**SUPPORTING INFORMATION**

# Determination of femtogram level plutonium isotopes in environmental and forensic samples with high-level uranium using chemical separation and ICP-MS/MS measurement

Xiaolin Hou[1,2,3,5*], Weichao Zhang[1,4], Yanyun Wang[1,4]

1 State Key Laboratory of Loess and Quaternary Geology, Shaanxi Key Laboratory of Accelerator Mass Spectrometry Technology and Application, Xi'an AMS Center, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

2 Center for Nuclear Technologies, Technical University of Denmark, DTU Nutech, Roskilde DK-4000, Denmark

3 CAS center of Excellence in Quaternary Science and Global Change, Xi'an 710061, China

4 University of Chinese Academy of Sciences, Beijing 100049, China

5 Open Studio for Oceanic-Continental Climate and Environment Changes, Pilot National Laboratory for Marine Science and Technology (Qingdao), Qingdao 266061, China

Supporting information includes a description of chemical separation of plutonium from environmental samples, 4 Tables and 3 Figures.

[*] Corresponding author at: DTU Nutech, E-mail: xiho@dtu.dk (Xiaolin Hou). Fax:45 46775357

## Chemical separation of plutonium from environmental samples

A chemical separation procedure using acid leaching, co-precipitation and chromatographic separation (Fig. S2) was used for separation of plutonium from sample matrix and interfering radionuclides. For the environmental soil samples, small stones and vegetation root were first removed, the samples were then dried, ground and sieved through an 80-mesh sieve. 1-30 g of soil samples, soil and sediment certified reference materials (depending on the level of plutonium) was weighed to a beaker, it was heated at 450 °C and remained overnight to remove the organic substance in the samples. After spiked a known amount of $^{242}$Pu (3.4 pg) as chemical yield tracer, the sample was leached with *aqua regia* at 150°C on a hotplate for 30 minutes, followed by leaching at 200°C for 2 hours. The leachate containing plutonium was separated by filtration through a glass fiber filter. Ammonium was added to the leachate to pH 8.5 to form hydroxides precipitation of plutonium with iron and other metals ions. The precipitate was separated by centrifuge and washed with 2 mol/L NaOH to remove the amphoteric elements (e.g. Al, V, etc.). The precipitate was then dissolved with HCl, and 0.2-1 g of $K_2S_2O_5$ (depending on sample size) was added to reduce plutonium to $Pu^{3+}$, meanwhile iron was reduced to $Fe^{2+}$. Ammonium was added to pH 8.5 to precipitate $Pu^{3+}$ and $Fe^{2+}$ as hydroxides, which was then separated by centrifuge. Concentrated $HNO_3$ was then added to dissolve the precipitate and meanwhile oxidize $Pu^{3+}$ to $Pu^{4+}$ using nitrite presents in the concentrated $HNO_3$, and the sample solution was adjusted to 1.0 mol/L $HNO_3$ medium. The prepared sample solution was loaded to a TEVA column (2 mL, 0.70 cm in diameter and 5 cm in length) which has been conditioned with 30 mL of 1.0 mol/l $HNO_3$. The column was rinsed with 120 mL of 1.0 mol/L $HNO_3$ and 60 mL of 6 mol/L HCl to remove matric elements, uranium and thorium. Plutonium on the column was finally eluted with 40 mL of 0.1 mol/L $NH_2OH \cdot HCl$ in 2 mol/L HCl. The eluate was evaporated to dryness on a hotplate, 5 mL of concentrated $HNO_3$ was added and the solution was evaporated to dryness again to decompose $NH_2OH \cdot HCl$ and remove HCl in the sample. The residue was finally dissolved in 0.5 mol/L $HNO_3$ and prepared in 3.5 mL for measurement of plutonium isotopes using ICP-MS/MS.

Table S1 ICP-MS/MS instrument settings for the measurement of Pu isotopes

| Conditions | Parameter | Value |
|---|---|---|
| ICP | RF Power | 1500W |
| | RF Matching | 1.60V |
| | Sampling Depth | 5.1mm |
| | Carries Gas | 0.70L/min |
| | Temperature of Spray Chamber | 2℃ |
| | Makeup Gas | 0.36L/min |
| Lens | Extraction Lens 1 | -190.0V |
| | Extraction Lens 2 | -10.0V |
| | Omega Bias | -110V |
| | Omega Lens | 19.5V |
| | Q1 Entrance | 3.7V |
| | Q1 Exit | -3.7V |
| | CRC focus | 6.7V |
| | CRC Entrance | -135V |
| | CRC Exit | -134V |
| | Deflect | 9.3V |
| | Plate Bias | -136V |
| Q1 | Q1 Bias | 1.6V |
| | Q1 Prefilter Bias | -1.5V |
| | Q1 Postfilter Bias | -9.9V |
| CRC | Octopole Bias | -7.6V |
| | Octopole RF | 180V |
| | Energy Discrimination | -19.9V |

