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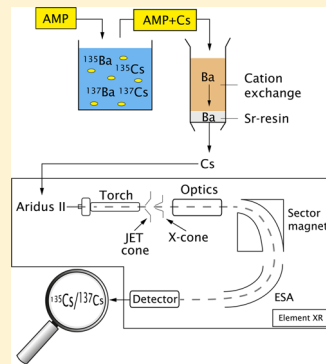
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Determination of Precise $^{135}\text{Cs}/^{137}\text{Cs}$ Ratio in Environmental Samples Using Sector Field Inductively Coupled Plasma Mass Spectrometry

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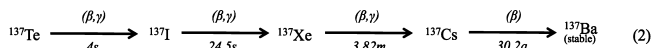
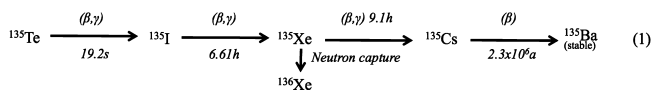
ABSTRACT: Recent advances in sector field inductively coupled plasma mass spectrometry (ICP-SFMS) have led to significant sensitivity enhancements that expand the range of radionuclides measurable by ICP-MS. The increasing capability and performance of modern ICP-MS now allows analysis of medium-lived radionuclides previously undertaken using radiometric methods. A new generation ICP-SFMS was configured to achieve sensitivities up to 80 000 counts per second for a 1 ng/L ^{133}Cs solution, providing a detection limit of 1 pg/L. To extend this approach to environmental samples it has been necessary to develop an effective chemical separation scheme using ultrapure reagents. A procedure incorporating digestion, chemical separation and quantification by ICP-SFMS is presented for detection of the significant fission product radionuclides of cesium (^{135}Cs and ^{137}Cs) at concentrations found in environmental and low level nuclear waste samples. This in turn enables measurement of the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio, which varies with the source of nuclear contamination, and can therefore provide a powerful dating and forensic tool compared to radiometric detection of ^{137}Cs alone. A detection limit in sediment samples of 0.05 ng/kg has been achieved for ^{135}Cs and ^{137}Cs , corresponding to 2.0×10^{-3} and 160 mBq/kg, respectively. The critical issue is ensuring removal of barium to eliminate isobaric interferences arising from ^{135}Ba and ^{137}Ba . The ability to reliably measure $^{135}\text{Cs}/^{137}\text{Cs}$ using a high specification laboratory ICP-SFMS now enables characterization of waste materials destined for nuclear waste repositories as well as extending options in environmental geochemical and nuclear forensics studies.



Radionuclide measurement by ICP-MS has traditionally focused on the longer-lived, low activity nuclides,^{1,2} as the technique was unable to match the sensitivities achievable by radiometric methods for shorter-lived radionuclides, such as ^{90}Sr and ^{137}Cs .^{1,3} Recent developments in ICP-MS now provide significantly improved sensitivity and offer the prospect of effectively measuring both shorter and longer-lived radionuclides, at ultralow concentrations (Figure 1). These improvements are important and expand the options available for environmental, contaminated land and nuclear waste assessments and even nuclear forensics.

This study focuses on method developments to enable quantification of ^{137}Cs ($t_{1/2} = 30.1$ years) and ^{135}Cs ($t_{1/2} = 2.3 \times 10^6$ years; Table 1).^{4,5} Both radionuclides are high yield fission products that have been or are released into the environment from nuclear power plants, reprocessing sites, nuclear accidents and atmospheric weapons test fallout.^{2,6,7} Cesium-137 is typically measured using gamma spectrometry in radiation protection, environmental monitoring and waste characterization fields.^{2,8,9} Cesium-135 is not currently considered to be radiologically significant, but is a major contributor to the long-term radionuclide inventory of deep geological repositories.^{2,7} The distribution and measurement of ^{135}Cs may also be applicable to understanding the behavior of thermohaline circulation and oceanic water bodies.¹⁰ Furthermore, the $^{135}\text{Cs}/^{137}\text{Cs}$ ratio varies with reactor, weapon, and fuel type (Figure 2) and can potentially be used as a forensic tool to identify the source of radioactive contamination.^{6,7}

Variations in $^{135}\text{Cs}/^{137}\text{Cs}$ originate from ^{135}Xe and ^{137}Xe fission products in the ^{135}Cs and ^{137}Cs decay chains (eqs 1 and



2). Xenon-135 is a potent neutron poison (neutron capture cross section 2.7×10^6 barns) that can transmute to ^{136}Xe , reducing the fission yield of ^{135}Cs , however there is no such competing reaction for ^{137}Xe affecting the ^{137}Cs yield.^{2,11} The time of neutron irradiation therefore has a significant impact on $^{135}\text{Cs}/^{137}\text{Cs}$. For example, in a nuclear reactor, there is long-term exposure to a high neutron flux, and ^{136}Xe produced by neutron capture by ^{135}Xe will compete with ^{135}Cs production from ^{135}Xe beta decay.^{7,12} By comparison, a nuclear weapon forms relatively more ^{135}Cs , as there is little ^{135}Xe existing at the time of the relatively transient but high neutron flux.¹² Accurate measurement can distinguish between different sources of contamination, which in turn will improve the modeling of anthropogenic radionuclide dispersion.³ Similar insights have

