

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

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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 sampling methods, such as flowing atmospheric-pressure afterglow (FAPA), are of high interest. However, with such direct sample introduction, matrix from ambient chemicals may introduce interferences 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 post-ionization separation. Such filtering reduces interferences for ambient sample inlet MSs and is particularly beneficial for ion-trap style mass analyzers, which comprise the majority of field-portable mass spectrometers. 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 FAPA-DMS may dramatically improve selectivity for fieldable mass spectrometers.

Synthesized metal-acetylacetonate complexes were prepared as 1-mg/mL solutions in acetonitrile. A 100- $\mu$ L sample solution were evenly applied on a mesh substrate (52% transmittance). A home-built FAPA device, employing helium as the discharge gas, was operated between 5 and 10 mA. The sample mesh was positioned in transmission mode and scanned across the path of the afterglow of the FAPA source at a rate 0.2 mm/s to allow a relatively continuous ion source introduction over an extended period (~10 min). A home-built DMS device consisting of two metal electrodes (15.0 mm  $\times$  4 mm) separated by a 0.4-mm gap was fitted to the inlet of a Thermo LTQ XL. The DMS electrodes were powered with an asymmetric RF field using flyback electronics from Sionex that offer dispersion voltages (DV) from 500 to 1450 V and compensation voltages (CV) from -15 V to 9.5 V with a scan rate of 1.667 V/s. An external pump was used to maintain a constant flow of ~1.2 L/min of transport gas through the DMS channel. Ions produced from the sample-containing mesh with FAPA were filtered or transmitted by the

DMS device across a range of DV and compensation CV voltages to characterize ion dispersion. Extracted ion signals obtained from the MS spectra were synchronized with the DMS method to obtain dispersion plots.

In this study, cobalt(II)acetylacetonate and nickel(II)acetylacetonate were sampled neatly, and as mixtures on a mesh substrate. A nominal fixed DV, scanned CV chronogram was obtained within 15 seconds while full dispersion plots were obtained in 5 minutes. From neat Co(II)acetylacetonate, DMS was shown to separate Co(II) ions from the associated Co(III) ions demonstrating a promising means of ion speciation. Additionally, the separation of Co(AcAc)<sub>2</sub> from neighboring Ni(AcAc)<sub>2</sub> of near masses demonstrates that the FAPA-DMS-MS hybrid could be a deployable analytical tool for on-site screening of radio-nuclear debris like uranium, other d- and f-block metals.

Novel Aspect: ambient ionization, rapid sampling, prefiltration and screening of inorganics by FAPA-DMS.