Isotopy ratio study of uranyl ion with Differential Mobility Spectrometry-Mass Spectrometry (DMS-MS)

Ifeoluwa Ayodeji

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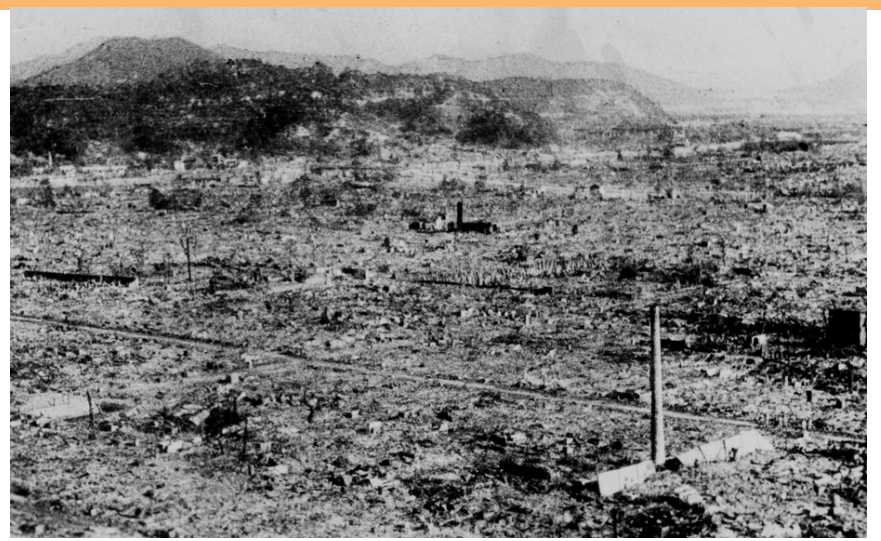
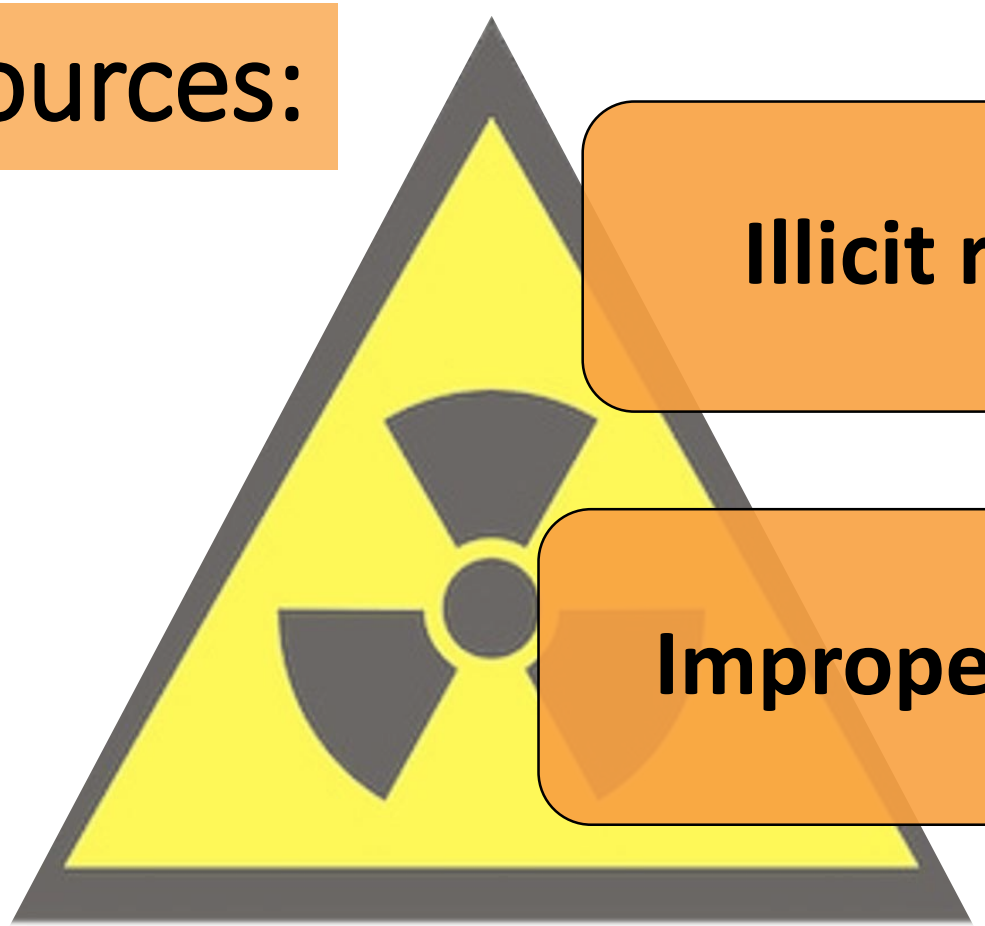
Why?

- Uranium and fission products are indiscriminately dispersed;
- A major health & environmental concern

World War II. Hiroshima, 0.8 km from the explosion Centre. 24 hours after the explosion of the atom bomb. Photo by Satsuo Nakata © ICRC Archives

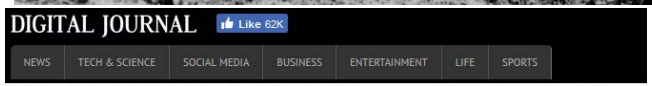


Sources:



