{135}Cs/^{137}Cs$ ratios determined with the developed method agreed all very well with previously published data (E_n score < 1).

Table 5 - Comparison of $^{135}Cs/^{137}Cs$ isotopic ratio of IAEA certified reference materials with those reported in the literature.

Sample name	Matrix	$^{135}Cs/^{137}Cs$ isotopic ratio[a] *(at/at)*	Reference	En score
IAEA-330	Spinach	0.29 ± 0.02 (n=4)	*Taylor et al. (2008)*	0.35 < 1
		0.29 ± 0.01 (n=2)	*Zheng et al. (2014)*	
		0.29 ± 0.02 (n=3)	*Snow et al. (2015)*	
		0.29 ± 0.04 (n=1)	*Zhu et al. (2020)*	
		0.28 ± 0.02 (n=3)	**This work**	
IAEA-375	Soil	0.30 ± 0.03 *(n=3)*	*Zheng et al. (2014)*	0.00 < 1
		0.29 ± 0.01 *(n=3)*	*Snow et al. (2015)*	
		0.30 ± 0.01 *(n=5)*	*Dunne et al. (2017)*	
		0.30 ± 0.04 (n=3)	*Zhu et al. (2020)*	
		0.30 ± 0.01 (n=3)	**This work**	

[a] *Decay corrected to April 26, 1986. The isotopic ratio presented are the average of the replicates with uncertainty at k = 2.*

Analysis of sediments impacted by Fukushima accident fallout. The $^{135}Cs/^{137}Cs$ ratios of the samples taken in the Niida River catchment are presented in Table 6 and were compared to the ratios published by studies characterizing the Fukushima fallout. The average measured $^{135}Cs/^{137}Cs$ ratios of 0.36 was comparable with reported ratios after the Fukushima accident ranging from 0.33 to 0.40.

Table 6 - Analytical results of $^{135}Cs/^{137}Cs$ isotopic ratio in environmental samples after the FDNPP accident.

Sample name	Matrix	$^{135}Cs/^{137}Cs$ isotopic ratio[a] *(at/at)*	Isotopic ratio reported in the literature		
			Matrix	$^{135}Cs/^{137}Cs$ *(at/at)*	Reference
Niida_2012	Sediment	0.36 ± 0.02 (n=3)	Rainwater	0.34 – 0.40	Ohno et al. (2014)
Niida_2015		0.36 ± 0.01 (n=3)	Soil	0.333 – 0.375	Zheng et al. (2014)
			Soil	0.341 – 0.366	Yang et al. (2016)
Niida_2020		0.38 ± 0.04 (n=1)	Moss	0.344 – 0.366	Zok et al. (2021)

[a] *Decay corrected to March 11th, 2011. The isotopic ratio presented are the average of the replicates with uncertainty at k = 2.*

Conclusions

A novel radiocesium measurement method was developed to quantify the $^{135}Cs/^{137}Cs$ ratio in low-activity environmental samples. The strategy adopted was first to assess the composition of the eluate obtained after the purification of 100 g of soil. From these results, the gas conditions in the collision-reaction cell (nature of gases, flow rates) were investigated by measuring a solution containing Cs and its measurement interferents. By adjusting the N_2O, He and NH_3/He mixture flow rates to 0.55, 1 and 4.79 $mL.min^{-1}$ respectively, robust measurement conditions were achieved leading to a maximal Cs signal sensitivity while ensuring a powerful interference suppression (background lower than 0.6 cps at m/z 135 and 137). To the best of our knowledge, this new method is the first technique incorporating the use of ammonia to effectively remove mass interference. Furthermore, it was observed that the gas flow rates to be introduced into the CRC were directly affected by the purity of the sample. There was therefore a real complementarity between the radiochemical treatment of the sample and its measurement by ICP-MS/MS. The true isotopic ratio was obtained after applying blank and mass bias corrections. Due to the lack of $^{135}Cs/^{137}Cs$ certified solution, the bias mass was corrected by the sample-standard bracketing approach with a solution previously qualified by TIMS. The developed method was successfully validated by the analysis of certified reference samples and sediment samples impacted by Fukushima fallout in Japan. In the future, the application of this novel method to the analysis of environmental samples will allow the estimation of the respective contributions of the main sources of radiocesium in the environment and provide a tool that will be usable over the long term, given ^{135}Cs is a long-lived isotope.

Supporting information

- Three figures of additional experimental details
- One table of optimal ICP-MS/MS measurement parameters.