Table S2 The standard solutions and setting values of Q1(m/z) and Q2(m/z) and possible ions measured for elimination of $^{238}U^{1}H^{+}$ ions using different reaction gasses

| Standard | Q1(m/z) | Q2(m/z) and possible ions species |
|---|---|---|
| $^{238}U$(20 ng/ml) | 238($^{238}U^{+}$) | 237, 238($^{238}U^{+}$), 239($^{238}UH^{+}$), 240($^{238}UH_2^{+}$), 252($^{238}UN^{+}$), 253($^{238}UNH^{+}$), 254($^{238}UO^{+}$,$^{238}UNH_2^{+}$), 255($^{238}UOH^{+}$, $^{238}UNH_3^{+}$) |
| $^{238}U$(1000 ng/ml) | 239($^{238}UH^{+}$) | 238($^{238}U^{+}$), 239($^{238}UH^{+}$), 240($^{238}UH_2^{+}$), 252($^{238}UN^{+}$), 253($^{238}UNH^{+}$), 254($^{238}UO^{+}$, $^{238}UNH_2^{+}$), 255($^{238}UOH^{+}$, $^{238}UNH_3^{+}$) |
| $^{239}Pu$(10 pg/ml) | 239($^{239}Pu^{+}$) | 238, 239($^{239}Pu^{+}$), 240($^{239}PuH^{+}$), 253($^{239}PuN^{+}$), 254($^{239}PuNH^{+}$), 255($^{239}PuO^{+}$, $^{239}PuNH_2^{+}$), 256($^{239}PuOH^{+}$, $^{239}PuNH_3^{+}$) |

Table S3 Results of measurement of intensity and fractions of the possible formed ions of $^{238}U$ in the DRC using ICP-MS/MS with the different reaction gasses

| Standard solution | Setting of Mass and possible ions Q1(m/z) | Q2(m/z) | Intensities of the measured signals, cps/ppb He (8.0 mL/min) | $NH_3$/He (0.6/8.8 mL/min) | $O_2$ (2.0 mL/min) | $CO_2$/He (1.2/8.0 mL/min) |
|---|---|---|---|---|---|---|
| $^{238}U$(20ppb) | $^{238}$(238U+) | 237 | 64.65 | 4.52 | $9.48\times10^2$ | 0.05 |
| | | 238($^{238}U^+$) | $6.29\times10^5$ | $4.78\times10^4$ | 0.01 | $2.89\times10^2$ |
| | | 239($^{238}UH^+$) | 9.45 | $2.66\times10^2$ | 0.01 | <0.001 |
| | | 240($^{238}UH_2^+$) | 0.07 | 0.48 | 54.17 | <0.001 |
| | | 252($^{238}UN^+$) | <0.001 | $6.93\times10^2$ | <0.001 | <0.001 |
| | | 253($^{238}UNH^+$) | <0.001 | $9.24\times10^4$ | <0.001 | <0.001 |
| | | 254($^{238}UO^+$,$^{238}UNH_2^+$) | <0.001 | $1.30\times10^4$ | $3.40\times10^4$ | $2.46\times10^5$ |
| | | 255($^{238}UOH^+$, $^{238}UNH_3^+$) | <0.001 | $4.09\times10^2$ | 13.80 | 99.44 |
| | | 256($^{238}UOH_2^+$) | <0.001 | <0.001 | 66.10 | <0.001 |
| $^{238}U$(1000ppb) | 239($^{238}UH^+$) | 238($^{238}U^+$) | 15.94 | 0.22 | 0.01 | 0.001 |
| | | 239($^{238}UH^+$) | 16.96 | 1.60 | 0.04 | 0.006 |
| | | 252($^{238}UN^+$) | <0.001 | 0.15 | <0.001 | <0.001 |
| | | 253($^{238}UNH^+$) | <0.001 | 0.33 | <0.001 | <0.001 |
| | | 254($^{238}UO^+$, $^{238}UNH_2^+$) | <0.001 | 5.90 | 0.99 | 2.43 |
| | | 255($^{238}UOH^+$, $^{238}UNH_3^+$) | <0.001 | <0.001 | 0.06 | 0.008 |
| | | 256($^{238}UOH_2^+$) | <0.001 | <0.001 | 0.002 | 0.005 |

