

Supporting information

Precise U and Pu isotope ratio measurements in nuclear samples by hyphenating capillary electrophoresis and MC-ICPMS

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Table S1. Instrumental settings for CE and its interface with MC-ICPMS.

Table S2. Operating conditions of the MC-ICPMS instrument.

SI experimental Section

Instrumental system

The instrumentation used in this work was composed of five main parts:

- A mass flow controller (MFC) (Fluigent, Villejuif, France)
- A high voltage generator (Spellman, Bochum, Germany)
- A laboratory-built CE module
- A specific laboratory-built interface to connect the CE module to the MC-ICPMS
- A Neptune Plus MC-ICPMS (ThermoFisher Scientific, Bremen, Germany)

The overall system was designed to facilitate manipulation in a glove box and to externalize as many parts as possible in order to avoid corrosion and to reduce technological waste. A schematic description of the complete instrumental system is presented in [Figure S1](#). Several feedthroughs were implanted in the glove box ([Figure S1](#), F) to connect electric wires to the high-voltage generator and PEEK tubing to the MFC.

The CE module presented in [Figure S2](#), made of PVC without any metal parts, was designed to facilitate manipulation in the glove box and to ensure that the electric field was safely applied. It comprised two main parts (A and B). The first one (A) had sealed passages in it, which were realized for the introduction of the pressure tubing of the MFC ([Figure S2](#), E1), the electrode ([Figure S2](#), E2) and the capillary ([Figure S2](#), E3). The first part was screwed on top of the second one (B) with a gasket at the interface between the two parts to ensure correct sealing of the module. The second part could contain vials of different sizes for the injection and separation steps. During the injection step, 1-mL vials were used. During the separation step, a larger 50-mL vial was employed and filled with 1 or 2 mL of electrolyte

solution. During this step, the electrode was immersed in the electrolyte solution before the electric field was applied to the capillary, as illustrated in [Figure S2](#). Fused silica capillaries (Polymicro Technologies, Phoenix, USA) with an internal diameter of 50 μm and a length of 95 cm were used. The end of the capillary was connected to the ICPMS via an interface detailed in the Supplementary information S3. The hyphenation to the MC-ICPMS was achieved using a Mira Mist CE nebulizer (Burgener, Mississauga, Ontario, Canada). This nebulizer, developed especially for CE, has already been described in previous publications⁴⁰ where its analytical performance is also emphasized. The Mira Mist CE enabled closure of the electric circuit at the extreme end of the capillary outlet using the background electrolyte as a makeup solution. The capillary outlet was positioned 2 mm before the nebulizer tip. This position was found to be optimal for the nebulization of the sample as described in a previous study.²⁹ The MFC was used to deliver the makeup solution at a flow rate of 10 $\mu\text{L min}^{-1}$. A specifically designed low volume cyclonic spray chamber (20 mL) was used at the interface. It was composed of 2 nebulizer inlets with an angle of 45° between them³¹: one for the Mira Mist CE nebulizer ([Figure S3, A](#)) and one for a Micro Mist nebulizer, with a nominal flow rate of 100 $\mu\text{L}\cdot\text{min}^{-1}$, ([Figure S3, B](#)) used to inject a standard during the separation in order to perform mass bias correction. The MFC was also employed to continuously deliver a 2% HNO_3 solution to the Micro Mist nebulizer and an injection valve was utilized to introduce the standard solution before and after the sample detection. After optimization of the two carrier gas flow rates ([Table S1](#)) the concentration of the reference isotopic standard was fixed at 10 $\mu\text{g g}^{-1}$.