Acknowledgements

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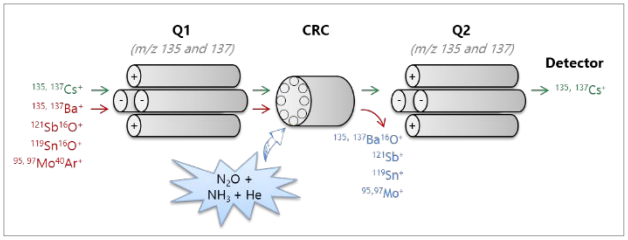
For Table of Contents Only



SUPPORTING INFORMATION

Innovative ICP-MS/MS method to determine the $^{135}Cs/^{137}Cs$ ratio in low activity environmental samples

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Number of pages in Supporting Information section: 5, including cover.

Number of Figures: 3.

Number of Tables: 1.

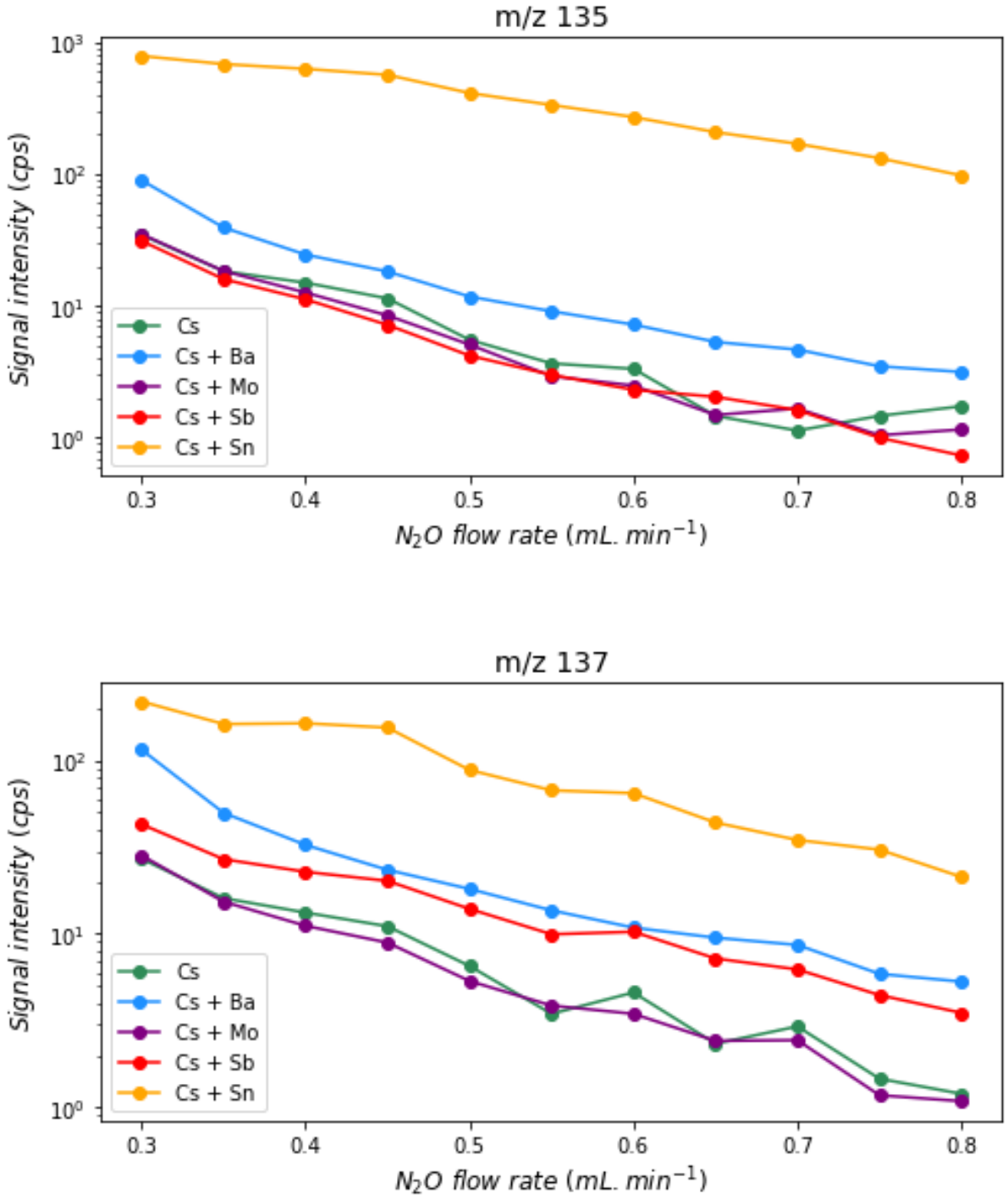

Figure S1 - Variation of signal intensities of ions with m/z 135 and 137 with N_2O flow rate for solutions containing Cs (10 ng.mL^{-1}) in the presence of one measurement interferent (Mo (3 ng.mL^{-1}), Sb (0.5 ng.mL^{-1}), Sn (50 ng.mL^{-1}) or Ba (5 ng.mL^{-1}).

