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Published in:
Talanta

Link to article, DOI:
10.1016/j.talanta.2020.121637

Publication date:
2021

Document Version
Peer reviewed version

Citation (APA):
Zhu, L., Hou, X., & Qiao, J. (2021). Determination of 135Cs concentration and 135Cs/137Cs ratio in waste samples from nuclear decommissioning by chemical separation and ICP-MS/MS. Talanta, 221, [121637]. https://doi.org/10.1016/j.talanta.2020.121637
Determination of $^{135}$Cs concentration and $^{135}$Cs/$^{137}$Cs ratio in waste samples from nuclear decommissioning by chemical separation and ICP-MS/MS

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Abstract:

Determination of $^{135}$Cs concentration and $^{135}$Cs/$^{137}$Cs atomic ratio is of great importance in characterization of radioactive waste from decommissioning of nuclear facilities. In this work, an effective analytical method was developed for simultaneously determination of $^{135}$Cs and $^{137}$Cs in different types of waste samples (steel, zirconium alloy, reactor coolant, ion exchange filter paper and spent ion exchange resin) by coupling AMP-PAN, AG MP-1M and AG 50W-X8 chromatographic separation with ICP-MS/MS measurement. Decontamination factors of $7.0 \times 10^6$ for Co, $6.0 \times 10^6$ for Ba, $4.2 \times 10^5$ for Mo, $3.2 \times 10^5$ for Sn and $2.1 \times 10^5$ for Sb were achieved using the chemical separation procedure. The overall chemical yields of cesium were higher than 85%. A detection limit of $3.1 \times 10^{-14}$ g/g for $^{135}$Cs was achieved for 0.2 g stainless steel sample or spent resin. The developed method was validated by analysis of standard reference materials (IAEA-375) and successfully applied for analysis of zirconium alloy, steel, ion exchange filter paper and spent ion exchange resin from nuclear power reactors. The obtained $^{135}$Cs can be used to evaluate the long-term environmental impact and provide useful information for waste disposal. The measured $^{135}$Cs/$^{137}$Cs in reactor coolant, as a characteristic information, might be useful for

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source identification and localization of leaked fuel element. The neutron flux of the leaked fuel element can be estimated based on the measured $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios in the reactor coolant water. The developed method is simple and rapid (8 samples/day) for the determination of $^{135}\text{Cs}$ concentrations and $^{135}\text{Cs}/^{137}\text{Cs}$ ratios in various waste samples from nuclear decommissioning.

**Keywords:** $^{135}\text{Cs}$, $^{135}\text{Cs}/^{137}\text{Cs}$, radioactive waste, characterization, decommissioning, ICP-MS/MS

### 1. Introduction

Since 1950s, nuclear energy has become an important energy in many countries. There are around 450 nuclear power reactors in operation at present, meanwhile, increased number of power reactors were closed and have being decommissioned [1]. Nuclear waste generated during the operation of nuclear power plants (e.g. ion exchange resin) and decommissioning needs to be safely deposited. Radiological characterization of these wastes is critically important for their safe repository. Among all radionuclides, long-lived radionuclides, especially the difficult-to-measure radionuclides such as $^{99}\text{Tc}$, $^{129}\text{I}$, $^{93}\text{Mo}$, $^{135}\text{Cs}$ and actinides are very important and highly challenging in the waste characterization.

As a high yield fission product (6.9% from $^{235}\text{U}$ fission), $^{135}\text{Cs}$ is a long-lived (2.3 Myr) pure beta emitter ($E_{\text{max}} = 268$ keV) with a very low specific radioactivity of 0.043 Bq/ng. Therefore, the measurement of $^{135}\text{Cs}$ by radiometric method, i.e. liquid scintillation counting or beta counting is hindered due to the co-existence of $^{137}\text{Cs}$, which has a short half-life (30 yr), similar fission yield as $^{135}\text{Cs}$ and high beta energy ($E_{\text{max}}= 1176$ keV). Neutron activation analysis (NAA) has been proposed for the determination of $^{135}\text{Cs}$ in high-level waste samples by converting $^{135}\text{Cs}$ to a gamma emitting radionuclide $^{136}\text{Cs}$ through neutron activation reaction. However, it cannot be used for determination of low level $^{135}\text{Cs}$ due to the high detection limits [2, 3]. Mass spectrometry is a sensitive measurement technique for the determination of long-lived radionuclides, which
enables measurement of femtogram level of $^{135}$Cs [4, 5]. Among them, thermal ionization mass spectrometry (TIMS) is one suitable technique for measurement of $^{135}$Cs due to its high sensitivity and less interferences [6, 7, 8, 9], but its less accessibility and capability make it difficult to be used for routine analysis of large number of samples. ICP-MS can also be used for measurement of $^{135}$Cs, but the isobaric interference ($^{135}$Ba), peak tailing of stable $^{133}$Cs and polyatomic interference ($^{95}$Mo$^{40}$Ar$^+$, $^{119}$Sn$^{16}$O$^+$) seriously limit its application in the measurement of $^{135}$Cs. The triple quadrupole ICP-MS can be used to significantly suppress peak tailing of $^{133}$Cs; in combination with collision reaction technique in this instrument, the interferences of $^{135}$Ba and polyatomic ions can be also eliminated, enabling it to measure low-level $^{135}$Cs, as well as $^{137}$Cs [10, 11, 12, 13]. However, nuclear waste samples usually contain high level of radioactivity of activation products, e.g. $^{60}$Co, $^{58}$Co, $^{125}$Sb, which might be more than 6 orders of magnitude higher than that of $^{135}$Cs, thus limits the direct measurement by ICP-MS due to the radioactive damage and contamination of the instrument. Therefore, chemical separation of cesium from complicated matrix, major radioactive radionuclides and interfering elements is needed prior to its measurement. Different separation methods, such as AMP adsorption, and ion exchange techniques could be used for this purpose [14, 15, 16].

In the decommissioning of nuclear reactors, all components of the materials which were exposed to neutron irradiation or contaminated by radioactive substances such as various metal used as construction materials in the reactor are dominant wastes. During the operation of nuclear power reactor, coolant water and spent fuel pool water are easily contaminated due to the leakage of nuclear fuel and the corrosion of the construction metals, which are routinely purified by mixed ion exchange column, resulting in a large amount of spent ion exchange resin wastes. These materials need to be characterized for various radionuclides, especially long-lived radionuclides
before repository. Meanwhile, the reactor coolant water and spent fuel pool water also need to be analyzed for various radionuclides for monitoring the contamination level and possible leakage of the nuclear fuel element. Many analytical methods have been reported for the determination long-lived radionuclides in waste samples from nuclear decommissioning and reactor operation for $^{99}$Tc, $^{93}$Zr and $^{129}$I [17, 18, 19, 20], but very few on the determination of $^{135}$Cs in waste samples. The reported method for the determination of $^{135}$Cs in the evaporated coolant water by NAA and ICP-MS showed a relatively high detection limit (0.4-2 Bq/L) for $^{135}$Cs [3], which is not suitable for ordinary coolant water and fuel pool water. Another method using ion chromatography and ICP-MS was also reported for the determination of $^{135}$Cs in irradiated UO$_2$ pellet with a relatively high detection limit up to 0.7 mBq/g [21]. To the best of our knowledge, the method for the determination of $^{135}$Cs in steel, zirconium alloy, filter and spent ion exchange resin from nuclear facilities is still not available.

