Rapid isotopy measurement of Uranium with Differential mobility spectrometry- Mass Spectrometry (DMS-MS)

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Introduction

Isotopy ratio (IR) analysis application has spanned beyond ecological process and archeological dating and is now widely used in nuclear forensics. The threat to human life associated with radionuclear materials requires a high throughput and rapid analytical technique for detection. Isotope ratio mass spectrometry (IRMS) – with magnetic sector analyzers is conventionally employed for IR measurement. Size, weight, and power (SWP) requirements and laborious and time-consuming sampling and analysis are concerns for the lab-based instrument.

With the heterogeneous nature of radionuclides and fission products, Differential Mobility Spectrometry (DMS) is a promising, rapid and portable analytical technique for ion prefiltration prior to MS analysis.

In earlier studies, we have demonstrated the DMS-MS hybrid for metal speciation and differentiation from chemical interferences. Herein, DMS is coupled to a linear ion trap MS for separation of uranyl ion from fission products and further IR analysis.

Why DMS-MS for Isotopy measurement?

- Portable
- Fast
- Simple sampling
- High Throughput:
  - Reduced chemical interference, High S/N ratio
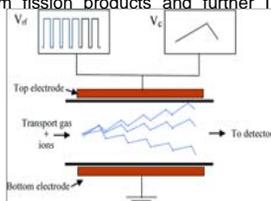 - Improved selectivity & sensitivity

Figure 1. Concept of differential mobility spectrometry.[2]

Methods

DMS methods: As shown in Figure 2, a planar DMS cell was custom-machined from a Vespel® SP-1 polyimide. The cell comprises two planar electrode with surface dimensions of 15.0 x 4.0 mm and separated by a 0.5 mm spacing to define the flow channel. Using the MS's vacuum pull, the transport gas flow through the DMS drift region was maintained at a 0.65 LPM flow rate.

The rf and dc potential, termed the dispersion voltage (DV) and compensation voltage (CV), respectively, were supplied to the electrodes by commercial Sionex electronic hardware. The electronics software is capable of supplying DV ranges from 500 to 1500 V_{p-p} and CV ranged from -50 to +15 V at configurable rates. Here, we employed scan rate of CV 0.416 V/sec. However, a DV and CV scan method was achieved in ~ 5 minutes to obtain a full dispersion plot.
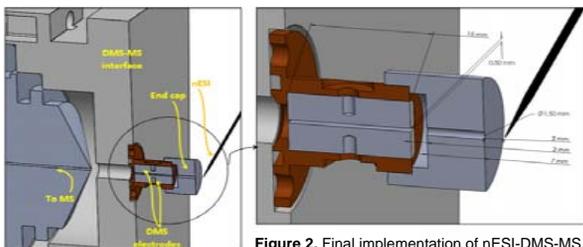
Figure 2. Final implementation of nESI-DMS-MS.

Methods

nESI- DMS-MS:
As shown in figure 3, the end cap guide ion into the DMS region. The potential was optimized to enhance transmission of positive ions. The DMS-MS interface (with a resemblance to the commercial DART vapor interface) was employed to couple the DMS cell to the front end of a commercial Thermo LTQ XL MS (figure 2)

Sampling:
For a reproducibility study of the DMS, 20 mM uranyl acetate was prepare in methanol solution.

Each from a 1000 ppm standard stock solution, mixtures of $UO_2(NO_3)_2.6H_2O$ and Sr $(NO_3)_2$ at 4 µM concentration each were prepared in methanol.

For IR measurements, a 1000 µg/mL certified reference material (CRM) of U_3O_8, 500 µg/mL was prepared.

All samples were nanosprayed at a flow rate of 1 µL/ min.

Data acquisition:
Data acquired on Thermo Xcalibur software were exported and synchronized using the Sionex Expert scanning method using Excel programming. CV, DV, and extracted ion signal were further processed to obtain differential mobility (DM) spectra. Full dispersion plots were processed by OriginPro 2015.
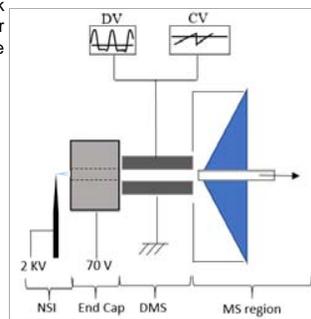
Figure 3. Schematic of the nESI-DMS-MS setup.