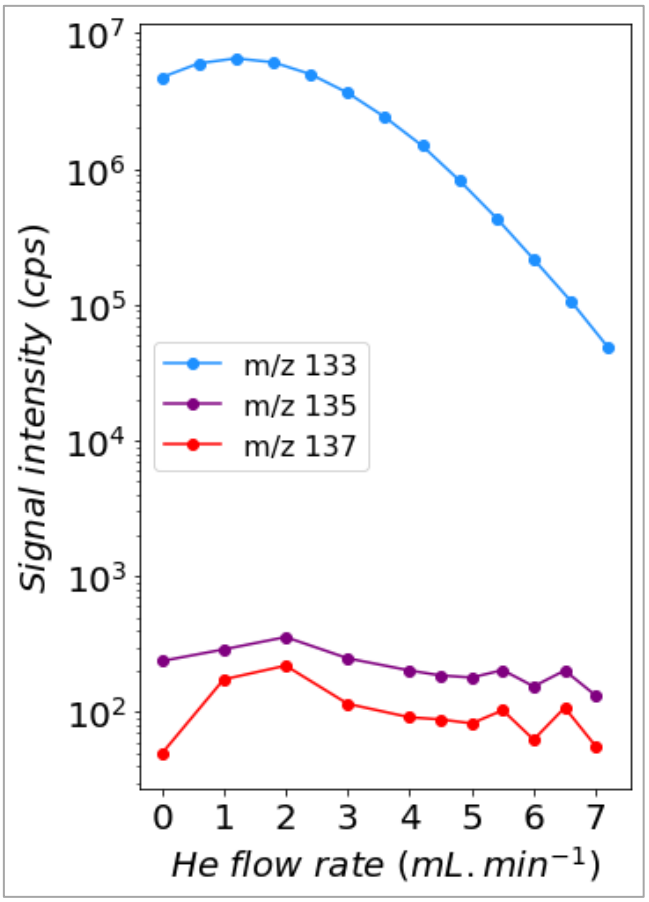

Figure S2 - Influence of the He flow rate on ^{133}Cs sensitivity and interference removal at m/z 135 and 137 in presence of N_2O at 0.52 mL.min^{-1} (flow rate adjusted to visualize a significant impact). Measurement of a solution of Cs, Mo, Sb, Sn and Ba concentrated to 10, 3, 0.5, 50 and 5 ng.mL^{-1} respectively.

