Pre-filtration of Transition Metals in Differential Mobility Spectrometry

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Introduction

For on-site screening of radiological debris for defense applications, rapid separation of inorganic mixtures is important. Conventional sample preparation and separation techniques are laborious but crucial for elemental analysis. Differential Mobility Spectrometry (DMS) also known as field asymmetric ion mobility spectrometry (FAIMS) is a powerful analytical technique for the gas phase differentiation and separation of ions based on the mobility under the influence of differential high and low electric field at or near atmospheric pressure. In contrast to other separation methods, it filters ion in the order of milliseconds.

Earlier work had been reported on the implementation of DMS for nano-sprayed inorganic salt solutions comprised of stable analogs, as substitutions for radioisotopes.[1,2] A complication associated with the introduction of sprayed ionization techniques is that the mechanism of the atomic ion-solvent cluster formation is yet to be fully understood, likely due to poor control of conditions between the source and the DMS. The separation and mobility behavior of ions partly depends on the dynamic nature of clustering/declustering conditions. Thus, an antechamber (Figure 1) is implemented herein to regulate ion conditions prior to the DMS inlet.

Here, we focus on the analyses of neighboring transition metals while investigating the dynamic behavior of ion- cluster formation as they drift through the DMS. While nano-electrospray (nESI) source will be employed for our baseline ionization technique, we will explore other Atmospheric Pressure Ionization (API) sources such as plasma ionization and laser desorption ionization.
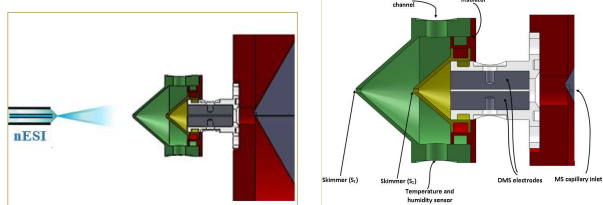

Figure 1. Schematics of nESI-DMS-MS set-up (left) and detailed view (right)

Principle of Differential Mobility Spectrometry

The separation capability of DMS depends on the field strength (E/N); which is the ratio of E (electric field) to N (gas density). At higher values of E/N above 40 Townsend unit (1 Td = 10^{-17} V·cm²), the mobility is no longer constant but becomes field dependent. This was based on the experiment of Mason and McDaniel [3] and the simplified equation can be represented as:

$$K(E/N) = K(0)[1 + \alpha_{eff}(E/N)]$$

As ions drift through the gap between the upper and lower parallel plate electrodes of the DMS cell simultaneously under the influence of influence of the transport gas flow and asymmetric radio-frequency electric field waveform (Figure 2a), they assumed A, B and C- type behavior (Figure 2b) described by the "effective alpha parameter"(α_{eff}). When $\alpha_{eff}(E/N) > 0$, the mobility coefficient ($K(E/N)$) of the ion-neutral increases with field strength, attributed to a clustering/ declustering model and described by "A-type" behavior. Conversely, when $\alpha_{eff}(E/N) < 0$, the behavior is explained by a hard sphere model and described as "C-type" behavior. When α_{eff} $(E/N) \sim 0$, the of the ions correspond to behavior switching from A-type to C-type behavior.
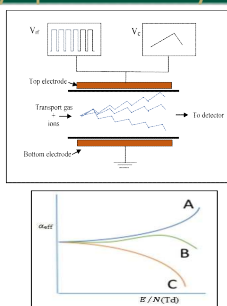

Figure 2. (a) Concept of differential mobility spectrometry. (b) effective alpha parameter $\alpha_{eff}(E/N)$ plot describing ion behavior under the influence of electric field.

Methods

API source
nESI: 2 kV was generated by the high voltage source of the commercial MS (Thermo LTQ-XL) and supplied to a coated,10 μm PicoTip emitter (Figure 3) inserted into a static NSI probe. The probe assembly adopted allow flexible X,Y, Z alignment of the NSI source ensuring ion transmission into the reaction chamber. ICP-MS grade transition metal standards (1 μg/mL) in 50/50 acetonitrile/ water mixture were infused at 1 μL/ min.
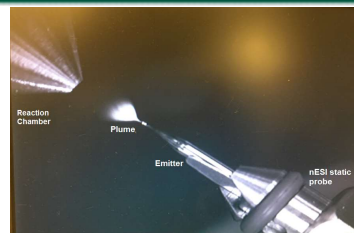

Figure 3. Nanosprayed jet plume as it exit the emitter tip into the reaction chamber.

Reaction Chamber
The reaction chamber is comprised of two skimmer (S_1 and S_2) separated by 10mm space. The voltage drop (ΔV) across the skimmer (not critical) is set between 50 to 100 V. The reaction chamber was designed to accommodate hot Nitrogen gas with/without a modifier vapor and the sensor probe to monitor the temperature within the chamber in real time.