Table S4 Results of measurement of intensity and fractions of the possible formed ions of $^{239}Pu$ in the DRC using ICP-MS/MS with the different reaction gasses

| Standard solution | Setting of two quadrupole | | Intensities of the measured signals, cps/ppb | | | |
|---|---|---|---|---|---|---|
| | Q1(m/z) | Q2(m/z) | He (8.0 mL/min) | $NH_3$/He (0.6/8.8 mL/min) | $O_2$ (2.0 mL/min) | $CO_2$/He (1.2/8.0 mL/min) |
| $^{239}Pu$(10ppt) | 239($^{239}Pu^+$) | 238 | 0.14 | 0.25 | <0.001 | 0.04 |
| | | 239($^{239}Pu^+$) | $1.03\times10^3$ | $1.17\times10^3$ | 3.47 | $3.48\times10^2$ |
| | | 240($^{239}PuH^+$) | <0.001 | 2.32 | <0.001 | 0.04 |
| | | 253($^{239}PuN^+$) | <0.001 | 0.04 | <0.001 | <0.001 |
| | | 254($^{239}PuNH^+$) | <0.001 | 7.32 | <0.001 | <0.001 |
| | | 255($^{239}PuO^+$, $^{239}PuNH_2^+$) | <0.001 | 5.63 | $2.33\times10^2$ | $2.33\times10^2$ |
| | | 256($^{239}PuOH^+$, $^{239}PuNH_3^+$) | <0.001 | 2.49 | 1.53 | 0.06 |

Table S5 Measurement results of the interferences of polyatomic ions of Pb and Tl to the measurement of plutonium isotopes

| Solution # | Counts rate (cps) at m/z 239 and 240 using ICP-MS | | Counts rate (cps) at m/z 239 or 240 by using ICP-MS/MS | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | No Gas | | No Gas | | He | | $NH_3$/He | | $CO_2$/He | |
| | m/z 239 | 240 | 239 | 240 | 239 | 240 | 239 | 240 | 239 | 240 |
| 3% $HNO_3$ | 0.77±0.38 | 0.13±0.12 | 0.20±0.20 | 0.03±0.06 | 0.50±0.10 | 0.10±0.10 | 0.27±0.15 | 0.07±0.06 | 0.07±0.06 | <0.01 |
| Tl-3%$HNO_3$ | <0.01 | 0.33±0.29 | <0.01 | 0.03±0.06 | <0.01 | <0.01 | <0.01 | 0.10±0.10 | 0.07±0.03 | 0.03±0.06 |
| Tl-0.1M HCl-3%$HNO_3$ | 0.23±0.04 | 0.60±0.32 | <0.01 | 0.07±0.07 | <0.01 | <0.01 | <0.01 | 0.00±0.00 | <0.01 | <0.01 |
| Pb-3%$HNO_3$ | <0.01 | 0.67±0.05 | 0.17±0.07 | 0.13±0.12 | <0.01 | <0.01 | 0.03±0.02 | 0.07±0.12 | <0.01 | 0.07±0.12 |
| Pb-0.1M HCl-3%$HNO_3$ | 0.40±0.17 | 0.63±0.27 | 0.03±0.02 | <0.01 | <0.01 | <0.01 | 0.20±0.02 | 0.03±0.06 | 0.03±0.06 | <0.01 |
| Hg-3% $HNO_3$ | 25±1 | 32±1 | 13±1 | 16±1 | 8.2±0.8 | 7.5±0.5 | 0.09±0.04 | 0.03±0.02 | 0.04±0.03 | 0.02±0.02 |
| Hg-0.1M HCl-3% $HNO_3$ | 24±1 | 26±1 | 12±1 | 14±1 | 6.5±0.6 | 7.5±0.6 | 0.20±0.07 | 0.04±0.03 | 1..9±0.3 | 0.03±0.02 |

