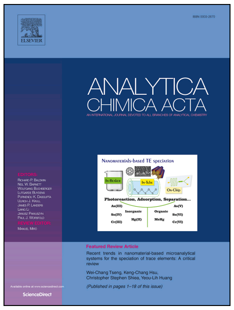

Determination of ^{135}Cs and ^{137}Cs in environmental samples: A review

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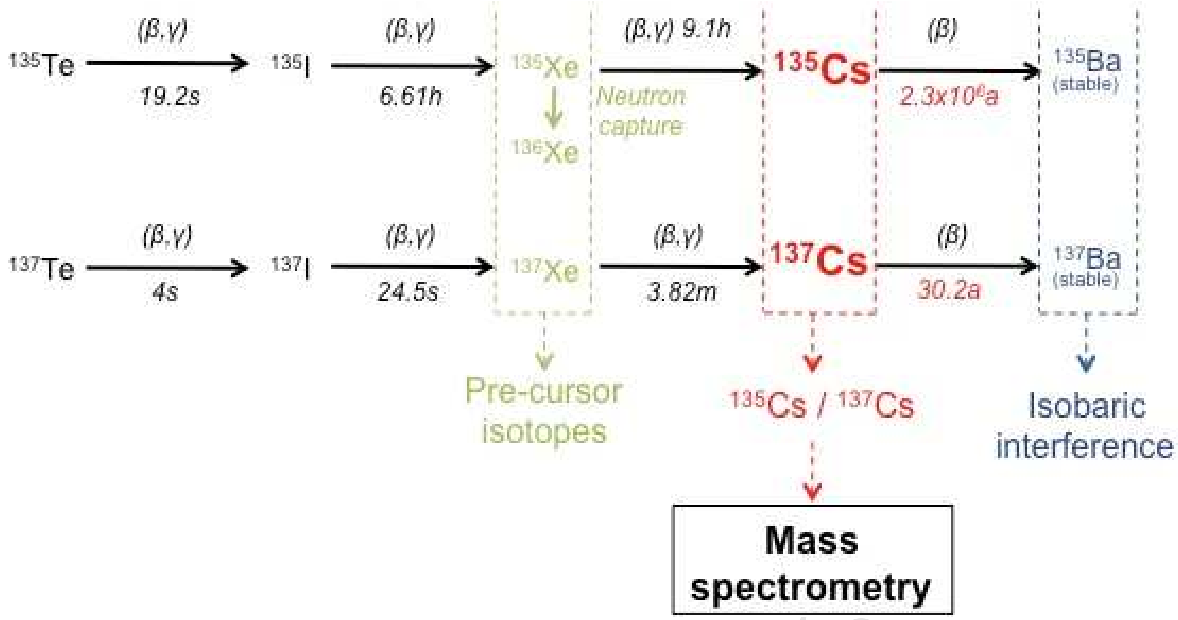
135Te
(β,γ)
19.2s
135I
(β,γ)
6.61h
135Xe
136Xe
(β,γ) 9.1h
Neutron capture
135Cs
(β)
2.3x10⁶a
135Ba (stable)
137Te
(β,γ)
4s
137I
(β,γ)
24.5s
137Xe
(β,γ)
3.82m
137Cs
(β)
30.2a
137Ba (stable)
Pre-cursor isotopes
135Cs / 137Cs
Isobaric interference
Mass spectrometry

Determination of ^{135}Cs and ^{137}Cs in environmental samples: A review

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Abstract

Radionuclides of caesium are environmentally important since they are formed as significant high yield fission products (^{135}Cs and ^{137}Cs) and activation products (^{134}Cs and ^{136}Cs) during nuclear fission. They originate from a range of nuclear activities such as weapons testing, nuclear reprocessing and nuclear fuel cycle discharges and nuclear accidents. Whilst ^{137}Cs, ^{134}Cs and ^{136}Cs are routinely measurable at high sensitivity by gamma spectrometry, routine detection of long-lived ^{135}Cs by radiometric methods is challenging. This measurement is, however, important given its significance in long-term nuclear waste storage and disposal. Furthermore, the ^{135}Cs/ ^{137}Cs ratio varies with reactor, weapon and fuel type, and accurate measurement of this ratio can therefore be used as a forensic tool in identifying the source(s) of nuclear contamination. The shorter-lived activation products ^{134}Cs and ^{136}Cs have a limited application but provide useful early information on fuel irradiation history and have importance in health physics.

Detection of ^{135}Cs (and ^{137}Cs) is achievable by mass spectrometric techniques; most commonly inductively coupled plasma mass spectrometry (ICP-MS), as well as thermal ionisation (TIMS), accelerator (AMS) and resonance ionisation (RIMS) techniques. The critical issues affecting the accuracy and detection limits achievable by this technique are effective removal of barium to eliminate isobaric interferences arising from ^{135}Ba and ^{137}Ba, and elimination of peak tailing of stable ^{133}Cs on ^{135}Cs. Isobaric interferences can be removed by chemical separation, most commonly ion exchange chromatography, and/or instrumental

separation using an ICP-MS equipped with a reaction cell. The removal of the peak tailing interference is dependent on the instrument used for final measurement. This review summarizes and compares the analytical procedures developed for determination of ^{135}Cs/^{137}Cs, with particular focus on ICP-MS detection and the methods applied to interference separation.

1. Sources and properties of caesium isotopes

High yield fission products ^{135}Cs and ^{137}Cs (Table 1) are present in environmental samples as a result of releases from nuclear power plants and reprocessing sites, nuclear accidents, and fallout from atmospheric weapons testing [1]. Caesium-137 is established as an important radionuclide in radiation protection, environmental monitoring, sediment dating, land erosion and waste disposal [2]. By comparison, ^{135}Cs is a long-lived radioisotope with a comparatively low radiation risk; however it is a significant contributor to the long term radiological risk associated with deep geological disposal [3]. Furthermore, the ^{135}Cs/^{137}Cs ratio varies with reactor, weapon and fuel type, and therefore can be used as a forensic tool to identify the source of radioactive contamination [1, 4-6]. Other isotopes of caesium include the activation products (^{134}Cs and ^{136}Cs, Table 1). These shorter-lived activation products (2.06 years and 13.2 days, respectively) provide information on fuel irradiation history and have importance in health physics terms but are not considered further here.

(Table 1)

Caesium-137 decays by beta emission to short-lived metastable isomer ^{137m}Ba, with maximum energies of 514 keV (94.4 % intensity) and 1175 keV (5.4 % intensity). This is immediately accompanied by gamma ray emission of 662 keV (85.1 %

intensity) to form ^{137}Ba [2]. Detection of ^{137}Cs is therefore achievable using beta counting or gamma spectrometry. Gamma spectrometry is generally favoured because it exploits the high gamma intensity of the 662 keV energy that is not susceptible to significant absorption. The ability to directly count most samples without the need for any chemical separation is also beneficial, and a high-purity germanium (HPGe) well detector can readily achieve a detection limit of ~2.5 mBq g^{-1} (for a 20 g sample counted for half a day), which is suitable for many environmental samples [3]. By comparison, ^{137}Cs measurement by beta counting in environmental samples requires chemical separation from other beta-emitting nuclides prior to measurement. Caesium-135 decays with a maximum beta particle energy of 269 keV, however, radiometric measurement by beta counting is prevented by ^{137}Cs also present in the sample with a radioactivity concentration that is typically 5 orders of magnitude higher.

Measurement of ^{135}Cs by mass spectrometry offers a considerable advantage because of the low specific radioactivity. Resonance ionisation mass spectrometry (RIMS) [7, 12], thermal ionisation mass spectrometry (TIMS) [8, 9, 10, 11], accelerator mass spectrometry (AMS) [13, 14], and most frequently ICP-MS (Table 6) [4, 5, 15-22], have been applied to ^{135}Cs/^{137}Cs measurement. Radionuclide measurement by ICP-MS has traditionally focused on the longer-lived, low specific radioactivity nuclides [3, 23], as the technique was unable to match the sensitivities achievable by radiometric methods for shorter-lived radionuclides such as ^{90}Sr and ^{137}Cs [23, 24]. Recently developed instruments now provide improved sensitivity and offer the prospect of measuring both shorter and longer-lived radionuclides, enabling quantification at ultra-low concentrations. Such improvements expand the options available for environmental, contaminated land and nuclear waste assessments and even nuclear forensics. The challenges for mass spectrometric measurement are removal of isobaric interferences from naturally occurring ^{135}Ba and ^{137}Ba (isotopic abundances 6.6 % and 11.2 %, respectively) and peak tailing from stable ^{133}Cs (isotopic abundance 100 %).