DMS methods
A planar DMS cell custom-machined from a Vespel® SP-1 polyimide features two 15-mm long and 4-mm wide aluminum separated by 0.5 mm gap (Figure 2). The transport gas flow through the DMS cell was set at ~ 1.2 L min⁻¹ maintained through an independent pump. The V_{rf} and V_c potentials are supplied by commercial Sionex electronic hardware and software to generate the 1.20 MHz V_{rf} in the range of 500 – 1500 V while V_c scan range from -45 V to 10 V. A 50 V offset voltage was supplied to the reaction chamber and DMS electrodes while the MS capillary inlet voltage and temperature is 50V and 200°C.

Data acquisition from Xcalibur was synchronized manually with the Sionex Expert software. Extracted ion signal data from full dispersion plot experiments were processed using Labview 2013 and OriginPro 2015.

Results

Results
A transparent mode (DMS – off) analysis was performed on sprayed 1 μg/mL of mixtures of first six ICP-MS grade transition metal standards. A full mass spectrum is shown in Figure 4. In the transparent mode, the Nitrogen flow rate and LTQ "in source fragmentation" voltage were optimized to 0.1 LPM and 100 V for high transmission and ionization of bare metal species respectively.
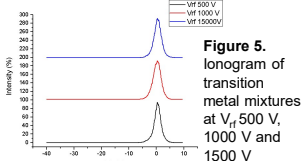

Figure 5. Ionogram of transition metal mixtures at V_{rf} 500 V, 1000 V and 1500 V
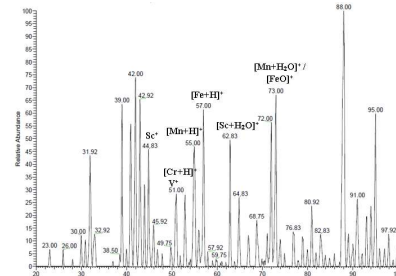

Figure 4. Mass spectrum of transition metal standard obtained in transparent mode (DMS-off)

Initial screening of the mixture was accomplished at fixed V_{rf} while V_{rf} while V_c scan was done in the range -40 to +9.5 V in 2 minutes (scan rate ~ 0.416 V_c/sec). The ionogram at 500 V, 1000 V and 1500 V is shown in figure 5.

Results

Sprayed ionization techniques coupled to DMS require a heated desolvation region. In this study, the nitrogen transport gas is heated to desolvate ions before entry into the DMS field . Thus, the influence of solvent-ion interaction on the separation of ions is minima. At 0.1 LPM nitrogen flow, the maximum temperature achieved in the interior part of the reaction chamber is 42 °C which is too low to desolvate the ions. A flow versus temperature/ ion intensity curves (Figure 6) was plotted to validate the optimum Nitrogen flow that will desolvate and also serve as transport gas.
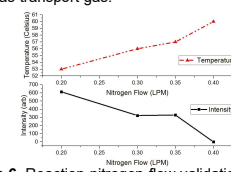

Figure 7. New reaction chamber design.
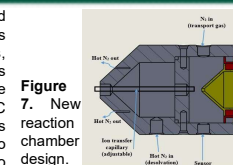
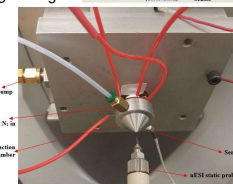

Figure 6. Reaction nitrogen flow validation

Figure 8. nESI-DMS-MS set-up

Conclusions

The filtering of transition metal cations is demonstrated at zero compensation voltages through the DMS cell indicates the viability of our DMS system for post-ionization separation. With the current configuration, separation of the metal species is not feasible. Therefore, the incorporation of a dopant is anticipated to facilitate DMS separation but introduced independently from the ionization source. Thus, we believe that the redesigned reaction chamber (figure 7) suffice while fully in control of the ion+ transport gas flow dynamics as it drift DMS region.

Future Directions

- In order to achieve an efficient heating of the reaction chamber and flexible transport gas control through the DMS cell, a re-designed reaction chamber will be machined.
- We will employ a calibrated vapor generator and sensor to control and monitor the DMS carrier gas humidity respectively. This shall help to thoroughly monitor and control the ion-cluster formation in real time.
- Simulated fluid dynamic modeling of gas transport supported by ion transport models through SIMION will be correlated with the controlled nESI experimental data obtained from the dispersion plot. This will be translated to their effective alpha parameters for comparison.
- We will pursue assembly of simplified, non-proprietary COTS electronics to achieve higher E/N values and thereby extend the understanding of cluster behavior from hydration energies.
- Other solventless API source will be explored for DMS filtration of inorganic species.

Acknowledgements

References

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2. Manolakos, S.; Sinatra, F.; Albers, L. N.; Hufford, K.; Alberti, J.; Nazarov, E. G.; Evans-Nguyen, T. *Anal. Chem.* **2016**.
3. Mason, E. A.; McDaniel, E. W. *NASA STIRecon Tech. Rep. A* **1988**, *89*.