Illicit release

Improper disposal



Nuclear waste in Kara Sea could spread to other continents

BY KAREN GRAHAM OCT 27, 2013 IN ENVIRONMENT LISTEN | PRINT

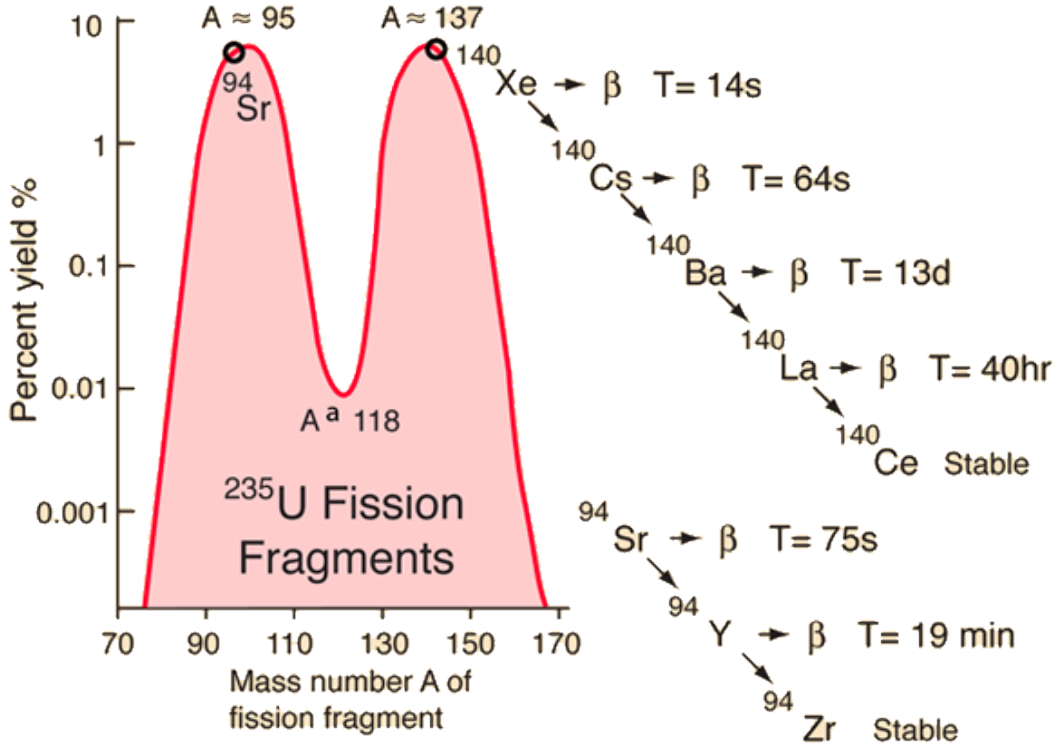
In 1992 the world learned the former Soviet Union had used the Arctic Ocean as a dumping ground for liquid and solid nuclear waste. The waste, including nuclear subs was mostly confined to an area off the coast of Novaya Zemlya, in the Kara Sea.

http://www.digitaljournal.com/article/361035

Fission products;

High Enriched Uranium (HEU) > 20% U-235

- Low Enriched Uranium (LEU , < 20% U-235)
- U-238; can used to produce Plutonium-239
- Fission products **(Sr, Ce, Cs, Xe,…)** may be highly unstable (radioactive).
- Stable fragments (Sr-90 & Cs-137) are extremely dangerous to environment (long-term effect).



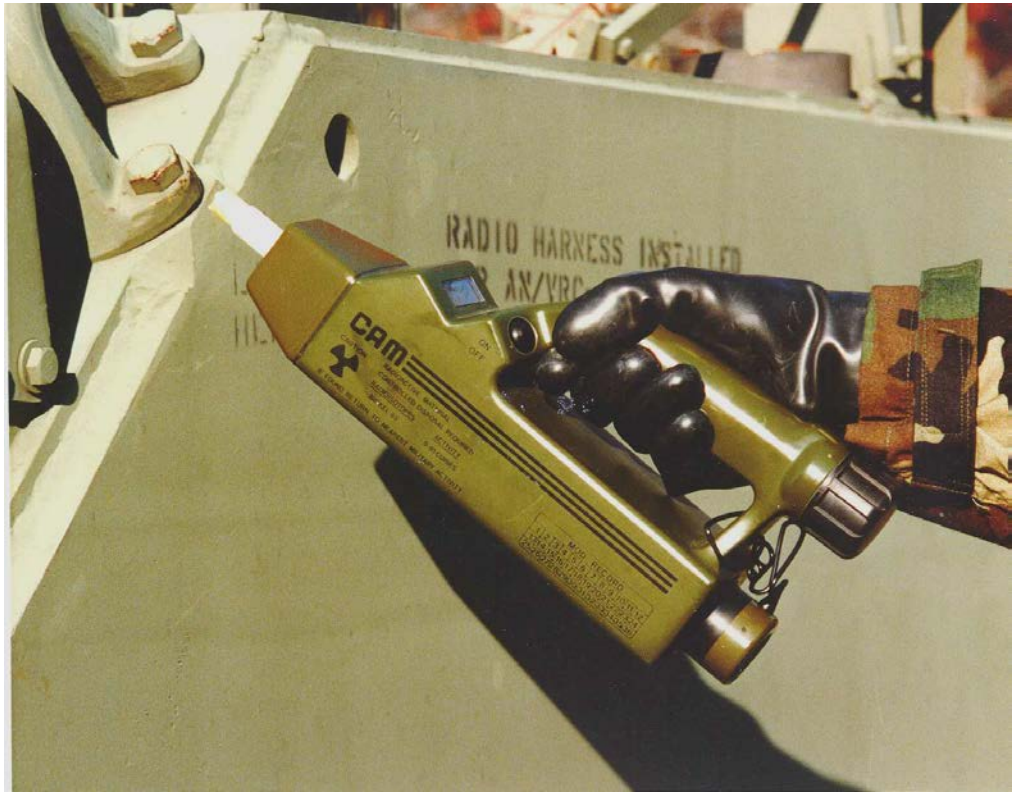
http://hyperphysics.phy-astr.gsu.edu/hbase/NucEne/fisfrag.html

All present in Harsh Environment

Why DMS for field sensing?

- Size, Weight & Power (SWaP) consideration
- High Throughput:
  - Sensitivity & selectivity,
  - High S/N ratio, reduces chemical interference.
- Simple sampling
- Rapid analysis