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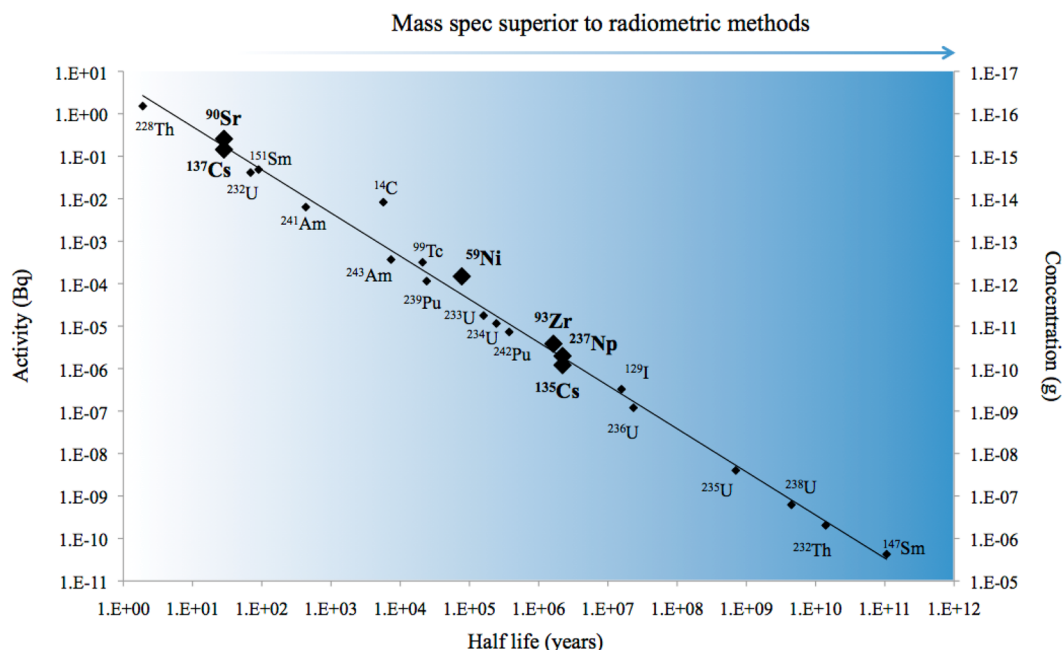


Figure 1. Half-life versus minimum detectable activity and concentration of selected radionuclides. Highlighted radionuclides (diamonds) reflect those that potentially benefit from advances in ICP-MS sensitivity. Activity and concentration values correspond to detection limits of 0.05 Bq/kg and 5 pg/kg, respectively.

Table 1. Properties of ^{135}Cs and ^{137}Cs ^{4,5}

radioisotope	half life (years)	^{235}U fission yield (%)	specific activity (Bq/g)	activity equivalent of 1 pg/g (Bq/g)
^{135}Cs	2.3×10^6	6.6	4.3×10^7	4.1×10^{-5}
^{137}Cs	30.1	6.2	3.2×10^{12}	3.2

been obtained using $^{134}\text{Cs}/^{137}\text{Cs}$ ratios, but application is limited by the relatively short half-life of ^{134}Cs (2.06 y).^{8,13,14} Measurement of $^{135}\text{Cs}/^{137}\text{Cs}$ is considerably less restricted, and can be a powerful tool in the field of nuclear forensics. In environmental studies this will provide significantly more information than detection of ^{137}Cs alone, and can build on analogous studies involving U and Pu isotopes that have already

provided valuable insights (Warneke et al.,¹⁵ and Lindahl et al.¹⁶).

While ^{137}Cs is commonly measured using high resolution gamma spectrometry, radiometric detection of ^{135}Cs is considerably more challenging, since it is a pure beta emitter with a relatively low specific activity (42.6 MBq/g). The nuclide also exists in the presence of ^{137}Cs , which has an activity concentration that is 5 orders of magnitude higher.² Mass spectrometry has been successfully applied to ^{135}Cs measurement; with ICP-MS the most frequently used approach (Table 2).^{6–9,11,17–20,24} The primary challenge is removal of isobaric ^{135}Ba and ^{137}Ba interferences, with isotopic abundances of 6.6% and 11.2%, respectively.²³ The resolution required to separate these isobars from ^{135}Cs and ^{137}Cs is greater than typical high resolution ICP-MS can achieve ($R = 10\,000$),²² therefore

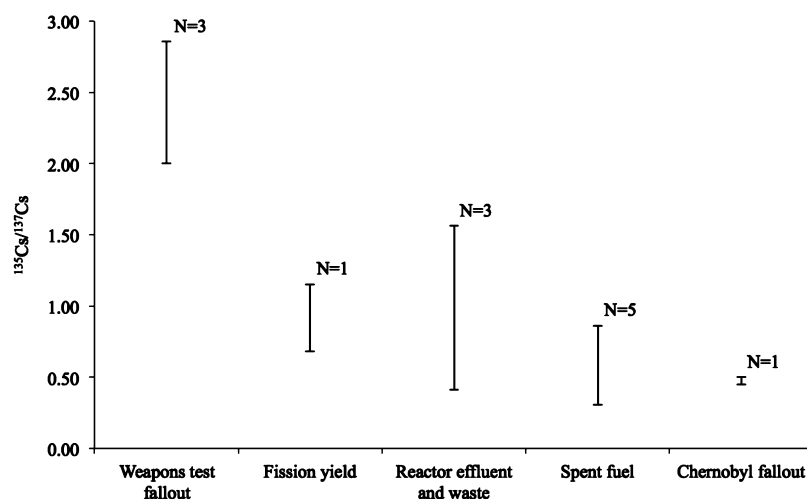


Figure 2. Summary of $^{135}\text{Cs}/^{137}\text{Cs}$ atom ratios for a range of sources measured by mass spectrometry^{6–8,19–21,23,24,37,40} Weapons fallout values have been decay corrected to 1963.