This work aims to develop an effective method for the determination of $^{135}$Cs concentration and $^{135}$Cs/$^{137}$Cs atomic ratio in different waste samples from nuclear decommissioning and waste repository. This will be implemented through establishing effective methods for releasing cesium from sample matrix by acid dissolution and leaching, removing dominant radioactive radionuclides and major interfering elements using chemical separation, and systematically optimization of measurement method of $^{135}$Cs using triple quadrupole ICP-MS with sufficiently suppressing isobaric interferences ($^{135}$Ba), tailing effect of $^{133}$Cs and interferences of polyatomic ions.

2. Experimental

2.1. Instrumentation
A tandem quadrupole ICP-MS/MS (Agilent 8800, Japan), equipped with a Ni sampler cone, a Ni skimmer cone, a spray chamber and a PTFE nebulizer, was employed to determine $^{135}$Cs and $^{137}$Cs in purified waste samples. The first quadrupole mass filter situated in front of the collision-reaction cell was used to select analyte ions (m/z=135 and 137) to enter the analysis system, and reject all other ions. N$_2$O (99.999% purity, Air Liquide Denmark) was introduced into the collision-reaction cell to eliminate the isobaric interference ($^{135}$Ba and $^{137}$Ba) by forming oxides of barium and polyatomic interference ($^{95}$Mo$^{40}$Ar$^+$, $^{97}$Mo$^{40}$Ar$^+$, $^{119}$Sn$^{16}$O$^+$ and $^{121}$Sb$^{16}$O$^+$) by splitting them to single ions. The analytes ions ($^{135}$Cs and $^{137}$Cs) were selected in the second quadrupole mass filter and measured by detector. Diluted stable Cs standard solution (10 $\mu$g/mL, LabKings, Netherlands) was used to optimize the instrumental parameters. A high performance sample introduction system (Apex-Q, Elemental Scientific Instruments, USA) was employed to further improve the sensitivity of cesium isotopes. The instrumental parameters used for the measurement of $^{135}$Cs and $^{137}$Cs are listed in Table 1.

Table 1. Optimized parameters for measurement of $^{135}$Cs and $^{137}$Cs by ICP-MS/MS

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>1500 W</td>
</tr>
<tr>
<td>Sampling position</td>
<td>6.0 mm</td>
</tr>
<tr>
<td>Plasma gas flow rate</td>
<td>15 L/min</td>
</tr>
<tr>
<td>Auxiliary gas flow rate</td>
<td>0.98 L/min</td>
</tr>
<tr>
<td>Nebulizer pump</td>
<td>0.1 rps</td>
</tr>
<tr>
<td>Nebulizer gas flow rate</td>
<td>0.98 L/min</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}$ flow rate</td>
<td>0.70 mL/min</td>
</tr>
<tr>
<td>OctP Bias</td>
<td>-5.5 V</td>
</tr>
<tr>
<td>OctP RF</td>
<td>180 V</td>
</tr>
<tr>
<td>Extract 1</td>
<td>-105 V</td>
</tr>
<tr>
<td>Extract 2</td>
<td>-200 V</td>
</tr>
<tr>
<td>Q1 Entrance</td>
<td>2 V</td>
</tr>
<tr>
<td>Q1 Exit</td>
<td>4 V</td>
</tr>
</tbody>
</table>
An HPGe gamma spectrometer (Canberra) with spectroscopy software Genie 2000) was used to determine the activity of radionuclides in waste samples (e.g. $^{137}$Cs by counting its 661.6 keV gamma rays) in this work. The resolution of this system is 1.83 keV for 1332 keV gamma line of $^{60}$Co and the relative counting efficiency is 25%. The detector was calibrated for counting efficiency using a mixed gamma standard.

2.2. Reagents, materials and samples

All reagents used in this study, including HNO$_3$, H$_2$SO$_4$, HCl, HF, H$_2$O$_2$, NH$_3$·H$_2$O were of analytical reagent grade. Ultra-pure water (18.2 MΩ·cm, Sartorius water purification system, arium pro VF) and purified HNO$_3$ (acid distilled system, Savillex DST-1000, USA) were employed for dilution of reagents, elution of cesium from cation exchange column and preparation of final Cs solution prior to ICP-MS/MS measurement. AMP-PAN (100-600 μm, Triskem International) resin and ion exchange resin (AG MP-1M and AG 50W-X8, 100-200 mesh, analytical grade, Bio-Rad Laboratory) were used for separation and purification of cesium.

Reference materials IAEA-375 (soil collected from Novozybkov, Bryansk, Russia in 1990), were purchased from the International Atomic Energy Agency (IAEA).

Different types of samples from nuclear power plants such as stainless steel and carbon steel from pressure vessel of nuclear reactor (which was exposed to the neutron flux during operation of the nuclear reactor), zirconium alloy from the construction of reactor (which was contaminated by the reactor water on the surface), leachate of ion exchange filter paper used for pre-concentration of radionuclides in coolant water of nuclear power reactors, ion exchange filter paper and spent ion exchange resins (which were used for purification of the reactor coolant water in different nuclear reactors, e.g. boiling water reactor and pressurized water reactor) were analyzed in this work. The detailed information of these samples are summarized in table 2.
Table 2. Information of waste samples used for the determination of $^{135}\text{Cs}$ and $^{135}\text{Cs}/^{137}\text{Cs}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of sample</th>
<th>Reactor type</th>
<th>Reactor No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-1</td>
<td>Zirconium alloy</td>
<td>BWR</td>
<td>R-1</td>
</tr>
<tr>
<td>Zr-2</td>
<td>Zirconium alloy</td>
<td>BWR</td>
<td>R-1</td>
</tr>
<tr>
<td>Zr-3</td>
<td>Zirconium alloy</td>
<td>BWR</td>
<td>R-2</td>
</tr>
<tr>
<td>Steel-1</td>
<td>Stainless steel</td>
<td>BWR</td>
<td>R-2</td>
</tr>
<tr>
<td>Steel-2</td>
<td>Carbon steel</td>
<td></td>
<td>R-1</td>
</tr>
<tr>
<td>Leachate-1&lt;sup&gt;a)&lt;/sup&gt;</td>
<td>Acid leachate of ion exchange filter paper</td>
<td>BWR</td>
<td>R-3</td>
</tr>
<tr>
<td>Leachate-2&lt;sup&gt;a)&lt;/sup&gt;</td>
<td>Acid leachate of ion exchange filter paper</td>
<td></td>
<td>R-4</td>
</tr>
<tr>
<td>Leachate-3&lt;sup&gt;a)&lt;/sup&gt;</td>
<td>Acid leachate of ion exchange filter paper</td>
<td>BWR</td>
<td>R-5</td>
</tr>
<tr>
<td>Filter paper&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>Mixed ion exchange filter paper</td>
<td></td>
<td>R-6</td>
</tr>
<tr>
<td>Resin-1&lt;sup&gt;c)&lt;/sup&gt;</td>
<td>Spent ion exchange resin</td>
<td>BWR</td>
<td>R-7</td>
</tr>
<tr>
<td>Resin-2&lt;sup&gt;c)&lt;/sup&gt;</td>
<td>Spent ion exchange resin</td>
<td></td>
<td>R-7</td>
</tr>
<tr>
<td>Resin-3&lt;sup&gt;c)&lt;/sup&gt;</td>
<td>Spent ion exchange resin</td>
<td>BWR</td>
<td>R-7</td>
</tr>
</tbody>
</table>

