



Method for ultra-trace cesium isotope ratio measurements from environmental samples using thermal ionization mass spectrometry



Mathew S. Snow^{a,b,*}, Darin C. Snyder^b, Nick R. Mann^b, Byron M. White^b

^a Department of Chemistry, Washington State University, PO Box 644630, Pullman, WA 99164-4630, USA

^b Idaho National Laboratory, PO Box 1625, Idaho Falls, ID 83415-2805, USA

ARTICLE INFO

Article history:

Received 29 January 2015

Received in revised form 18 March 2015

Accepted 23 March 2015

Available online 30 March 2015

Keywords:

Cesium-135

Cesium-137

Ammonium molybdophosphate

ABSTRACT

¹³⁵Cs/¹³⁷Cs isotope ratios can provide the age, origin and history of environmental Cs contamination. Relatively high precision ¹³⁵Cs/¹³⁷Cs isotope ratio measurements from samples containing femtogram quantities of ¹³⁷Cs are needed to accurately track contamination resuspension and redistribution following environmental ¹³⁷Cs releases; however, mass spectrometric analyses of environmental samples are limited by the large quantities of ionization inhibitors and isobaric interferences which are present at relatively high concentrations in the environment. We report a new approach for Cs purification from environmental samples. An initial ammonium molybdophosphate-polyacrylonitrile (AMP-PAN) column provides a robust, selective method for extracting Cs under a wide variety of sample matrices and mass loads. Application of a novel cation exchange separation approach using AMP-PAN results in more than two orders of magnitude greater Cs/Rb separation factors than commercially available strong cation exchangers. Final sample purification using a microcation column (AG50W resin) enables consistent 2–4% (2σ) measurement errors for samples containing 3–6000 fg ¹³⁷Cs, representing the highest precision ¹³⁵Cs/¹³⁷Cs ratio measurements currently reported for soil samples at the femtogram level.

Published by Elsevier B.V.

1. Introduction

Cs isotope ratios can provide the age, origin and history of Cs contamination within the environment. While ¹³³Cs is the only stable isotope of Cs (and thus represents 100% naturally occurring Cs), other isotopes of Cs (notably ¹³⁴Cs, ¹³⁵Cs and ¹³⁷Cs) are created in varying quantities during nuclear fission of ²³⁵U and ²³⁹Pu [1,2]. While the distinct gamma emissions and relatively short half lives (2.065 and 30.01 yrs respectively) of ¹³⁴Cs and ¹³⁷Cs result in the concentrations of these isotopes being easily detected via gamma spectrometry, quantification of ¹³⁴Cs/¹³⁷Cs ratios is only possible for the first few years after the occurrence of a fission event (due to the rapid decay of ¹³⁴Cs). In contrast, ¹³⁵Cs has a very long half life (2.3E6 yrs) and thus mass spectrometric analysis of ¹³⁵Cs/¹³⁷Cs ratios shows promise as a contaminant tracer for much longer time scales (Fig. 1). Furthermore, ¹³⁵Cs/¹³⁷Cs ratios can provide a

sensitive indicator of specific fission conditions including neutron energies [2–4], fluxes, the duration of the fission event [4], chemical fractionation of isobaric precursors [5], and the time which has elapsed since fission took place [4]. These properties have resulted in ¹³⁵Cs/¹³⁷Cs ratio usage for a variety of environmental applications including contamination source term tracking of large scale ¹³⁷Cs environmental releases (including releases from Chernobyl, Fukushima, Sellafield, and global nuclear weapons fallout) [1–8], identifying the source term and history of low level ¹³⁷Cs releases from radiological disposal facilities [9], and calculating sedimentation/erosion rates [2].