Table 2. Summary of ICP-MS Measurements of ^{135}Cs and ^{137}Cs ^a

ref	measurement	sample	digestion	major separation	LOD
17	ICP-QMS	spent nuclear fuel pellets and solutions	aqua regia	cation exchange	
18	ICP-QMS	waste tank sludges and supernates	microwave digestion	Ba(OH) ₂ precipitation	209 ng/L
8	ICP-QMS	high activity waste and spent fuel	7 M HNO ₃	cation exchange	16 ng/L
9	ETV-ICP-MS	^{137}Cs standard solution		ETV	0.2 ng/L
24	DRC-MC-ICP-MS	spent fuel pellets	9.2 M HNO ₃	anion exchange (fission product removal)	
7	DRC-ICP-QMS	soil and sediment samples	lithium metaborate fusion	AMP, anion exchange	0.2 ng/L
11	ICP-QMS	spiked groundwater		HPLC	1 pg/L (^{137}Cs)
19	CE-ICP-QMS	simulated spent fuel, samples from PUREX process and MOX fuels	4 M HNO ₃	capillary electrophoresis	6000 ng/L (ICP-QMS)
	CE-ICP-SFMS				4 ng/L (ICP-SFMS)
20	MC-ICP-MS	spent nuclear fuels		anion exchange (U and Pu removal)	

^aETV, electro-thermal vaporization; DRC, dynamic reaction cell; CE, capillary electrophoresis.

complete chemical separation prior to measurement is critical in achieving accurate ^{135}Cs and ^{137}Cs measurements. In addition, depending on the sample matrix, high concentrations of stable ^{133}Cs (100% isotopic abundance) can lead to peak tailing on ^{135}Cs and impact the detection limits achievable.^{7,23}

The most frequently used chemical separation procedure utilizes ammonium molybdophosphate (AMP) and/or ion exchange chromatography.^{6,7,11,20,21,23–28} AMP ($[\text{NH}_4]_3\text{PMo}_{12}\text{O}_{40}$) is an inorganic ion exchanger that has been applied to ^{137}Cs separation/preconcentration from sea and fresh waters, acidic nuclear wastes, and solid materials including spent fuel, soils and sediments.^{29–31} The structure consists of phosphomolybdate ions ($\text{PMo}_{12}\text{O}_{40}$)^{3–} surrounded by three ammonium ions (NH_4^+) that can exchange with Cs^+ .^{29,30,32,33} The reaction is highly selective toward Cs, with K_d values of around 10^4 cm³/g routinely achievable.³¹ Anion and cation exchange chromatography has been used in both single stage^{8,17,21,23,26} and multistage separations.^{6,7,27,28} Strong acid cation exchange resin, specifically Bio-Rad AG50W, has frequently been applied to ^{135}Cs and ^{137}Cs separation,^{21,23,25–28} with Cs elution achieved using both HCl^{23,26–28} and HNO₃.²¹

Extending the application of ^{135}Cs measurements for environmental and nuclear forensics studies is dependent on the development of robust techniques for ultralow level measurement of ^{135}Cs . This paper reports a state-of-the-art ICP-SFMS study for low-level measurement of ^{135}Cs and ^{137}Cs through a combination of a highly efficient chemical separation of interfering elements along with improvements in ICP-SFMS sensitivity. The method now permits a high specification laboratory instrument to be used for a range of applications in the fields of nuclear and environmental forensics and nuclear waste characterization and demonstrates the extended range of nuclides that can now be effectively measured by mass spectrometry.

EXPERIMENTAL SECTION

Reagents and Materials. Stable Cs and Ba standard solutions were prepared from 1000 mg/L elemental stock solutions (Inorganic Ventures) in 0.1% HNO₃ (v/v). Sub-boiled HNO₃ and sub-boiled HCl (Saville DST-1000, Minnesota, USA), and high purity deionized water (resistivity higher than 18.2 MΩ) produced from a Q-Pod Millipore System (Merck, York, UK) were used throughout.

To minimize introduction of Ba during the procedure, digestion and chemical separation steps were carried out in a Class 100 workstation contained in a Class 1000 clean laboratory. Vials, pipet tips and columns were cleaned in 10% HNO₃ for at least 24 h prior to use. Heavy duty PFA jars with lids (Saville, USA) were used for digestion. Similar open jars were used to collect the Cs fraction following cation exchange. PFA jars were cleaned before and after use using 50% HCl (v/v) at 100 °C for 24 h, followed by 50% HNO₃ (v/v) at 100 °C for 24 h. Cation exchange chromatography was performed in a HEPA filtered cabinet. The resin was soaked overnight in 6 M HNO₃, loaded onto the column and then conditioned with 40 mL 6 M HNO₃ to elute residual Ba (concentrations range from 5 to 10 μg/L). This cleaning step had no notable impact on the performance of the column with regards to Cs separation/purification.