The isotope ratios were determined using a Neptune Plus MC-ICPMS (Thermo Scientific, Bremen, Germany) modified to accommodate a glove box around the ion source. The operating parameters are detailed in [Table S2](#). Faraday cups were equipped with 10^{11} and 10^{12}

ohm resistors. $10^{12} \Omega$ resistances were set up for the less abundant U isotopes (234 and 236). The configuration (C1) used for the measurement of IRMM184 and IRMM187 is presented in **Table S2**. $10^{12} \Omega$ resistances were set up for the less abundant U isotopes (234 and 236). A special configuration was used for the nuclear spent fuel sample analysis with a first set up (C2) used for the acquisition of the Pu isotopes signals and a second set up (C3) used for the acquisition of the U isotopes signals. All the configurations used are presented in **Table S2**. The analysis was conducted at low mass resolution with an acquisition time set at 0.131 seconds. The Faraday amplifier gains were calibrated daily before the analytical session yielding a reproducibility of the electric gain better than 20 ppm per day.

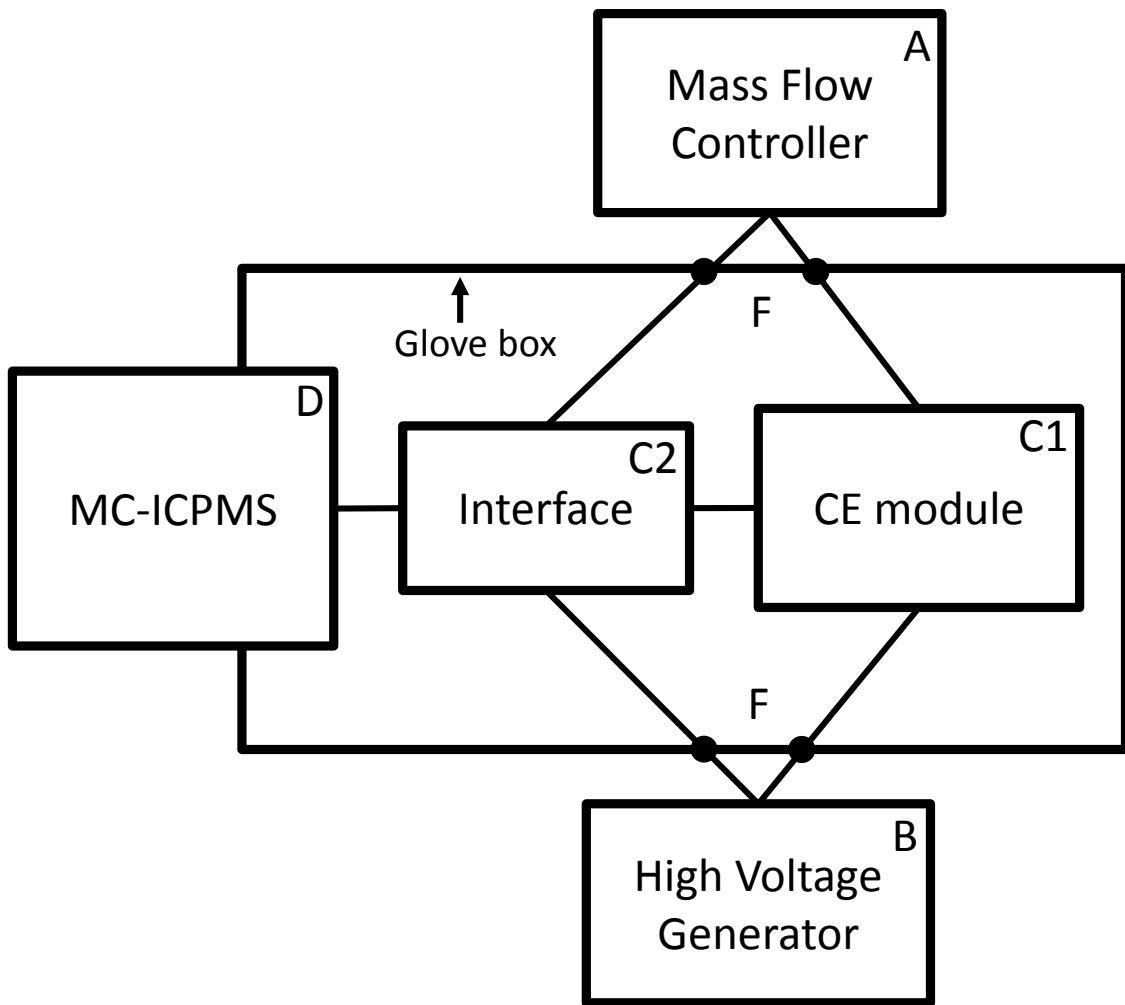


Figure S1

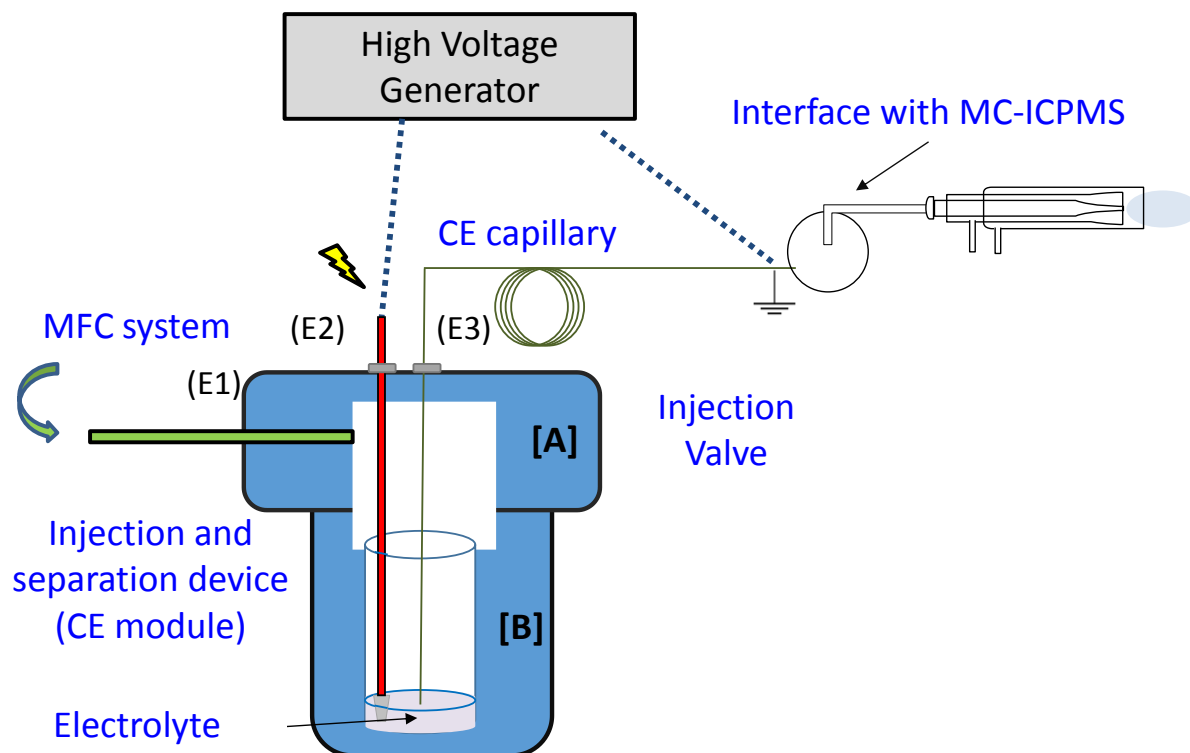


Figure S2

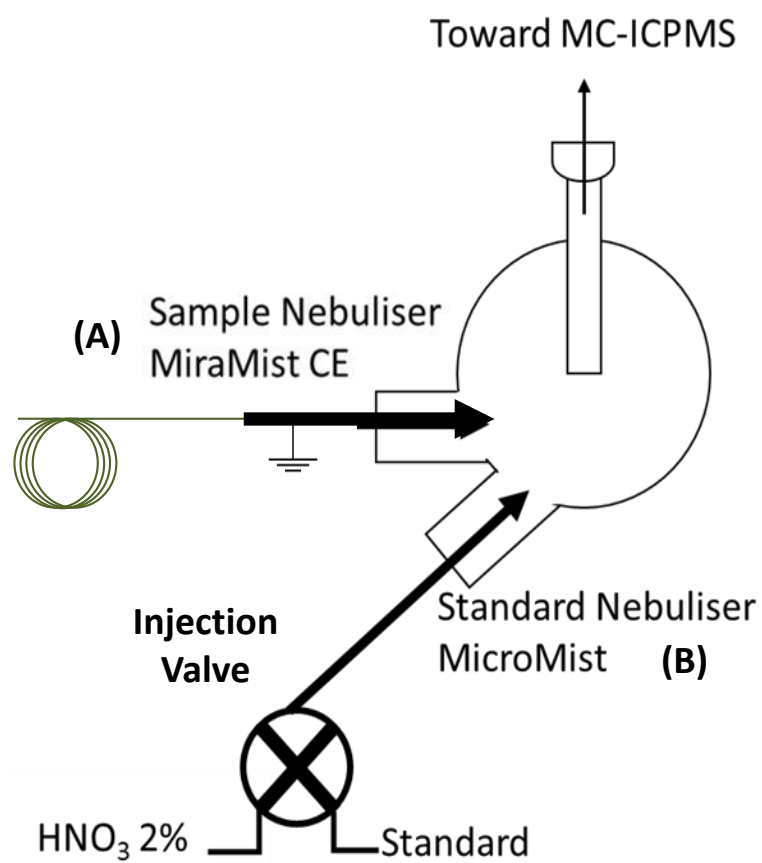


Figure S3

CE system and interface to MC-ICPMS	
Instrument	Laboratory-built CE system
Voltage	+ 20 kV
CE/ITP capillary	Bare fused silica, inner diameter 50 μm , outer diameter 365 μm , length 95 cm
Sample injection	Pressure 200 mbar during 5 seconds
CE background electrolyte	Acetic acid 0.25 - 0.4 M pH: 3 adjusted with ammonia
First nebuliser (A)	Micro Mist (0.1 mL min ⁻¹)
Carrier gas (Ar) flow rate	0.25 L min ⁻¹
Second nebuliser (B)	Mira Mist CE (0.01 ml.min ⁻¹)
Makeup electrolyte	background electrolyte
Makeup electrolyte flow rate	10 $\mu\text{L min}^{-1}$
Carrier gas (Ar) flow rate	0.70 L min ⁻¹
Spray chamber	cyclonic spray chamber (Volume: 20 mL)

Table S1

