

Analysis of Volatile Organic Compounds from Gasoline Samples Using Radio-Frequency Ionization/Mass Spectrometry



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OVERVIEW

Results from analysis of volatile organic compounds (VOCs) using principal component analysis (PCA) and radio-frequency ionization/Fourier transform ion cyclotron resonance mass spectrometry (RFI/FT-ICR MS) are reported.

Commercially available gasoline samples with three different grades and from three different gas stations were classified using PCA and RFI/FT-ICR MS data.

INTRODUCTION

Recently, we introduced a novel RFI technique coupled to FT-ICR mass spectrometers for VOC analysis [1]. This new ionization method is a sensitive and efficient technique. For example, under an identical ionization time and similar acetone neutral pressures, the observed signal-to-noise ratio was enhanced by ~6 fold for RFI/FT-ICR MS (as compared to conventional electron impact (EI)/FT-ICR MS detection [1]).

Our goal is to evaluate the utility of RFI for MS fingerprinting of VOC mixtures. We present RFI/FT-ICR MS results from analysis of VOCs present in different gasoline samples. We also show how results from RFI/FT-ICR MS can be used for multivariate data analysis and classification of different grades of gasoline samples and gasoline samples from different gas stations.

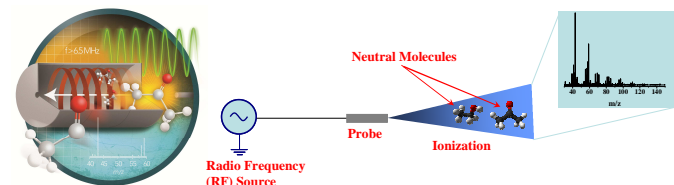


Figure 1. Radio frequency ionization (RFI) is a novel ionization technique that we recently introduced for mass spectrometry analysis of volatile and semi-volatile organic molecules. In RFI, a radio-frequency signal is used to ionize neutral organic molecules in the ultrahigh-vacuum region of FT-ICR mass spectrometers [1].

METHODS

Samples: The gasoline samples were collected from three different gasoline stations in Waco, TX. A 100- μ L volume of each of the samples was transferred into a separate sealed glass vial. Room temperature headspace VOCs (present in gasoline samples) were transferred into a heated (~200 °C) expansion reservoir and subsequently introduced into the FT-ICR vacuum chamber through a heated (~200 °C) transfer line and a pulsed valve (~120 °C). Samples were analyzed in multiple runs to ensure the reproducibility of FT-ICR mass spectra.

RFI: A home-built RF power supply [2] was used to generate the radio-frequency signals for RFI. An optimized RF signal of 6.5 MHz (~200 V_{pp}) was applied to the quadrupole ion guide (QIG) rods of the 9.4 T FT-ICR mass spectrometer. The RFI duration was 200 ms.

FT-ICR MS: An IonSpec FT-ICR mass spectrometer (former IonSpec Corp. - now a division of Agilent Technologies, Santa Clara, CA) equipped with a 9.4 T superconducting magnet (Cryomagnetics Inc., Oakridge, TN) was used to acquire the RFI/FT-ICR mass spectra. RFI-generated ions were trapped in an open-ended ICR cell for 1 s. The trapped ions were excited (4 ms) using a dipolar frequency sweep excitation and detected in the broadband mode. Fourier transformation of 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 2, 4, and 6. All RFI/FT-ICR mass spectra were calibrated internally using m/z values for the molecular and fragment ions of known VOC standards such as ethanol, benzene, and toluene.

Data Analysis: Principle component analysis (PCA) was performed in MATLAB 7.0 (The Math Works Inc., Natick, MA). Prior to PCA, all of the MS intensity data were normalized (to one) and mean-centered.

RESULTS

(I) RFI/FT-ICR Mass Spectra of Commercially Available Gasoline Samples (three different grades)

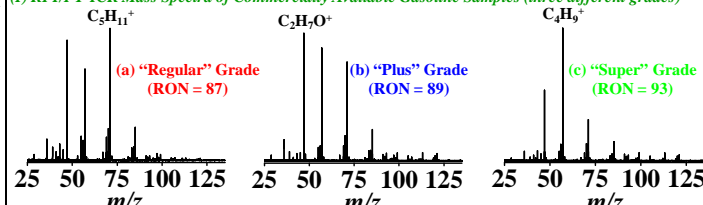


Figure 2. RFI/FT-ICR mass spectra of three commercially available gasoline grades. The research octane numbers (RONs) for mass spectra in (a), (b), and (c) correspond to 87, 89, and 93, respectively. The most abundant peak in each mass spectrum is labeled.