2. Environmental level and behaviour of ^{135}Cs and ^{137}Cs

2.1. Inputs of ^{135}Cs and ^{137}Cs

The difficulty in quantifying ^{135}Cs and its relatively low radiation hazard means historical detection and environmental monitoring of radiocaesium has focused on ^{137}Cs. The most significant sources are releases from operations at nuclear power plants and fuel reprocessing facilities. For example, at the Sellafield reprocessing facility, Cumbria, UK, atmospheric and marine discharges of ^{137}Cs have been measured since 1952 (Figure 1) [25, 27]. Peak values in 1974-1978 were attributed to corrosion of Magnox fuel elements in the storage ponds, which were brought under control initially through the use of zeolite absorbers in the ponds, and then from 1985 when the operation of the site ion-exchange effluent plant (SIXEP) began [28]. A second reprocessing facility that makes a significant contribution to marine discharges in NW European seas is the Areva La Hague plant, France, with discharges monitored since 1966 (Figure 1) [26]. Additionally, milling, cropping and reprocessing operations at the Dounreay Fast Reactor (DFR) and Materials Test Reactor (MTR) sites on the North coast of Scotland led to the production of sand-sized (up to several mm diameter) ‘hot particles’ (fuel debris) that predominantly consisted of ^{137}Cs and ^{90}Sr (Table 2) [30]. Whilst the majority of waste produced was dealt with at licensed disposal and storage facilities on site, some particles were accidentally released into the sites low level liquid effluent system and released into the marine environment [30, 31].

(Figure 1)

A number of nuclear weapon-based research facilities were developed in the 1940's and 1950's, including the Hanford Site (Washington, USA); the Savannah River Site (South Carolina, USA); and Chalk River Laboratories (Ontario, Canada). As the requirement to develop nuclear weapons ceased, clean-up of the sites became the primary aim, given the large amount of solid and liquid wastes produced, and the risks these posed to the local environment. For example, at the Savannah River Site, ^{137}Cs was primarily produced as a by-product in nuclear fuel and targets, with smaller amounts produced by test reactors, neutron activation analysis, spontaneous fission, and fuel reprocessing [32]. Aqueous discharges were primarily measured in seepage or containment basins, and to a lesser extent in site streams. In the 1950's and 1960's tens of terabecquerels were released into site streams, after which discharges were significantly reduced with improvements in process operations, such as installation of deionisers and filters in the site basins [32].

(Table 2)

During its operational lifetime, the Hanford Site produced two-thirds of the total plutonium generated for nuclear weapons in the United States [33]. Half of the chemical waste is present in underground tanks and storage facilities, with the remainder in soil, groundwater and burial grounds [33]. Separated ^{137}Cs and ^{90}Sr primarily exist as capsules at the waste encapsulation storage facility (WESF), and vitrified glass, with ^{135}Cs considered a minor impurity [34, 35].

Fallout from atmospheric weapons' test has resulted in widespread ^{137}Cs contamination (Table 2). The majority of aboveground testing occurred in the Northern hemisphere between the late 1940's and early 1960's. Depending on the yield of the explosion, radioactive debris is partitioned into the troposphere and stratosphere, with fallout primarily detected in the hemisphere of origin [36]. A study of the spatial distribution in the Northern hemisphere showed higher fallout in the Kuroshio and Kuroshio extension areas (20-40°N), and the Gulf Stream area (30-50°N), both of which are areas of higher precipitation and exchange between the troposphere and stratosphere [117]. Environmental radiocaesium contamination has also been produced following nuclear accidents, in particular at Chernobyl in 1986, and at the Fukushima Dai-ichi nuclear power plant (NPP) in 2011 (Table 2) [36-44]. Initial deposition from Chernobyl releases were measured in Scandinavia, Belgium, the Netherlands and Great Britain, extending to Southern and central Europe [36]. More recently, the accident at Fukushima following a magnitude 9 earthquake and resulting tsunami lead to significant atmospheric and aqueous releases of ^{137}Cs, and represented the largest accidental source of radionuclides into the ocean in terms of measured concentration [38, 42-44]. Around 80% of atmospheric ^{137}Cs released was deposited into the sea [21, 40], with only a small proportion of atmospheric fallout (~2 %) deposited on land areas other than Japan [40].

2.2. Environmental concentrations of ^{135}Cs and ^{137}Cs

The ^{137}Cs activity in a range of sample types and locations is summarized in Table 3. The environment surrounding Sellafield has been monitored for ^{137}Cs activity for a number of years, with areas of interest including water and surface sediments at beaches along the Cumbrian and Northern Ireland coasts. Additionally, flat lying salt marshes bordering the Irish Sea have been proven to produce a chronological record of historical Sellafield discharges through measurement of ^{137}Cs activities in vertical sediment core samples [45]. Marine biota around Sellafield is monitored as part of the UK Food Standards Agency national monitoring program, as these represent the primary route for ^{137}Cs uptake into the food chain. The ^{137}Cs activity is also measured in a range of samples throughout the UK including rainwater, fresh water and seawater.

(Table 3)

In the seas surrounding Japan, values decreased between the 1960's (due to weapons test fallout) and 2010, due to a combination of ocean mixing and ^{137}Cs decay [38, 39]. Even in the relatively short time following the Fukushima accident, the peak ^{137}Cs activities measured in seawater samples decreased by several orders of magnitude within several months of the accident as a result of ocean mixing, with a similar rate of decrease after one year [38, 44]. Caesium-137 measured in surface water of the Pacific are estimated to reach the US coastline 4-5 years after the accident, with activities on the order of <3 Bq m^{-3} [44]. Caesium-137 has been detected in marine biota, however dose calculations suggest minimal impact to biota or humans as a result of direct exposure in ocean waters, with doses dominated by naturally occurring radionuclides ^{210}Po and ^{40}K [38].

Low surface water activities in oceans in the Southern hemisphere are a result of lower input from atmospheric weapons testing, compared to oceans in the Northern hemisphere, which have additional inputs including discharges from reprocessing facilities, and fallout from the Chernobyl accident (Table 4) [46-51]. In addition, disposals of solid and liquid waste from Russian nuclear facilities into the Ob and Yenisey rivers then drain into the Eastern Arctic Ocean [48, 50, 51]. The majority of ^{137}Cs discharged from the Chelyabinsk site into the Techa River (a tributary of the Ob) was retained in sediments close to the site [46, 47].

(Table 4)

Effluents from the Chalk River Laboratories, Ontario, Canada, have been discharged into the Ottawa River over the last 60 years. A recent study found that, other than at some sites immediately adjacent to outfall, there has been little impact of ^{137}Cs discharges from the Chalk River Laboratories on radionuclide concentrations in river sediments [52]. Activities measured upstream of Chalk River Laboratories were due to fallout from atmospheric weapons test fallout, with the higher activities measured downstream a result of a combination of Chalk River Laboratories releases and weapons test fallout [52]. At the Hanford site, Washington, USA, ^{137}Cs activities were monitored in Columbia and Snake River sediments from 1988 to 2004. The activity in groundwater was not considered to be a viable pathway, given the strong sorption to sediments [122].

2.3. Environmental behavior of caesium isotopes

The conservative behavior of Cs in seawater (<1 % attached to marine particles) [38] combined with the routine detection of ^{137}Cs by gamma spectrometry has led to widespread application as a tracer for assessing ocean circulation and the fate of nuclides discharged into the marine environment [53]. The ^{137}Cs activity in the North Atlantic and Arctic Oceans have been extensively studied, given the multiple sources of contamination [54, 55, 56, 57]. Direct discharges from Sellafield are transported northwards out of the Irish Sea, before entering the North Sea, with further northward transport through the Norwegian Sea to the Arctic Ocean and Greenland Sea [53, 56]. The transit time for ^{137}Cs between discharge from Sellafield and detection in the Greenland Sea is approximately 10 years, therefore higher activities measured along the East coast of Greenland compared to elsewhere in the Arctic and North Atlantic are a signature of older aqueous discharges [46, 47, 49, 59].

The ^{137}Cs activity concentration in the seas around Japan reduced by a factor of 10^3 within several months of the Fukushima accident, and 10^5 within 1 year, due to rapid horizontal and vertical mixing [38, 42, 44]. Despite the behavior of Cs being considered to be conservative, a substantial release of radioactivity and/or high concentrations of marine particles can result in a significant part of ^{137}Cs binding to suspended particles, leading to long term contamination by deposition on the seafloor.

