

## RiO5 METHOD (26)

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**$^{135}\text{Cs}$  and  $^{135}\text{Cs}/^{137}\text{Cs}$  atom ratio**— Ammonium Molybdophosphate (AMP) — soil, litter, lichen, particles

Determination of  $^{135}\text{Cs}$  and  $^{135}\text{Cs}/^{137}\text{Cs}$  atom ratio in environmental samples by combining AMP adsorption and simple-column chromatographic separation to triple-quadrupole inductively coupled plasma-mass spectrometry

### Disclaimer

It is the responsibility of each analyst to follow established practices when handling and examining the samples referenced in this Rio5 Cookbook. Although the methods may have been tested by each laboratory identified as the source, each user must perform a validation procedure to ensure the validity of their results. Woods Hole Oceanographic Institution, its officers, directors and employees are not responsible for any of the data or the results that may be achieved from using the information in the Rio5 Cookbook and disclaim all liability for the same.



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## 1 SCOPE

The challenge of determination of  $^{135}\text{Cs}$  and  $^{137}\text{Cs}$  isotopes using ICP-MS, are the isobaric interferences from Ba isotopes. Because of the high Ba concentration in the environment (for example,  $550 \text{ mg kg}^{-1}$  in soil (Yamasaki et al., 2001)),  $^{135}\text{Ba}$  (abundance = 6.59%) and  $^{137}\text{Ba}$  (abundance = 11.2%) could cause an extremely high background signal at  $m/z$  135 and 137, deteriorating the limit of detection for  $^{135}\text{Cs}$  and  $^{137}\text{Cs}$ . Furthermore, Mo in the environmental samples (ca.  $2 \text{ mg kg}^{-1}$  in soil) could result in polyatomic interferences,  $^{95}\text{Mo}^{40}\text{Ar}^+$  and  $^{97}\text{Mo}^{40}\text{Ar}^+$ . Minor polyatomic interferences are  $^{119}\text{Sn}^{16}\text{O}^+$  and  $^{121}\text{Sb}^{16}\text{O}^+$  (ca.  $3 \text{ mg kg}^{-1}$  Sn and  $2 \text{ mg kg}^{-1}$  Sb in soil) on  $^{135}\text{Cs}$  and  $^{137}\text{Cs}$  measurements, respectively. In addition, the high concentration of stable Cs ( $^{133}\text{Cs}$ ) in environmental samples will also interfere with  $^{135}\text{Cs}$  analysis, because of the peak tailing effect. Therefore, it is key to eliminate the major interferences (Ba and Mo) and minor interferences (Sb and Sn).

## 2 EQUIPMENT and CHEMICAL REAGENTS

### 2.1 Equipment and consumables

- A triple-quadrupole ICP-MS/MS device (Agilent, Model 8800).
- A MicroMist micro-uptake glass concentric nebulizer.
- A sector-field ICP-MS (SF-ICP-MS, Element 2, Thermo Fisher Scientific).
- Nitrous oxide gas (as 20%  $\text{N}_2\text{O}$  mixed with 80% He) (Sumitomo Seika Chemicals Co., Ltd., Tokyo, Japan).
- Helium and argon gases (Taiyo Nippon Sanso Corp., Tokyo, Japan).
- Anion-exchange resin (AG MP 1M, 100–200 mesh,  $\text{Cl}^-$  form) and cation exchange resin (AG 50WX8, 100–200 mesh,  $\text{H}^+$  form) (Bio-Rad).
- a  $0.45\text{-}\mu\text{m}$  syringe filter (Sartorius Stedim Biotech, Goettingen, Germany)

### 2.2 Tracers

- Single-element standard solutions ( $1000 \text{ mg L}^{-1}$ ) of Ba, Cs, Sb, Mo, and Sn (Kanto Chemical Co., Inc., Tokyo, Japan).
- A standard solution of Cs ( $0.2 \text{ ng mL}^{-1}$ ) and Ba ( $1 \text{ ng mL}^{-1}$ ).
- Soil reference material (IAEA-375) (International Atomic Energy Agency, IAEA).

### 2.3 Chemical reagents

- Analytical reagent grade: nitric acid ( $\text{HNO}_3$ ), hydrochloric acid (HCl), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).
- Ultrapure grade  $\text{HNO}_3$  (Tama Chemicals, Tokyo, Japan)

- Milli-Q purified water (18.2 M $\Omega$  cm).
- Ammonium molybdophosphate (AMP) (Kishida Chemical Co., Ltd., Osaka, Japan).