# The concentrations of Tl, Pb and Hg are 500 ppb

Table S6 Analytical results of $^{239}Pu$ in simulated samples with high U/Pu ratio by chemical separation and ICP-MS/MS measurement with $CO_2$ – He as the reaction gas

| Sample code | Sample mass, mL | Chemical yield, $^{242}Pu$ | $^{239}Pu$ spiked ($10^{-15}$ g/mL) | $^{239}Pu$ intensity, cps | Measured $^{239}Pu$ ($10^{-15}$ g/mL) | Division |
|---|---|---|---|---|---|---|
| Procedure Blank | 7.00 | 93.4% | 0 | 0.15±0.03 | 0 | |
| Sample-1 | 7.00 | 88.2% | 4.10±0.05 | 2.62±0.15 | 4.12±0.31 | 0.5% |
| Sample-2 | 7.00 | 92.0% | 4.10±0.05 | 3.02±0.18 | 4.23±0.32 | 3.2% |
| Sample-3 | 7.00 | 93.5% | 4.10±0.05 | 2.81±0.20 | 4.18±0.35 | 1.4% |

Sample-1, 2 and 3 are the spiked solution containing $4.1\times10^{-15}$ g/mL $^{239}Pu$ and $4.0\times10^{-3}$ g/mL uranium. The samples was prepared in 3.2-3.5 ml 0.5M HNO3 solution for ICP-MS/MS measurement.