In soils, ^{137}Cs is generally immobilized at the surface, with an approximately exponential decline in activity concentration with depth [60, 62]. The extent of immobilization is dependent on the type and content of clay minerals, as well as pH, organic content and the potassium and ammonium content [60]. The sorption strength of Cs on clay minerals and subsequent transport through soil layers is dependent on the mineralogical content [61]. Layer-type silicate minerals can bind Cs by electrostatic interactions with anionic surfaces in the interlayer or basal plane, as well as dissociated edge hydroxyl groups, forming outer sphere complexes. Alternatively, stronger inner sphere complexes are formed through electronic bonding at external sites, in the interlayer of clay minerals, or at frayed edge sites [32, 61]. Caesium shows a particularly high affinity for sorption at frayed edge sites, where Cs can coordinate directly to basal oxygen on adjacent siloxane (Si-O-Si) sheets [61]. The difference in the strength of the complexes formed means ^{137}Cs can be used as a tracer to investigate soil migration and composition, and, in the case of inner spheres complexes, further suggests that Cs redistribution into the environment is the result of physical processes associated with erosion, transport and deposition [62]. Such processes are also a concern for sediment samples, such as remobilisation of Sellafield-contaminated sediments on the Irish Sea bed, which have been acting as a source of ^{137}Cs since the 1980's [25]. An estimated 300 TBq ^{137}Cs was remobilised in the tidal area around Sellafield from 1989 to 2009, and in 2012 was responsible for a transfer rate of ~6 TBq yr^{-1}, effectively doubling the input from direct aqueous discharges [28]. At the Savannah River Site, there was minimal contamination from direct atmospheric releases, however a notable airborne source was suspension of Cs-containing soil in dried-out basins that had previously received aqueous discharges [32].

2.4. Variation in ^{135}Cs/^{137}Cs values

The average fission yield ^{135}Cs/^{137}Cs isotope ratio value (calculated from a compilation of individual ^{135}Cs and ^{137}Cs fission yields) ranges from 0.93-1.24, with an average value of 1.01 [116]. However, there is a significantly wider range in accumulated fission yield isotope ratios (Figure 2), originating from the difference in behavior of ^{135}Xe and ^{137}Xe fission products in the ^{135}Cs and ^{137}Cs decay chains (Equations 1 and 2). Xenon-135 is a potent neutron poison (neutron capture cross section of 2×10^{6} barns) that can transmute to ^{136}Xe, reducing the fission yield of ^{135}Cs, whereas there is no such competing reaction for ^{137}Xe affecting the ^{137}Cs yield [3]. The accumulated fission yield isotope ratio is therefore dependent on the irradiation history, in particular the neutron flux and irradiation time.

$$\begin{tikzcd}[column sep=large] {}^{135}\mathrm{Te} \arrow[r, "(\beta{,}\gamma)", "19.2s"'] & {}^{135}\mathrm{I} \arrow[r, "(\beta{,}\gamma)", "6.61h"'] & {}^{135}\mathrm{Xe} \arrow[r, "(\beta{,}\gamma)\ 9.1h"] \arrow[d, "Neutron\ capture"] & {}^{135}\mathrm{Cs} \arrow[r, "(\beta)", "2.3x10^{6}a"'] & \underset{\text{(stable)}}{{}^{135}\mathrm{Ba}} \\ & & {}^{136}\mathrm{Xe} & & \end{tikzcd} \quad (1)$$

$$\begin{tikzcd}[column sep=large] {}^{137}\mathrm{Te} \arrow[r, "(\beta{,}\gamma)", "4s"'] & {}^{137}\mathrm{I} \arrow[r, "(\beta{,}\gamma)", "24.5s"'] & {}^{137}\mathrm{Xe} \arrow[r, "(\beta{,}\gamma)", "3.82m"'] & {}^{137}\mathrm{Cs} \arrow[r, "(\beta)", "30.2a"'] & \underset{\text{(stable)}}{{}^{137}\mathrm{Ba}} \end{tikzcd} \quad (2)$$

In nuclear weapons, higher ^{135}Cs/^{137}Cs atom ratios are a result of little ^{136}Xe production at the time of high neutron flux [63]. The ^{135}Cs/^{137}Cs production ratio for nuclear weapons has been estimated to be close to 1 [8, 10], with an age-corrected value of 2.7 calculated by Snyder et al. (2012), based on correcting to the 1963 global fallout peak [10]. By comparison, in a nuclear reactor, lower atom ratio values are expected because of long-term exposure to a high neutron flux, in which the increased fraction of ^{135}Xe converted to ^{136}Xe results in reduced ^{135}Cs production from ^{135}Xe beta decay [4, 63]. Isotope ratios range from 0.41-1.56 for reactor effluent and waste, with an average value of 0.99 [1, 4, 11]. This range of values is greater than for any other source, which may be the result of changes in operating conditions and fuel type over a reactors lifetime [4]. Depleted ^{135}Cs/^{137}Cs values compared to the fission yield ratio have been measured in samples near the Chernobyl site, with a corrected value at the time of the accident in 1986 of 0.28-0.32 [4]. Depleted ratios were also measured in rainwater and environmental samples (litter, lichen and soil) following the Fukushima accident. Zheng et al. (2014) measured samples collected to the northwest of the nuclear power plant in forests of the Fukushima prefecture, with a range in isotope ratios of 0.333-0.343 (reference date for ^{137}Cs decay correction was 11th March 2011) [22]. This similarity suggested that Cs isotopes deposited in this region were released from the same source [22]. Higher ^{135}Cs/^{137}Cs isotope ratios of 0.355-0.375 were measured in samples 20 km south and 230 km south-west of the nuclear power plant. The results were in good agreement with similar studies of ^{135}Cs/^{137}Cs ratios measured in rainwater [6], and plant samples [9].

(Figure 2)

Accurate measurement of ^{135}Cs/^{137}Cs ratios can distinguish between different sources of contamination, which in turn will improve modeling the dispersion of anthropogenic radioactivity. The absence of a certified ^{135}Cs/^{137}Cs reference material prevents direct comparison between studies, with published ratios for ^{137}Cs standards ranging from 0.66-1.96 [1, 4, 5, 8]. Furthermore, the high variation in values measured makes it challenging to determine how effective ^{135}Cs/^{137}Cs measurement is as a forensic tool, and knowledge of source conditions would be beneficial in constraining variations between sites. To overcome this, when investigating environmental samples contaminated by the Fukushima accident, Zheng et al. (2014) compared the ^{135}Cs/^{137}Cs ratio measured for IAEA-375 (collected in the 30km Chernobyl exclusion zone) with the value obtained for the same sample by Taylor et al. (2007), with values of 0.52±0.045 and 0.50±0.05, respectively [4, 21]. Isotope ratio values can potentially support similar approaches applied to uranium and plutonium isotopes [36, 64]. For example, ^{240}Pu is produced by neutron capture of ^{239}Pu, therefore $^{240}Pu/^{239}Pu$ also varies between reactor type (0.23-0.67) and weapon production (0.01-0.07) [25]. For a high neutron flux, $^{240}Pu/^{239}Pu$ is expected to increase as $^{135}Cs/^{137}Cs$ decreases [4].

3. Separation of Cs from environmental samples

The key procedural stages for detection of $^{135}Cs/^{137}Cs$ in solid samples are digestion, separation from interferences using chemical and/or instrument based techniques, and quantification. The techniques that have been applied to each procedural stage are summarized in Table 5.

3.1. Sample digestion

A sufficient amount of solid sample is dried, ground, and sieved to get a homogeneous and representative sample for analysis. Ashing of the sample decomposes organic matter, with temperatures up to 500^0C reported with no loss of Cs [4]. Alternatively, hydrogen peroxide can be added to the digest to decompose organic matter [22]. Digestion techniques include HNO_3 [21] a combination of HNO_3 and HF [8], *aqua regia* [7], and lithium borate fusion [4, 5], which was first used in a radioanalytical context by Croudace et al. (1998) [65]. In samples where Cs is strongly sorbed to clay minerals as an inner sphere complex, the more aggressive lithium metaborate fusion technique has been necessary to achieve a quantitative recovery of Cs, as *aqua regia* acid leaching does not fully liberate radiocaesium [5]. Spent fuel samples have been successfully digested using HNO_3 [66], *aqua regia*

[15], acid digestion using a closed vessel microwave [16], and lithium metaborate fusion [4].

3.2. Chemical Separation

Ion exchange and extraction chromatography are the most common techniques with regards to radiocaesium separation. A number of materials have been developed for ^{137}Cs separation [67, 68], with the aim to combine decontamination of interferences with high analyte recovery. The majority of materials are used for the separation of ^{137}Cs from fission products and alkali metals, namely Na and K. For mass spectrometric measurement, quantitative Cs recovery is critical, particularly for low-level environmental samples. This section therefore focuses primarily on separation procedures that have been applied prior to mass spectrometric determination of ^{135}Cs and ^{137}Cs.

3.2.1. Ammonium molybdophosphate (AMP)

AMP [$(NH_4)_3PMo_{12}O_{40}$] is an inorganic ion exchanger that has been used in the selective removal of Cs from sea and fresh waters, acidic nuclear wastes, and solid materials after decomposition including spent fuel, soils and sediments [1, 4, 5, 7, 10, 11, 12, 21, 22, 69]. The phosphomolybdate ion $(PMo_{12}O_{40})^{3-}$ is a hollow sphere composed of 12 octahedral MoO_6 groups and a central PO_4 group, with ammonium ions ($3NH_4^+$) and associated water molecules located between these negative ion spheres. Separation is based on exchange or co-precipitation of Cs^+ with NH_4^+ ions (equation 3). The reaction is rapid, and highly selective under acidic conditions, with >95 % recoveries and a distribution coefficient (K_d) of 10^4 mL g^{-1} is routinely achievable [5, 70]. The highest selectivity is observed in ~1-3 mol L^{-1} HNO_3, as only monovalent cations (particularly Cs) can stably pack into the molybdophosphoric acid lattice and form an insoluble compound. Under weaker acid and neutral conditions, Cs uptake remains high, however there is a reduction in selectivity [71, 72].