Results

DMS reproducibility study.
From a uranyl acetate solution, with a fixed DV 1200 V and CV scan -15 to +9.5 V, DM spectrum of UO_2^+ extracted ion signal was obtained at different CV rates as shown in figure 4. Each repeated dispersed ion peak was filtered out at CV ~10 V.

For each scan duration, twenty trials were obtained and the average area under curve (AUC) for twenty peaks plotted against scan duration to obtain the DM calibration plot as shown in figure 5.
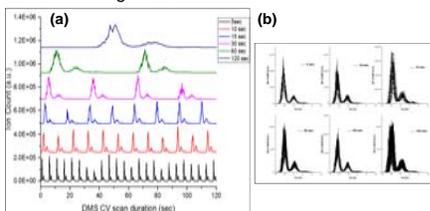
Figure 4. At DV 1200 V DM-spectrum of uranyl ion at fixed DV and different CV scan (-15 – 9.5 V) rates. (b) DIP filtered out at CV ~10 V
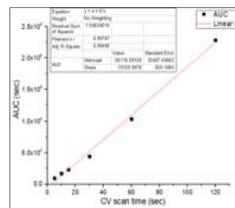
Figure 5. Plot showing linearity of UO_2^+ ion AUC as the CV scan increases
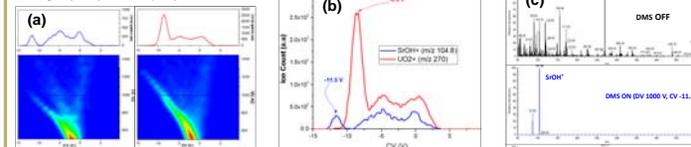
Results

DMS for ion filtration

Figure 6. (a) Dispersion plot of the extracted ion of SrOH+ and UO2+; (b) DM Spectrum of the ionic species at fixed DV of 1000 V and (c) corresponding mass spectrum at DMS OFF and DMS ON at ions DV and CV combination.
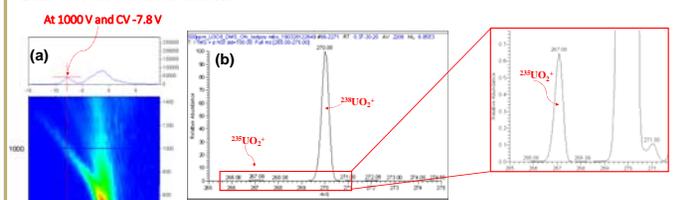
DMS for IR measurement

Figure 7. (a) Dispersion plot of the extracted ion of UO_2^+ from CRM of U_3O_8 for isotopy analysis (b) Mass spectrum data at a fixed DV 1000V and CV -7.8 V for 30 minutes.

	Average	SD	% Error
DMS OFF	0.0091	0.000595	0.26 %
DMS ON	0.0071	0.000497	0.02%
ACTUAL (CRM)	0.0073		

Conclusions

❖ DMS is capable of filtering uranyl ions from fission products like strontium.

❖ DMS can be used for **sample pre-filtration** prior to further characterization.

❖ **DMS** coupled to an **Ion Trap MS** - the most common portable MS, demonstrated a potential capability for isotopy ratio analysis in the field.

Future Directions

- IR measurement of certified reference materials using comparative methods
- Study of temperature and humidity effects on the performance of DMS separation.
- Development of simplified, non-proprietary COTS electronics to achieve and extend the applied RF waveforms across higher E/N values.

Acknowledgements

References

1. Manolakos, S.; Sinatra, F.; Albers, L. N.; Hufford, K.; Alberti, J.; Nazarov, E. G.; Evans-Nguyen, T. *Anal. Chem.* **2016**.
2. Ayodeji, I.; Vazquez, T.; Bailey, R.; Evans-Nguyen, T. *Anal. Methods* **2017**
3. Ayodeji, I.; Vazquez, T.; Song, L.; Donovan, J.; Badal, S. P.; MacLean, G. M.; Shelley, J. T.; Evans-Nguyen, T. , *Int. J. Mass Spectrom.* **2019**.