Methods which enable relatively high precision ¹³⁵Cs/¹³⁷Cs ratio measurements from environmental samples containing femtogram quantities of ¹³⁷Cs are currently needed. Although samples taken near the center of a plume after a major release event often contain very large quantities of ¹³⁷Cs [8,10,11], the application of ¹³⁵Cs/¹³⁷Cs ratio measurements to mapping the fringes of the plume and tracking ¹³⁷Cs transport from the source as a function of time due to environmental processes (e.g. sorption/desorption [12,13], diffusion [14], ¹³⁷Cs particulate resuspension/redistribution [9,15,16], etc.) require very sensitive, precise ¹³⁵Cs/¹³⁷Cs measurement capabilities. Furthermore, as the concentration of ¹³⁷Cs in an environmental sample from a given source term decreases, the contribution of other background

Abbreviations: Cs, cesium; AMP-PAN, ammonium molybdophosphate-polyacrylonitrile; TIMS, thermal ionization mass spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry.

* Corresponding author at: Idaho National Laboratory, PO Box 1625, Idaho Falls, ID 83415-2805, USA.

E-mail address: mathew.snow@inl.gov (M.S. Snow).

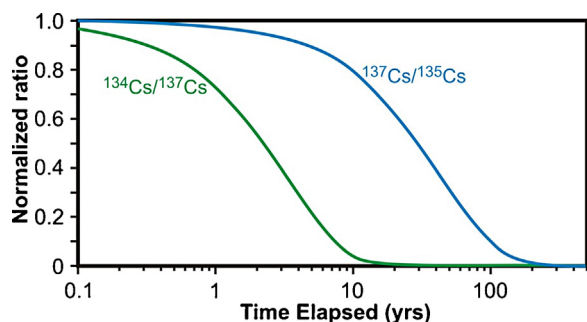


Fig. 1. Effect of time on $^{134}\text{Cs}/^{137}\text{Cs}$ and $^{135}\text{Cs}/^{137}\text{Cs}$ ratios (note that $^{137}\text{Cs}/^{135}\text{Cs}$ is plotted rather than $^{135}\text{Cs}/^{137}\text{Cs}$). In addition to enabling contamination tracking over a longer time period, $^{135}\text{Cs}/^{137}\text{Cs}$ ratios provide a sensitive indicator of specific fission conditions including neutron energies, fluxes, fission event durations, and chemical fractionation of precursor elements.

sources (such as global nuclear weapons fallout, which is ubiquitously scattered across the globe) to the observed $^{135}\text{Cs}/^{137}\text{Cs}$ ratio in the sample increases, introducing the challenge of discriminating between Cs from global nuclear weapons fallout and Cs from a source of interest [9]. Improvements in the precision of $^{135}\text{Cs}/^{137}\text{Cs}$ ratio measurements at the femtogram level would enable more precise identification of the source term of the ^{137}Cs and improve quantification of non-fallout Cs in a given sample.

Several methods for purifying Cs from environmental samples have been previously suggested. The first method, proposed by Lee et al. and later used by Chen et al., performs Cs purification of dissolved sediment samples using two sequential cation exchange columns (Bio-rad AG50W resin) prior to mass spectrometry analysis [1,2]. However, several major drawbacks to this approach include (1) the restriction to relatively small sample masses (in order to minimize the load solution volume on the initial cation column and thus enable effective Cs separation from the bulk matrix), (2) the lack of robustness of the initial cation column calibration to different sample matrices, mass loads, and types, and (3) the relatively low selectivity of most commercially available cation exchange resins for Cs over similar cations (such as the alkali metals) [17].

In 2007 an improved method was proposed by Taylor et al. [3]; this method employs an initial Cs concentration step by contacting the dissolved sample with ammonium molybdophosphate (AMP) powder. The extremely high selectivity of AMP for Cs provides a very robust initial separation of Cs from the bulk sample matrix. AMP is subsequently dissolved under basic conditions and passed through an anion exchange column and a cation exchange column prior to Cs isotope analysis using quadrupole based dynamic reaction cell-inductively coupled plasma-mass spectrometry (DRC-ICP-MS). The ultimate precision of this technique has been demonstrated by several groups studying rainwater and vegetation samples collected near the Fukushima Daichi site, where $^{135}\text{Cs}/^{137}\text{Cs}$ ratio measurement precision as low as 0.6–2% (2σ) have been reported from samples containing >60 fg of ^{137}Cs [8,18].

