

# A Novel Radio-Frequency Ionization Method for the Analysis of Wide Classes of Volatile Organic Compounds

## Organic Compounds

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### OVERVIEW

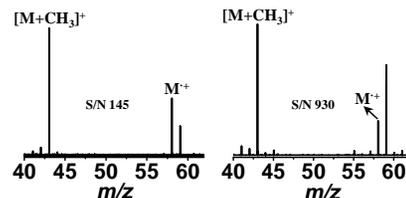
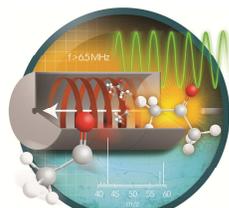
• Results from radio-frequency ionization (RFI)/Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) for analysis of VOCs and semi-volatile organic compounds (1). RFI is a robust and highly sensitive ionization technique (as compared to electron impact ionization (EI)) for VOC analysis (Figure 1). In a previous report, we discussed the details of acetone and poly(dimethylsiloxane) (PDMS) ionization using RFI [1].

• Ion trajectory calculations are used to simulate the experimentally observed side band artifacts in RFI/FT-ICR mass spectra that utilize “off-axis” ICR ion injection.

### INTRODUCTION

Recently, we introduced a novel radio-frequency ionization (RFI) method coupled to FT-ICR MS for analysis of VOCs and semi-volatile organic compounds [1]. RFI is a robust and highly sensitive ionization technique (as compared to electron impact ionization (EI)) for VOC analysis (Figure 1). In a previous report, we discussed the details of acetone and poly(dimethylsiloxane) (PDMS) ionization using RFI [1].

Our aim is to utilize both experimental and theoretical (*viz.*, ion trajectory simulation) approaches and investigate the mechanism(s) of ion generation in RFI. In this presentation, results from RFI of a wide classes of compounds and ion trajectory simulations are presented.



**Figure 1.** (left) EI/FT-ICR and (right) RFI/FT-ICR mass spectra of acetone. The ionization sensitivity (IS) of RFI is higher than the IS of conventionally used 70 eV EI for analysis of VOCs. For example, RFI yielded signal/noise (S/N) ratios roughly six times higher than those generated by EI (70 eV) for ionization of acetone.

**Scheme 1.** Radio frequency ionization (RFI) is a novel ionization technique that we recently introduced for mass spectrometry analysis of volatile and semi-volatile organic molecules.

### METHODS

**Samples:** All of the standard VOCs used in this study were purchased from Sigma (Sigma-Aldrich, St. Louis, MO) and used without further purification.

A 20- $\mu$ L volume of each of the standard VOC samples was transferred into a sealed glass vial. The headspace from each VOC standard (at room temperature) was then transferred into a heated ( $\sim$ 200  $^{\circ}$ C) expansion reservoir and subsequently introduced into the FT-ICR vacuum chamber through a heated ( $\sim$ 200  $^{\circ}$ C) transfer line and a pulsed-valve ( $\sim$ 120  $^{\circ}$ C).

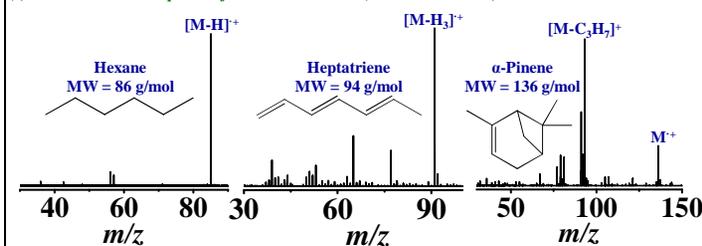
**RFI:** The radio-frequency signals for RFI was generated using a home-built RF power supply. [2] Optimized RF signal at 6.5 MHz ( $\sim$ 200  $V_{b,p}$ ) was applied to the quadrupole ion guide (QIG) rods for 200 ms.

**FT-ICR MS:** RFI/FT-ICR mass spectra were acquired with an IonSpec FT-ICR mass spectrometer (former IonSpec Corp. - now a division of Agilent Technologies, Santa Clara, CA) equipped with a 9.4 tesla superconducting magnet (Cryomagnetics Inc., Oakridge, TN). The RFI-generated ions were trapped in the ICR cell for 1 s and subsequently excited (4 ms) using a dipolar frequency sweep excitation prior to detection in broadband mode. Fourier transformation of the acquired time-domain signals (128 k data points) with one zero fill and Blackman window apodization followed by magnitude calculation and frequency-to- $m/z$  conversion yielded the RFI/FT-ICR mass spectra shown in Figures 1, 2, 3, and 4.

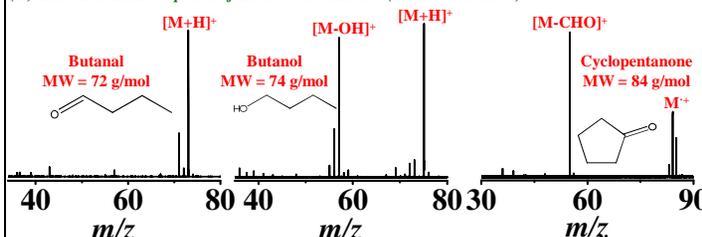
**Simulations:** Ion trajectory simulations were performed using SIMION 8.1 (Scientific Instrument Services, Inc., NJ) on a 2.5 GHz Pentium 4 PC with 1.25 GB RAM (Dell, Inc., Round Rock, TX). ICR cell and quadrupole ion guide (QIG) dimensions/positions for SIMION simulations (Figure 5) were kept identical to experimental conditions (Figure 4).