$[NH_4^+]_i + Cs^+ \rightleftharpoons NH_4^+ + [Cs]_i$ where i is the ion sorbed onto AMP (3)

The fine powder crystalline structure of AMP is often modified by impregnation onto an inert support material, such as silica gel [73], asbestos [71], and polyacrylonitrile (PAN) [74]. In batch separations, a small quantity of AMP (~100 mg per 10 mL sample) is mixed with the sample, followed by separation by centrifuging and/or filtration [4, 5, 7, 21, 22]. The interaction time with AMP ranges from several minutes [7] to 1 hour [4], with a similar recovery across this timescale. Longer reaction times can negatively impact ^{137}Cs recovery as a result of displacement with other ions, or AMP degradation [67]. Chromatographic separations have been applied to high volume aqueous samples, including seawater [57, 75, 76], which despite the high ionic strength does not impact AMP performance with regards to Cs separation [69].

AMP+Cs has been successfully dissolved in alkali solutions including NaOH [1] and NH_4OH [4, 5, 12, 21, 22]. Prior to ICP-MS quantification, dissolved AMP and bound Cs is taken forward for ion exchange chromatography separation.

3.2.2. Insoluble hexacyanoferrates

Transition metal hexacyanoferrates show rapid, selective and quantitative separation of ^{137}Cs [77-82]. For example, potassium nickel hexacyannoferrate (KNiFC) has been effectively used in batch and chromatographic separation of ^{137}Cs from samples including nuclear waste and large volume aqueous solutions [75, 79, 83-88]. As with AMP, the exchanger is commonly precipitated onto an inert support material e.g. colloidal silica or PAN [69, 75]. The K_d for Cs decreases with increasing concentrations of K and NH_4, with the linear decrease at NH_4 concentrations greater than 0.1 M suggesting Cs uptake is via a cation exchange reaction, and that NH_4-based alkali solutions can effectively elute Cs [89-91]. KNiFC has achieved quantitative separation of ^{137}Cs in neutral, acidic and alkaline solutions [69], with the highest chemical and thermal stability in neutral or slightly acidic conditions [75, 83].

KNiFC has been reported to achieve K_d values one order of magnitude higher for Cs than AMP [79]. A 25 mL KNiFC-PAN column achieved 93 % ^{137}Cs recovery from a 100 L acidified seawater sample at a flow rate of 300 mL min^{-1}, compared to 89 % recovery using 25 mL AMP-PAN [75]. However, the higher uptake of Ba onto KNiFC is a concern for ICP-MS procedures. Zheng et al. (2014) compared powdered AMP and KNiFC-PAN for Cs/Ba decontamination. Whilst both materials showed >98.7 % uptake of Cs after a 1 hour reaction time in a 1.6 mol L^{-1} HNO_3 solution, Ba uptake onto KNiFC-PAN was 21 %, compared to 12 % for powdered AMP [22].

3.2.3. Ion exchange chromatography

Both anion and cation exchange chromatography have been applied to Cs separation, either specifically from Ba or as a bulk matrix separation stage. Given that the decontamination factor from interferences required in order to obtain accurate ^{135}Cs/^{137}Cs ratio data varies with sample type, ion exchange chromatography has been used as a single separation stage for spent fuel, sediments, and spiked groundwater [8, 15, 19, 20], and in multi-stage separations for reactor effluent, and environmental samples including leaf litter, lichen soils and sediments (Table 6) [1, 4, 5, 9, 10, 11]. Ion exchange chromatography is a versatile and selective technique, however potential disadvantages are long elution times and the large volumes of acids and resin required [63, 92].

Strong acidic cation exchange resin (Dionex 50W and Bio Rad AG50W) have been applied to ^{135}Cs and ^{137}Cs separation [5, 8, 9, 11, 21, 22, 93]. The resin is composed of sulphonic acid functional groups covalently bonded to a styrene divinylbenzene polymer lattice. Elution has been achieved with 0.3-2 mol L^{-1} HCl [11], and 1 mol L^{-1} HNO_3 [93], whilst divalent Ba^{2+} is retained on the resin. A more rapid breakthrough of Ba is observed in HNO_3 than HCl due to alkaline earth elements forming a univalent cationic ion-pair complex of the form $Ba(II)NO_3^+$ [94].

Moreno et al. (1999) investigated three Dionex ion exchangers coupled online to ICP-MS for Cs/Ba separation [2], of which CS5 resin using a 1 mol L^{-1} HNO_3 eluent gave the most effective separation. This was determined from the precision of ^{134}Cs/^{137}Cs ratios measured by gamma spectrometry, and accuracy of ion chromatography-ICP-MS measurement of ^{133}Cs/^{135}Cs and ^{135}Cs/^{137}Cs, which was compared to values obtained by KORIGEN code calculations (a package that calculates fuel depletion during irradiation and decay). Precision and accuracy values of 2.5 % and 5 % were achieved, respectively [2]. Dionex CS5 is a high-resolution column with both anion and cation exchange capacity (sulphonic acid and quaternary ammonium functional groups), with Cs effectively eluted in 0.03-1 mol L^{-1} HNO_3 [15].

Ion exchange has been applied as a second stage clean-up following AMP separation [4, 5, 9, 21, 22]. AMP dissolved in alkali can be loaded onto anion exchange resin (Dowex AGMP-1M), with Mo retained as negative MoO_4^{2-}, whilst Cs^+ and Ba^{2+} are eluted [4, 21, 22]. The eluted fraction is then loaded onto cation exchange resin (Dowex AG50WX8) for separation of Cs from Ba. Alternatively, the dissolved AMP can be loaded directly onto a cation exchange column, with Mo eluted in the load and following a Milli-Q water wash, whilst Cs and Ba are retained on the resin [5].

3.2.4. Extraction chromatography

Extraction chromatography combines the ease of use of ion exchange chromatography with selectivity of solvent extraction [95]. Calixarenes are macrocyclic extractants that have been extensively applied to ^{137}Cs separation, for example from acidic nitrate solutions [96], acidic liquid waste [97], spent nuclear fuel [98] and Savannah River Site tank wastes [99].

Calixarenes are made up of phenolic units (C_6H_5OH) linked by methylene groups (CH_2^+) [68]. Rotation around this group allows the formation of a number of conformations and unique cavities, and therefore selectivity towards different ions [100]. Calix[4]arenes with crown-6 ethers show the highest selectivity, as the crown-6 cavity size (1.70 Å) is similar to the ionic radius of Cs (1.67 Å), giving Cs/Na and Cs/K separation factors exceeding 10^4 and 10^2, respectively [98, 99, 101-104].

The general method for extraction of Cs (Equation 4, [105]) is to contact organic (calixarene) and aqueous (HNO_3) phases, followed by centrifuging and measurement of ^{137}Cs in the two phases by gamma spectrometry. Contact time has ranged from 1 minute [99] to 12 hours [106]. Caesium has been retained in the organic phase at HNO_3 concentrations from 1-4 mol L^{-1}, with elution achieved using ~0.05 mol L^{-1} HNO_3 or Milli-Q water (due to the low K_d for Cs), or 6-8 mol L^{-1} HNO_3 (because of competitive extraction of HNO_3) [105]. Chromatographic separation has been successfully applied by impregnation of the calixarene onto inert materials including Amberlite XAD-7 (Sigma Aldrich) [106], SiO_2 particles [107, 108], and Aberchrom CG-71 prefilter resin material (Triskem) [104], with the latter setup achieving a Ba decontamination factor of 2,900.

$$Cs^{+}_{(aq)} + NO_3{}^{-}{}_{(aq)} + Cx_{org)} + nH_2O_{(aq)} \rightleftharpoons [CsCx]^{+} \cdot [NO_3{}^{-} \cdot nH_2O]_{org} \qquad (4)$$

Where *Cx* is the calixarene

Calixarenes offer straightforward extraction and elution of Cs, and the limited number and volume of reagents can reduce Ba contamination introduced during the procedure, which is particularly beneficial for detection of low-level environmental samples [104]. Extraction chromatography resins are expensive, but are often regarded as an economically and technically justifiable option [109].

Depending on the decontamination factors required, a multi-stage chemical separation procedure may be required. However, this increase in the number and volume of reagents used risks a higher Ba procedural blank concentration, which has an increasingly significant impact on the detection limits achievable as the $^{135}Cs/^{137}Cs$ concentration decreases [104].