Digestion and Separation of Cs. Aqua regia acid leaching, lithium metaborate fusion (Fluxana, Germany) and sodium hydroxide sintering (Analytical reagent grade, Fisher chemicals, UK) were evaluated as digestion techniques for Cs dissolution using an Irish Sea marine sediment (contaminated with Sellafield-derived radionuclides), having a ^{137}Cs concentration of ~0.34 pg/g (1.1 Bq/g) and Ba concentration of ~380 μg/g, determined by gamma spectrometry and ICP-QMS, respectively. Recovery of ^{137}Cs was assessed by gamma spectrometry (Table 3). For borate fusion, 5 g of sediment and 5 g lithium metaborate are mixed in a Pt–Au 5% crucible

Table 3. Caesium-137 Recovery from Irish Sea Sediment Samples Contaminated by the Releases from the Sellafield Reprocessing Plant Using Various Digestion Methods (Estimated Time for the Full Process)

digestion method	^{137}Cs recovery (%)	time to completion (h)
aqua regia acid leach and filtration/centrifuge	78 ± 3	4
acid leaching in ultrasonic bath + evap	80 ± 6	2
lithium metaborate fusion and digestion	100 ± 6	5
single attack NaOH sinter in silica crucible	90 ± 9	5
double attack NaOH sinter in silica crucible	100 ± 10	10
acid leach + NaOH sinter	100 ± 9	10

and heated at 950 °C for 10 min using a Vulcan flame fusion system (Fluxana, Germany). The resulting melt is poured into a PTFE beaker containing Milli-Q water to form a frothy glass. The water is decanted, replaced with 8 M HNO₃, and then transferred to an ultrasonic bath for 30 min to accelerate the digestion and dissolution of the frothy glass. The mixture is then left on a hot plate at 80 °C with a PTFE magnetic stirrer for 4 h and finally vacuum filtered.

For aqua regia acid leaching, 5 g of sediment is added to a PFA jar, followed by addition of 100 mL of aqua regia to the sediment in 10 mL increments, allowing any effervescence to subside before adding the next fraction. The sample is then transferred to a hot plate at 80 °C with a PTFE magnetic stirrer at 300 rpm for 4 h. The contents of the beaker are then centrifuged for 5 min at 4500 rpm, and the supernatant transferred to a clean PFA jar and evaporated to dryness.

For sodium hydroxide sintering, 5 g of sediment is transferred to a quartz crucible, followed by addition of 10 mL 6 M NaOH. The sample is evaporated to dryness by heating with an infrared lamp, and then ignited at 450 °C for 4 h. After cooling, 10 mL of Milli-Q water is added to the ignited sample, and then transferred to a hot plate at 80 °C, with regular stirring until all solid material is liberated from the base of the beaker. The contents of the beaker are transferred to a centrifuge tube and centrifuged for 10 min at 4500 rpm. The supernatant is transferred to a clean PFA jar and evaporated to dryness. The effectiveness of a double NaOH sinter, and acid leaching followed by NaOH sintering were also investigated.

Cation exchange chromatography and AMP separation (Figure 4) were investigated using Milli-Q water, acidic solutions and digested sediment samples spiked with natural or radioactive Cs and Ba standards. An AMP-based separation medium was prepared by loading AMP onto inert silica gel support material (Phase Separations Ltd., UK) following the method described by Baker (1975).³⁵ The effect of AMP mass, interaction time and HNO₃ concentration on Cs recovery and selectivity was assessed. For the combined separation procedure, AMP+Cs dissolution prior to cation exchange was tested using analytical reagent grade ammonium hydroxide and sodium hydroxide (Fisher Chemicals, Leicestershire, UK). Uptake of Cs and separation from interfering species by cation exchange chromatography (AG50W-X8, 8% cross-linked, 100–200 mesh, Bio-Rad laboratories, California, USA) was assessed at 1–4 M HCl and HNO₃ concentrations for a 3 × 0.7 cm column. Finally, for more complex sediment samples, a final stage extraction chromatography cleanup of Cs from Ba prior to quantification was investigated using Sr resin (Triskem International). This has not previously been tested; however in ~3 M HNO₃ Sr-resin is known to exhibit good retention of Ba, while showing no affinity toward Cs.⁴²

Measurement of Cs by ICP-SFMS and Gamma Spectrometry. Low-level ¹³⁵Cs and ¹³⁷Cs measurements were performed using a Thermo Element 2XR ICP-SFMS. Ions are focused according to their mass to charge ratio through a sector magnetic field, followed by energy focusing in an electro-static analyzer (ESA). A single Faraday detector and dual mode secondary electron multiplier (SEM) make up the detection system, with a linear dynamic range of >10¹².²²

The instrument can be equipped with the Jet interface (consisting of a high capacity dry interface turbo pump and a specially designed sample cone)). When combined with a desolvating sample introduction system and X-skimmer cone, this setup can yield significant improvements in sensitivity.³⁴

The impact of the Jet interface in conjunction with an Aridus II desolvating sample introduction system (Cetac, Omaha, USA) on sensitivity was determined using 0.01–10 ng/L stable ¹³³Cs standards. The Aridus II was fitted with a self-aspirating Saville C-flow nebulizer operating at an uptake rate of 100 μL/min.

For digestion and chemical separation procedures, samples spiked with radioactive Cs (mixed ^{135,137}Cs) and ¹³³Ba standards were counted as concentrates following separation using a Canberra well-type HPGe detector with an efficiency of 10% at 662 keV (corresponding to the gamma photopeak energy for ¹³⁷Cs/^{137m}Ba). Analysis of the energy spectra and calculation of radionuclide activity was performed using Fitzpeaks software (JF Computing, Stanford in the Vale, UK). Samples spiked with natural Cs and Ba standards were assessed using a Thermo-Scientific X-series II benchtop ICP-QMS. A coverage factor of *k* = 2 for uncertainties in measured values has been used consistently throughout.

