Flowing Atmospheric-Pressure Afterglow Drift Tube Ion Mobility Spectrometry

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Abstract

Here, a Flowing Atmospheric-Pressure Afterglow Discharge (FAPA) is coupled for the first time as a desorption/ionization source to a home-built standalone Drift Tube Ion Mobility Spectrometer (DTIMS). The DTIMS features a Bradbury-Nielsen gate and an axial ion-repeller electrode to facilitate ion introduction into the drift region. Current-voltage behavior of the plasma created in FAPA demonstrates that the plasma belongs to the normal glow region. Ion mobility spectra for different analytes, including 2,6-Di-tert-butylpyridine as a standard, acetone, and acetaminophen, were investigated and their corresponding reduced mobilities calculated. The FAPA source improves the DTIMS as a portable analytical tool and permits the direct desorption and ionization of analytes (solids, liquids, gas).

Introduction

Drift Tube Ion Mobility Spectrometry (DTIMS) is an ion separation technique at atmospheric pressure where ions are separated based on their individual mobilities as they pass though the drift gas under a uniform electric field. DTIMS features excellent detection limits, fast responses, low costs, and portability which allows identification and quantification of trace substances like pharmaceuticals, explosives and environmental toxins. [1]

The ionization source is critical to the performance of DTIMS. Different kinds of ionization sources like radioactive sources, including nickel (^{63}Ni) and americium (^{241}Am), and non-radioactive sources, including corona discharge, low-temperature plasma probe (LTP), and electrospray ionization, have been used in DTIMS. Radioactive sources produce stable and reproducible signals, but ion generation rates are low and result in weak signal intensity and small dynamic range. Corona discharge gives higher ion signal than radioactive sources by about one order of magnitude, but it can typically only be used for gaseous samples and deterioration of signal stability happens due to the erosion of anode tip. Electrospray ionization source is mainly used for liquid samples and requires time-consuming and accurate sample preparation process. LTP has been coupled to DTIMS to directly desorb and ionize samples, however, samples were introduced in the high voltage region which restricts the safe sampling and accessibility. [2]

FAPA uses an atmospheric pressure glow discharge that generates excited species and ions and its effluent is used to directly desorb and ionize the sample (solid, liquid, or gas) with minimal sample preparation, thus it significantly improves the potential of DTIMS as a portable analytical tool. [3]

Here, we coupled FAPA as an ionization source to a standalone DTIMS for the first time. Samples are desorbed and ionized outside the DTIMS high voltage region to ensure safe sampling and accessibility.

Methods: FAPA Source

An atmospheric-pressure glow discharge is sustained between a stainless steel pin cathode and a stainless steel Swagelok tube fitting in a concentric geometry. Inner-electrode distance is 2.5 mm and a glass capillary (L = 4 cm, 1.56 mm i.d.) extends from the anode to direct the plasma reagent species toward the desorption/ionization region. Instead of helium, nitrogen is used as a discharge plasma gas to prevent secondary discharge formation between the FAPA source and DTIMS inlet. Plasma-gas flow rate is set to 750 ml/min, the current to 20 mA and the resulting anode voltage is 635 V. The FAPA source glass capillary is angled 40° relative to sample.

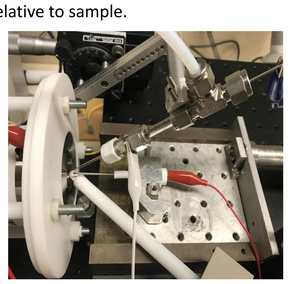

Figure 1. FAPA setup.

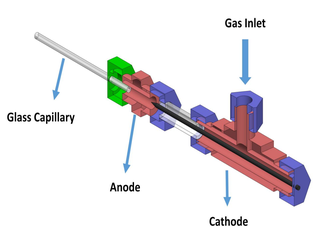

Figure 2. Section view of FAPA.