(Table 5)

Measurement techniques for ^{135}Cs/^{137}Cs

4.1. Neutron Activation Analysis (NAA)

Caesium-135 has a thermal neutron capture cross section of 9 barns, and its activation product ^{136}Cs ($t_{1/2}$ = 16 days), formed through (n, γ) reaction, emits gamma rays at energies of 818, 1048 and 1235 keV [109]. Chao and Tseng (1996) separated caesium from the fission and activated products in radioactive wastes using AMP, which was then dissolved in NaOH and immobilised on a cation exchange column (Amberlite 200) for irradiation [1]. The main gamma emitting radionuclides detected were ^{134}Cs, ^{136}Cs, and ^{137}Cs. An earlier study by Stamm (1973) did not include AMP separation, leading to detection of other peaks (namely ^{22}Na) and increasing the limit of detection [110].

Whilst NAA avoids isobaric Ba interferences, the detection limit is affected by the concentration of ^{133}Cs, its activated product ^{134}Cs, and ^{137}Cs [3]. NAA has focused on radioactive waste samples with high ^{135}Cs, ^{137}Cs concentration, and applying a similar procedure to environmental samples would be challenging, not least because of the need for a nuclear reactor to form this activated product.

4.2. Mass spectrometric detection

Mass spectrometry, most commonly ICP-MS, has been effectively applied to the measurement of ^{135}Cs/^{137}Cs, with the extent of separation from isobaric Ba interferences a critical factor in the detection limits achievable. For low level environmental samples, measurements must also not be affected by tailing from stable ^{133}Cs on ^{135}Cs. The abundance sensitivity is a measure of the contribution of the tail from the peak at mass 133 to the peak at mass 135, with a value of approximately 1×10^{-9} required to completely remove the tailing effect [4, 6, 8, 21]. The abundance sensitivity required is dependent on the ^{133}Cs/^{135}Cs ratio in the starting sample, whilst the ability to remove peak tailing effects varies significantly with instrument type (Table 7).

(Table 6)

4.2.1. ICP-MS

Caesium-135 and ^{137}Cs quantification has been achieved using quadrupole (ICP-QMS) [2, 6, 15, 16, 18], and sector field (ICP-SFMS) instruments [5, 66], with the latter offering greater sensitivity, albeit at a higher cost [60].

The sample introduction system affects analyte sensitivity, transport efficiency and sample uptake, and for higher activity samples is contained in a glove box [2, 15]. Traditional concentric and cross flow nebulizers suffer from high sample uptake rates (up to ~1 mL min^{-1}) and poor introduction efficiency (<1 %) [4]. Analytical sensitivity is improved through the use of more efficient micro-concentric, direct injection or desolvating nebulizers [19] that can achieve up to 100 % analyte transport efficiency and a sample uptake rate as low as 50 µL min^{-1}.

Sample introduction has been applied as a Cs separation stage. For example, an electrothermal vaporisation (ETV) system using an appropriate chemical modifier can discriminate against Ba, based on selective volatisation of Cs [18]. Song et al. (2001) investigated 12 chemical modifiers and determined potassium thiocyanate (KSCN) to be the most effective with regards to Cs signal enhancement and Ba separation [18].

A volatilization temperature of 1100^0C was used for vaporization of Cs in a 10^4 excess of Ba, with a Ba signal increase at mass 135 of only 1 %. The detection limit of ^{135}Cs was calculated as 0.2 ng L^{-1} (8.2×10^{-6} Bq L^{-1}). Advantages of ETV-ICP-MS include limited sample preparation and high introduction efficiency (70-100 %) [18]. However, chemical separation is required prior to ETV in real samples where a greater Ba decontamination factor is required.

Capillary electrophoresis (CE-ICP-MS) has been applied to ^{135}Cs/^{137}Cs separation in plutonium uranium redox extraction (PUREX) and mixed oxide fuel (MOX) samples, with separation achieved by Ba^{2+} having a shorter migration time in the capillary than Cs^{+}, due to its higher charge and corresponding faster migration rate [66]. The procedure used low microlitre sample volumes and nanolitre scale sample injection, achieving ^{133}Cs detection limits of 6,000 ng L^{-1} and 4 ng L^{-1} in ICP-QMS and ICP-SFMS, respectively. Whilst other procedures have achieved lower limits of detection, capillary electrophoresis separation is potentially applicable to environmental samples, given that the speed and effectiveness of separation and low reagent volumes used compares favourably to ion exchange based procedures.

Online separation has been applied to Cs and Ba separation prior to ICP-MS analysis. This can minimise reagent volumes, achieve a more efficient Ba separation and thus improve the detection limits achievable [2, 4, 15, 67]. Capillary electrophoresis (CE-ICP-MS) has been applied to online ^{135}Cs/^{137}Cs separation in plutonium uranium redox extraction (PUREX) and mixed oxide fuel (MOX) samples, with separation achieved by Ba^{2+} having a shorter migration time in the capillary than Cs^{+}, due to its higher charge and corresponding faster migration rate [66]. The procedure used low microlitre sample volumes and nanolitre scale sample injection, with resulting ^{133}Cs detection limits of 6,000 ng L^{-1} and 4 ng L^{-1} in ICP-QMS and ICP-SFMS, respectively. Whilst other procedures have achieved lower limits of detection, capillary electrophoresis separation is potentially applicable to environmental samples, given that the speed and effectiveness of separation and low reagent volumes used compares favourably to ion exchange based procedures. Isnard et al. (2009) achieved a ^{135}Cs and ^{137}Cs detection limit of 2 pg L^{-1} (8.2×10^{-8} Bq L^{-1}) and 1pg L^{-1} (3.2×10^{-3} Bq L^{-1}), respectively, using on-line chromatographic separation with a CG3 IonPac guard column (Dionex, USA), which was effectively applied to measurement of ^{135}Cs/^{137}Cs in a spiked groundwater matrix [19]. Following AMP and anion exchange separation, Taylor et al. (2008) achieved online Cs/Ba separation by attaching a Dionex CS12A 3×150 mm cation exchange column onto a high performance liquid chromatography (HPLC) module, and coupling this system with ICP-MS. This setup was effectively applied to measurement of ^{135}Cs/^{137}Cs in sediment samples [4].

Instruments equipped with a dynamic reaction cell (DRC) have been applied to Cs separation [4, 20]. The aim is to use an appropriate gas to react with Ba and convert it to a non-interfering product, whilst having little or no impact on Cs [111], with N_2O, and CH_3Cl used as reactive gases [4, 20]. For example, the reaction between Ba and N_2O to form BaO is exothermic (-236.8 kJ mol^{-1}), whereas the reaction with Cs is thermodynamically unfavorable (+106.3 kJ mol^{-1}) [20]. Kinetic data from Lavrov et al. (2004) supports this, indicating the reaction for Ba has an efficiency of 32 %, compared to 0.01 % for Cs [112]. A recently developed ICP-MS (Agilent 8800 ICP-QQQ) has been applied to ^{135}Cs/^{137}Cs detection in rainwater and environmental samples contaminated following the accident at the Fukushima Daiichi NPP [6, 21, 22]. The instrument is equipped with a quadrupole mass filter in front of an octopole reaction cell and second quadrupole mass filter in an MS/MS configuration. Using N_2O as a reactive gas, a ^{135}Cs and ^{137}Cs detection limit of 10 pg L^{-1} (equivalent to 4.1×10^{-7} Bq L^{-1} and 3.2×10^{-2} Bq L^{-1}, respectively) was achieved in a Ba-free solution, compared to 100 pg L^{-1} (4.1×10^{-6} Bq L^{-1}) and 270 pg L^{-1} (8.6×10^{-1} Bq L^{-1}) for ^{135}Cs and ^{137}Cs, respectively, in solutions containing 100 µg L^{-1} Ba. These values are higher than the instrumental and method detection limits achievable using ICP-SFMS [5]. However, an advantage of the triple quad instrument is the combination of chemical and instrument-based separation using the reaction cell. Furthermore, the two quadrupoles can achieve a theoretical ^{133}Cs/^{135}Cs abundance sensitivity of 10^{-14} [21, 22], which is higher than any other ICP-MS.

A procedure recently developed using a Thermo Element 2XR ICP-SFMS achieved an instrumental detection limit of 1 pg L^{-1} for stable ^{133}Cs. The absence of instrument-based separation meant highly efficient chemical separation techniques using high purity reagents and clean laboratory conditions was required to minimise Ba contamination prior to sample introduction. Following AMP and combined cation exchange+ Sr-resin extraction chromatography separation, a method detection limit of 50 pg L^{-1} for ^{135}Cs and ^{137}Cs was calculated (equivalent to 2.1×10^{-6} Bq L^{-1} and 1.6×10^{-1} Bq L^{-1}, respectively), which is notably higher than the instrument detection limit [5]. This was improved to 20 pg L^{-1} (equivalent to 8.2×10^{-7} Bq L^{-1} and 6.4×10^{-2} Bq L^{-1}, respectively) with the addition of a calixarene extraction chromatography separation stage [104].