RESULTS AND DISCUSSION

Effect of Digestion Method on Cs Recovery. Lithium borate fusion (metaborate, tetraborate, or mixtures) has been shown to be one of the best and most rapid opening-out techniques for environmental materials, such as silicates, carbonates, oxides, etc.³⁶ No significant volatilization of Cs during the borate fusion procedure was observed (Table 3), as the Cs becomes largely trapped in the borate melt. The filtered solution is retained for chemical separation. Cesium was not detected on the solid residual phase (containing nanocrystalline silica and boric acid).

Alternative, although inferior, methods for sample digestion investigated included double NaOH sintering and aqua regia acid leaching followed by evaporation and NaOH sintering. A single NaOH sinter using 5 mL of 6 M NaOH achieved a Cs recovery of 76 ± 7%, increasing to 90 ± 9% when the volume was increased to 10 mL. A unique feature of sintering is that it acts as a separation stage for Cs from actinide elements, as ²⁴¹Am present in the sediment was retained in the solid hydroxide phase.

A consistent Cs recovery of 78 ± 3% was achieved by aqua regia, with no additional Cs recovered following repeated leaching of the solid residue, or increased contact time (up to 24 h). This implies that a component of the Cs is being effectively retained in the sediment, which is most likely through retention in clay minerals. A 100% recovery of ²⁴¹Am, which shows no such affinity for clay minerals, is evidence for this partial retention mechanism. Layer-type silicate minerals are the major sorbents in soil that bind Cs by electrostatic interactions, or stronger bonds through partial electron sharing between Cs and ligand sites of the clay mineral. Within the interlayer of clay minerals, complexes are formed through electronic bonding at external basal sites or frayed edge sites.³⁷ The mineralogical associations of Cs means recovery using aqua regia leaching is likely to vary significantly between sample types; in the case of clay-rich samples, borate fusion is a more suitable technique.

Chemical Separation of Cs Prior to Quantification. Recoveries of >95% and a *K_d* for Cs of ~1 × 10⁴ mL/g are achievable using AMP. Selectivity toward Cs reduces as HNO₃ concentration decreases, leading to sorption of other ions including Ba, with *K_d* increasing from <1 mL/g in 1 M HNO₃ to 56 ± 5 mL/g in Milli-Q water. At lower acid concentrations, AMP acts as a generic ion exchanger, whereas in 1–4 M HNO₃

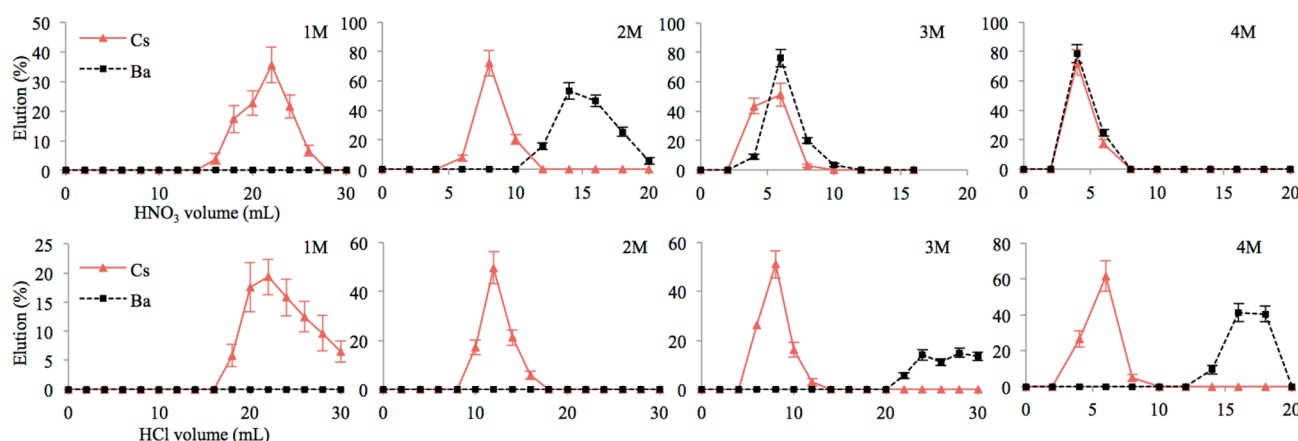


Figure 3. Elution profiles for Cs and Ba in 1–4 M HNO₃ and 1–4 M HCl from a 3 × 0.7 cm DOWEX AG50W-X8 cation exchange column.

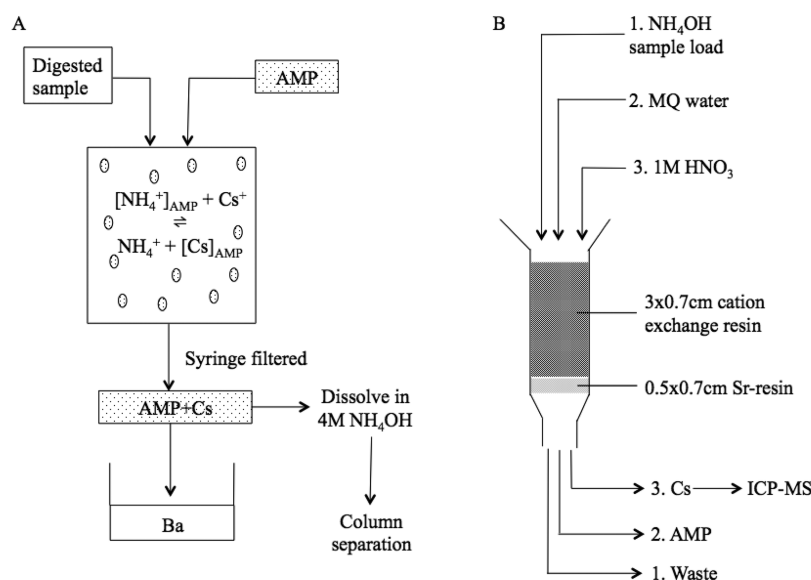


Figure 4. Summary of chemical separation procedure for ¹³⁵Cs and ¹³⁷Cs, incorporating (A) AMP and (B) cation exchange and extraction chromatography.