Methods: DTIMS

The home-made DTIMS is composed of thirteen 10 mm thick stainless steel (SS) rings, separated by 2 mm PTFE rings, stacked together and connected through resistors (1MΩ) to create a uniform electric field. A home-built high voltage power supply was adjusted to 5.4 kV and connected to SS ring at the entrance of the 15.9 cm DTIMS cell to produce an electric field of 340 V/cm. An axial ion-repeller electrode, made up of Tungsten with smoothed tip, was biased to a potential of 10.5 kV to enhance the ion injection into the DTIMS. The Bradbury-Nielsen gate (BNG) is composed of two series of parallel nickel-chromium wires (0.1 mm thickness) with a separation-distance of 0.5mm to create an orthogonal electric field relative to the ion passage. A home-built pulse generator (250 us pulse width at a frequency of 31 HZ) is connected to the BNG to inject the ions into the drift region for separation. An aperture SS grid is placed 1mm from the Faraday plate. The ion current is amplified by a home-built electrometer with a gain of 10^8, that after further amplification is fed to the A/D converter and the resulting ion mobility peak is displayed on the monitor. Dry nitrogen gas (13X molecular sieve) was passed through the DTIMS cell with a flow of 750 ml/min.

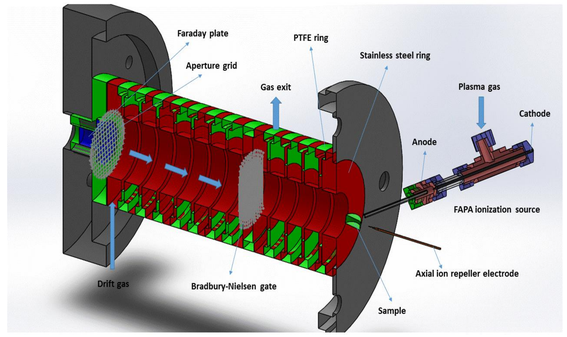

Figure 3. Drift Tube Ion Mobility Spectrometer schematic diagram cross section.

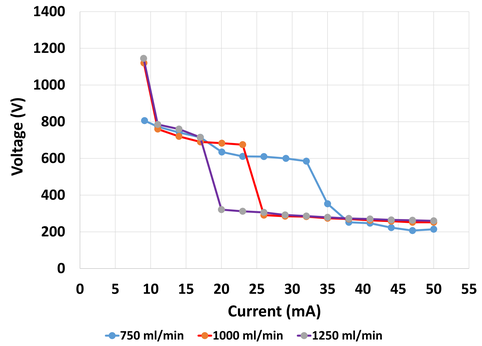

Figure 4. Characteristic current-voltage curve for FAPA.

Results

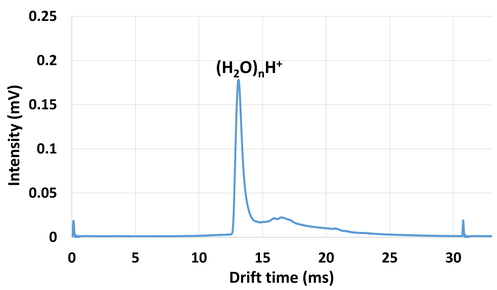

Figure 5. Ion mobility spectrum of reactant ions formed in FAPA source at 12.9ms (no sample).

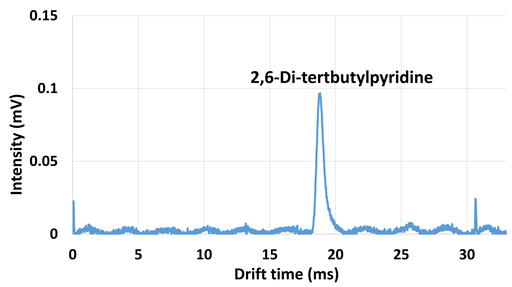

Figure 6. Ion mobility spectrum of 2,6-Di-tertbutylpyridine at 19.1ms

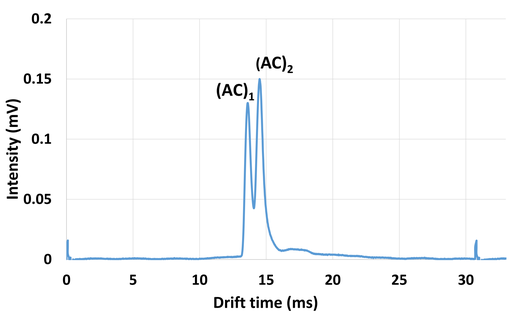

Figure 7. Ion mobility spectrum of monomer and dimer of acetone at 13.8 and 14.3 ms, respectively (AC_1 and AC_2).