## 2.4 Solutions

- 1.5M NH<sub>4</sub>OH,
- 0.15 M NH<sub>4</sub>OH
- 4% HNO<sub>3</sub>
- 1.5 M HCl

## 3 PROCEDURE

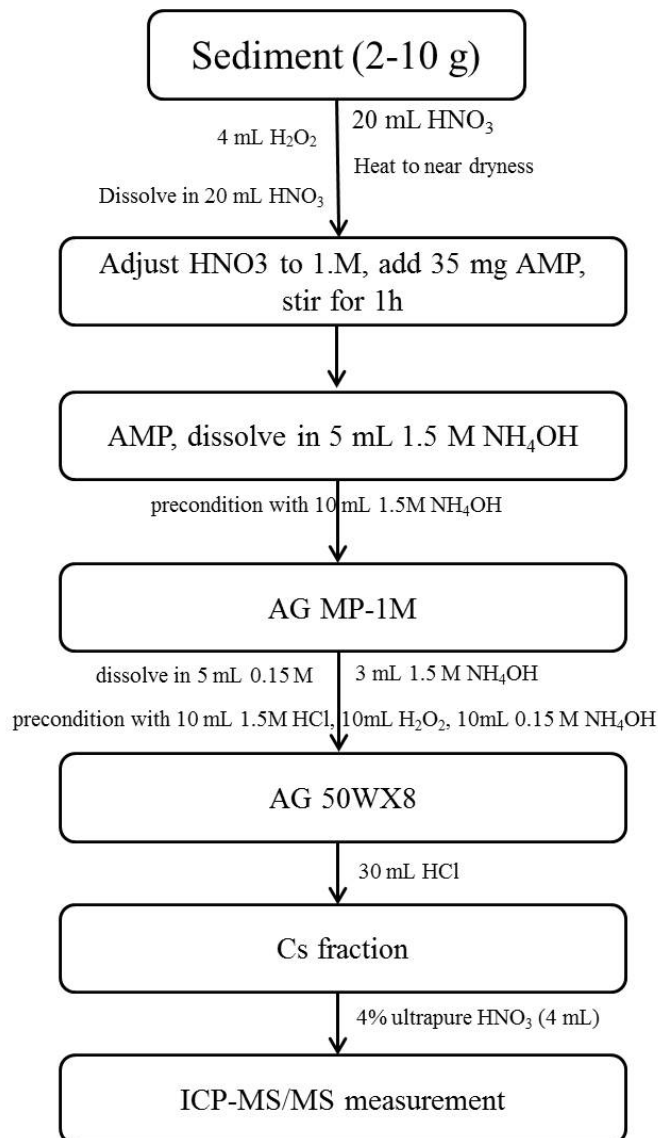
1. Dry sample at 80 °C overnight and ash at 450 °C for 2 h.
2. Weigh samples (2-10 g), add 20 mL HNO<sub>3</sub>, heat at 160 °C for over 2 h, add 4 mL H<sub>2</sub>O<sub>2</sub>.
3. Heat to near dryness, dissolve the residual in 20 mL HNO<sub>3</sub>, filter.
4. Take out 0.1 mL the filtered sample solution (analysis of stable Cs, yield monitor), adjust the rest to 1.6 M HNO<sub>3</sub> by adding Milli-Q water.
5. Add 35 mg AMP, stir for 1h and filter 0.45  $\mu$ m, and dissolve in 5 mL 1.5 M NH<sub>4</sub>OH.
6. Load AG MP-1M column (precondition with 10 mL 1.5M NH<sub>4</sub>OH), and then wash the column using 3 mL 1.5 M NH<sub>4</sub>OH, evaporate to dryness, and dissolve in 5 mL 0.15 M NH<sub>4</sub>OH.
7. Load the AG 50W-X8 (precondition with 10 mL 1.5M HCl, 10mL H<sub>2</sub>O<sub>2</sub>, 10mL 0.15 M NH<sub>4</sub>OH). And then wash the column using 10 mL 0.15 M NH<sub>4</sub>OH, 10 mL water.
8. Elute Cs from the column with 30 mL HCl, evaporate to dryness, dissolve in 4% ultrapure HNO<sub>3</sub> (4 mL) and send to ICP-MS/MS analysis.

## 4 REFERENCES

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- Yang, G.S., Tazoe, H., Yamada, M., 2016. Rapid determination of <sup>135</sup>Cs and precise <sup>135</sup>Cs/<sup>137</sup>Cs atomic ratio in environmental samples by single-column chromatography coupled to triple-quadrupole

inductively coupled plasma-mass spectrometry. Anal. Chim. Acta 908, 177-184.