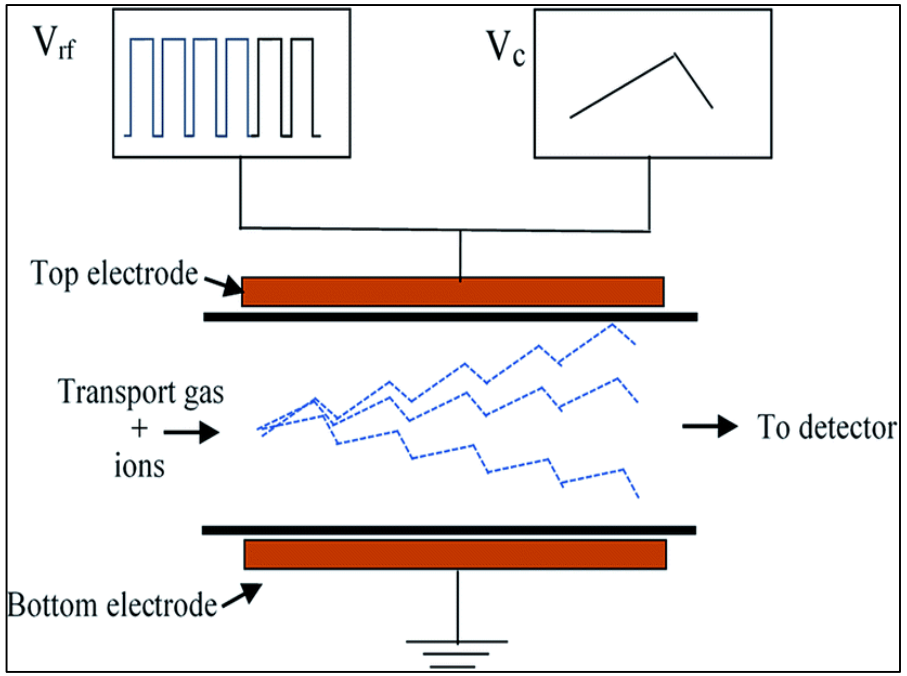
Military grade handheld IMS



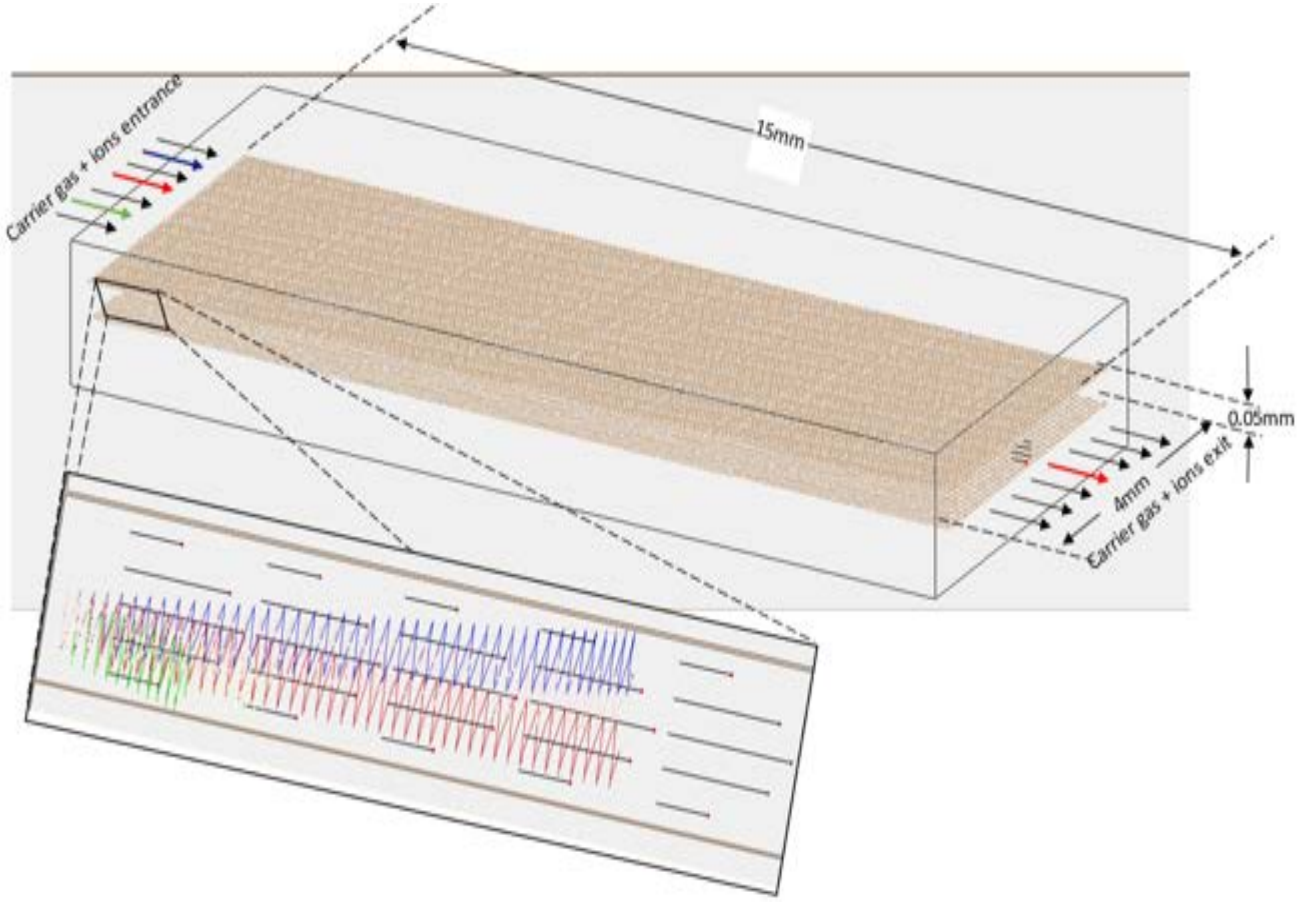
http://web.nmsu.edu/~pfunk/IMS.html(accessed 10/10/2018)

Differential Mobility Spectrometry

- Variant of Ion Mobility Spectrometry (IMS)
- Ion drift in non-linear motion
- Separate under the influence of an asymmetric RF field (V_{rf} or DV) and counterbalancing DC field (V_c or CV)
- Ambient ion filter