### RESULTS

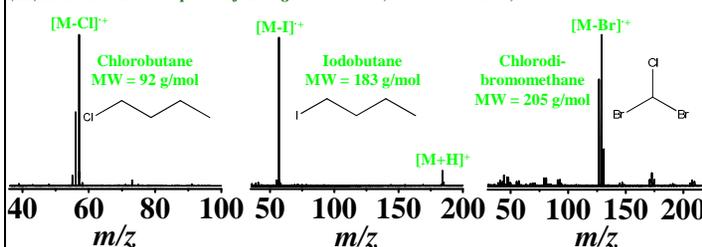
#### (I) RFI/FT-ICR Mass Spectra of Alkanes & Alkenes (Positive-Ion Mode)



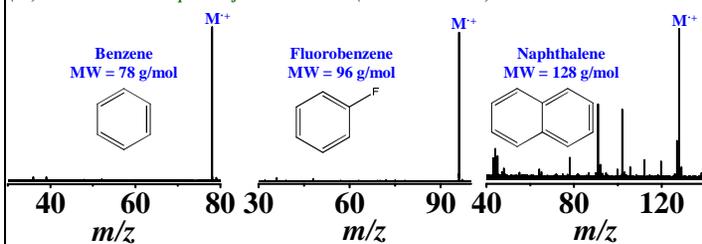
#### (II) RFI/FT-ICR Mass Spectra of Alcohols and Ketones (Positive-Ion Mode)



#### (III) RFI/FT-ICR Mass Spectra of Halogenated VOCs (Positive-Ion Mode)

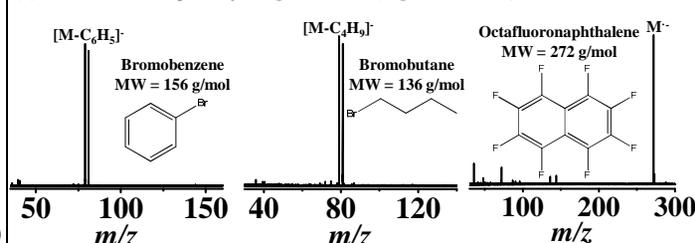


#### (IV) RFI/FT-ICR Mass Spectra of Aromatic VOCs (Positive-Ion Mode)



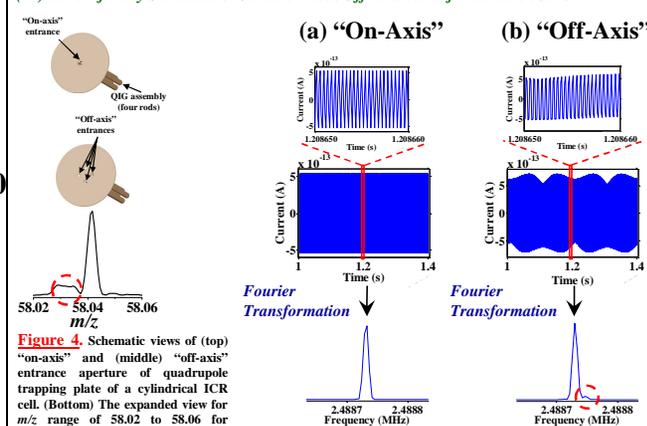
**Figure 2.** (Sections I to IV) RFI/FT-ICR mass spectra of different classes of volatile organic compounds in positive-ion mode.

#### (V) RFI/FT-ICR Mass Spectra of Halogenated VOCs (Negative-Ion Mode)



**Figure 3.** RFI/FT-ICR mass spectra of halogenated volatile organic compounds in the negative ion mode.

#### (VI) Ion Trajectory Simulations: On-Axis versus Off-Axis Ion Injection Into ICR Cell



**Figure 4.** Schematic views of (top) “on-axis” and (middle) “off-axis” entrance aperture of quadrupole trapping plate of a cylindrical ICR cell. (Bottom) The expanded view for  $m/z$  range of 58.02 to 58.06 for experimentally obtained acetone RFI/FT-ICR mass spectrum. The side band artifact (shown within the red dash circle) results from “off-axis” ion entrance into the ICR cell.

### CONCLUSIONS

• Radio-frequency ionization (RFI) technique is capable of ionizing different classes of VOCs.

• Both positive and negative ions are generated in RFI.

• Ion trajectory simulation results suggest that “off-axis” entrances of ions into ICR cell is the primary cause of peak splittings and appearance of side bands in RFI/FT-ICR mass spectra.

### REFERENCES

- [1] Zekavat, B.; Solouki, T., *Angewandte Chemie International Edition*, 2013, 52, 2426-2429.
- [2] Zekavat, B.; Szulejko, J. E.; LaBrecque, D.; Solouki, T., *Proceedings of the 57th ASMS Conference on Mass Spectrometry and Allied Topics 2009*, Philadelphia, PA.

### ACKNOWLEDGEMENTS

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