PWR: pressurized water reactor; BWR: boiling water reactor; a) leachate of ion exchange filter paper used for pre-concentration of reactor coolant water; b) Mixed ion exchange filter paper used for pre-concentration of spent fuel pool water; c) Mixed ion exchange resin for purification of reactor coolant water.
2.3. Pretreatment of different types of waste samples

2.3.1. Stainless steel and carbon steel

Steel samples were transferred to a beaker and dried by heating on a hot plate at 150°C for 1-2 hours. 0.05-0.3 g of dried sample was weighed to a round flask. The steel samples were dissolved with 20-30 mL of 5 M H₂SO₄ at 180°C for 1-2 hours. Then the obtained sample solution was transferred to a tube after removing the residue still remained in some sample (e.g. carbon steel, a tiny amount of black residue floats on the dissolved sample solution after the dissolution, which might be carbon in the steel).

2.3.2. Zirconium alloy

The zirconium alloy samples, as one piece of 5-10 cm² surface area, were collected from a nuclear reactor as construction material that was exposed and surface contaminated by reactor water. The sample in a beaker was first dried by heating at 150 °C for 1 hour. The dried sample was measured for surface area and total weight. The zirconium alloy samples were then measured using an HPGe gamma spectrometry for gamma emitting radionuclides (mainly ⁶⁰Co and ¹²⁵Sb). The sample was then leached with 30-50 mL of *aqua regia* at 180°C on a hot plate. The solution was transferred to a bottle and the zirconium alloy was measured again using gamma spectrometry. The sample was leached again with *aqua regia* if the total gamma activity remaining on the residue was more than 5%. All leachates were combined in a bottle and weighed, which was used for the determination of ¹³⁵Cs and ¹³⁷Cs. This process was applied to dissolve all deposited radionuclides on the surface of the zirconium alloy.

2.3.3. Spent ion exchange resin

About 0.2 g sample was transferred to a 50 mL centrifuge tube and weighed. Radionuclides in the resin were measured by an HPGe gamma spectrometry. After measurement, 30 mL of 5 M HNO₃
was added to the centrifuge tube, shaking for 0.5 h to leach cesium. The leachate was transferred to a bottle after centrifuging for 10 minutes at 3000 rpm. The residue was rinsed with 5 mL 5 M HNO₃ for 2 times, and the leachate and rinsing solution were combined for further separation of cesium. The residue of resin was dried and measured by gamma spectrometry.

2.3.4. Filter paper

The ion exchange filter paper sample that have been used to concentrate radionuclides from reactor coolant water was weighed into a beaker, about 10 mL of concentrated H₂SO₄ was added to digest for 20-30 min. 10 mL of concentrated (65%) HNO₃ was then added and heated at 200°C on a hot plate for 30 min. 15 mL of H₂O₂ was added to the sample and heated at 200 °C for 30-60 min. After cooled down, 70 mL water was carefully added to the sample. The leachate was collected by filtering through a glass fiber filter (0.45 µm pore size). The residue was rinsed 3 times using 10-20 mL of 1 M HNO₃. Radionuclides in the leachate and residue of filter were measured by HPGe gamma spectrometry for measurement of cesium recovery in this step.

2.3.5. Leachate of filter paper

The mixed ion exchange filter paper that was used to concentrate radionuclides from 2.5 L coolant water of different nuclear reactors was leached using the same method as above, the obtained leachate was used for determination of radiocesium.

2.4. Chemical separation of cesium from waste samples

An aliquot of solution (15-40 mL) of the dissolved metal, leachate of zirconium alloy, spent ion exchange resin and filter paper was weighed to a beaker, 1.0 µg of stable cesium (Cs standard, Lab Kings, Netherlands) was added to the solution as carrier and chemical yield tracer. For high concentration of acid in the dissolved solution or leachate, H₂O was added to adjust the acid concentration to 1 M HNO₃ media. 0.2 mL 30% H₂O₂ was added to sample solution to form an
oxidizing media. The solution was loaded to a 1.0 mL AMP-PAN resin column (100-600 μm, φ7 mm × 5 cm). After rinsing with 45 mL of 1 M HNO₃ and 15 mL of H₂O, Cs retained on the column was eluted with 8 mL of 1.5 M NH₃·H₂O from the column. The eluate was directly loaded onto a 2 mL anion exchange column (AG MP-1M, φ7 mm × 5 cm, Cl⁻ form), the column was rinsed with 5 mL of 1.5 M NH₃·H₂O. Cesium in the effluent and washing solution was combined, and then loaded onto a 10 mL cation exchange column (AG 50W-X8, φ1.0 cm × 20 cm, H⁺ form). The column was rinsed with 40 mL of 1.5 M NH₃·H₂O, followed by 20 mL H₂O and 70 mL of 1 M HNO₃. Cesium was finally eluted from the AG 50W-X8 column using 70 mL of 1 M HNO₃. The eluate was evaporated to near dryness on a hot plate, the residue was dissolved with 3 mL of 0.3 M HNO₃ (distilled) for the determination of ¹³⁵Cs, ¹³⁷Cs and ¹³³Cs by ICP-MS/MS. Figure 1 shows a schematic diagram of the separation procedure for cesium.

Fig. 1. Schematic diagram of chemical procedure for separation of cesium from different nuclear waste samples
3. Results and discussion