only monovalent cations (particularly Cs) can stably pack into the molybdophosphoric acid lattice.^{38,39} K_d values decrease at >4 M HNO₃, indicative of H⁺ ion competition with Cs for sorption sites.^{31,32}

Cesium uptake reached a maximum after approximately 60 min contact time, and remained constant over a measurement period of 24 h. Contact times of 5 min have been previously used;⁴⁰ however, in this study Cs was detected in the filtered solution at contact times of under 30 min. AMP was effectively dissolved in either 4 M NaOH or 4 M NH₄OH.

There was no significant difference in Cs recovery over an AMP mass range of 10–100 mg/mL solution, with the lower value of 10 mg/mL comparable to previous investigations.^{7,40} Filtration of AMP achieved a Cs recovery of ~85%, with the remainder retained on the filter paper. This value improved to ~90% when the alkali solution was left to interact with AMP for several minutes before filtering.

The elution profiles for Cs and Ba at 1–4 M acid concentrations for a 3 × 0.7 cm cation exchange column were determined (Figure 3). A lower wash volume and higher Cs recovery was achieved for HNO₃ compared to HCl. However, above 2 M HNO₃ Ba and Cs were detected in the

same wash fractions, and at 4 M HNO₃ the elution profiles are almost indistinguishable. By comparison, a good separation of Cs can be achieved in 1–3 M HCl, although Ba was detected in the Cs fraction at 4 M HCl. The more rapid elution of Ba in HNO₃ than HCl is due to alkaline earth elements forming a univalent cationic ion-pair complex of the form Ba(II)NO₃⁺.⁴¹

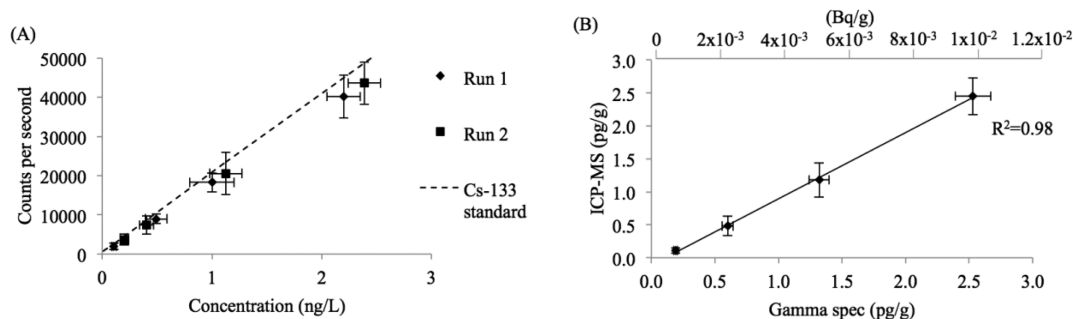
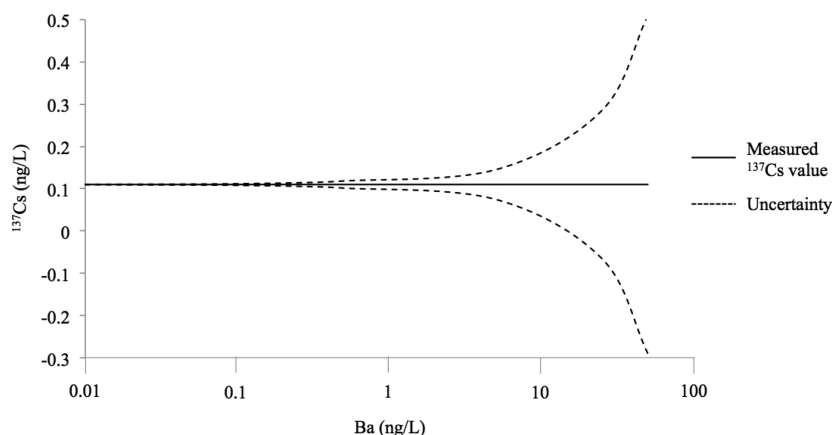
Cesium is loaded directly onto a cation exchange column from the alkaline AMP digest. Removal of residual alkaline solution entrained in the column is required prior to the acid wash, which was achieved using a 30 mL Milli-Q water wash, which also removes remaining dissolved AMP from the column. Molybdenum concentration declined to a maximum of 2 µg/L in the water washings compared with 36–42 mg/L in the original alkali load fraction, with <2% of the Cs detected in the water washings.