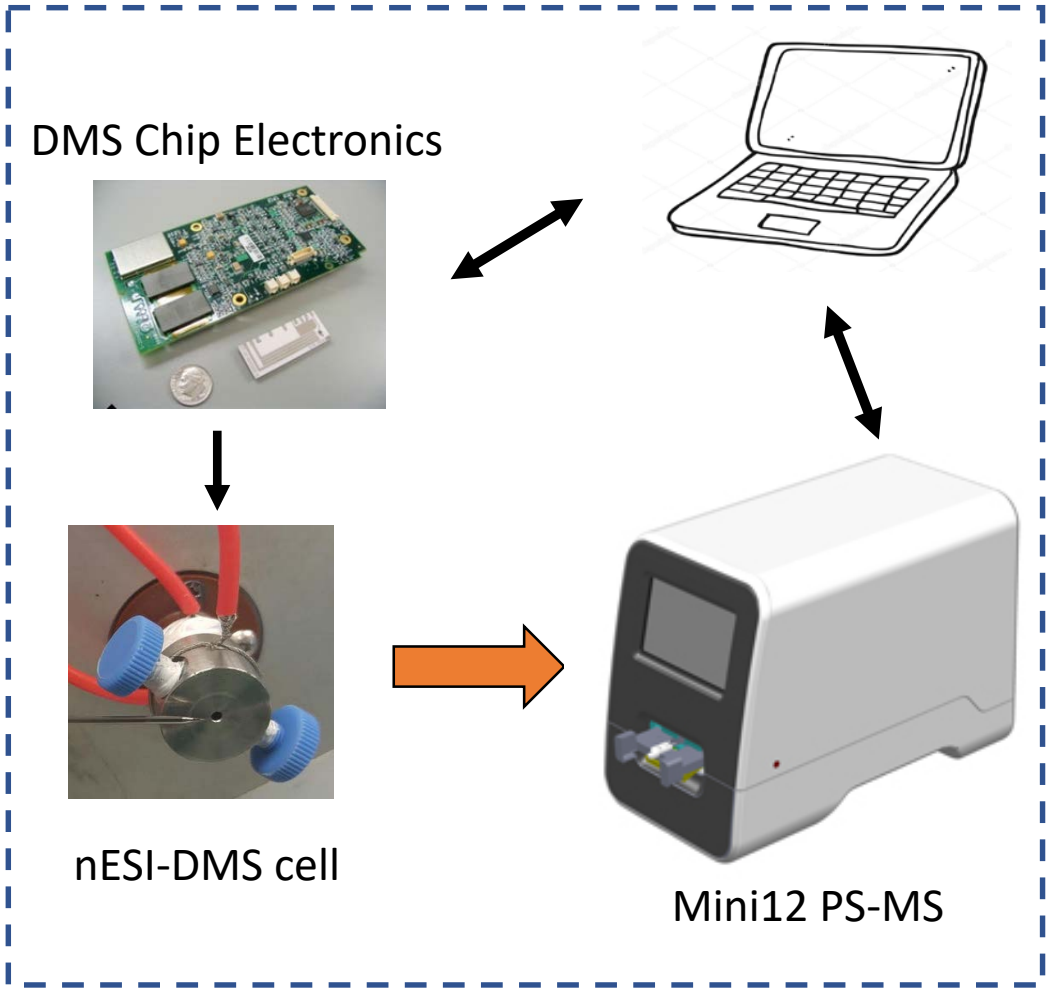
*I. Ayodeji, Anal. Methods, 20170914, **9**, 5044–5051*



Ion trajectory under the influence of asymmetric RF field in a plainer DMS

DMS-MS for Isotopy measurement

How portable ?



- Thermo 253 Plus-Isotope Ratio MS

https://assets.thermofisher.com/TFS-Assets/CMD/brochures/BR-30333-IRMS-253-Plus-BR30333-EN.pdf(accessed 10/10/2018)

Anal. Chem., 2014, 86 (6), pp 2909–2916; Ouyang group

Experimental

DMS:

Sionex fly-back electronics
Transport gas flow rate: 0.65 LPM
CV scan: - 15 V to 9.5 V at 0. 5 V step size for 15 sec
DV scan: 500 V to 1450 V at 50 V step size
Full CV and DV scan = ~ 5min

MS:

Thermo LTQ XL
Nano-electrospray: 2 KV
Capillary inlet potential: 35 V
Source fragmentation potential: 100 V

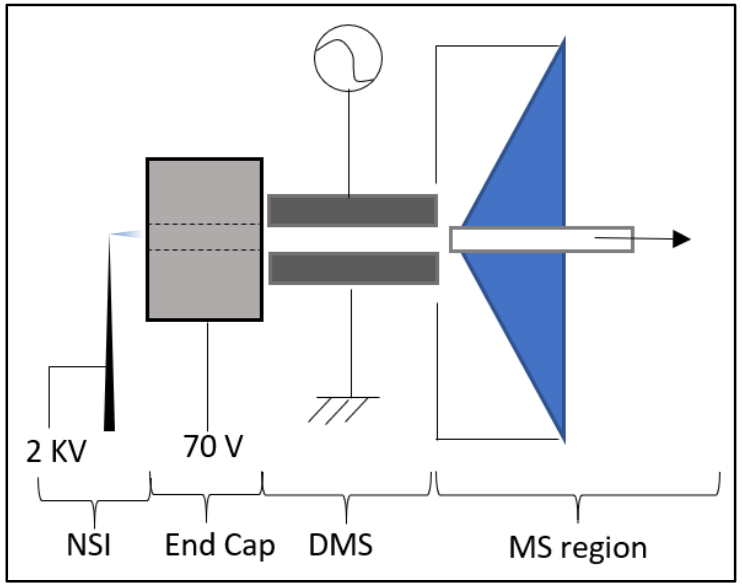
Sampling:

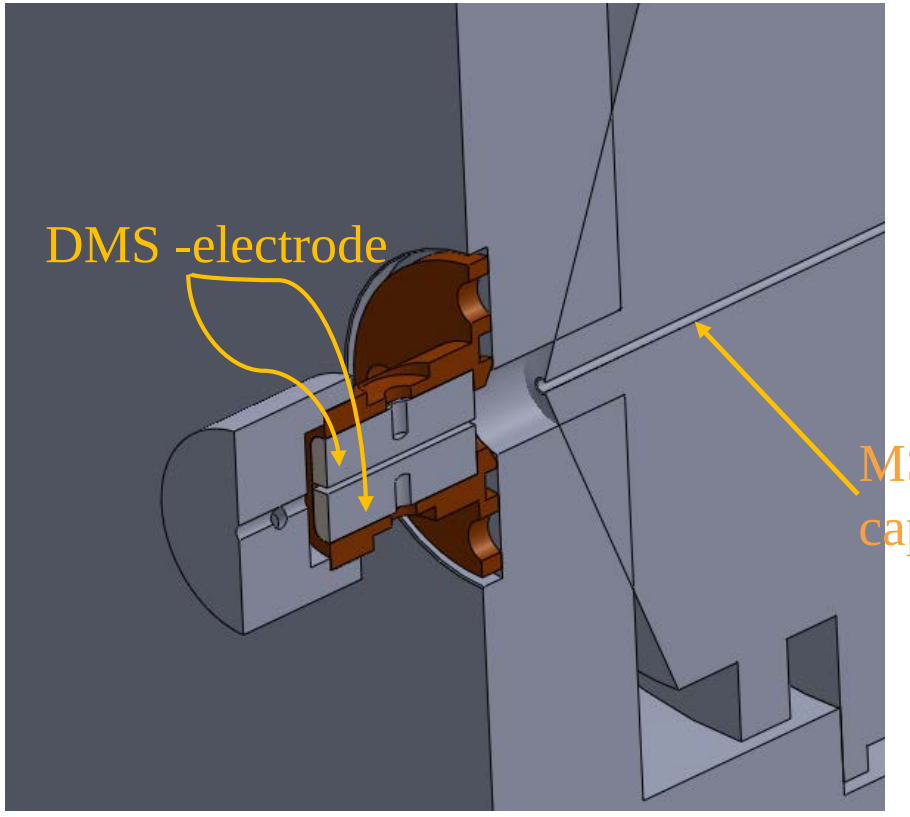
Concentration prepared as;