3.1. Release of cesium from solid waste samples

Two types of metal samples from nuclear reactors are often required for radiochemical analysis depending on the source of radionuclides in it, i.e. induced and surface samples. For metals used in the nuclear reactor components which are close to the reactor core and exposed to the neutron flux of the reactor, radionuclides are mainly generated by neutron activation reaction of the isotopes of elements present in the metal samples, with small fraction of fission products of $^{235}$U present in the metal samples as impurity. This type of samples is called induced samples. Some fission products leaked from the damaged nuclear fuel elements and activation products corroded from other part of the reactor construction materials into the reactor water might be deposited on the surface of the components of the nuclear power plants. For samples which are located outside of the reactor core and not exposed to the neutron flux, the radionuclides are mainly deposited from the reactor water. Since all radioactive substances in this type of samples are surface contamination, they are called surface samples. Therefore, two different methods were used for releasing radiocesium from them, total dissolution and leaching to dissolve the surface deposited radionuclides. Acid dissolution using 5 M H$_2$SO$_4$ solution at 180$^\circ$C was applied to dissolve stainless steel and carbon steel samples to release all radioactive substance including radiocesium into the solution for further separation of individual radionuclides such as $^{36}$Cl, $^{55}$Fe, $^{63}$Ni. The experiments showed that all steel sample can be completely dissolved by 3-6 M H$_2$SO$_4$. Heating the solution can significantly improve the dissolution speed. It was observed that concentrated H$_2$SO$_4$ could not dissolve the steels. This might be attributed to the formation of oxides on the surface of the metal, which prevent the further reaction of H$_2$SO$_4$ with metal. For 2.0 gram of stainless steel and carbon steel samples, all materials can be completely dissolved within 2 hours.
In carbon steel and some stainless steel samples, small amount of black substance was observed after the dissolution, which float on the surface of the solution. After separation and washing with diluted acid (HNO₃), the measurement using gamma spectrometry did not show any measurable gamma emitters, so the activity (mainly ⁶⁰Co) in the residue was more than 7 orders of magnitude lower compared to the value in the original sample. Combustion at 900°C in air or oxygen atmosphere can ash this substance, indicating it should be carbon. Since it does not contain any measureable radioactivity, this insoluble black residue was removed without further treatment. *Aqua regia* has been widely used for dissolution of steels [22, 23], however, it contains huge amount of chloride, and the obtained solution cannot be used for the determination of ³⁶Cl. If only radiocesium is determined, the steel materials can be dissolved using *aqua regia*, which is also relatively faster compared to using only H₂SO₄.

Zirconium alloy is difficult to be dissolved using HNO₃, HCl, H₂SO₄ or *aqua regia*. HF has to be used, and the dissolution is very slow [24, 25]. However, for the surface contamination sample, the radioactivity originated from the deposition of various ions present in the reactor water through nuclear fuel leakage and corrosion of the construction materials. The dissolution of the materials deposited on the surface of zirconium can effectively release radiocesium and other radionuclides to the solution. In this work, *aqua regia* was selected to dissolve the radioactive contamination on the zirconium alloy surface in a heating reflux system. The experiment showed that *aqua regia* can effectively remove the radioactive substance on the surface, without dissolving the zirconium alloy matrix. By measuring the activity of residual ⁶⁰Co on the zirconium material, it was observed that more than 95% of the radioactivity could be removed by digestion using *aqua regia* at 180°C for 2 hours. However, zirconium alloy might be also used inside the reactor, which was also exposed to the neutron flux. In this case, the radioactivity in this sample will be produced by both
surface contamination and neutron activation. It was observed that the radioactivity in one zirconium sample investigated in this work (Zr-3) could not be effectively removed by dissolution using *aqua regia*. By addition of HF to the digestion system, the radioactivity was slowly removed from the sample; meanwhile, zirconium material was also dissolved which was indicated by the reduction of the mass of the remained zirconium material. This sample dissolved by a mixed acid of HNO₃ + HCl + HF was also analyzed for radiocesium in this work.

Filter papers consisting of anion and cation resins were used to pre-concentrate radioactive ions from about 10 L of water collected from a spent nuclear fuel pool. Cesium often presents as cation in water, which can be retained on cation exchange resin. High concentration of HNO₃ is often used to elute cations retained in cation exchange resin [12, 16]. To improve the release efficiency of cesium and other radionuclides, the cartridge filter paper was digested with 8 M H₂SO₄ for 30 min followed by 14 M HNO₃ at 200°C for 30 min and H₂O₂ for 30 min., sequentially. The leachate was separated and combined with the rinsing solution. The measurement of the residue and the original sample by gamma spectrometry showed that only less than 2% of ⁶⁰Co remained in the residue after leaching.

The mixed bed ion exchange column has been routinely used to purify reactor coolant water, to remove ions entered into the water from the corrosion of the construction materials and leaked from damaged nuclear fuel elements, to ensure the quality of the coolant water and reduce the radioactive level of the coolant water. Radiocesium present as Cs⁺ in water is easily retained on the cation exchange resin. Correspondingly, high concentration of HNO₃ has potential to extract Cs⁺ from the cation exchange resin [4]. In this work, an aliquot of ion exchange resin was analyzed for radiocesium. Acid leaching using 5 M HNO₃ was investigated to leach radiocesium from the ion exchange resin. By measurement of the residual ¹³⁷Cs on resin using gamma spectrometry, it
was found that radiocesium can be quantitatively extracted from the resin (> 99.9%) after leaching with 5 M HNO₃ for 30 min (Table 3.). These results indicate that leaching with 5 M HNO₃ is sufficient for extraction of cesium from the mixed ion exchange resin.

Table 3. Leaching rate of $^{137}$Cs from mixed ion exchange resin using 30 mL of 5 M HNO₃

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight/g</th>
<th>Before extraction (×10³, Bq/g)</th>
<th>After extraction (Bq/g)</th>
<th>Recovery of $^{137}$Cs/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin-1</td>
<td>0.202</td>
<td>2.40 ± 0.02</td>
<td>1.18 ± 0.03</td>
<td>99.95 ± 0.01</td>
</tr>
<tr>
<td>Resin-2</td>
<td>0.135</td>
<td>9.79 ± 0.07</td>
<td>0.35 ± 0.02</td>
<td>99.99 ± 0.01</td>
</tr>
<tr>
<td>Resin-3</td>
<td>0.180</td>
<td>151.9 ± 0.6</td>
<td>13.0 ± 0.2</td>
<td>99.99 ± 0.01</td>
</tr>
</tbody>
</table>