(Table 7)

Time independent fractionation is an issue affecting accurate isotope ratio measurements by ICP-MS. This instrumental mass bias must be corrected for in order to achieve accurate and precise isotope ratio values. One cause of this are space charge effects, as lighter ions are deflected to a greater extent than heavier ions during ion extraction, leading to fractionation towards the heavier isotope relative to the true value [113]. The absence of a ^{135}Cs/^{137}Cs certified reference material makes accurate mass bias correction challenging, and limits the ability to compare results between studies [4]. To suggest their method was applicable to isotope ratio measurements, Ohno and Muramatsu (2014) showed that measurements of ^{134}Cs/^{137}Cs by ICP-QQQ were consistent with values determined by Ge semiconductor analysis to within the analytical error [6]. Isnard et al. (2009) applied a sample standard bracketing technique using natural ^{121}Sb, ^{123}Sb and ^{151}Eu, ^{153}Eu to correct for mass bias, as the average mass of these isotopes is close to that of ^{137}Cs [113]. Barium-138 (natural abundance 71.7 %) has been used to assess the effectiveness of separation at masses 135 and 137, however any interference correction will reduce the accuracy of ^{135}Cs/^{137}Cs values. Caesium-137 values can be verified by gamma spectrometry, however if a significant correction is required this will not validate the ^{135}Cs result [13, 93, 114].

4.2.2. Thermal ionisation mass spectrometry (TIMS)

Lee et al. (1993) was the first to develop a procedure for measuring ^{135}Cs/^{137}Cs in environmental samples using TIMS. The instrument was equipped with a static quadrupole lens and static retarding potential repeller (RPQ) that acted as an energy and directional filter to remove ^{133}Cs ions scattered in the tail, improving the abundance sensitivity to 1×10^{-9} [8]. More recently, TIMS was applied to measurement of ^{135}Cs/^{137}Cs in effluent from three reactor sites, with significant variations between the three sites (0.41-1.30) highlighting that various factors over a reactor lifetime influences isotope ratio values [11]. The same instrumentation and sample preparation was applied to sediment core samples to highlight fractionation of ^{135}Cs and ^{137}Cs following aboveground nuclear tests at the Nevada Nuclear test site [10]. The difference in half-life of gaseous precursors of ^{135}Cs and ^{137}Cs, and washout due to wind or flooding events were highlighted as reasons for isotope fractionation [10].

Measurement of ^{135}Cs/^{137}Cs by TIMS is affected by time-dependent isotopic fractionation, as lighter isotopes are preferentially evaporated from the filament. The lack of an available certified Cs isotopic standard makes it difficult to measure mass fractionation, however, relative to the total estimated uncertainties, the fractionation effects have been predicted to be small [11]. Alternatively, mass fractionation can be corrected by measuring ^{133}Cs/^{137}Cs and ^{135}Cs/^{137}Cs ratios during the analysis, with Isnard et al. (2009) recording a relative bias ranging from 0.5-1.5 %, and a relative standard deviation lower than 0.1 % for all isotope ratios measured [113].

The isotopic fractionation affecting TIMS and ICP-MS, as well as the absence of a certified reference material to verify accuracy of ^{135}Cs/^{137}Cs measurements, led to Isnard (2009) comparing the two techniques for uranium oxide and mixed oxide fuel samples. The agreement between the two approaches was good, with a relative difference of 0.2-0.5 % for the two samples, measured following chemical separation. This suggests a combination of measurement procedures can be used to verify the measured isotope ratio values [113]. TIMS has also been applied to ^{135}Cs/^{137}Cs detection in environmental samples contaminated by the Fukushima Daiichi accident [9]. No correction was made for instrumental mass fractionation, however there was good agreement between the ^{134}Cs/^{137}Cs ratio measured by TIMS (1.02±0.07) and gamma spectrometry (1.04±0.003) [9]. For samples containing 5 Bq ^{137}Cs, the analytical uncertainty for ^{135}Cs/^{137}Cs was ~0.1 %.

4.2.3. Resonance ionisation mass spectrometry (RIMS)

In RIMS analysis, one or more lasers are tuned to Cs atomic transition wavelengths to achieve a very high selectivity [3]. Subsequent mass spectrometry combined with resonant excitation and ionization results in excellent separation from Ba interferences, a high ionisation efficiency, high transmission and low instrument background [12]. Pibida et al. used both RIMS and TIMS to determine the chronological age of nuclear fuel burn up samples through measurement of ^{135}Cs/^{137}Cs [12]. Following digestion and chemical separation, samples were loaded into a graphite furnace and atomised by gradually increasing the temperature of the furnace. Selectivity was achieved through tuning the laser frequencies for both ^{135}Cs and ^{137}Cs. For low-level detection of ^{135}Cs/^{137}Cs in environmental samples, improvements in overall efficiency and chemical separation were required [12]. The absence of a commercially available instrument is the primary limitation to this approach [3]. In addition, optimisation of instrument efficiency and chemical preparation is time-consuming compared to other mass spectrometric approaches [57].

4.2.4. Accelerator mass spectrometry (AMS)

AMS measurement of ^{135}Cs/^{137}Cs is limited by the high energies required to separate Cs and Ba isobars, which makes separation a complex and costly process [13]. A method to produce a beam of Cs anions, and production of suitable yield tracers to determine the efficiency of the process are also required [14]. A Ba reduction of 2×10^{-5} was achieved by preparing Cs as CsF_2^-, which forms an anion that is preferentially produced in the ion source over BaF_2^-. The compound was prepared by mixing the sample with PbF_2 at a ratio of 1:5 by volume. Stable Cs was used as a sputtering source, with a theoretical ^{135}Cs/^{133}Cs detection efficiency of 7×10^{-15} [13]. It may be possible to incorporate ^{134}Cs as a yield tracer into the sputtering source [14], or alternatively use rubidium as a source, providing the stable Cs content is sufficiently low. As with RIMS, the lack of a commercially available instrument and complex and time-consuming instrumental setup prevents the application of AMS to routine ^{135}Cs/^{137}Cs detection.

5. Conclusions

Caesium-135 and ^{137}Cs are high yield fission products, whose presence in the environment is a result of anthropogenic nuclear activities. Caesium-137 is of major importance in decommissioning, environmental process studies and monitoring and radiation safety, whereas ^{135}Cs would be a major contributor to the long-term radiological risk associated with deep geological disposal. Advances in mass spectrometry (specifically ICP-MS) have put the technique at a stage where it can accurately detect low-level environmental concentrations of ^{135}Cs and ^{137}Cs. This also enables the measurement of ^{135}Cs/^{137}Cs values that can be used to identify the source of radioactive contamination, and therefore has the potential to be a powerful forensic tool in environmental studies. A limitation is the application of $^{135}Cs/^{137}Cs$ ratios to series of isolated studies, with the absence of certified reference materials and inconclusive evidence over the site history being limiting factors in comparing variations between, and even within studies.

The detection limits achievable are strongly controlled by the extent of separation of isobaric Ba interferences, and elimination of peak tailing from stable ^{133}Cs on ^{135}Cs. AMP and/or ion exchange chromatography are the most common methods for chemical separation of Cs from Ba, whilst extraction chromatography using a calixarene offers a highly selective and costly alternative. Coupling the separation stage online to the instrument reduces contamination by minimising reagent volumes and analyst exposure, for example through ion exchange, electro thermal vaporisation or capillary electrophoresis.

Sector field ICP-MS (ICP-SFMS) is a highly sensitive approach that enables detection of $^{135}Cs/^{137}Cs$ in low-level environmental samples. At these concentrations, the detection limits achievable are determined by Ba contamination in the resins and reagents used, or that introduced during the separation procedure, rather than the capabilities of the instrument. An alternative approach is to use ICP-QMS equipped with a Dynamic Reaction Cell, with N_2O and CH_3Cl used as reactive gases for removal of Ba. The instrumental detection limit is higher than ICP-SFMS, however reaction-cell separation can eliminate residual Ba not removed by chemical separation. Furthermore, the abundance sensitivity is superior to ICP-SFMS, which is beneficial to samples such as soils and sediments with a high stable ^{133}Cs concentration. Recently, a triple quadrupole ICP-MS (ICP-QQQ) has been applied to measurement of ^{135}Cs/^{137}Cs in environmental samples contaminated by the accident at the Fukushima Daiichi Nuclear Power Plant, combining chemical and reaction-cell based Ba separation with the highest abundance sensitivity of any ICP-MS instrument. Whilst the instrumental sensitivity is lower than that of sector-field instruments, for real samples the method detection limits are comparable.

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Table 1. Properties of radiocaesium isotopes.

