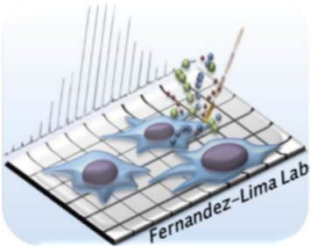
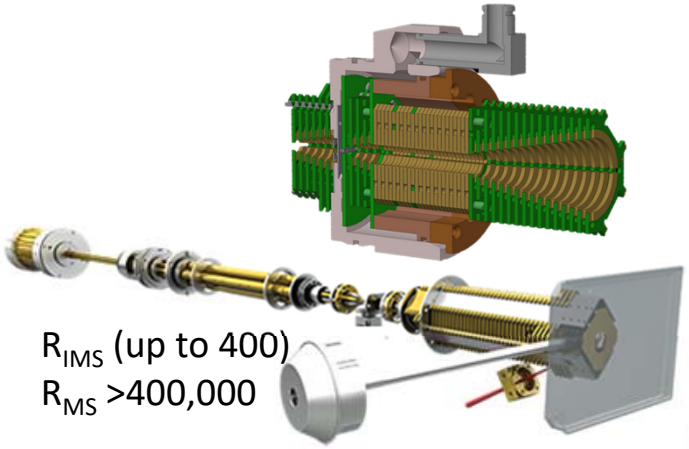
FIU | Center for Aquatic Chemistry and Environment

NSF Center of Research Excellence in Science and Technology

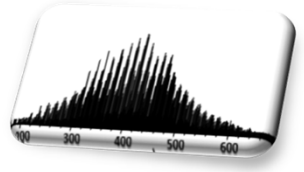


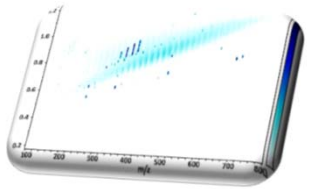
Unraveling the Structural Complexity and Diversity of Dissolved Organic Matter using TIMS-FT-ICR MS

Dennys Leyva, Lilian V. Tose, Jacob Porter, Jeremy Wolff, Rudolf Jaffé and Francisco Fernandez-Lima



R_{IMS} (up to 400)
R_{MS} >400,000



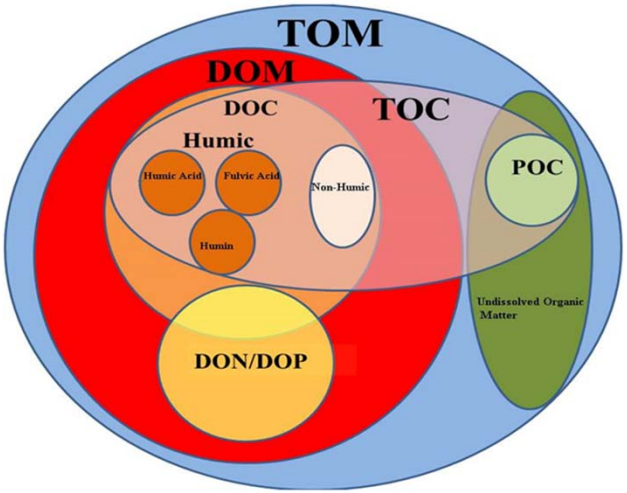


American Chemical Society Florida Section FAME 2019

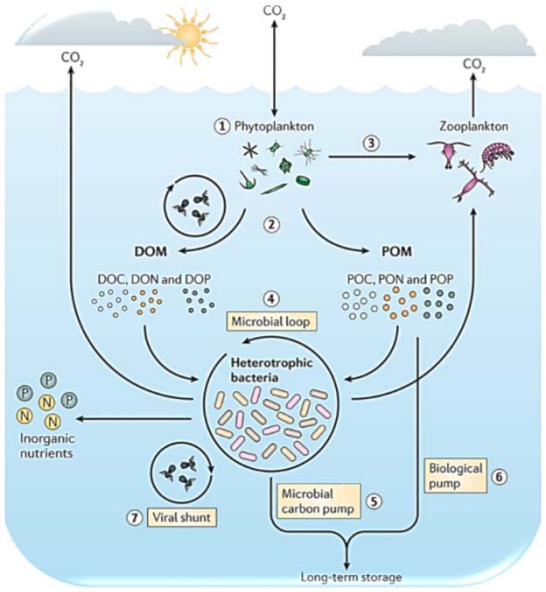
Motivation

Dissolved Organic Matter (DOM): Complex mixture from bacteria, algal and high plant organic matter degradation.