3.2. Chemical separation of cesium from waste samples

Since waste samples from nuclear reactors such as steel, zirconium alloy and spent ion exchange resin contain high level radionuclides (> 10⁶ Bq/g, mainly $^{60}$Co, $^{125}$Sb, $^{14}$C, $^{3}$H, $^{55}$Fe, $^{63}$Ni, etc.), all these radionuclides have to be removed before ICP-MS measurement of radiocesium to avoid the radioactive contamination of the measurement instrument. Meanwhile, the matrix elements also have to be removed to improve the measurement sensitivity and eliminate the polyatomic ion interferences. Based on the specific adsorption of Cs⁺ on ammonium phosphomolybdate (AMP) by replacing NH₄⁺ in the AMP and better separation feature of chromatography, AMP-PAN column chromatography was selected in this work to separate Cs from the matrix elements and most of the radionuclides in the sample solution. The preliminary experiments showed that $^{60}$Co, $^{125}$Sb, $^{55}$Fe, $^{63}$Ni, $^{3}$H and $^{14}$C were not retained on the AMP-PAN resin, and therefore can be effectively removed from cesium. The measurement results indicated that $^{60}$Co in the sample
solution was removed by AMP-PAN column chromatography by a factor of more than $3 \times 10^4$, resulting in less than 0.2 Bq in the eluate of Cs from the column. To improve the stability of AMP-PAN resin and remain high retention for cesium, the acidity of the sample solution was reduced to less than 1.0 M by dilution with H$_2$O. The adsorption experiments of Cs on AMP-PAN resin from different solution showed that the presence of HF, H$_2$SO$_4$, HNO$_3$ and HCl of less than 1.0 M does not significantly influence the retention efficiency of cesium on AMP-PAN resin. It has been reported that AMP is quite stable in less than 0.1 M of HNO$_3$, HCl, H$_2$SO$_4$ and HF, and the solubility of AMP increases with the concentration of the acid. In 1 M HF, the solubility of AMP in 24 hours contact time increases to 43 g/L from only less than 3.6 g/L in 0.1 M HF solution and 0.36 g/L in 0.1 M HNO$_3$ solution [26]. It is therefore important to reduce the concentration of the acid to less than 1.0 M for HNO$_3$ and HCL, and less than 0.1 M for HF. Meanwhile, it is also important to reduce the contact time of sample solution with AMP-PAN resin. Since the adsorption of Cs$^+$ on AMP is a rapid process, and ion exchange equilibrium can be quickly reached in less than 30 min, the flow rate of sample loading on AMP-PAN column can be increased to 2-5 mL/min. It has been reported that at a flow rate of 35 mL/min for 5 mL column, the recovery of Cs was still as high as 93% [27]. In this work, a 1 mL AMP-PAN column was used and flow rate of loading solution was 2 mL/min. It was observed that the color of AMP-PAN column was changed from yellow to blue when loading the solution of stainless steel, indicating that AMP was reduced to phosphorus molybdenum blue by Fe$^{2+}$. In order to solve this problem, 1.0 mL of 30% H$_2$O$_2$ was added to sample solution prior to the AMP-PAN separation process, to oxidize Fe$^{2+}$ to Fe$^{3+}$ and to form an oxidative media, which was proved to be efficient and critical for successful separation of cesium by AMP-PAN column.
Cesium retained on AMP-PAN resin was eluted with 1.5 M NH₃ by directly dissolving AMP from the column. Meanwhile, a high concentration of MoO₄²⁻ present in the eluate, which interferes with the ICP-MS measurement of ¹³⁵Cs and ¹³⁷Cs by polyatomic ions of Mo isotope with Ar (⁹⁵Mo⁴⁰Ar⁺, ⁹⁷Mo⁴⁰Ar⁺). An anion exchange chromatography (AG MP-1M resin) was applied to remove MoO₄²⁻, while radiocesium as cation passed through the anion exchange column and remained in the effluent. The measurement of Mo in the solution before and after column separation showed that a decontamination factor of $1 \times 10^6$ was achieved by this process.

The major interferences for the measurement of ¹³⁵Cs and ¹³⁷Cs are isobars, i.e. stable ¹³⁵Ba and ¹³⁷Ba. Based on the different selectivity (affinity) of Cs and Ba, cation exchange chromatography was used for elimination of barium from radiocesium. Based on our previously established method [28], cesium was purified using a 10 mL of AG 50W-X8 column with a decontamination factor of more than $1.0 \times 10^5$. Meanwhile, an overall decontamination factor for ⁶⁰Co was further improved to be more than $7.0 \times 10^6$. The measurement of the final eluate using LSC indicates that the overall remaining activity of the final solution was less than 10 Bq, this also implies that the decontamination factors for other dominant radionuclides including ¹²⁵Sb, ⁵⁵Fe, ⁶³Ni, ³H and ¹⁴C were more than $1 \times 10^5$ for the steel samples. The efficient removal of these dominant radionuclides in waste samples enable the measurement of radiocesium by mass spectrometry in ordinary chemical laboratory without contaminating the instrument and radiation risk to operator.

The decontamination factors for Ba, Mo, Sb and Sn in the whole procedure (Figure 1.) were measured to be $6.0 \times 10^6$, $4.2 \times 10^5$, $3.2 \times 10^5$ and $2.1 \times 10^5$, respectively, which is comparable with the published data [10, 12]. This efficiently eliminated interferences from these elements on the measurement of ¹³⁵Cs and ¹³⁷Cs by ICP-MS/MS.
3.3. Measurement of $^{135}\text{Cs}$ and $^{137}\text{Cs}$ by ICP-MS/MS

According to the previous study [11, 12], the main interferences for the measurement of $^{135}\text{Cs}$ and $^{137}\text{Cs}$ by ICP-MS were isobaric interference such as $^{135}\text{Ba}^+$ and $^{137}\text{Ba}^+$, and polyatomic interference such as $^{95}\text{Mo}^{40}\text{Ar}^+$, $^{97}\text{Mo}^{40}\text{Ar}^+$, $^{119}\text{Sn}^{16}\text{O}^+$ and $^{121}\text{Sb}^{16}\text{O}^+$. Although most of Ba (with a decontamination factor of $6.0 \times 10^6$) in the samples has been removed by the chemical separation, it is still not sufficient for the measurement of low-level $^{135}\text{Cs}$ because of extremely high ratios of $^{135}\text{Ba}/^{135}\text{Cs}$ and $^{137}\text{Ba}/^{137}\text{Cs}$ in most of samples. It has been widely reported that Ba can be well eliminated by reaction with N$_2$O in a collision-reaction cell in ICP-MS [29, 30] by forming BaO$^+$ but not for Cs$^+$. It was observed that the signal intensity of Ba$^+$ was significantly suppressed with the increased flow rates of N$_2$O in the reaction cell, while the Cs$^+$ signal intensity only slightly reduced with the flow rate of N$_2$O. At a N$_2$O flow rate of 0.70 mL/min, $^{135}\text{Ba}^+$ signal intensity was significantly suppressed by a factor of $10^5$, whilst the sensitivity of Cs decreased only by a factor of 5-10, causing the improved $^{133}\text{Cs}/^{135}\text{Ba}$ signal intensity ratios of $2 \times 10^4$. In combination with the chemical separation, an overall suppression of Ba$^+$ signal of $10^{11}$ was achieved, thus the interference of Ba on the $^{135}\text{Cs}$ and $^{137}\text{Cs}$ measurement was sufficiently eliminated (Figure 2.). In the final purified cesium solution, the concentration of Ba was lower than 0.2 ng/mL, which is corresponding to a contribution of less than 0.2 cps on the m/z of 135 and 137 under the optimal measurement condition, similar as the procedure blank of 0.3 cps, therefore can be ignored. By employing two sequential quadrupole mass filter, the abundance sensitivity was improved from $10^{-7}$ to $10^{-11}$ practically. Before the chemical separation, only 1.0 µg of stable $^{133}\text{Cs}$ was spiked to the sample for chemical yield monitoring, making the $^{135}\text{Cs}/^{133}\text{Cs}$ ratios of higher than $10^9$, therefore the interference of $^{133}\text{Cs}$ peak tailing to the $^{135}\text{Cs}$ and $^{137}\text{Cs}$ was eliminated by this approach. However, it is important that not too much stable cesium (e.g. >0.1 mg) should be added.
before chemical separation to avoid a low $^{135}\text{Cs}/^{133}\text{Cs}$ ratio in the final separated samples, which might make the peak tailing of $^{133}\text{Cs}$ too high compared to the $^{135}\text{Cs}^+$ signal at m/z =135, and consequently cause failure for accurate determination of $^{135}\text{Cs}$.