A major weakness with the batch AMP powder contact step is that this method does not effectively separate Cs from the alkali metals or Ba [17,20], which represent potential isobaric and/or ionization inhibiting interferences. While this may not be a major concern for matrices containing relatively low concentrations of these elements (such as rainwater or vegetation samples), it can represent a significant concern for more complicated matrices (such as soils and seawater, which frequently contain mg quantities of the alkali metals per gram of soil or mL of seawater) [21]. In order to minimize potential ionization inhibition and isobaric interferences by these elements (and thus maximize measurement

sensitivity and precision [23]), procedures utilizing AMP powder must rely on subsequent cation exchange purification to provide sufficient Cs/Rb, K, Ba separation [3,18,20]. However, while most commercially available cation exchangers enable nearly quantitative separation of Cs from Ba [20,22], these exchangers show little selectivity for Cs over K and Rb, resulting in inefficient (and often incomplete) separations [17,22]. The inability to completely separate Cs from the alkali metals (which in turn can result in significant Cs ionization suppression [23]) represents a major limiting factor in the sensitivity and precision for Cs isotope ratio measurements.

One alternative which has not yet been reported is to exploit the extremely high uptake affinity and selectivity of AMP for Cs by performing cation exchange separations of Cs using AMP. While such an approach is not practical using AMP alone (due to the challenges associated with handling the powder), the combination of AMP with polyacrylonitrile (PAN) binder results in a physical form of AMP that is easily adapted to chromatographic separations [24–28]. AMP has a much higher selectivity for Cs over the alkali earth metals than any current commercially available cation exchanger, with selectivities that are 22 and 1200 times greater for Cs/Rb and Cs/K separations than are reported for Dowex 50 in 0.1 M NH_4NO_3 [17]. These dramatically superior selectivities provide the potential for much higher Cs separation factors than any purification method previously reported.

In this work, we report a systematic analysis of three sample preparation methods for Cs isotope ratio measurements from environmental samples using thermal ionization mass spectrometry (TIMS). An initial AMP-PAN column enables robust Cs separation from a wide variety of sample matrices. A cation exchanging step on the initial AMP-PAN column (using dilute NH_4NO_3) is employed in order to separate Cs from Na and K. Quantitative recovery of Cs from the AMP-PAN resin is performed by stripping Mo and Cs off the PAN backbone under basic conditions, followed by subsequent separation of Cs from Mo using anion exchange. Three separate approaches for final sample purification prior to TIMS analysis are evaluated: (1) Cs purification using a commercially available strong cation exchanger (Biorad AG50W-X4) in a fashion similar to that performed by Taylor et al. and Zheng et al. [3,20], (2) cation exchange purification using AMP-PAN, and (3) cation exchange using AMP-PAN followed by final purification using the commercially available strong cation exchanger.

2. Experimental

AMP-PAN was obtained directly from the Czech Technical University of Prague; all other reagents in this study were trace metals grade or better. Initial method development was performed using separate 6 g aliquots of NIST 2710a soil spiked with ~1000 fg of an available ^{137}Cs tracer. Later sample compositions ranged from a variety of different soil, seawater, and vegetation samples (grass, clover, spinach, and rice) with initial ^{137}Cs loads ranging from 0.3 up to 6000 fg of ^{137}Cs . Soil samples were dry ashed in a muffle furnace at 650 °C for 20 hours, following which 0.5 g of the dry ashed soils were added to individual CEM microwave digestion vessels; for vegetation samples, up to 0.25 g of vegetation were added to each vessel without prior treatment. After sample addition, 4 mL of 16 M HNO_3 and 4 mL 29 M HF were added to each vessel. Vessels were immediately sealed and microwaved using a CEM MARS 5 microwave digestion system. Operating conditions for the digestion sequence are given elsewhere (Table S-1, Supporting Information). After cooling, 30 mL of a 44 g/L boric acid solution was added to each vessel, following which vessels were re-microwaved using the same power sequence described previously. Upon cooling, samples were transferred with three 3.5 M HNO_3 rinsings into a Nalgene CES 0.45 μm filter unit and filtered.

Download English Version:

<https://daneshyari.com/en/article/1193598>

Download Persian Version:

<https://daneshyari.com/article/1193598>

[Daneshyari.com](https://daneshyari.com)