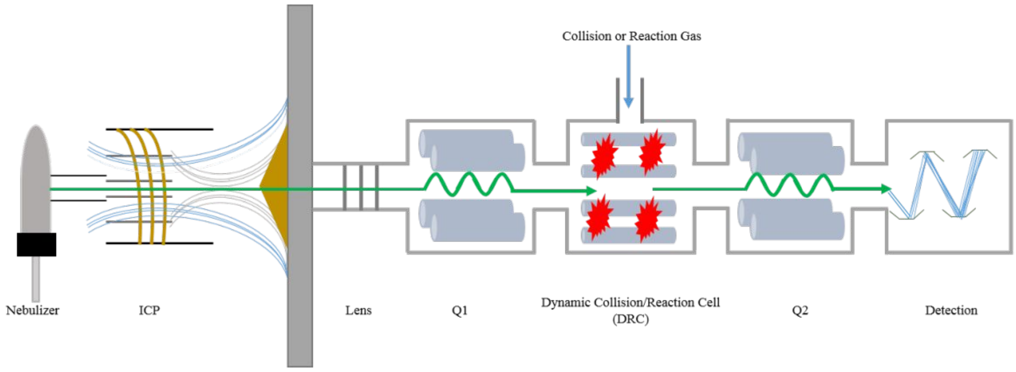


Figure S1 Schematic diagram of ICP-MS/MS for measurement of $^{239}Pu$

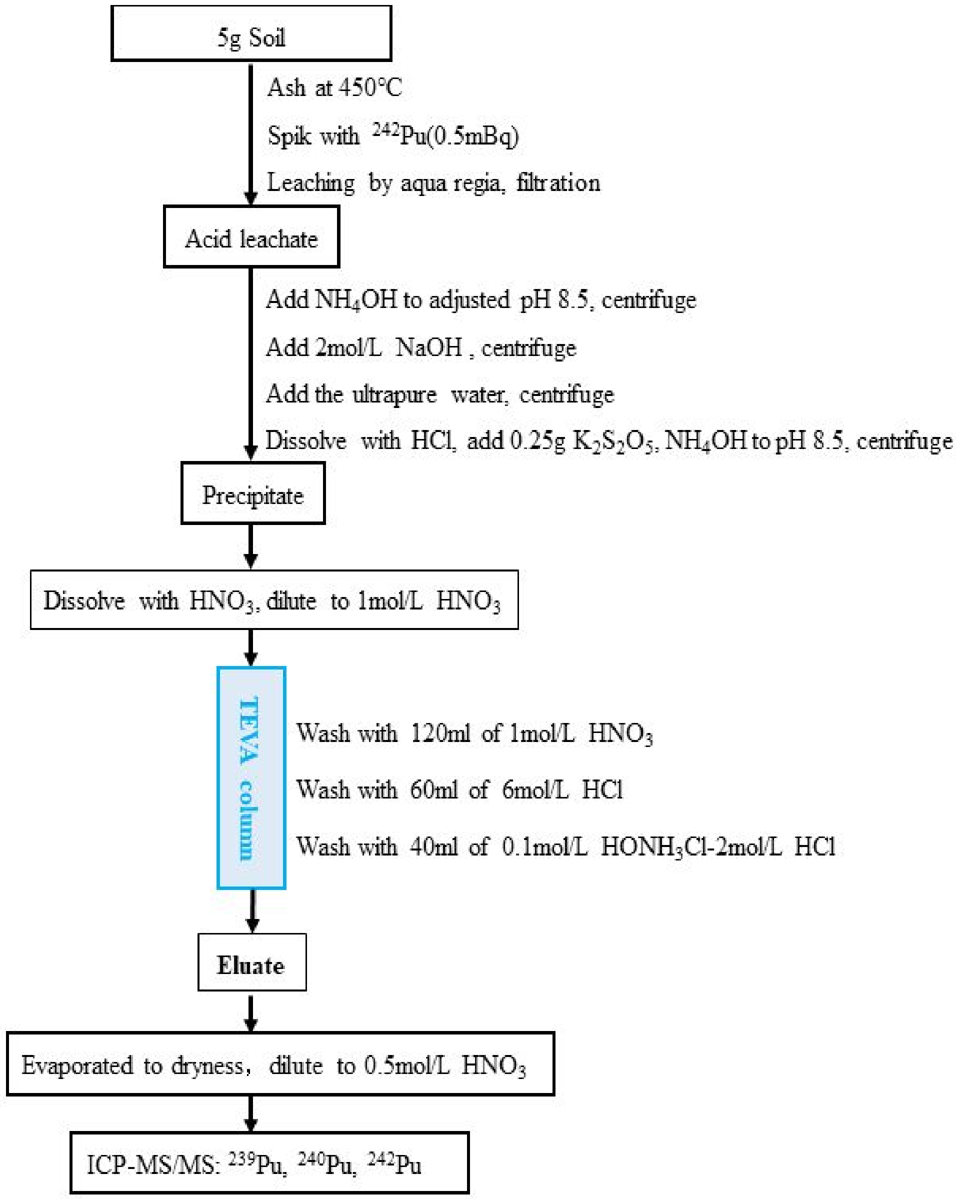


Figure S2 Schematic diagram of chemical separation and purification of Pu isotopes in soil or sediment samples from the environment