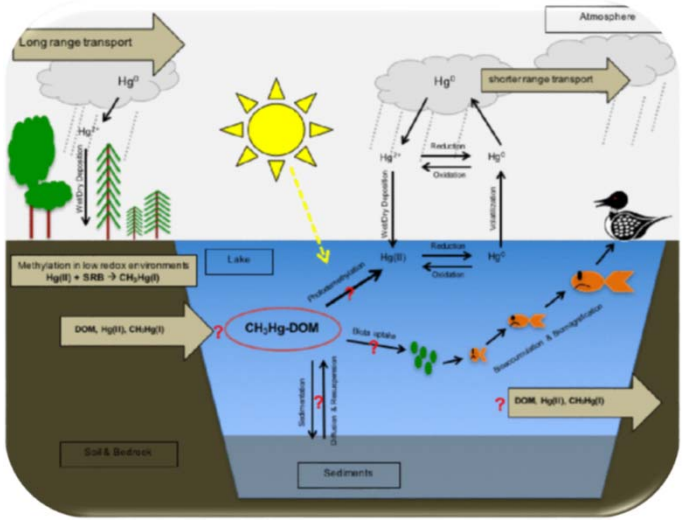
Role in aquatic environments



T. Pagano, M. Bida and J. E. Kenny, Water, 2014, 6, 2862.



Nature Reviews Microbiology 12, 686 698 (2014)

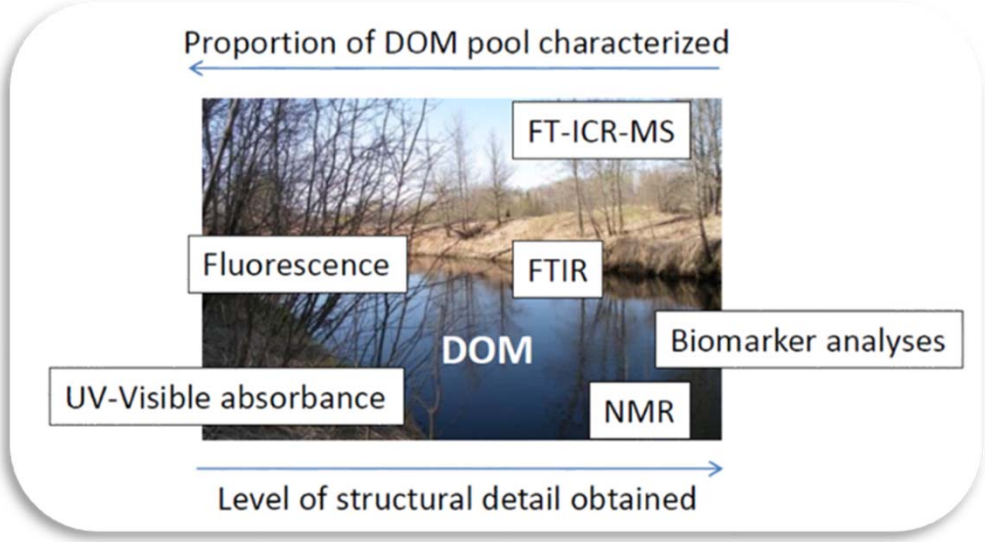


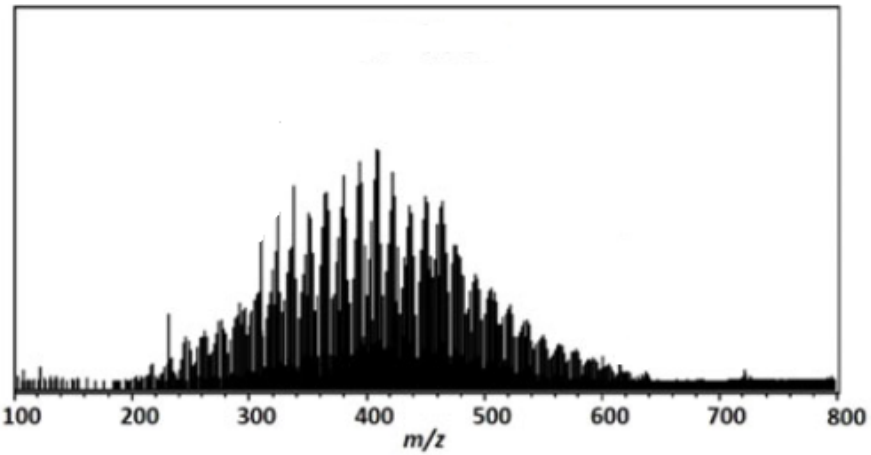
Bulletin of Environmental Contamination and Toxicology (2018) 100:14–25

A full understanding of DOM impact in climate change, ecology, and toxicology, requires a comprehensive knowledge of their molecular composition and structure.