MC-ICPMS system									
Instrument	Neptune Plus Thermo Scientific								
RF Power	1300 W								
Plasma gas flow rate	16 L min ⁻¹								
Auxiliary gas flow rate	1 L min ⁻¹								
Data acquisition	1 block, between 1 and 15690 cycles 0.131 s integration								
Cup configuration for IRMM 184 and 187 analysis - C1									
Faraday cup	L4	L3	L2	L1	C	H1	H2	H3	
Isotopes	²³² Th	²³³ U	²³⁴ U	²³⁵ U	²³⁶ U	237	²³⁸ U	239	
Resistance (Ω)	10 ¹¹	10 ¹¹	10 ¹²	10 ¹¹	10 ¹²	10 ¹¹	10 ¹¹	10 ¹¹	
Cup configuration for nuclear fuel samples (first set up) - C2									
Faraday cup		L3	L2	L1	C	H1	H2	H3	
Isotopes		²³⁵ U	²³⁶ U	²³⁸ U	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu	
Resistance (Ω)		10 ¹¹	10 ¹²	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹	
Cup configuration for nuclear fuel samples (second set up) - C3									
Faraday cup				L1	C	H1	H2	H3	H4
Isotopes				²³⁴ U	²³⁵ U	²³⁶ U	237	²³⁸ U	239
Resistance (Ω)				10 ¹²	10 ¹¹	10 ¹²	10 ¹¹	10 ¹¹	10 ¹¹

Table S2