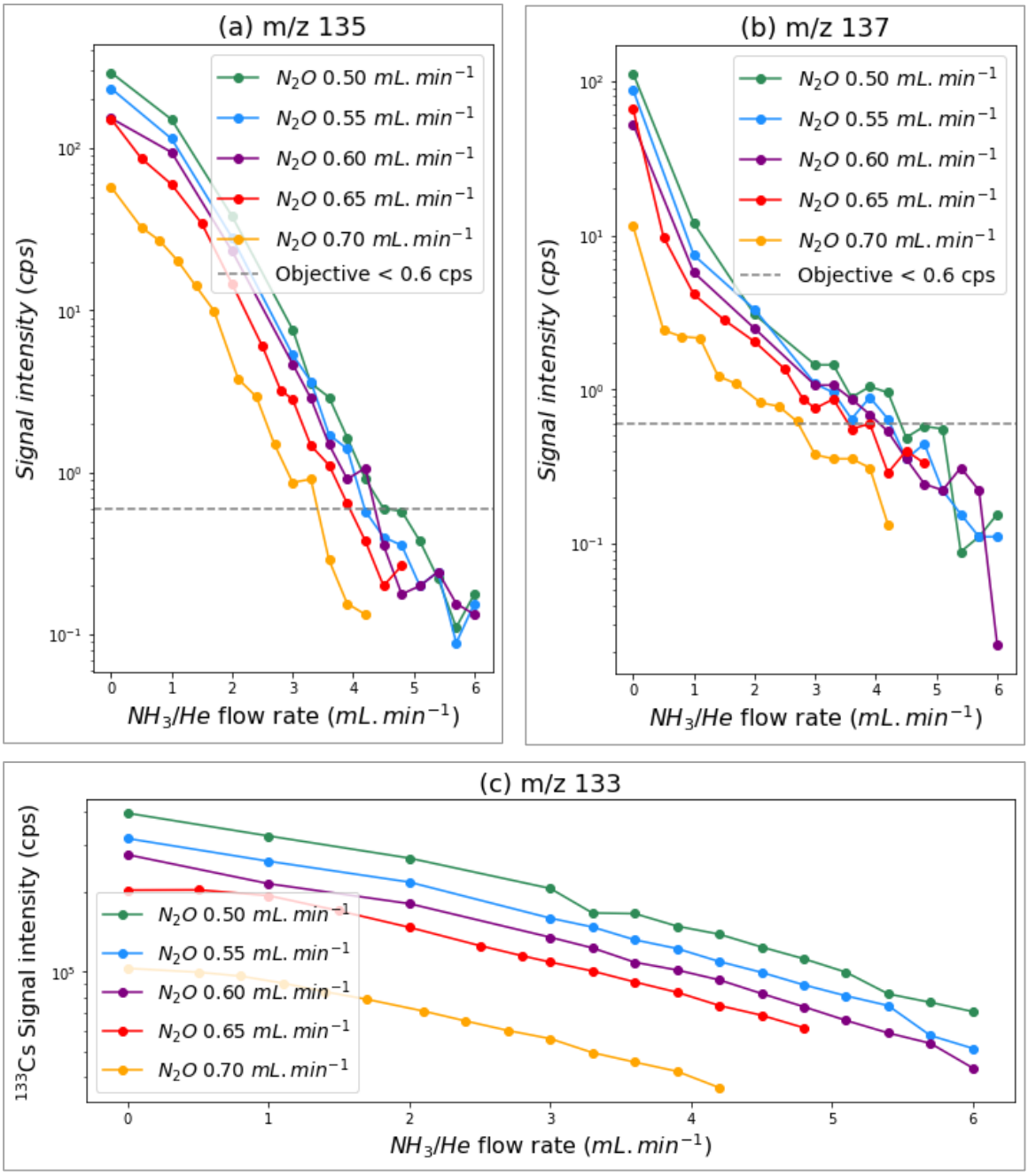

Figure S3 : Variation of signal intensities at m/z 135 (a), 137 (b) and 133 (c) as a function of the NH_3/He flow rate introduced in the CRC and a fixed N_2O flow. For these tests, the measured solution contained 10 ng.mL^{-1} of stable Cs, 3 ng.mL^{-1} of Mo, 0.5 ng.mL^{-1} of Sb, 50 ng.mL^{-1} of Sn and 5 ng.mL^{-1} of Ba.

Table S1 - ICP-MS/MS parameters for $^{135}Cs/^{137}Cs$ isotopic ratio measurement

Parameters	Settings
Sample introduction	
Sample uptake	80 s (0.30 rps)
Stabilization time	40 s
Probe rinse	20 s (0.30 rps)
Spectrum acquisition	
Q2 peak pattern	3 points
Replicates	5
Sweeps/replicates	1000
Plasma	
RF power	1550 W
RF matching	1.27 V
Sample Depth	5.4 mm
Nebulizer gas	1.11 $L.min^{-1}$
Option gas	0.0 %
Nebulizer pump	0.10 rps
S/C temperature	2 °C
Makeup gas	0.00 $L.min^{-1}$
Lenses	
Extract 1	-19.0 V
Extract 2	-235.0 V
Omega bias	-110 V
Omega lens	12.0 V
Q1 entrance	2.0 V
Q1 exit	2.0 V
Cell focus	3.0 V
Cell entrance	-50 V
Cell exit	-58 V
Deflect	1.0 V
Plate bias	-50 V
Q1	
Q1 bias	-1.0 V
Q1 prefilter bias	-8.5 V
Q1 postfilter bias	-10.0 V
Cell	
He flow	1 $mL.min^{-1}$
3^{rd} gas flow	NH_3/He – 48% (4.79 $mL.min^{-1}$)
4^{th} gas flow	N_2O – 52 % (0.55 $mL.min^{-1}$)
OctP bias	-4.0 V
Axial acceleration	2.0 V
OctP RF	160 V
Energy discrimination	-7.0 V