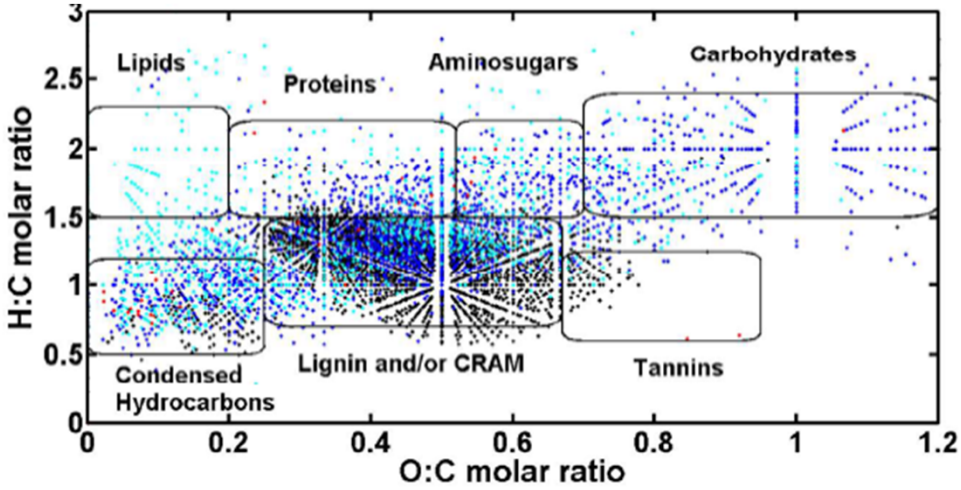
Analytical approaches

Bulk vs molecular level characterization





DOM MS spectrum



Diversity in molecular classes

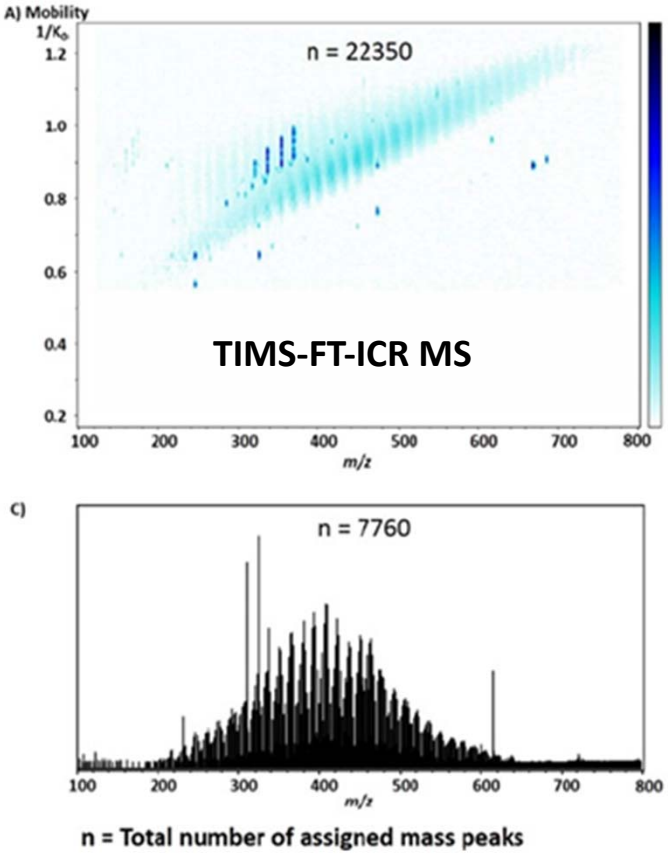
Challenges in DOM structure elucidation

- High structural heterogeneity
- Wide range of molecular weights
- **Isomeric diversity**