Radio-isotope	Half life (years)	^{235}U fission yield (%)	Specific activity (Bq g^{-1})	Mass equivalent to activity of 1 Bq (pg)
^{134}Cs	2.1	7.7	6.4×10^{15}	0.02
^{135}Cs	2.3×10^{6}	6.6	4.1×10^{7}	24491.3
^{136}Cs	0.04	6.3	3.7×10^{17}	4.1×10^{-4}
^{137}Cs	30.2	6.2	3.2×10^{12}	0.3

Table 2. Summary of ^{137}Cs inventories

Location	Contamination type	Date	^{137}Cs released	Reference
Global weapons testing	Atmospheric fallout	1950's-1960's	545-765 PBq	[117-121]
Sellafield, UK	Aqueous discharges	1952-2011	41.3 PBq	[25, 27, 28]
La Hague, France	Aqueous discharges	1966-2011	1.0 PBq	[26]
Chernobyl, Ukraine	Atmospheric	1986	42.5 TBq	[37]
Fukushima, Japan	Atmospheric	2011	13-53 PBq	[38, 42] [38, 42-44]
	Aqueous discharges	2011	3.5-27 PBq	[21]
	Inventory in damaged reactor cores	2011	77.5 kg	[21]
Dounreay, UK	Hot particles	1960's-1970's	1.4-5.5 MBq (^{137}Cs+^{90}Sr)	[30, 31]
Hanford, USA	Tank waste inventory summation	1994	2.0×10^3 PBq	[123]
	Waste capsules	2013	37 PBq (^{137}Cs+^{90}Sr)	[34]
	Vitrified glass	2013	296 PBq (^{137}Cs+^{90}Sr)	[34]

Table 3. Summary of ^{137}Cs activities in multiple locations and sample types

Location	**Sample type**	**Source of contamination**	**Date**	**^{137}Cs concentration**	**Reference**
Northern hemisphere	Global fallout	Weapons test fallout	1970	3830-5090 Bq m^{-2} (55°N) - 280-900 Bq m^{-2} (85°N)	[117-121]
Southern hemisphere	Global fallout	Weapons test fallout	1970	440-530 Bq m^{-2} (15°S) - 580-810 Bq m^{-2} (35°S)	[117-121]
Northern hemisphere oceans	Seawater	Weapons test fallout, reprocessing facilities, Chernobyl	2012	3-5 Bq m^{-3}	[46-51]
Southern hemisphere oceans	Seawater	Weapons test fallout	2012	<1 Bq m^{-3}	[46, 47]
Cumbria, UK	Coastal sands and muds	Sellafield	2011	39-450 Bq kg^{-1}	[27]
Northern Ireland coast	Coastal sands and muds	Sellafield	2011	1-35 Bq kg^{-1}	[27]
Irish Sea	Seawater	Sellafield	2011	$<3\times10^{-5}$-1.2×10^{-4} Bq kg^{-1}	[27]
Japan seawater	Seawater	Weapons test fallout	1960 2010	~30 Bq m^{-3} 1-4 Bq m^{-3}	[38, 39]
Discharge channels from Fukushima NPP	Water	Fukushima	2011	4×10^{7} Bq m^{-3} (at time of accident) 25,000 Bq m^{-3} (4 months after accident)	[38, 44]
Baltic and	Seawater	Chernobyl	1986	10-10,000 Bq m^{-3}	[38]

Black Seas			2012	<10-100 Bq m^{-3}	
Chalk River	River water	Chalk River Laboratories		85 Bq kg^{-1} (upstream) 198 Bq kg^{-1} (downstream)	[52]
Columbia and Snake River	Sediments	Hanford	1988-1994	2-7×10^{-6} Bq kg^{-1} (dry weight)	[122]

Table 4. Estimate of Arctic Ocean inventories in 1993 [46].

Source	**^{137}Cs (PBq)**
Global fallout	4
Runoff of global fallout	1
Sellafield discharges	10-15
USSR river discharges	1-5
Chernobyl	1-5
Total	**17-30**

Table 6. A summary of analytical methods for measurement of ^{135}Cs and ^{137}Cs.

Ref	**Sample**	**Separation**	**Measurement method**	**Recovery**	**Detection limit**
[8]	Coastal sediment	Cation exchange with AG50W-X8	TIMS	>90 %	
[15]	Spent nuclear fuel pellets, solutions	Cation exchange with CG3+CS3	ICP-QMS	-	
[1]	Radioactive waste	AMP Cation exchange with Amberlite 200	NAA	-	
[16]	Waste tank sludges and supernates	$Ba(OH)_2$ precipitation using ammonium hydroxide	ICP-QMS	-	209 ng L^{-1}
[114]	High activity waste, spent fuel	On-line cation exchange comparing multiple resins	ICP-QMS	-	16 ng L^{-1} (^{133}Cs)
[18]	^{137}Cs standard	ETV sample introduction	ETV-ICP-MS	96-99 %	0.2 ng L^{-1} (^{135}Cs) 8.2×10^{-6} Bq L^{-1}
[7]	Freshwater lake sediment	AMP	RIMS, TIMS	70 %	
[12]	Nuclear fuel burn up samples	Extraction chromatography with Eichrom TRU resin; AMP	RIMS, TIMS	82 %	7 Bq (^{135}Cs) 0.6 Bq (^{137}Cs)
[20]	Spent fuel pellets	Anion exchange with AG50W-X4; HPLC with Interchim uptisphere SCX	DRC-MC-ICP-MS	-	
[4]	Soil and sediment	AMP; Anion exchange with AG-MP; On-line cation exchange with CS12A	DRC-ICP-QMS	-	0.2 ng L^{-1} (^{133}Cs)
[19]	Spiked groundwater	On-line cation exchange with CG3	ICP-QMS	-	2 pg L^{-1} (^{135}Cs) 8.2×10^{-8} Bq L^{-1} 0.9 pg L^{-1} (^{137}Cs) 2.9×10^{-3} Bq L^{-1}

[11]	Reactor effluents	AMP; Anion and cation exchange	TIMS	-	
[93]	Spent fuel solutions	Cation exchange	ICP-QMS	-	
[10]	Sediment cores	AMP-PAN Anion and cation exchange	TIMS	-	
[6]	Rainwater	-	ICP-QQQ-MS		10 pg L^{-1} (^{135}Cs) 4.1×10^{-7} Bq L^{-1} 10 pg L^{-1} (^{137}Cs) 3.2×10^{-2} Bq L^{-1}
[66]	Simulated spent fuel	Capillary electrophoresis sample introduction	CE-ICP-QMS CE-ICP-SFMS	-	6000 ng L^{-1} (^{133}Cs) 4 ng L^{-1} (^{133}Cs)
[113]	Spent fuel	Anion exchange using AG1x4 HPLC with interchim uptisphere SCX	TIMS, MC-ICP-MS	-	
[22]	Litter, lichen, soils	AMP Anion exchange AG MP-1M Cation exchange AG 50W-X8	ICP-QQQ-MS	-	0.01 ng L^{-1} (^{135}Cs) 4.1×10^{-7} Bq L^{-1} 0.006 ng L^{-1} (^{137}Cs) 1.9×10^{-2} Bq L^{-1}
[9]	Environmental samples	AMP Anion exchange Cation exchange AG 50W-X8	TIMS	-	-
[5]	^{137}Cs standard	AMP Cation exchange with AG 50W-X8 Extraction chromatography (Sr-resin)	ICP-SFMS	>85%	0.05 ng L^{-1} (^{133}Cs)

Table 7. Abundance sensitivity values for ^{133}Cs on mass 135 for different mass spectrometry instruments

Reference	**Instrument**	**Abundance sensitivity**
[8]	TIMS (Finnegan MAT262Q)	10^{-10}
[4]	ICP-DRC-MS (Perkin Elmer DRC II)	10^{-10} (theoretical)
[6]	ICP-SFMS (Thermo Element 2XR)	10^{-5} (low resolution) 10^{-6} (medium resolution)
[6, 21]	ICP-QQQ-MS (Agilent 8800)	10^{-14} (theoretical)
[13]	AMS	10^{-15}

Table 5. Summary review of procedural stages applied to extraction and detection of ^{135}Cs/^{137}Cs

Analytical stage	**Key considerations**	**Procedure**	**Strengths**	**Potential problems**	**References**
Sample Digestion	Removal of organic matter from soils and sediments Opening-out of minerals Quantitative Cs recovery	Acid leaching	Rapid Straightforward	Limited recovery in more complex sample matrices	5, 7, 8, 15, 21, 22, 66
		Microwave digestion	Controlled temperature and pressure conditions	Limited to small sample sizes (< 1g)	16
		Borate fusion	High Cs recovery	Typically 1100^{0}C required but Cs effectively trapped in melt	4, 5, 60, 65
Chemical separation	Cs recovery Ba decontamination	AMP	• High Cs selectivity and Ba decontamination • Effective in multiple sample matrices	Dissolution in alkali solution and further ion exchange separation required prior to detection	1, 4, 5, 7, 22, 10, 11, 12, 21, 57, 69, 71, 73, 75, 76
		KNiFC	High Cs recovery	• Lower selectivity than AMP	75, 79, 83-88