## 5 FLOW CHART



## 6 IMAGES

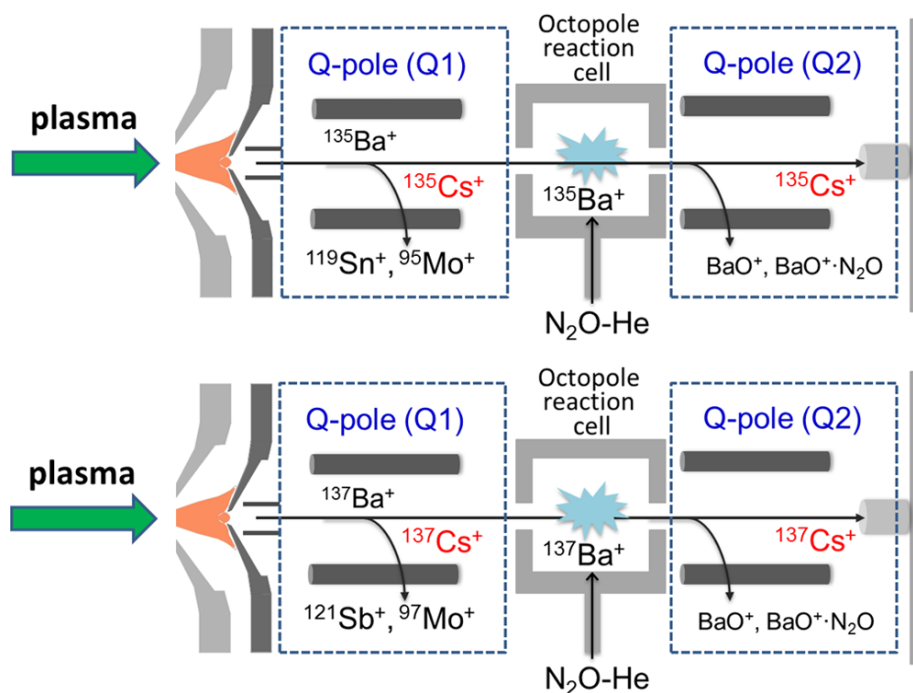


Figure 1. Schematic of ICP-MS/MS and ion-molecule reactions for  $^{135}\text{Cs}$  and  $^{137}\text{Cs}$  measurements. Target ions are separated from matrix ions by Q1 set at  $m/z$  135 and 137, respectively, and they enter the collision/reaction cell, where they react with  $\text{N}_2\text{O}$  to separate Cs/Ba, eliminate  $\text{MoAr}^+$  polyatomic interference, and suppress the formation of  $\text{SbO}^+$  and  $\text{SnO}^+$ . Finally, Q2 is set to measure the desired  $^{135}\text{Cs}$  and  $^{137}\text{Cs}$  (Zheng et al., 2014).

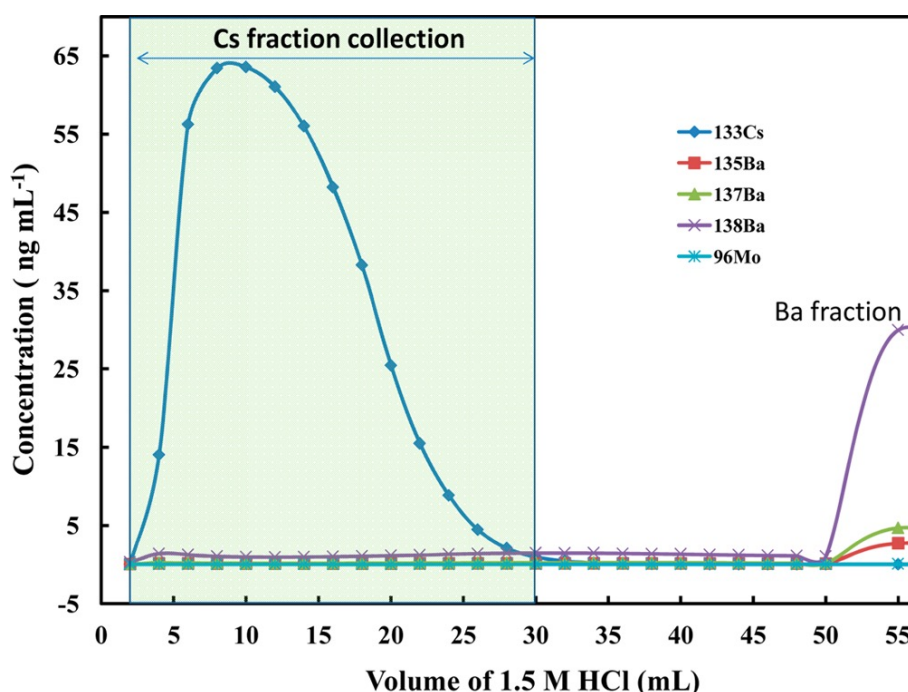


Figure 2. Elution profiles of Cs and Ba in IAEA-375 soil reference material obtained by cation-exchange chromatographic separation (AG 50WX8 resin) (Zheng et al., 2014).