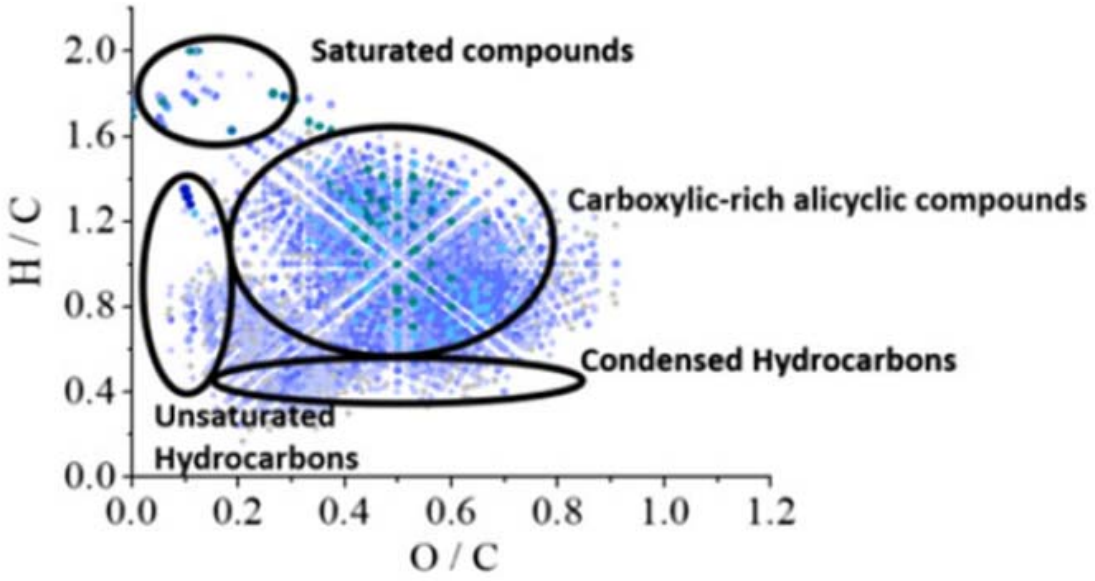
Environ Sci-Proc Imp., 16(9): 2064-2079, 2014

Coupling TIMS with FT-ICR MS in SRFA analysis

How can TIMS help to understand the complexity of DOM?