3.4. Validation of the analytical method and analytical quality control

Due to the lack of certified reference material for $^{135}\text{Cs}$ concentration or $^{135}\text{Cs}/^{137}\text{Cs}$ ratio in the similar sample matrices as the samples analyzed in this work, a soil reference material IAEA-375 (soil collected from Chernobyl accident contaminated area in Russia), in which the $^{137}\text{Cs}$ concentration and $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratio have been reported in literature, was analyzed to evaluate the developed method. The measured $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratio (0.30 ± 0.02) (n=3, decay corrected to April 1986) in IAEA-375 agrees well with the reported value (0.27-0.32) (decay corrected to April 1986) in the literature [13, 31, 32], demonstrating that the developed method is reliable and accurate for the determination of $^{135}\text{Cs}$ and $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratio.

The major isotopes which might cause isobaric and polyatomic ion interferences for ICP-MS measurement of $^{135}\text{Cs}$ and $^{137}\text{Cs}$ were measured in the final sample solution to monitor the possible

Fig. 2. Mass spectra of $^{135}\text{Cs}$ and $^{137}\text{Cs}$ measured by ICP-MS/MS in separated waste samples
interferences of their corresponding ions. These include $^{138}\text{Ba}$ (abundance of 71.7%) for monitoring the level of $^{135}\text{Ba}$ and $^{137}\text{Ba}$ isobars, $^{98}\text{Mo}$ (abundance of 24.1%) for $^{95}\text{Mo}^{40}\text{Ar}^+$, $^{97}\text{Mo}^{40}\text{Ar}^+$, $^{120}\text{Sn}$ (abundance of 32.6%) for $^{119}\text{Sn}^{16}\text{O}^+$, and $^{123}\text{Sb}$ (abundance of 42.6%) for $^{121}\text{Sb}^{16}\text{O}^+$. Since Mo, Sn and Sb might be the major component of some sample (e.g. stainless steel) and Mo presented in AMP might be not well removed, this step was used to confirm the sufficient elimination of all these interferences and therefore ensure the analytical quality.

3.5. Performance of the developed analytical method

The reported separation procedure of cesium from waste samples is simple and fast, and can be completed in one day for one batch of 8 samples. In combination with ICP-MS/MS measurement, it can be used for the determination of $^{135}\text{Cs}$ concentration and $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratio in various waste samples from nuclear facilities. The overall recovery of cesium was more than 85% (typically more than 95% and 90% for sample pretreatment and chemical separation preparation, respectively). The concentrations of Ba, Mo, Sn and Sb in the final separated samples were normally lower than 0.1, 1, 0.4, and 0.4 ng/mL, respectively, indicating successful removal of interfering elements by the chemical separation procedure (AMP-PAN and ion exchange resin AG MP-1M and AG 50W-X8). The count rates at m/z 135 and 137 in the procedure blanks were measured to be 0.3 ± 0.2 cps, and the sensitivity of $3.39\times10^5$ cps for 1 ng/mL of stable Cs was achieved in the ICP-MS/MS measurement using Apex Q for sample introduction. A detection limit of $6.2\times10^{-15}$ g (0.26 µBq) for $^{135}\text{Cs}$ can be estimated based on a procedure blank of 0.3 ± 0.2 cps, 3.0 mL of the final solution, and 85% recovery of cesium. For 0.2 g of metal sample or exchange resin, the detection limit will be $3.1\times10^{-14}$ g/g (1.3 µBq/g). For leachate or water of 100 ml, the detection limit will be $6.2\times10^{-14}$ g/L (2.6 µBq/L). This is more than 3 orders of magnitude lower
than the reported level by NAA and ICP-MS [3]. The improved detection limit enable the successful determination of ultra-low level $^{135}\text{Cs}$ in various types of waste samples from nuclear facilities which was slightly contaminated by the leakage of nuclear fuel elements or exposed to neutron irradiation.

3.6. Analysis of different waste samples for $^{135}\text{Cs}$ concentrations and $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios

3.6.1. Radiocesium in steel and zirconium alloy

Stainless steel, carbon steel and zirconium alloy samples collected from decommissioning of nuclear power plants were analyzed for $^{135}\text{Cs}$ concentrations and $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios (Table 4.). The $^{135}\text{Cs}$ levels in zirconium alloy as surface contaminated sample were presented as Bq/m$^2$ surface area, to be $0.293 \pm 0.014$ Bq/m$^2$ in Zr-1, $0.127 \pm 0.010$ Bq/m$^2$ in Zr-2 and $1.97 \pm 0.13$ Bq/m$^2$ in Zr-3, varying by a factor of 15. The different $^{135}\text{Cs}$ levels in these samples should be attributed to different contamination level of the components where the zirconium materials were sampled. A similar $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios of (0.238-0.244) were measured in Zr-1 and Zr-2 samples which were sampled from the same reactor and have relative low $^{135}\text{Cs}$ level. While, a relatively higher $^{135}\text{Cs}/^{137}\text{Cs}$ ratio of 0.311 was measured in the sample Zr-3 which was sampled from another reactor (Reactor 2), and a relatively higher $^{135}\text{Cs}$ level in this sample was observed. The difference of the $^{135}\text{Cs}$ levels and $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios in these samples should be attributed to their different sources of $^{135}\text{Cs}$ in these samples. The similar $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios (0.238-244) in Zr-1 and Zr-2 from the same nuclear reactor indicates that $^{135}\text{Cs}$ and $^{137}\text{Cs}$ in these two samples originated from the same leaked nuclear fuel or fuels experienced the same neutron irradiation and burnup level. The slightly different $^{135}\text{Cs}$ level ($0.127-0.293$ Bq/m$^2$) on the surface of these two samples might be attributed to the different deposition of the leaked radionuclides on
the two sites where these samples were sampled due to the different geometry and location of these two sites in the reactor. The significantly higher $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratio of 0.311 in Zr-3 compared to other two zirconium samples indicates that its originated source of the leaked nuclear fuel has been exposed to a relatively lower neutron flux. Based on the production of $^{135}\text{Cs}$ and $^{137}\text{Cs}$ by neutron induced fission of $^{235}\text{U}$ or $^{239}\text{Pu}$ in the reactor and the extremely high neutron reaction cross section of $^{135}\text{Xe}$, the decay precursor of $^{135}\text{Cs}$, the $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios are negatively correlated with the neutron flux [16]. However, it might also be resulted from the different cooling time after the shutdown of the nuclear reactor.