	Quantitative Cs recovery Subsequent measurement technique			• Quantitative Cs recovery challenging	
		Ion exchange chromatography	Versatile Selective On-line separation possible	• Long elution times • High reagent volumes required	1, 4, 5, 8, 9, 10, 11, 15, 19-22, 63, 92, 93
		Extraction chromatography	Direct sample introduction to ICP-MS	• High cost • Cannot act as a single separation stage for complex matrices	5, 96-99, 101-104, 105-108
Radiometric detection	Sensitivity Interference correction	NAA	• No Ba interference • Gamma spectrometry detection of ^{135}Cs through ^{136}Cs	• Activation process creates interferences and raises backgrounds if no chemical separations done • Reactor facility required	3, 110
ICP-MS detection	Sensitivity Interference removal	ETV-ICP-MS	• Further Ba decontamination • Reduced sample preparation time • High sample introduction	Previous chemical separation required for more complex sample matrices	18

	Interference correction Instrument type Sample introduction system Instrumental setup Peak tailing of ^{133}Cs Mass independent fractionation Limit of detection of instrument and procedure		efficiency		
		CE-ICP-MS	• Further Ba decontamination • Low sample volume	Previous chemical separation required for more complex sample matrices	66
		Online ICP-MS	Lower reagent volumes and more efficient separation than offline methods	Lower sample throughput compared to offline separation	2, 4, 15, 67
		ICP-QMS	• Straightforward instrument preparation • Robust	• High LOD • Restricted to higher activity samples	2, 15, 16, 18
		ICP-DRC-MS	• Cell-based Ba separation	Higher LOD than ICP-SFMS	4, 20
		ICP-QQQ-MS	• Cell-based Ba separation • High abundance sensitivity	Higher LOD than ICP-SFMS	6, 21, 22
		ICP-SFMS	• High sensitivity • Low detection limit	LOD dependent on chemical separation prior to sample introduction	5, 66
Alternative mass		TIMS	Used in combination with ICP-MS and RIMS	• Mass dependent fractionation • ICP-MS a favourable technique	8, 9, 113

spectrometric detection		RIMS AMS	High sensitivity	• Time consuming preparation • Low instrument availability	3, 7, 12 13, 14

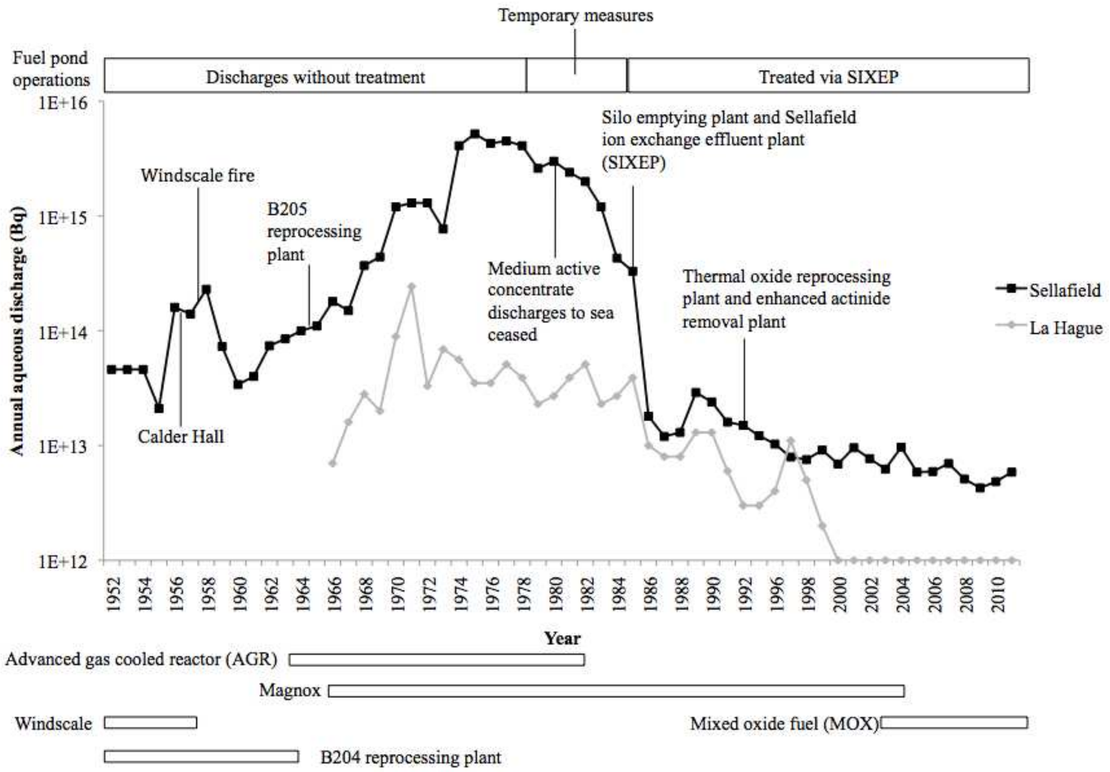

Figure 1. Annual aqueous discharges from the Sellafield and La Hague reprocessing sites, and major changes in Sellafield site operations. Discharge data from Gray et al. (1995), RIFE reports [25, 27], Warneke et al. (2002) [29] and AREVA La Hague [113].

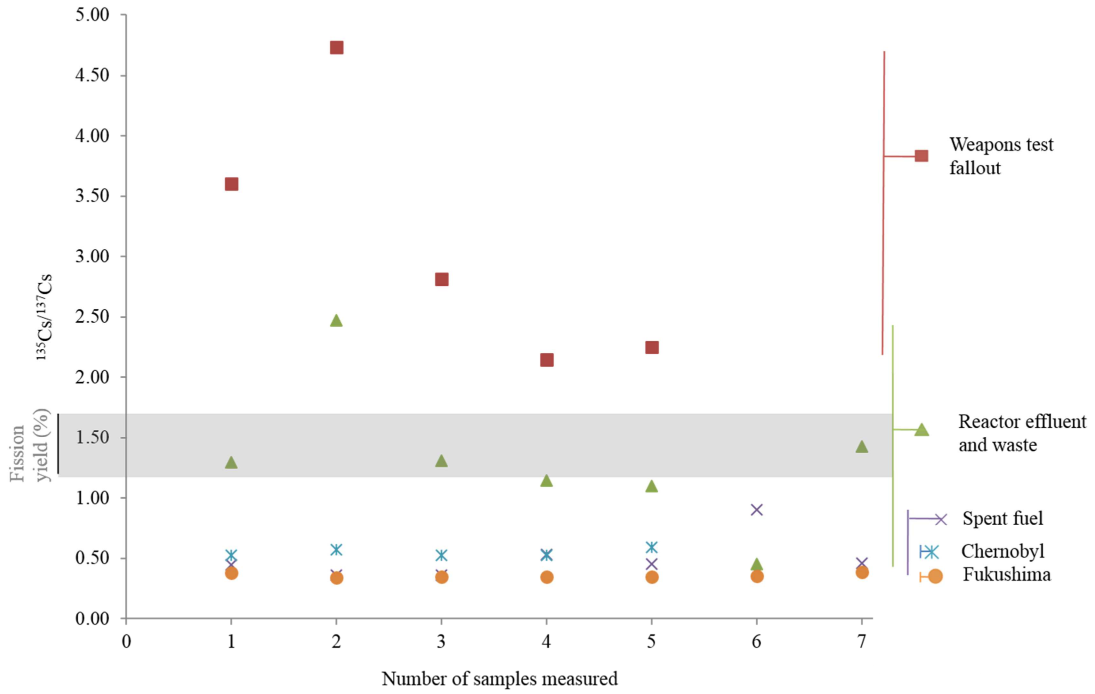

Figure 2. Summary of $^{135}Cs/^{137}Cs$ atom ratios for a range of sources measured by mass spectrometry [1, 2, 4-8, 10, 11, 20-22, 66, 113, 93] All values have been corrected to 2015.

- ^{135}Cs and ^{137}Cs are present as a result of anthropogenic nuclear activities
- Measurement has implications for multiple aspects of the nuclear industry
- Advances in mass spectrometry enable low-level detection of ^{135}Cs and ^{137}Cs
- Accurate measurement of the ^{135}Cs/^{137}Cs ratio can identify the contamination source
- Detection limits are controlled by removal of interferences from stable Ba and Cs

Ben Russell completed his PhD at the University of Southampton in 2014, investigating the application of sector field inductively coupled plasma mass spectrometry (ICP-SFMS) for low-level nuclear waste characterisation, focusing on radiocaesium isotopes and strontium-90. The project combined novel and efficient chemical separation techniques with high sensitivity ICP-SFMS quantification, resulting in two lead-author peer-reviewed papers. Since completing his PhD, Dr Russell has worked in the radioactivity group at the National Physical Laboratory, London, with the primary role of setting up and running the ICP-MS department.

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