$UO_2(NO_3)_2.6H_2O$ = 10 µM; 0.5 mM (Isotopy study)
$Sr(NO_3)_2$ = 4 µM
in methanol

nESI sample flow rate: 1µL/ min

Set-up

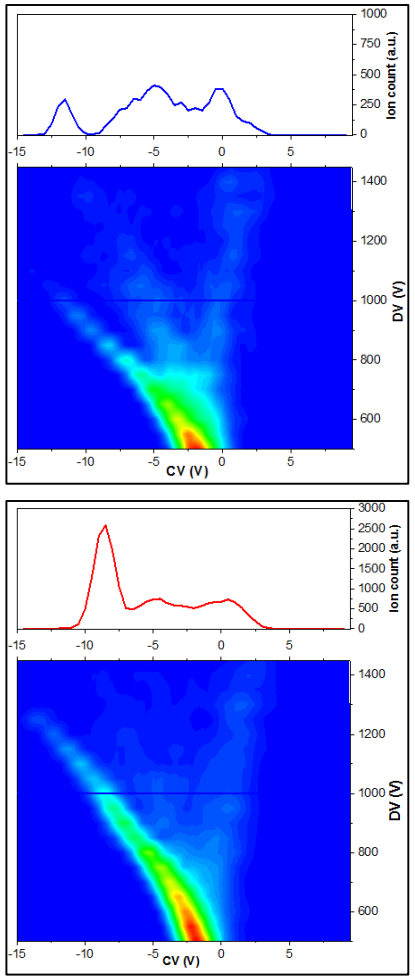




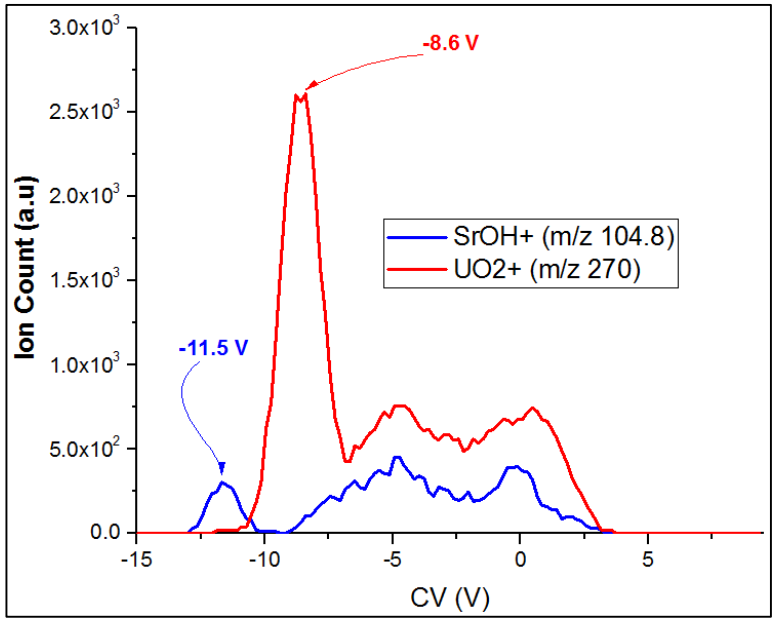
Result

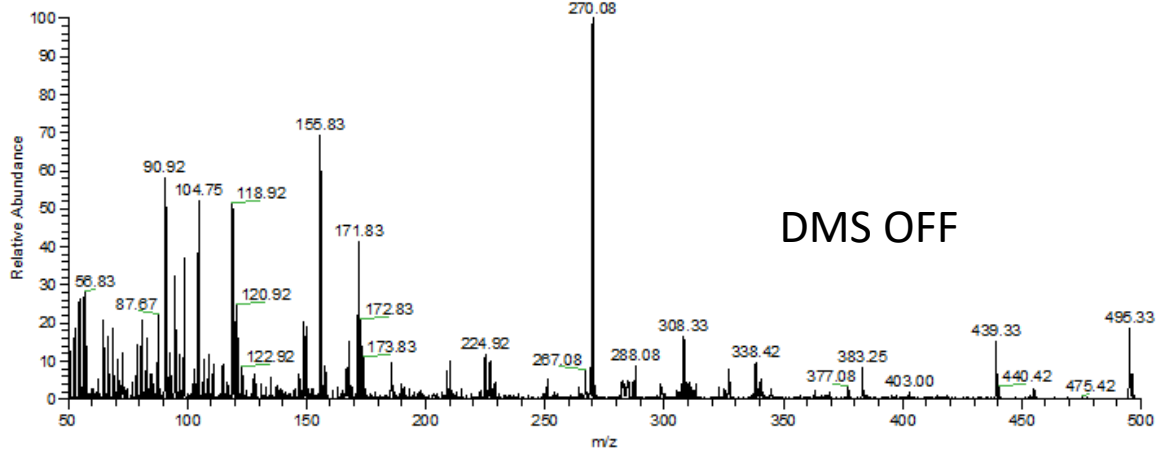
DMS as ion filter

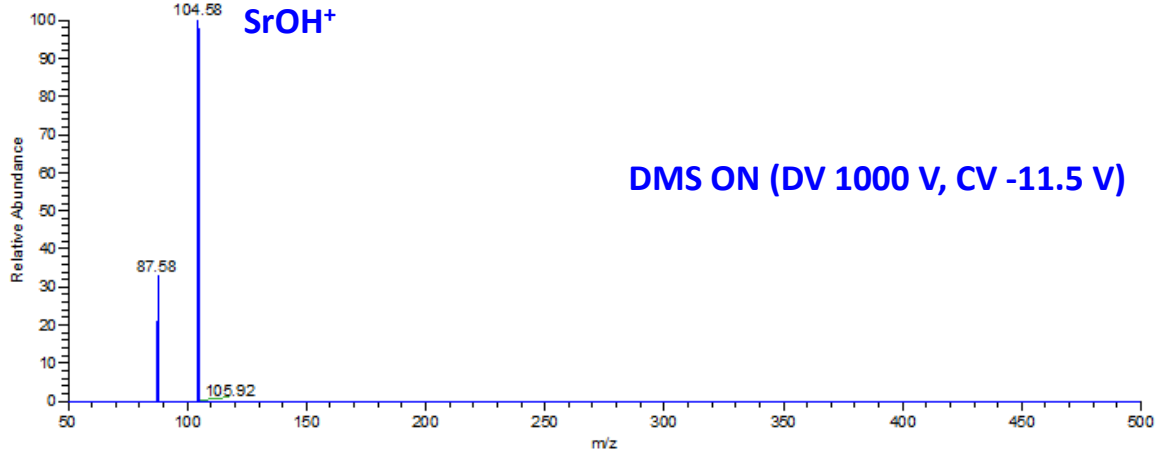
DV Scan 500 – 1450 V, CV Scan -15 to 9.5 V