The level of $^{135}\text{Cs}$ in most of steel samples (as construction materials) including carbon steel sample (steel-2) was below the detection limit of the analytical method, which is more than 2 orders of magnitude lower than those in the zirconium samples. A high atomic ratio of $^{135}\text{Cs}/^{137}\text{Cs}$ up to $0.761 \pm 0.201$ and low concentrations of $(1.11 \pm 0.33) \times 10^{-4}$ Bq/g for $^{135}\text{Cs}$ and $11.1 \pm 3.3$ Bq/g for $^{137}\text{Cs}$ were measured in one stainless steel (steel-1) sample (Table 4). The radiocesium in the stainless steel might have two sources, surface contamination from reactor coolant or fission of uranium ($^{235}\text{U}$) impurity in the steel. A few orders of magnitude lower $^{135}\text{Cs}$ and $^{137}\text{Cs}$ level in steel compared to that in zirconium sample indicate the surface contamination from the leaked fuel is not significant. Since the steel used as construction materials is located outside of the reactor core with a relatively low neutron flux, and the uranium impurity in steel is normally very low (e.g. <40 ng/g) [33], the levels of $^{135}\text{Cs}$ and $^{137}\text{Cs}$ produced in the steel samples were very low, and the $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratio was quite high.

3.6.2. Radiocesium in filter paper

Three leachate and one filter paper samples were analyzed for $^{135}\text{Cs}$ and $^{137}\text{Cs}$. The measured $^{135}\text{Cs}$ concentrations in three leachate samples vary from $(8.50 \pm 1.41) \times 10^{-8}$ Bq/mL to $(1.18 \pm 0.12) \times 10^{-7}$
The total content of $^{135}$Cs in filter paper is $(1.46 \pm 0.16) \times 10^{-3}$ Bq. Each filter sample consists of three components, microporous filter paper, cation exchange and anion exchange filter paper, and these filter papers were used to pre-concentrate radiocesium and other elements from reactor coolant water or spent fuel pool water. The results measured in the filter paper and filter paper leachate reflect the level of radiocesium in these water samples. Radiocesium in reactor coolant water has three sources: (1) release of radioactive gases (e.g. $^{135}$Xe) from fuel elements, which is decayed to $^{135}$Cs and trapped in the reactor coolant water; (2) release of fission products into reactor coolant due to fuel leakage; (3) fission products of uranium which was leaked from fuel elements to the coolant or as an impurity in coolant [34]. The different concentrations of radiocesium in reactor coolant were attributed to different quantities and/or the severity of fuel leakage, as well as the cleaning process used. The monitoring of $^{135}$Cs concentrations and $^{135}$Cs/$^{137}$Cs in reactor coolant might be used to identify leakages of fuel elements and provide information to locate the position of fuel failure in a single fuel element leakage occurred. The significantly different level of $^{135}$Cs in these samples reflect the different sources of radiocesium in reactor coolant and fuel pool water. The high level of $^{135}$Cs in the filter paper leachate-3 and filter paper might reflect the significant contribution of fuel elements leakage in this reactor and the spent fuel pool.

The measured $^{135}$Cs/$^{137}$Cs atomic ratios in three filter paper leachate samples from reactors R3-R5 vary from $0.126 \pm 0.021$ to $0.295 \pm 0.029$. The $^{135}$Cs/$^{137}$Cs ratios in samples from R3 and R5 (0.279-0.295) were similar to that in Chernobyl accident derived samples (0.27-0.32, see the values in IAEA-375, IAEA-330), while a lower atomic ratio of $^{135}$Cs/$^{137}$Cs (0.126) was observed in filter paper leachate-2 from R4, indicating that radiocesium in this sample probably originated from the core parts of reactors with a high neutron flux.
The $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratio in the filter paper of pool water was $0.735 \pm 0.081$, and a relatively high $^{135}\text{Cs}$ level (1.46 mBq) compared to the filter paper leachate (total 100 ml leachate was used) was observed in this sample. This filter paper was used to pre-concentrate radionuclides from a nuclear fuel pool water. Sources of radiocesium in this filter paper should originated from the leakage of spent fuel or dissolution of the deposited fission products on the outer surface of the spent fuel assembly. The high $^{135}\text{Cs}$ level might indicate a relatively significant leakage of fuel in the cooling pool. The high $^{135}\text{Cs}/^{137}\text{Cs}$ ratio (0.735) might be attributed to that the spent fuel stored in the fuel pool had been unloaded from the reactor for a relatively long time (e.g. > 35 years).

### 3.6.3. Radiocesium in spent ion exchange resin

The concentrations of $^{135}\text{Cs}$ in three ion exchange resin samples were 14.1-892 mBq/g. These ion exchange resins have been used to purify coolant water of a pressurized water reactor. The significantly different $^{135}\text{Cs}$ concentrations in these samples might be attributed to the different volume of coolant water that has been purified by these resins and original concentration of $^{135}\text{Cs}$ in the coolant (i.e. different level of leakage of the spent fuel in the reactors). The $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios in three spent ion exchange resin samples are quite similar and range within 0.415-0.447, with an average of $0.436 \pm 0.030$. This is similar to the reported value in the coolant of the same type of reactor (VVER-440) [35], but higher than the ratio in the filter paper leachate samples from boiling water reactor. This also indicate that the leaked fuel elements had been exposed to a relatively lower neutron flux in this reaction.

Based on these results, zirconium alloy, filter and spent ion exchange resin samples are featured with a high concentration of $^{135}\text{Cs}$, which needs to be considered during repository in view of long-term environmental and ecological impact; whilst the stainless steel and carbon steel only contain
activation products, which are normally relatively short lived radionuclides (e.g. $^{60}$Co, $^{125}$Sb, $^{55}$Fe, $^{63}$Ni, $^3$H and $^{14}$C), and have less long-term radiation impact.

Table 4. Radiocesium concentration and $^{135}$Cs/$^{137}$Cs atomic ratio in waste samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{135}$Cs/$^{137}$Cs</th>
<th>$^{135}$Cs activity</th>
<th>$^{137}$Cs activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-1$^a$</td>
<td>0.238 ± 0.012</td>
<td>(0.293 ± 0.014) Bq/m$^2$</td>
<td>(9.38 ± 0.23) $\times 10^4$ Bq/m$^2$</td>
</tr>
<tr>
<td>Zr-2$^a$</td>
<td>0.244 ± 0.019</td>
<td>(0.127 ± 0.010) Bq/m$^2$</td>
<td>(3.96 ± 0.19) $\times 10^4$ Bq/m$^2$</td>
</tr>
<tr>
<td>Zr-3$^a$</td>
<td>0.311 ± 0.021</td>
<td>(1.97 ± 0.13) Bq/m$^2$</td>
<td>(4.84 ± 0.23) $\times 10^5$ Bq/m$^2$</td>
</tr>
<tr>
<td>Steel-1$^a$</td>
<td>0.761 ± 0.201</td>
<td>(1.11 ± 0.33) $\times 10^{-4}$ Bq/g</td>
<td>(11.1 ± 3.3) Bq/g</td>
</tr>
<tr>
<td>Filter paper leachate-1$^b$</td>
<td>0.279 ± 0.046</td>
<td>(8.50 ± 1.41) $\times 10^{-8}$ Bq/mL</td>
<td>(2.32 ± 0.35) $\times 10^2$ Bq/mL</td>
</tr>
<tr>
<td>Filter paper leachate-2$^b$</td>
<td>0.126 ± 0.021</td>
<td>(7.18 ± 1.21) $\times 10^{-7}$ Bq/mL</td>
<td>(4.35 ± 0.28) $\times 10^4$ Bq/mL</td>
</tr>
<tr>
<td>Filter paper leachate-3$^b$</td>
<td>0.295 ± 0.029</td>
<td>Bq/mL</td>
<td>(3.03 ± 0.22) Bq/mL</td>
</tr>
<tr>
<td>Filter paper$^b$</td>
<td>0.735 ± 0.081</td>
<td>(1.18 ± 0.12) $\times 10^{-5}$ Bq/mL</td>
<td>152 ± 11 Bq</td>
</tr>
<tr>
<td>Resin-1$^b$</td>
<td>0.446 ± 0.032</td>
<td>(1.46 ± 0.16) $\times 10^{-3}$ Bq</td>
<td>(2.40 ± 0.02) $\times 10^3$ Bq/g</td>
</tr>
<tr>
<td>Resin-2$^b$</td>
<td>0.415 ± 0.022</td>
<td>(1.41 ± 0.10) $\times 10^{-2}$ Bq/g</td>
<td>(9.79 ± 0.07) $\times 10^3$ Bq/g</td>
</tr>
<tr>
<td>Resin-3$^b$</td>
<td>0.447 ± 0.035</td>
<td>(5.33 ± 0.29) $\times 10^{-2}$ Bq/g</td>
<td>(1.52 ± 0.01) $\times 10^5$ Bq/g</td>
</tr>
</tbody>
</table>

