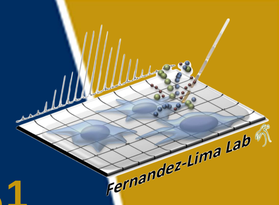
Development of New Analytical Tools for the Study of Dissolved Organic Matter



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Overview

Dissolved organic matter (DOM) is present in many aquatic ecosystems and is important for many biological systems. With the recent development of Trapped Ion Mobility Spectrometry (TIMS) and its coupling to time of flight (ToF) and Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometries (MS), in this project we evaluate new analytical workflows for the analysis of DOM. In addition, the coupling of pre-separaton techniques based on liquid chromatography (LC) were evaluated to reduce sample complexity during ionization and increase the orthogonality of the separation. The advantages of the LC-TIMS-ToF MS platform were illustrated for the separation of structural isomers and a complex mixture of DOM. Results show that the high mobility resolving power of the TIMS analyzer permits the separation of structural isomers and allowed determining accurate collision cross sections (CCS). The analysis of the Suwanee River Fulvic Acid (SWRFA) by LC-TIMS-ToF MS provided new insights into the structural complexity of DOM mixtures and opened new avenues for further exploration of LC separations.

Introduction

Dissolved organic matter (DOM) is present in many both salt water and fresh water ecosystems and is used by microorganisms to support aquatic ecosytems.[1] DOM also acts as a filter for sunlight that passes through water, protecting aquatic species.[2] There are varying types of compounds, including aromatic compounds, that make up the composition of DOM samples.[3] There can be some similarities between different DOM samples collected from different locations or from the same location during different hydroperiods. However, there are distinct differences, indicating that there can be different biogeochemical processes taking place or different influences from the environment.[4] Previous work conducted by Norbert Hertkorn, Mourad Harir, Kaelin Cawley, and Rudolf Jaffe containing proton nuclear magnetic resonance spectrometry (1H NMR) and fourier transform ion cyclotron resonance (FT-ICR) data for different DOM standards provided a reference for selecting the isomeric standards used in this project.[4] In the present work, we further expand the analysis of DOM by coupling LC-TIMS, adding orthogonal separations prior to mass analysis.

[1]Lawrence R. Pomeroy. *Bioscience*, Vol. 24, No. 9. Sept., 1974. 499-504

[2]Kenneth S. Johnson, Kenneth H. Coale, and Hans W. Jannasch. *Analytical Chemistry*, Vol. 64, No.22, Nov. 15, 1992. 1065-1075A

[3]Chen, M., Maie, N., Parish, K., and Jaffé, R., *Bio-geochemistry*, Vol. 115, 2013. 167–183

[4]Norbert Hertkorn, Mourad Harir, Kaelin Cawley, Rudolf Jaffe. *Biogeosciences Discuss.*, Vol. 12, 2015. 13711-13765

Experimental Methods

Figure 1.Schematics of the FT-ICR MS instrument used to analyze the SWRFA standard

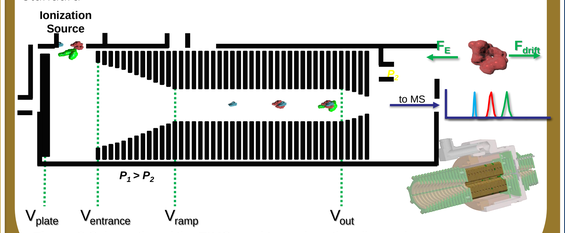

Figure 2.Schematics of the TIMS used to analyze the all samples

Fernandez-Lima F, Blase RC, Russell DH. 2011. International Journal of Mass Spectrometry 298:111-8

Fernandez-Lima F, Kaplan DA, Park MA. 2011. Review of Scientific Instruments 82:126106

Fernandez-Lima F, Kaplan DA, Suetering J, Park MA. 2011. International Journal for Ion Mobility Spectrometry 14:93-8

Experimental Methods

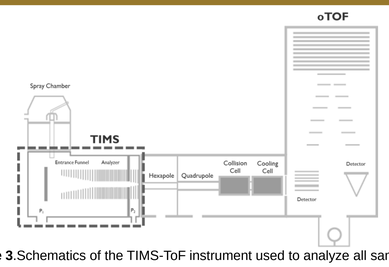

Figure 3.Schematics of the TIMS-ToF instrument used to analyze all samples

Fernandez-Lima F, Blase RC, Russell DH. 2011. International Journal of Mass Spectrometry 298:111-8

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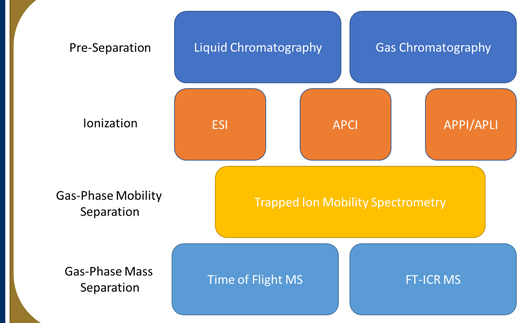
State of the Art MS



Experimental Results

Mobility Separation – ToF MS

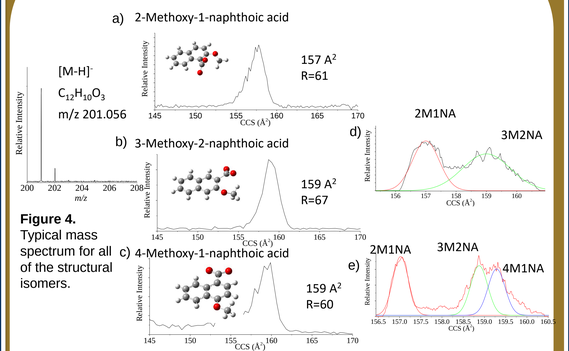


Figure 4. Typical mass spectrum for all of the structural isomers.