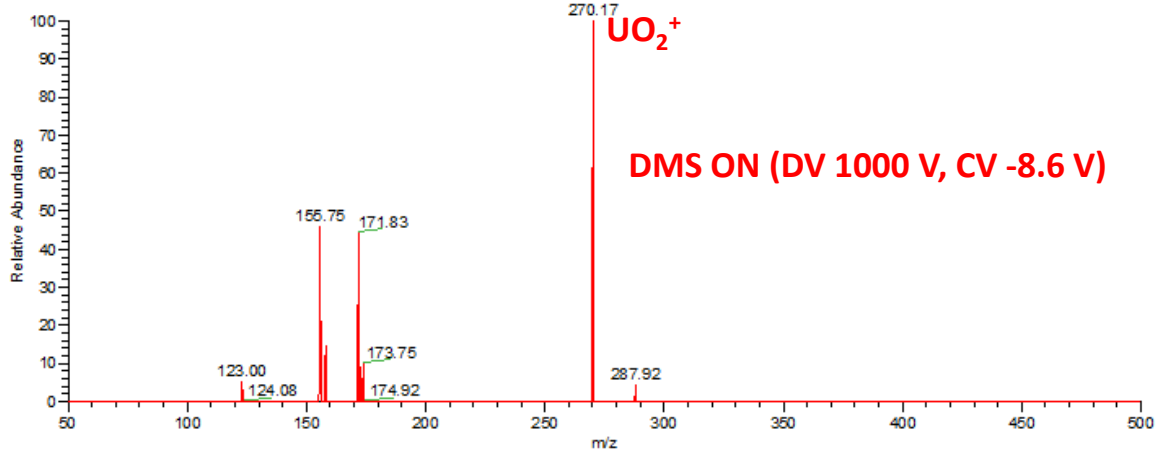


Fixed DV 1000 V, CV Scan -15 to 9.5 V





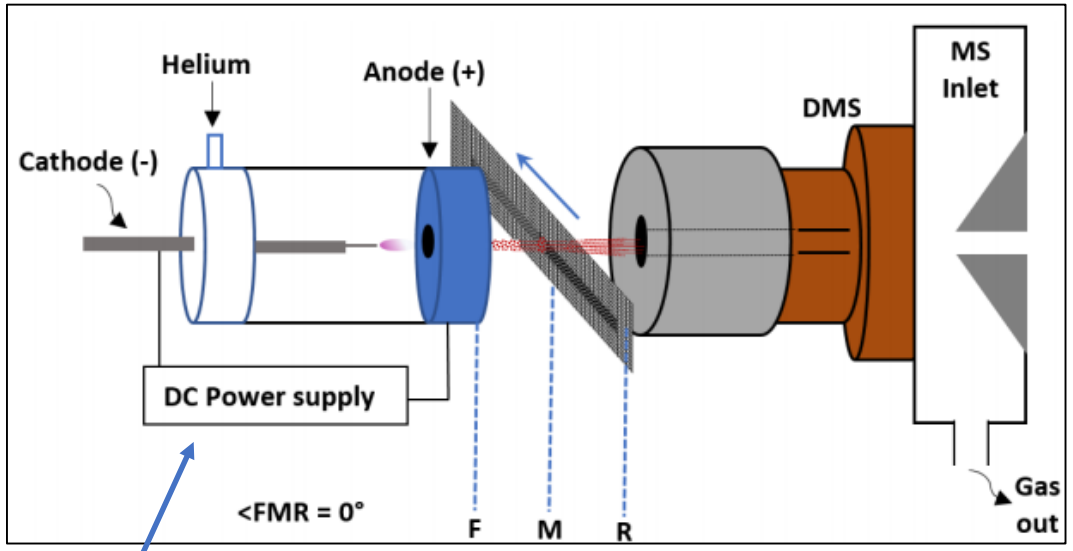




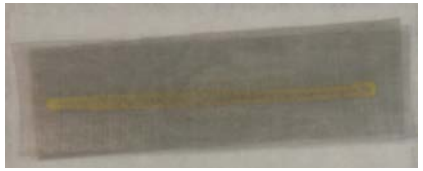
Result

Uranium Isotopy measurement

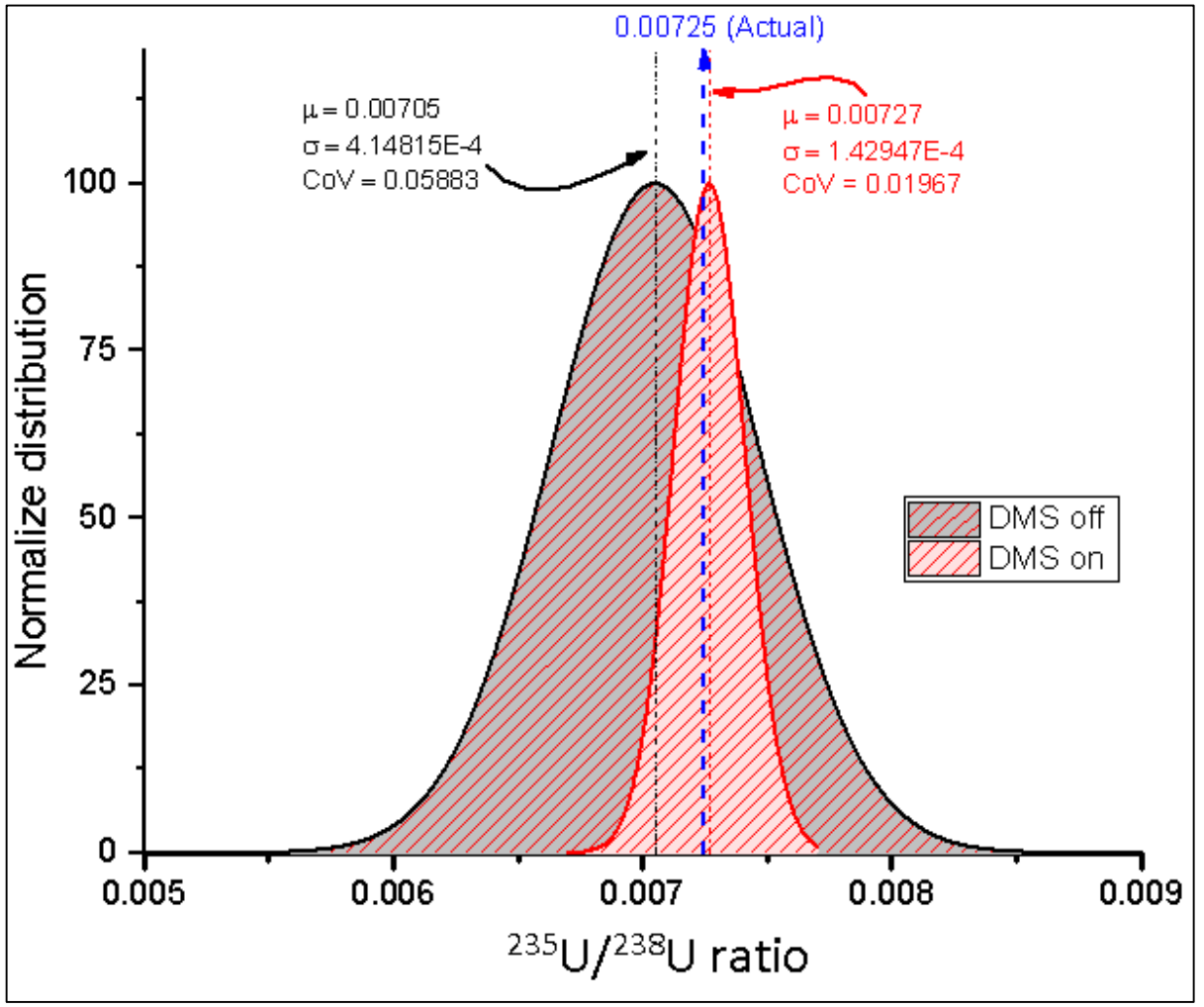
Previous work using FAPA-DMS-MS Orbitrap



Flowing Atmospheric Pressure Afterglow (FAPA)



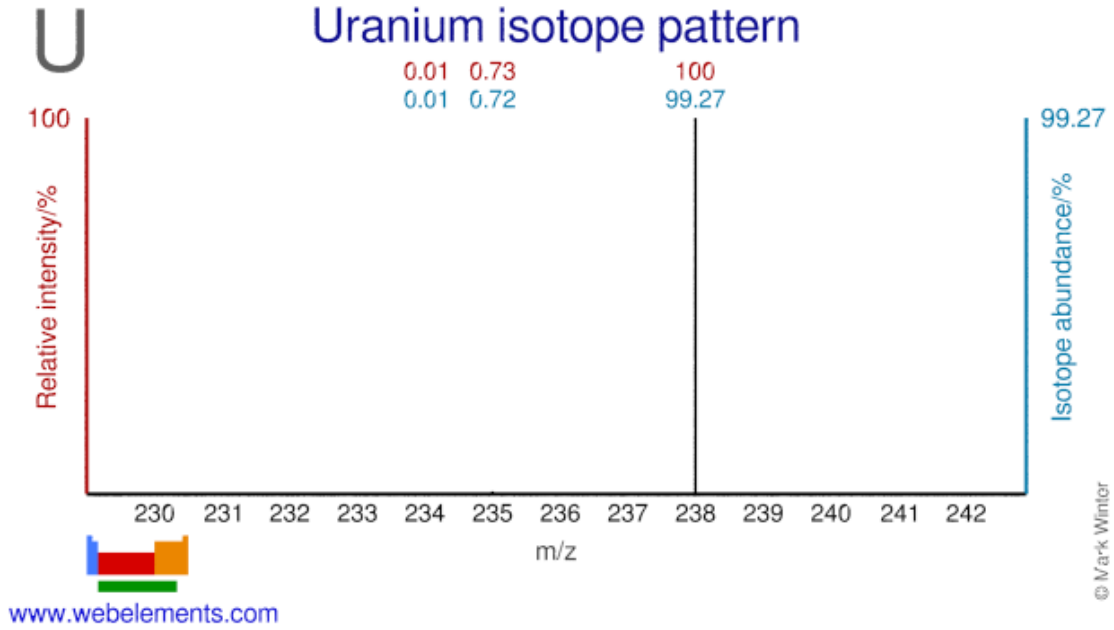
SS-mesh with 5 x 20uL $UO_2(AcAc)_2$ solution



Normal distribution curves of $^{235}U/^{238}U$ ratio at DMS off and DMS on (DV =1100 V and CV = -1.06 V); MS-MS at hcd 50 eV.

Result

Uranium Isotopy with DMS-trap MS



Initial challenges encountered.

1. Low y-axis resolution.

Naturally, Uranium main isotopes are:

^{235}U = 0.720% & ^{238}U = 99.274% (stable isotope).

2. Low x-axis resolution on trap analyzer

Solution ✓

1.

- Increase MS maximum injection time and microscan
- Short m/z range to increase ion trap capacity
- Increase concentration.