$^a$ decay corrected to the shutdown date of the reactors; $^b$ decay corrected to Sep 2019.

$^{135}$Xe as precursor of $^{135}$Cs in the fission products of $^{235}$U and $^{239}$Pu at m=135 has an extremely high thermal neutron-capture cross section up to $2.6 \times 10^6$ barns, the $^{135}$Cs/$^{137}$Cs ratios in the nuclear fuel vary significantly with neutron flux and irradiation time (burnup of fuel). The $^{135}$Cs/$^{137}$Cs atomic ratio from nuclear detonation is about 1.0 at the time of explosion due to very short neutron irradiation time during explosion and the similar cumulative fission yields of $^{135}$Cs (6.54%) and
$^{137}\text{Cs}$ (6.21%), but this ratio is decreased to 0.13-0.45 in nuclear reactor coolants and 0.6-0.8 in construction materials of reactors as measured in this work. The $^{135}\text{Cs}/^{137}\text{Cs}$ ratio in the reactor material can be used to estimate the neutron flux where the materials has been exposed. Therefore, besides the radiological characterization of nuclear waste, the method presented in this work can also be used to identify the source of radiocesium and estimate the exposed neutron flux of the leaked spent fuel. By measuring $^{135}\text{Cs}/^{137}\text{Cs}$ ratio in primary circuit coolant of reactor in combination with the operating parameters of the reactor, the location of leaking fuel element might be identified. However, this might be not practically applicable if several damaged nuclear fuel elements occurred in a reactor, the measured ratio of $^{135}\text{Cs}/^{137}\text{Cs}$ will be an integrated value of all leaked radiocesium from the damaged fuel elements. The $^{135}\text{Cs}/^{137}\text{Cs}$ ratio was also correlated with the operation history of reactor (thermal neutron flux and shutdown of reactor), the measured $^{135}\text{Cs}/^{137}\text{Cs}$ can be used to calculate the thermal neutron flux in the reactor using formula [2, 35]. For example, based on the obtained $^{135}\text{Cs}/^{137}\text{Cs}$ atomic ratios on the surface of zirconium samples and the simplified calculation algorithm as follows, the thermal neutron flux in the two reactors where the leaked fuel located can be calculated to be $4.3 \times 10^{13}$ cm$^{-2}$ s$^{-1}$ and $2.7 \times 10^{13}$ cm$^{-2}$ s$^{-1}$, respectively.

$$\frac{^{135}\text{Cs}}{^{137}\text{Cs}} \times \text{CFY}(137) = \frac{\lambda(135\text{Xe})}{\lambda(135\text{Xe}) + \sigma(135\text{Xe}) \times \Phi_{th}} \times [\text{CFY}(135)-\text{IFY}^{135}\text{Cs}-\text{IFY}^{135}\text{Ba}]+\text{IFY}^{135}\text{Cs}$$

Where:

- CFY(137) is cumulative fission yield for mass 137 (6.21%);
- CFY(135) is cumulative fission yield for mass 135 (6.54%);
- IFY$^{135}\text{Cs}$ is the independent fission yield for $^{135}\text{Cs}$ (0.55%);
- IFY$^{135}\text{Ba}$ is the independent fission yield for $^{135}\text{Ba}$ (0.004%);
- $\lambda(135\text{Xe})$ is the decay constant of $^{135}\text{Xe}$ ($2.12 \times 10^{-5}$ s$^{-1}$);
- $\sigma(135\text{Xe})$ is the thermal neutron capture cross section of $^{135}\text{Xe}$ ($2.6 \times 10^{6}$ b);
Фth is the thermal neutron flux in the reactor.

4. Conclusion

An analytical method was developed for determination of $^{135}$Cs concentration and $^{135}$Cs/$^{137}$Cs atomic ratio in different type of radioactive waste samples (such as stainless steel, zirconium alloy, leachate of filter, filter, and spent ion exchange resin) by coupling AMP-PAN, AG MP-1M and AG 50W-X8 chromatographic separation with ICP-MS/MS measurement. High radioactivity of $^{60}$Co was efficiently removed by the chemical separation procedure with decontamination factors of $7 \times 10^6$. The interfering elements such as Ba, Mo, Sn and Sb for the ICP-MS measurement of $^{135}$Cs and $^{137}$Cs were highly removed using the chemical separation. Meanwhile, by using N$_2$O as reaction gas and sequential quadrupole mass filter, the isobaric interference of $^{135}$Ba and $^{137}$Ba and the peak tailing of stable $^{133}$Cs were efficiently suppressed, and a detection limit of $3.1 \times 10^{-14}$ g/g for $^{135}$Cs was achieved for 0.2 g stainless steel sample or spent resin. The developed method was simple and rapid, which can be used for the inventory evaluation of $^{135}$Cs in a large diversity of waste samples from nuclear decommissioning. With the developed method, $^{135}$Cs concentration and $^{135}$Cs/$^{137}$Cs atomic ratio were first successfully determined in zirconium alloy, stainless steel, carbon steel, filter and spent ion exchange resin from reactors in operation and under decommissioning, which is critically important for waste characterization and final repository. The $^{135}$Cs/$^{137}$Cs atomic ratio has been demonstrated to be useful in identifying the source of $^{135}$Cs and the leaked fuel elements, as well as in estimating the neutron flux of leaked fuel experienced in the reactor.

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Notes: The authors declare no competing financial interest.
Reference


https://doi.org/10.1080/00223131.2014.891954

https://doi.org/10.1016/j.talanta.2017.06.033

DOI: 10.1016/j.aca.2015.12.041


https://doi.org/10.1016/j.talanta.2016.06.008