The AMP and cation exchange separation procedure can routinely achieve >85% Cs recovery. However, for more complex sample matrices such as soils or sediment, a final stage clean up is generally required. Results from Sr resin column tests (Figure 4b) showed a distribution coefficient for Cs of <10 mL/g in 1–3 M HNO₃, compared to 120–130 mL/g for Ba under the same conditions. Given the low level environ-

Table 4. Detection Limits Achievable with ^{133}Cs Standards, and for a Radioactive Standard Solution by ICP-SFMS Compared to Radiometric Techniques

detection method	^{133}Cs sensitivity (counts/ng/L)	LOD (ng/L)		LOD (mBq/L)	
		^{133}Cs	^{137}Cs	^{135}Cs	^{137}Cs
ICP-SFMS-standard ^a	720 \pm 26	0.02			
ICP-SFMS-Aridus II + Jet Interface + X-skimmer cone (initial)	20,050 \pm 164	0.004			
ICP-SFMS-Aridus II + Jet interface + X-skimmer cone (maximum)	82,033 \pm 790	0.001	0.05	2.1×10^{-3}	160
gamma spectrometry			0.001		3.2

^aStandard cones, rotary pump, pc3 spray chamber, and self-aspirating nebulizer.

**Figure 5. (A) Cesium-135 measured following peak correction using the natural $^{135}\text{Ba}/^{138}\text{Ba}$ isotope ratio. (B) Comparison of ICP-MS and gamma spectrometry measurements for ^{137}Cs standard solution. Points in panels A and B represent an average of 4 repeat runs.****Figure 6. Impact of Ba procedural concentration on the measurement precision of a 0.1 ng/L ^{137}Cs solution.**

mental concentrations aiming to be measured, Sr resin is very suitable for final removal of Ba. A further advantage is that it is possible to combine the Sr resin with the cation exchange resin in a single column (Figure 4). A 30 mL of 1 M HNO_3 wash quantitatively elutes Cs from a column consisting of 3×0.7 cm cation exchange resin overlying a 0.5 cm plug of Sr resin. Any residual Ba eluted from the cation exchange resin is retained on the Sr resin until the wash volume exceeds 40 mL. This approach minimizes the number and volume of reagents used compared to two separate columns, decreasing the Ba procedural blank concentration. The AMP and combined cation exchange/extraction chromatography separation procedure can consistently deliver a Ba decontamination factor of $>1 \times 10^8$. The process also reduced the boron content of the Cs fraction by a factor of 1.3×10^5 – 8.7×10^6 in samples digested by borate fusion, with typical concentrations of 30–60 $\mu\text{g/L}$ in final Cs fraction.

Quantification of Cs by ICP-SFMS and Gamma Spectrometry. The optimal instrumental setup (Table 4) uses a combination of the Cetac Aridus II desolvating sample

introduction system, the Jet interface and the X-skimmer cone. This setup recorded an initial Cs sensitivity of around 20 000 counts per ng/L, compared to 700 counts per ng/L when operating with a standard interface and sample introduction system (Peltier-cooled cyclonic spray chamber (PC³, Elemental Scientific), 200 $\mu\text{L}/\text{min}$ PFA nebulizer, standard nickel sample and skimmer cones, and a Pfeiffer Duo 5 interface rotary pump). The improvement is consistent with data quoted by the manufacturer, who recorded 20 000 counts for a 1 ng/L Indium standard when operating with the Jet interface and either the Aridus II or Apex Q (Elemental Scientific) desolvating sample introduction systems, compared to 1000 cps with the standard setup.³⁴

Further tuning with the optimal setup described can consistently produce sensitivities of ~ 30 000 counts per ng/L, and a maximum of 80 000 counts per ng/L, corresponding to a detection limit of 1 pg/L (calculated as the concentration of 3 times the standard deviation of the background at mass 133). The optimal instrument sensitivity is therefore capable of

detection limits that can rival radiometric techniques for short-lived radionuclides such as ^{137}Cs (Table 4).

Repeat measurements of a ^{137}Cs standard solution (AEA Technology QSA) with a Ba concentration of approximately 5 mg/L was used to determine the validity of the separation and ICP-SFMS procedure described in this study. At a concentration of 1 ng/L, the average $^{135}\text{Cs}/^{137}\text{Cs}$ value was 0.97 ± 0.05 ($n = 8$). The absence of a certified $^{135}\text{Cs}/^{137}\text{Cs}$ reference material prevents direct comparison between studies, with published ratios for ^{137}Cs standards ranging from 0.66 to 1.96.^{6,7,23} Sensitivities measured for ^{135}Cs , ranging from 18 300 to 19 300 counts per ng/L, are lower but in good agreement with the average ^{133}Cs sensitivity (20 500 counts) over the same runs (Figure 5A). At a ^{137}Cs concentration of 2.5 ng/L, gamma spectrometry and ICP-MS results are in good agreement (2.45 ± 0.28 ng/L and 2.53 ± 0.14 ng/L for ICP-SFMS and gamma spectrometry, respectively) (Figure 5B). At 0.1 ng/L, there is an increased discrepancy between the two techniques (0.11 ± 0.04 ng/L for ICP-SFMS and 0.19 ± 0.04 ng/L for gamma spectrometry) due to the smaller signal and relative increase in ^{137}Ba contribution.

Barium derived from the sample and the reagents used in the chemical separation procedure is the primary limitation to the detection limits achievable, as opposed to the capability of the instrument itself. The extent of Ba separation can be monitored and corrected for using ^{138}Ba (natural abundance 71.7%) and known $^{135}\text{Ba}/^{138}\text{Ba}$ and $^{137}\text{Ba}/^{138}\text{Ba}$ ratios. However, any correction will increase the uncertainty in measured values and will have a more significant impact with increasing contamination and lower radiocaesium concentrations (Figure 6). The accuracy of this correction is also dependent on accounting for instrumental mass bias, which is a drawback to the ICP-MS technique. The absence of a standard material with a certified $^{135}\text{Cs}/^{137}\text{Cs}$ value makes mass bias correction challenging.^{7,20} A linear correction was applied based on repeated measurements of stable $^{135}\text{Ba}/^{138}\text{Ba}$ and $^{137}\text{Ba}/^{138}\text{Ba}$ values in Cs-free solutions on the day of measurement (eq 3)

$$t = m \times (1 + \Delta Mf) \quad (3)$$

where t and m are the true and measured ratios, respectively, ΔM is the difference in mass of the two isotopes, and f is the mass bias correction factor. Given the instrumental sensitivity, a linear correction was considered to be acceptable rather than exponential or power laws.

