Coupling of Flowing Atmospheric Pressure Afterglow and Differential Mobility Separation toward Fieldable Post-Detonation Debris Analysis by Mass Spectrometry

Ifeoluwa Ayodeji *; Timothy Vazquez, Linxia Song*; Ronelle Bailey*; Joanna Donovan* and Theresa Evans-Nguyen *

Department of Chemistry, University of South Florida, Tampa, FL*

Jacob T. Shelley **

Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, NY**

Introduction

For nuclear forensics and other defense applications, fieldable screening technologies based on portable mass spectrometers (MSs) require simplified sample-preparation methods, often off of surfaces. For this reason, various direct ambient desorption/ionization (ADI) sampling methods, such as flowing atmospheric-pressure afterglow (FAPA), are of high interest.

Direct sampling may introduce matrix species that interfere with the analyte of interest leading to both false positives and negatives. Differential mobility spectrometry (DMS) is a technology which can provide an additional method of sample clean up, post-ionization. By selectively filtering matrix components, DMS can reduce chemical noise prior to MS analysis and is particularly beneficial for ion-trap style mass analyzers, which comprise the majority of field-portable mass spectrometers.

In our earlier work, d-block metal salt solution mixtures were nano-sprayed to the front end of a DMS cell prior to MS analysis. As a stable analog for radioisotopes, each metal ion was filtered out at certain dispersion voltage (DV) and compensation voltage (CV) combinations in the order of milliseconds.[1,2] We have also implemented coupling a solvent-less and plasma-based ADI; Direct analysis in Real Time (DART) with DMS.[3] This hybrid was successfully used for the separation of drug mixtures.

Herein, we explore coupling a FAPA desorption/ionization source with DMS for ambient sampling of inorganic compounds. Furthermore, we study the use of complexation reagents to enhance selectivity of this method. Ultimately, simplified sample preparation employing a FAPA-DMS hybrid may dramatically improve selectivity for fieldable mass spectrometers.
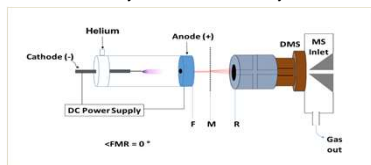

Figure 1. Schematic of the FAPA-DMS-MS setup. The angle between the FAPA, mesh and reaction chamber inlet (R) is at 0° while |FM| = 8 mm and |MR| = 7 mm. b) Final implementation.

Methods

FAPA source

As initially implemented by Shelley et al, an atmospheric-pressure glow discharge was formed between a stainless-steel pin cathode and a brass plate anode held in place by a quartz discharge chamber with an electrode gap of ca. 7 mm (Figure 1 and 2).[4] A 1.6-mm hole in the anode plate allowed discharge species to enter the atmosphere and, thereafter, interact with analyte deposited evenly on the mesh (M).

The glow discharge was sustained at currents between 5 and 10 mA, and voltage of ca. -550 V, with a custom-built high-voltage power supply (Prosolia Inc., Indianapolis, IN).[5] To obtain steady signals from samples during the collection of dispersion plots, an initial optimization of helium flow rate was accomplished. At 1.0 LPM, a stable signal was achieved at ~ 3 min when sample were desorbed/ consumed on a single spot of the sampled mesh as shown in figure 3.

To further produce a stable signal, evenly applied sample was scanned orthogonally in a continuous fashion through the afterglow of the FAPA at a rate of 0.2 mm s^{-1} with a one-dimensional translation stage.
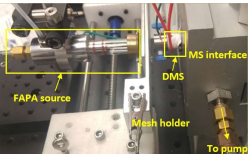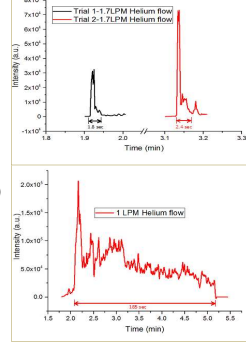

Figure 2. Final implementation of FAPA-DMS-MS.

Figure 3. Intensity stability rate of Co[(AcAc)$_2$+H]$^+$ at 1.7 LPM (a) and 1.0 LPM (b) Helium flowrate.

Methods

DMS methods

The operational scheme of the DMS is depicted in Figure 3. A planar DMS cell was custom-machined from a Vespel® SP-1 polyimide. The cell employs two rectangular stainless-steel electrode surfaces with dimensions 15.0 x 4.0 mm and separated by a 0.5 mm gap (G) to define the flow channel. An ~1.2 L min^{-1} transport gas flow was maintained externally by a pump and flowmeter. The 1.20 MHz radio-frequency dispersion voltage (DV) and compensation voltage (CV) potentials are supplied and controlled by the commercial Sionex electronic hardware and software. DV ranged from 500 to 1500 V$_{p-p}$ and CV ranged from -50 to +15 V. A fixed DV and CV scan was achieved in 2 min while a full dispersion plot was achieved in 5 min (scan rate ~ 0.416 V/sec).

MS method

Mass spectra were acquired with a commercial LTQ XL linear ion-trap mass spectrometer. It was optimized to accommodate the combination of the home-built FAPA source interfaced to DMS. Key instrument parameters were as follows: inlet capillary temperature at 200 °C; capillary voltage at 15 V; tube lens voltage at 80 V; source fragmentation energy after the skimmer at 0 V; m/z scan range of 50 to 500; microscan at ~ 8.4 Hz with maximum injection time of 10 ms; the automatic gain control (AGC) turned on.