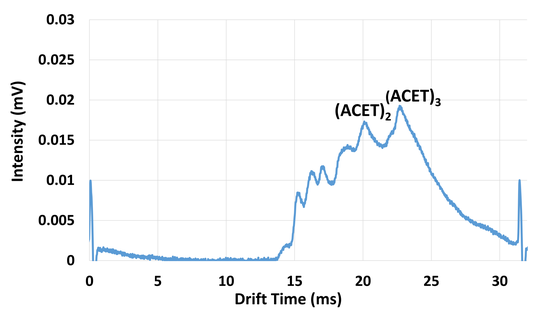

Figure 8. Ion mobility spectrum of dimer and trimer of acetaminophen at 20.1 and 22.5ms, respectively ($ACET_2$ and $ACET_3$

Results

- Figure 4 demonstrates that plasma corresponds to the normal glow region in FAPA. [3]
- Reduced mobility coefficient (K_0) which represents the validity of mobility values was calculated for 2,6 dtBP as a standard according to equation (1) and is well consistent with the literature values. [4]

$$K_0 = \left(\frac{L}{t_d E}\right) * \frac{273}{T} * \frac{P}{760} = 1.41 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \qquad (1)$$

L: Drift region length = 10cm, E: Electric field = 340 V/cm, t_d: Drift time = 19.1 ms, T: Temperature = 297 K, P: Pressure = 760 Torr

- Two intense ion mobility spectra were obtained for acetone with corresponding reduced mobilities of 1.88 cm2 V-1 s-1 for the monomer and 1.95 cm2 V-1 s-1 for the dimer. [2]
- Ion mobility spectra for acetaminophen tablet gives two peaks with corresponding reduced mobilities of 1.34 cm2 V-1 s-1 for the dimer and 1.2 cm2 V-1 s-1 for the trimer. [5] Other observed peaks are pertinent to the sample tablet matrix.
- Reactant ion peaks, mainly clustered hydronium ions, give a reduced mobility of 2.09 cm2 V-1 s-1.

Conclusions

- Successful coupling of FAPA source to DTIMS as a desorption/ionization source and identification of different analytes (solids, liquids, gas).
- Nitrogen plasma gas prevented secondary plasma formation and current-voltage curve demonstrates the normal glow region.
- Reduced mobility coefficient (K_0) calculated for 2,6-Di-tertbutylpyridine agrees with literature values and proves the validity of mobilities observed for analytes.

Future Work

- Systematic optimization of FAPA parameters: plasma gas flow rate, potential, current, angles, distances, etc.
- Obtain figures of merit for various analytes of interest under optimized FAPA conditions.
- Incorporate heating capabilities to the DTIMS to allow increased operating temperature to remove background peaks and reduce memory effect.

References

[1] M. Tabrizchi T. Khayamian, and N. Taj. Design and optimization of a corona discharge ionization source for ion mobility spectrometry. Review of Scientific Instruments 71, 2321 (2000)

[2] Mohammad T. Jafari. Low-Temperature Plasma Ionization Ion Mobility Spectrometry. Anal. Chem. 2011, 83, 3, 797-803

[3] Shelley JT, Wiley JS, Chan GC, Schilling GD, Ray SJ, Hieftje GM. Characterization of direct-current atmospheric-pressure discharges useful for ambient desorption/ionization mass spectrometry. J Am Soc Mass Spectrom. 2009 May, 20(5):837-44.

[4] G. Kaur-Atwal, G. O'Connor, A. Aksenov, V. Bocos-Bintintan, C. L. Paul Thomas, C. Creaser. Chemical standards for ion mobility spectrometry: a review. *Int J Ion Mobil Spectrom* 2009, *12*, 1.

[5] G. A. Eiceman, D. A. Blyth, D. B. Shoff, A. P. Snyder. Screening of solid commercial pharmaceuticals using ion mobility spectrometry. *Anal Chem* 1990, *62*, 1374.

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