Correcting for Ba decontamination means the optimal detection limit (1 pg/L) is lower than has been achieved for ^{135}Cs and ^{137}Cs (average 0.05 ng/L over the run data presented in Figure 5; Table 4). The LOD for real samples is calculated as the concentration of 3 times the standard deviation of the background at masses 135 and 137 in the procedural blank. Developing thorough cleaning procedures for resins, columns and labware, and use of high purity reagents significantly reduced the Ba procedural blank from 40–50 to 3–5 ng/L for Irish Sea sediment contaminated by the releases from the Sellafield reprocessing plant. The difficulty in reducing this value further suggests Ba is present as a result of general environmental contamination, with minimum concentrations of 1.9 ± 0.1 , 1.0 ± 0.1 , and 0.7 ± 0.04 ng/L measured in sub-boiled HNO_3 , Milli-Q water, and 2% HNO_3 , respectively. Coupling the chemical separation online with ICP-SFMS^{7–9,11,19} may reduce the procedural blank further by minimizing reagent volumes and achieving a more efficient Cs/Ba separation. Alternatively, a separation technique using a

calixarene (Calix[4]arene-bis(*tert*-octylbenzo-crown-6)) has been investigated by the author. This has been proven to show high Cs selectivity and elution of Cs in dilute HNO_3 that enables direct sample introduction, reducing the procedural time and environmental Ba contamination.⁴³

The procedure developed demonstrates an advance in the sensitivities achievable for ICP-MS measurement of $^{135}\text{Cs}/^{137}\text{Cs}$ in environmental samples, with the instrument capable of reaching a detection limit to as low as 1 pg/L. The methodology developed enables low-level measurement of $^{135}\text{Cs}/^{137}\text{Cs}$, which has the potential to be a powerful forensic tool in identifying the source of radioactive contamination compared to measurement of ^{137}Cs alone.

CONCLUSIONS

The method presented provides precise determination of $^{135}\text{Cs}/^{137}\text{Cs}$ using ICP-SFMS in environmental and other samples. These medium (^{137}Cs) and long-lived (^{135}Cs) fission product radionuclides are of growing importance in waste characterization at nuclear sites and repositories where they contribute to the long-term radionuclide inventory. They are of additional interest as the environmental $^{135}\text{Cs}/^{137}\text{Cs}$ signature reflects contributions from one or more sources (variations in reactor type, fuel burn-up, weapons' characteristics) and accurate measurement can therefore be applied to nuclear forensics to identify the source of radioactive contamination and as a dating tool in some circumstances.

Detection at low levels has been achieved by development of a robust procedure incorporating digestion of solid samples, chemical separation and quantification by ICP-SFMS. The Thermo Element XR combined with the CETAC Aridus II desolvating sample introduction system, Jet interface and X-skimmer cone can achieve up to 80 000 counts for a 1 ng/L ^{133}Cs solution, a 100-fold increase compared to the standard instrument setup. In the current method the best detection limit achieved for a pure ^{133}Cs standard solution is 1 pg/L, which puts ICP-SFMS in a position where it can begin to equal radiometric techniques in terms of sensitivities achievable for medium-lived radionuclides such as ^{137}Cs .

The main factor affecting the ultra low-level measurement of ^{135}Cs and ^{137}Cs is the concentration of isobaric ^{135}Ba and ^{137}Ba contamination in the measurement solution. This necessitates a correction using natural Ba isotope ratios, leading to increasing uncertainty with decreasing ^{135}Cs and ^{137}Cs concentration. A future aim is to further reduce this contamination, as the ICP-SPMS instrumental detection limits for pure Cs are 2 orders of magnitude lower than are practically measurable in sediment samples (because of residual Ba contamination). Sample preparation has focused on minimizing the number and volume of reagents used and has been performed using the cleanest possible conditions and reagents. At the low levels being aimed for, the Ba concentration inherently present in the reagents is often higher than that of ^{135}Cs and ^{137}Cs in the samples.

The sensitivities achieved are applicable to measurement of the key fission product Cs isotopes in environmental samples, and the methodology developed can be extended further. For example, other long-lived, low abundance radionuclides, such as ^{59}Ni and ^{93}Zr (activation and fission products, respectively), are not detectable by radiometric techniques, but like ^{135}Cs will contribute to the long-term radionuclide inventory of any geological repository. Furthermore, ^{90}Sr is a medium-lived radionuclide of significant interest with regards to waste

disposal and environmental monitoring. Traditionally, ICP-MS has offered reduced analytical time for ^{90}Sr compared to radiometric techniques at the expense of sensitivity. The analytical development described involving instrumental setup offered in this study may provide the improvement in sensitivity that can make ICP-MS a realistic alternative for routine analysis of ^{90}Sr . This combined with a higher sample throughput, offers more rapid assessment and clean up of nuclear sites, and with potential economic benefits.

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Notes

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