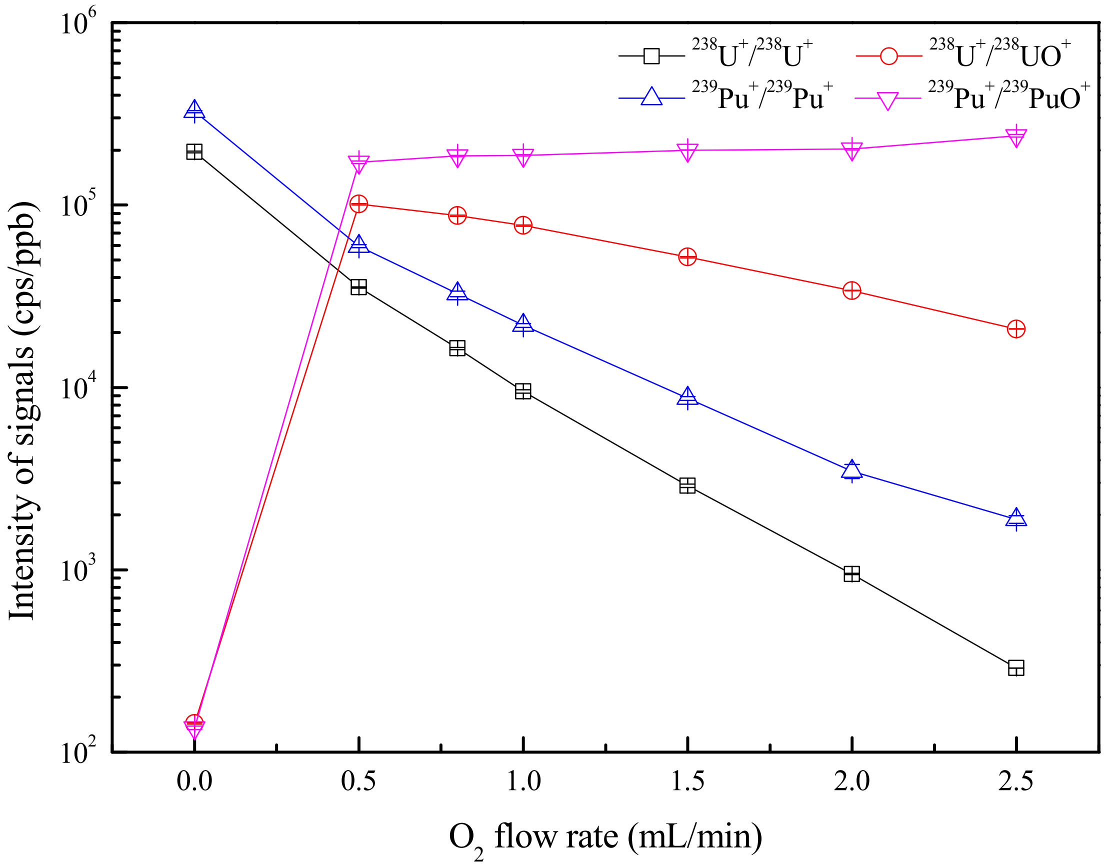


Figure S3 Variation of the signal intensities of $^{238}U^+$ and $^{239}Pu^+$ and their reaction product ions ($^{238}U^{16}O^+$, $^{239}Pu^{16}O^+$) in DRC with the flow rate of $O_2$ as reaction gas measured in uranium standard solution ($^{238}U$) and $^{239}Pu$ standard solution using ICP-MS/MS.

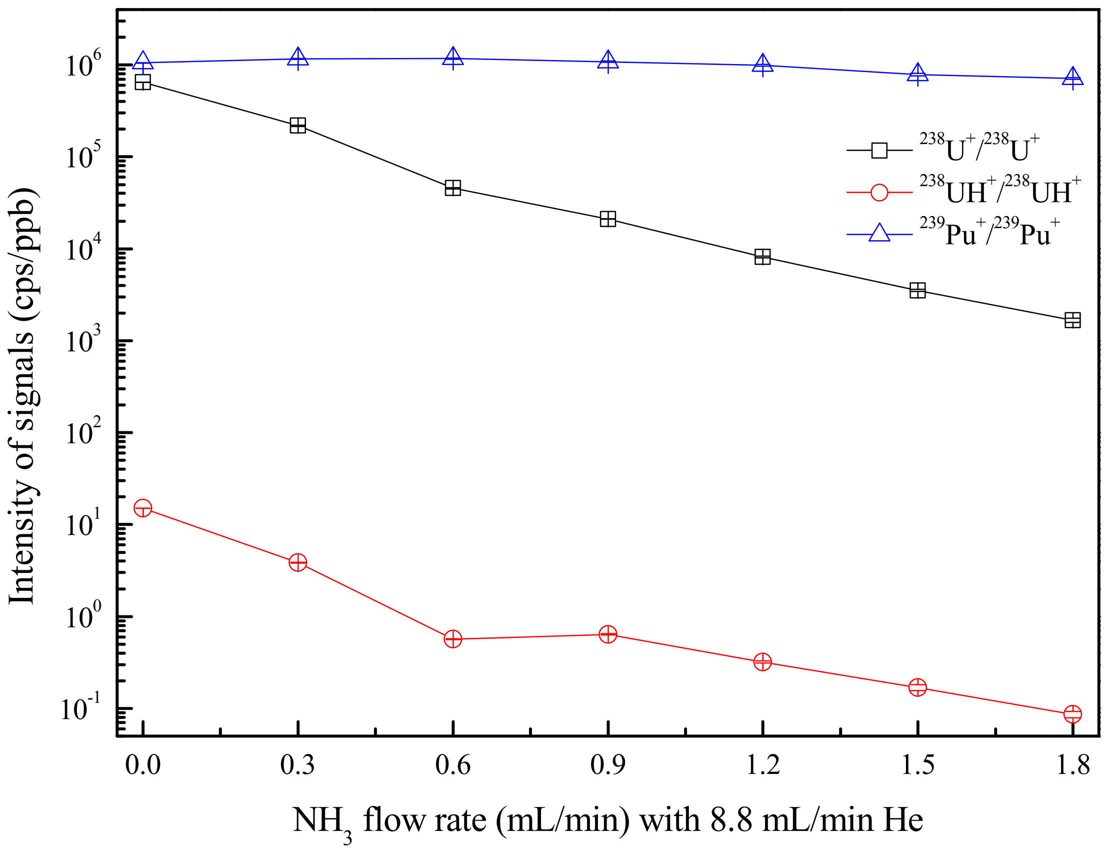


Figure S4 Variation of the signal intensities of $^{238}U^+$, $^{238}U^1H^+$ and $^{239}Pu^+$ with the flow rate of $NH_3$ (mixed with 8.8 ml/min He) as reaction gas measured in uranium standard solution ($^{238}U$) and $^{239}Pu$ standard solution using ICP-MS/MS.