(II) PCA of RFI/FT-ICR Mass Spectra of Three Gasoline Grades (total of thirty samples)

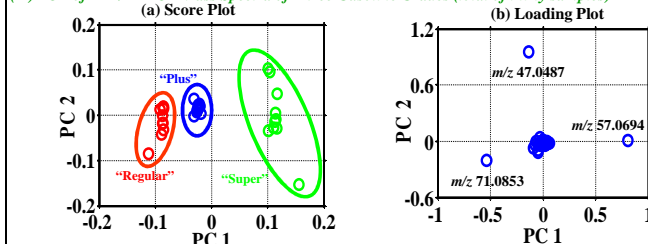


Figure 3. (a) Score and (b) loading plots obtained from PCA of RFI/FT-ICR mass spectra of three different grades of gasoline. The PCA score and loading values correspond to ten RFI/FT-ICR mass spectral replicates for each gasoline sample grade.

(III) RFI/FT-ICR Mass Spectra of Gasoline Samples (RON 87) From Three Different Gas Stations

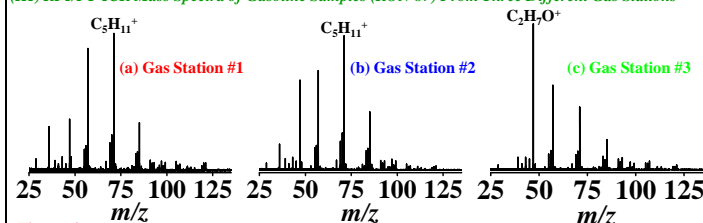


Figure 4. RFI/FT-ICR mass spectra of gasoline samples (regular grade) from three different gas stations. The most abundant peak in each mass spectrum is labeled.

(IV) PCA of RFI/FT-ICR Mass Spectra of Gasoline Samples (RON 87) From Three Different Gas Stations

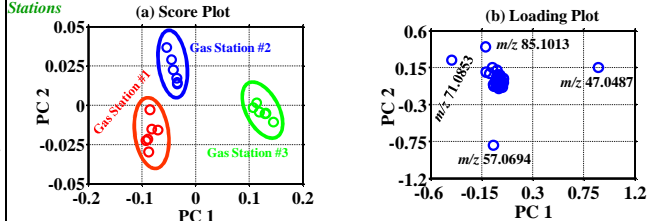


Figure 5. (a) Score and (b) loading plots obtained from PCA of RFI/FT-ICR mass spectra of gasoline samples (regular grade) from three different gas stations. The PCA score and loading values correspond to six RFI/FT-ICR mass spectral replicates for gasoline sample from each gas station.

Table 1. List of the observed m/z values and assigned chemical compositions for the ionic species observed in RFI/FT-ICR mass spectra of the analyzed commercially available gasoline samples. All chemical compositions were assigned based on mass measurement errors of less than 5 ppm.