Sampling

100 µL of neat 0.05 mg/mL Co(AcAc)$_2$, 1 mg/mL of Ni(AcAc)$_2$, and 50/50 v/v mixture of both were prepared in acetonitrile from solid complexed metals, and deposited evenly on the stainless steel sampling mesh.

Data acquisition

Data obtained from Thermo 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.
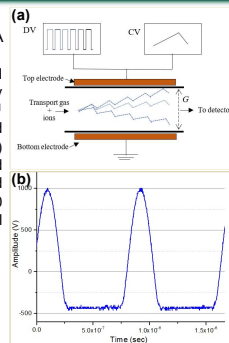

Figure 3. a) Concept of differential mobility spectrometry. b) A typical DMS electronics DV scan output signals obtained from the oscilloscope.

Results

A transparent mode (DMS voltages – off) analysis was done on the sample solution mixtures to obtain all peaks of interest. A full mass spectrum is shown in figure 4. For a neat 100 µL volume Co(AcAc)$_2$, the capability of DMS as ion pre-filter is notably observed as shown in figure 5. In 5a), Protonated acetylacetonate ion {[(AcAc)+H]$^+$; m/z =101} dispersed ion peaks (DIP) were filtered out from the residual ion peak (RIP) at DV < 1000 V. In contrast, for [Co(AcAc)$_2$]$^+$ with m/z = 257, the DIP produces a distinct separation from its RIP at higher DV field as shown in figure 5b. The mass spectrum of the filtered [Co(AcAc)$_2$]$^+$ ion is shown in figure 6.
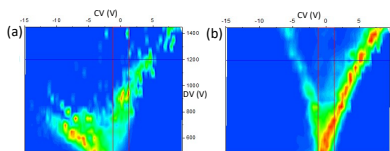

Figure 4. FAPA- DMS Mass Spectrum of all Co(AcAc)$_2$ and Ni(AcAc)$_2$ mixtures in DMS transparent mode

Figure 5. a) Dispersion plot of [(AcAc)+H]$^+$; m/z =101. b) [Co(AcAc)$_2$]$^+$; m/z =257
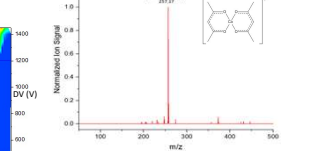

Figure 6. Neat mass spectrum of Co(III) at fixed DV 1200 V and CV -4.5 V

Results

At a single V$_{rf}$ 1200 V monitoring, the dispersed extracted ion of [Co(AcAc)$_2$]$^+$ and [Co(AcAc)$_2$+H]$^+$ representing Co(II) and Co(III) ions respectively is shown in figure 7. A notable separation of the two-oxidation state establishes the performance of DMS as a viable analytical tool for metal speciation.
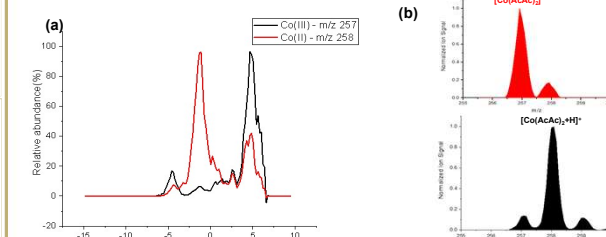

Figure 7. a) Extracted ion chronogram of Co(III) and Co(II) ion at DV 1200 V. They are transmitted at V$_c$ -4.5 V and -1.1 V respectively. b). Zoomed mass spectrum of Co(III) at CV -4.5 V (top) and Co(II) at CV -1.1V (bottom)

Conclusions

The data presented reveals the first integration of a FAPA ionization source with DMS, which together have potential for portable screening applications. The combined gas phase ion production and pre-filtration of complexed metals of neighboring masses: Cobalt(II)acetylacetonate and Nickel(II)acetylacetonate occurs within 15 seconds comprising a complete CV scan. The ability to separate selected ions is promising for metal speciation. Further investigation of this technique will focus on potential on-site screening of radio-nuclear debris and environmental contaminants.

Future Directions

- Optimizing FAPA ionization source for bare metal salts for d- and f-block elements
- Exploring on-line synthesis of gas phase metal from solid to enhance plasma-based ionization of inorganics.
- Introduction of dopants to enhance ion-neutral interactions, hence improving DMS separation.
- 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. Sinatra, F. L.; Wu, T.; Manolakos, S.; Wang, J.; Evans-Nguyen, T. G. Anal. Chem. 2015, 87 (3), 1685–1693.
2. Manolakos, S.; Sinatra, F.; Albers, L. N.; Hufford, K.; Alberti, J.; Nazarov, E. G.; Evans-Nguyen, T. Anal. Chem. 2016.
3. Ayodeji, I.; Vazquez, T.; Bailey, R.; Evans-Nguyen, T. Anal. Methods 2017
4. Shelley, J. T.; Wiley, J. S.; Hieftje, G. M. Anal. Chem. 2011, 83 (14), 5741–5748.
5. Badal, S. P.; Michalak, S. D.; Chan, G. C.-Y.; You, Y.; Shelley, J. T. Anal. Chem. 2016, 88 (7), 3494–3503.