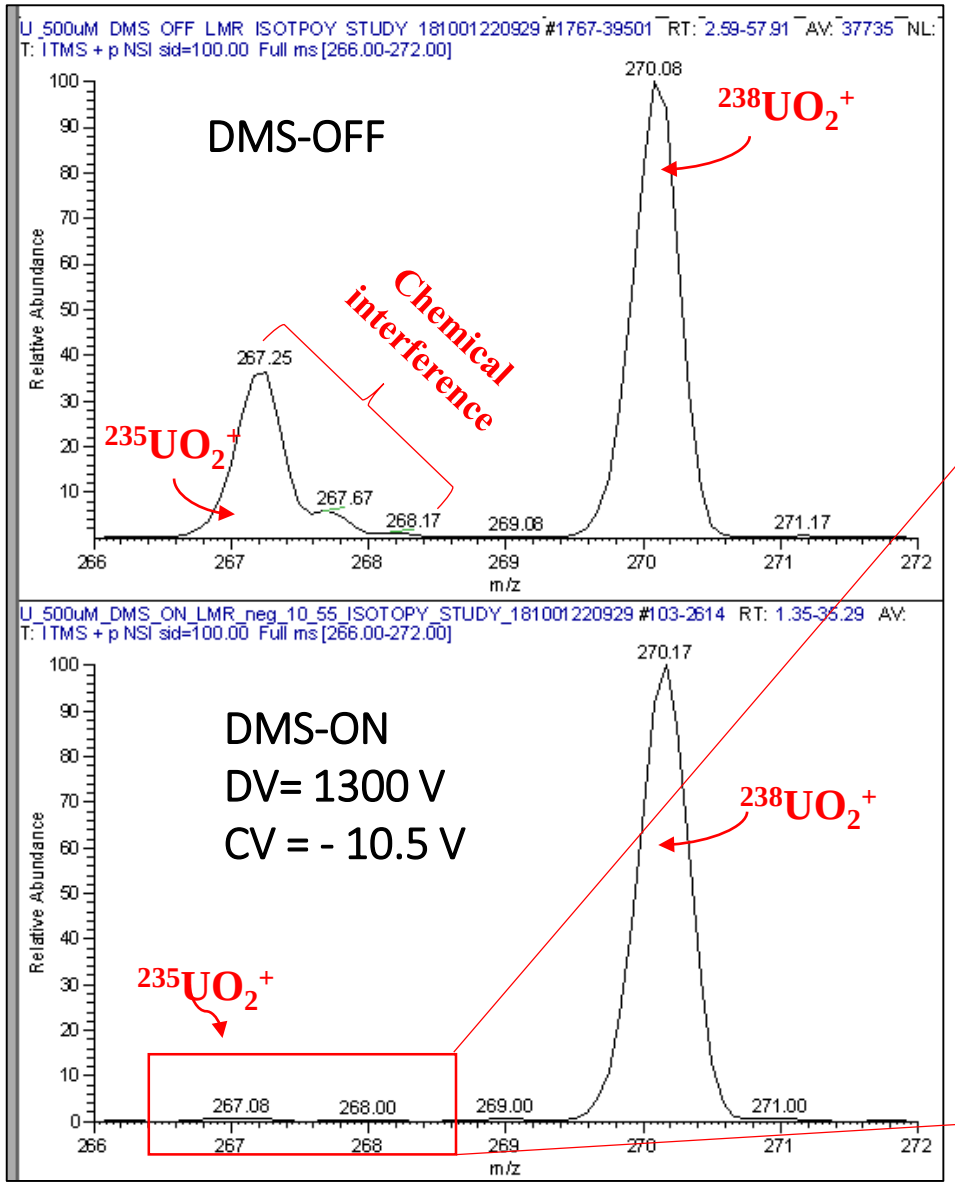
2.

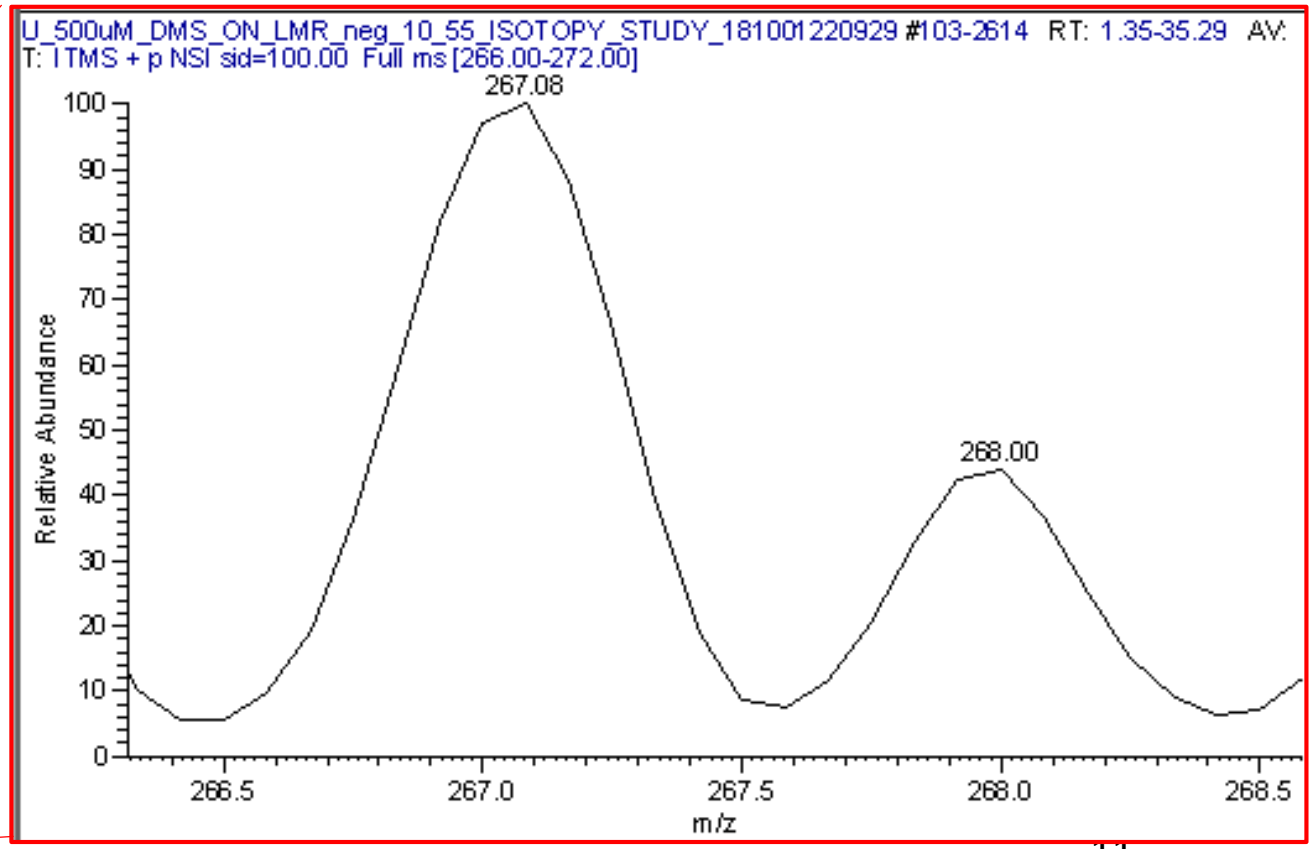
- DMS capable of filtering out interfering chemical noise

Result

$^{235}UO_2^+$/ $^{238}UO_2^+$ ratio

	Average	SD
DMS OFF	0.349335	0.061379
DMS ON	**0.007077**	0.006768





Summary

- DMS is capable of filtering selected metal ions in an ambient environment in order of milliseconds.
- DMS can be used for **sample pre-concentration** prior to further analysis.
- DMS coupled to trapped based mass analyzer can be deployed on the field for isotopy ratio analysis of Uranium

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euroHEMS 2018 student award