Figure 5. a-c) Typical low resolution mobility spectra for representative DOM isomers. d) Low resolution separation of a binary mixture of structural isomers, and e.) high resolution separation of a ternary mixture of isomers.

Experimental Results

LC and Mobility Separation – ToF MS

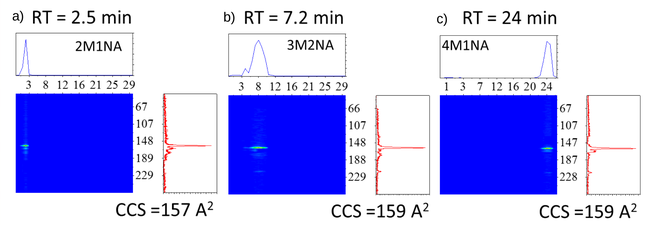


Figure 6. a-c) 2D LC-IMS contour maps of three structural isomers for *m/z* 201.06 using LC-TIMS-ToF MS. Notice the orthogonality between the LC and IMS separations.

SWRFA LC-ToF MS vs FT-ICR MS

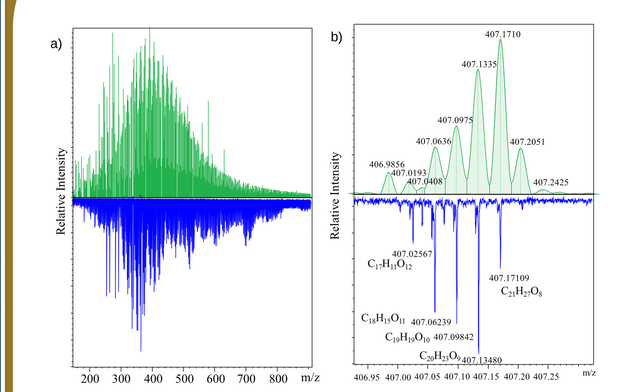


Figure 7. a) Typical ESI negative mode mass spectra of SWRFA standard using LC-ToF MS (green) and FT-ICR (blue), and b) Close up of *m/z* 407.
c) The number of peaks per nominal mass for the LC-ToF MS (green) and FT-ICR MS (blue), (g, d-e) Van Krevelen plots using LC-ToF MS (Left) and FT-ICR MS (Right)

Notice that the LC-ToF MS spectrum is able to identify the primary features of the SWRFA but the FT-ICR is able to resolved a greater number of features.

Experimental Results

LC-TIMS MS SWRFA

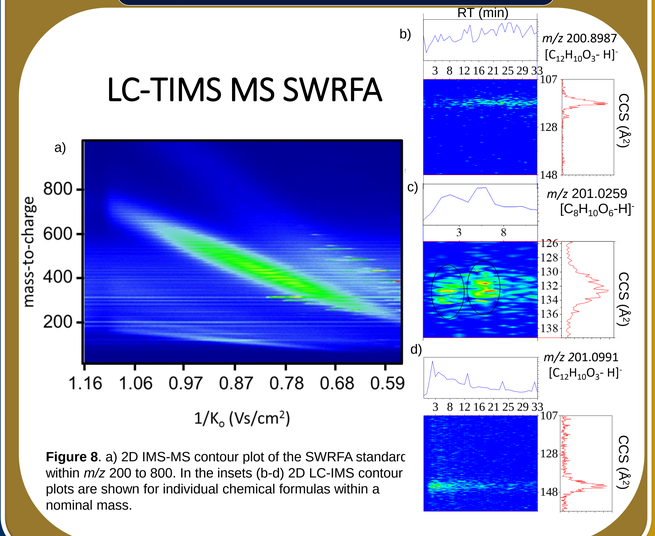


Figure 8. a) 2D IMS-MS contour plot of the SWRFA standard within *m/z* 200 to 800. In the insets (b-d) 2D LC-IMS contour plots are shown for individual chemical formulas within a nominal mass.

Conclusions

TIMS provides fast gas phase separation of isomers, as is shown. Coupling LC with TIMS increases the separation potential of the TIMS by adding another dimension of separation for structures with similar collision cross sections. Utilizing LC-TIMS-ToF MS gives complementary orthogonal separation of the isomers. We compared the number of features identified by ToF MS and FT-ICR and found that the ToF provided primary intense features, but the FT-ICR provided more features overall and allowed for the determination of chemical formulas. Next step is to further evaluate the analytical capabilities using TIMS FT-ICR MS.

Acknowledgments

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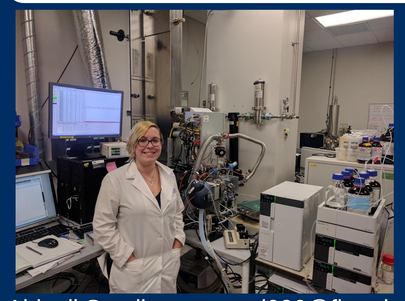

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