Obs. m/z	Chemical Composition	Obs. m/z	Chemical Composition	Obs. m/z	Chemical Composition	Obs. m/z	Chemical Composition	Obs. m/z	Chemical Composition
29.0384	C ₂ H ₅ ⁺	55.0542	C ₄ H ₇ ⁺	73.0651	C ₆ H ₉ O ⁺	96.0932	C ₇ H ₁₂ ⁺	117.0713	C ₈ H ₁₆ ⁺
31.0178	CH ₂ O ⁺	56.0621	C ₄ H ₈ ⁺	75.0806	C ₆ H ₁₀ O ⁺	97.1012	C ₇ H ₁₃ ⁺	119.0854	C ₈ H ₁₇ ⁺
39.0228	C ₃ H ₃ ⁺	57.0336	C ₄ H ₈ O ⁺	77.0597	C ₆ H ₁₀ O ₂ ⁺	98.1093	C ₇ H ₁₄ ⁺	120.0933	C ₈ H ₁₈ ⁺
41.0385	C ₃ H ₄ ⁺	57.0694	C ₄ H ₉ ⁺	78.0468	C ₆ H ₁₁ ⁺	99.1170	C ₇ H ₁₅ ⁺	121.1012	C ₈ H ₁₉ ⁺
42.0465	C ₃ H ₆ ⁺	59.0492	C ₄ H ₁₀ O ⁺	79.0544	C ₆ H ₁₂ ⁺	100.1223	C ₇ H ₁₆ ⁺	122.1081	C ₈ H ₂₀ ⁺
43.0180	C ₃ H ₇ O ⁺	61.0285	C ₄ H ₁₀ O ₂ ⁺	81.0702	C ₆ H ₁₃ ⁺	102.0659	C ₇ H ₁₇ O ₂ ⁺	125.1329	C ₈ H ₂₁ ⁺
43.0542	C ₃ H ₇ ⁺	63.0222	C ₄ H ₁₁ ⁺	82.0773	C ₆ H ₁₄ O ⁺	103.0535	C ₇ H ₁₈ ⁺	127.1468	C ₈ H ₂₂ ⁺
44.0248	C ₃ H ₈ O ⁺	65.0392	C ₄ H ₁₂ ⁺	83.0857	C ₆ H ₁₅ ⁺	105.0700	C ₇ H ₁₉ ⁺	133.0993	C ₁₀ H ₁₃ ⁺
45.0335	C ₃ H ₈ ⁺	66.0460	C ₄ H ₁₃ ⁺	84.0934	C ₆ H ₁₆ O ⁺	106.0781	C ₈ H ₂₀ ⁺	134.1103	C ₁₀ H ₁₄ ⁺
46.0416	C ₃ H ₉ O ⁺	67.0544	C ₄ H ₁₄ ⁺	85.1013	C ₆ H ₁₇ ⁺	107.0854	C ₈ H ₂₁ ⁺	135.1164	C ₁₀ H ₁₅ ⁺
47.0487	C ₃ H ₉ O ⁺	68.0629	C ₄ H ₁₅ ⁺	89.0380	C ₆ H ₁₈ ⁺	109.0992	C ₈ H ₂₃ ⁺	139.1115	C ₁₀ H ₁₇ O ⁺
51.0232	C ₄ H ₅ ⁺	69.0701	C ₄ H ₁₆ ⁺	91.0537	C ₆ H ₁₉ ⁺	110.1085	C ₈ H ₂₄ ⁺		
52.0311	C ₄ H ₇ ⁺	70.0777	C ₄ H ₁₇ O ⁺	92.0619	C ₆ H ₂₀ ⁺	111.1161	C ₈ H ₂₅ ⁺		
53.0386	C ₄ H ₉ ⁺	71.0478	C ₄ H ₁₈ O ⁺	93.0698	C ₆ H ₂₁ ⁺	112.1240	C ₈ H ₂₆ ⁺		
54.0470	C ₄ H ₁₁ ⁺	71.0853	C ₄ H ₁₉ ⁺	95.0854	C ₆ H ₂₂ ⁺	113.1326	C ₈ H ₂₇ ⁺		

(V) The Use of a Wire Ion Guide (WIG) For Improving RFI/FT-ICR Mass Spectral Appearances

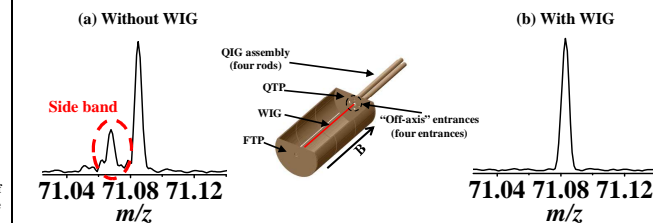


Figure 6. Expanded region between m/z 71.02 and 71.14 from RFI/FT-ICR mass spectra of a commercially available gasoline sample acquired (a) without and (b) with the use of a wire ion guide (WIG) device [3]. The middle panel shows the schematic view of an ICR cell with WIG device positioned in the center of ICR and parallel to magnetic field direction. FTP: Filament Trapping Plate; QTP: Quadrupole Trapping Plate. Note: The RFI/FT-ICR mass spectra of gasoline samples showed peak splittings and side bands for the RFI-generated ions (presumably caused by the "off-axis" entrance of the RFI-generated ions into the ICR cell [1]). With the use of a WIG device, we were able to eliminate peak splittings and side bands.

CONCLUSIONS

- The RFI/FT-ICR mass spectra of gasoline samples showed the presence of similar VOCs that are generally detected by gas chromatography (GC)/EI/FT-ICR MS [4].
- The MS results presented here show the utility of RFI for MS fingerprinting of complex VOC mixtures such as gasoline.
- Combined use of RFI-FT-ICR MS and PCA is a suitable approach for classification of gasoline samples based on their VOC compositions.

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