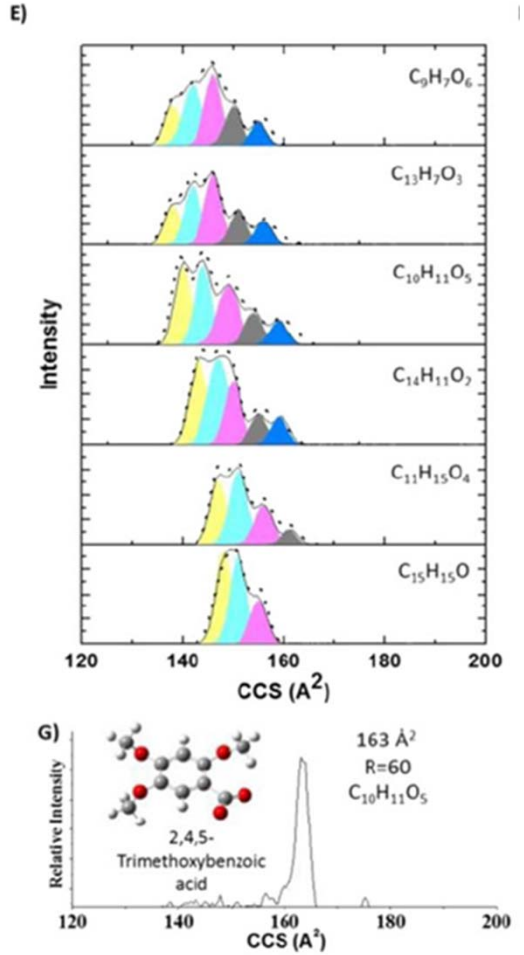
n = Total number of assigned mass peaks

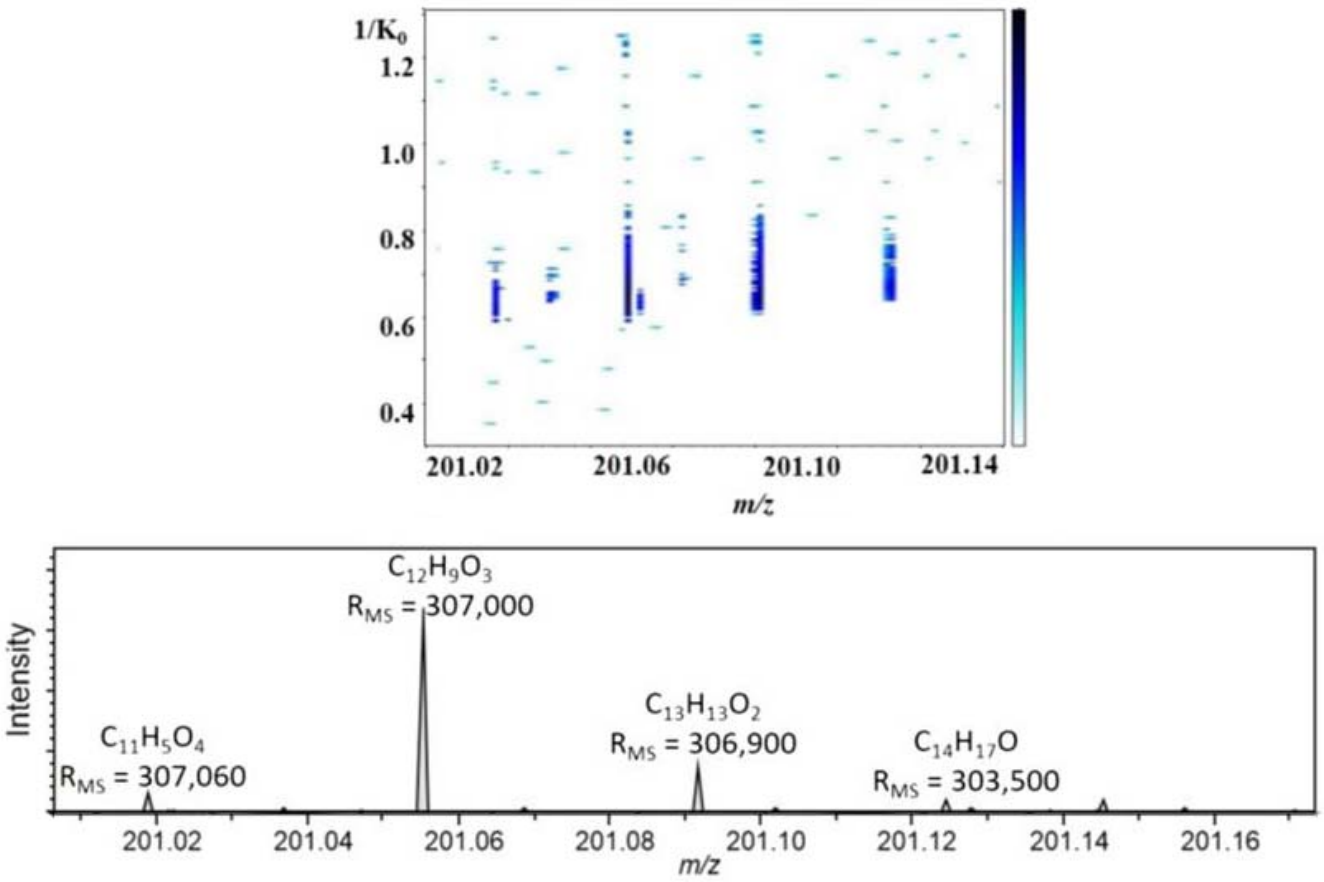


3050 chemical formulas assigned in SRFA standard

L. V. Tose, P. Benigni, **D. Leyva**, A. Sundberg, C. E. Ramírez, M. E. Ridgeway, M. A. Park, W. Romão, R. Jaffé and F. Fernandez-Lima, *Rapid Communications in Mass Spectrometry*, 2018, 32, 1287-1295.

Isomeric content in SRFA standard





IMS-MS (top) and MS (bottom) projections from the SRFA analysis at m/z 201

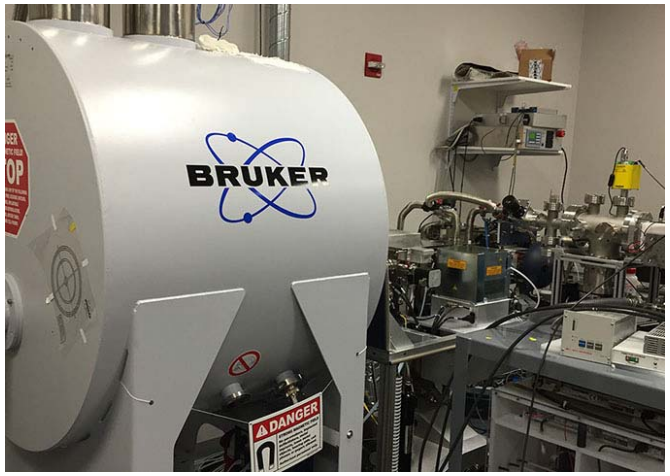
We provided, for the first time, a lower cutoff estimation of the number of molecular isomers in the SRFA standard.

Experimental

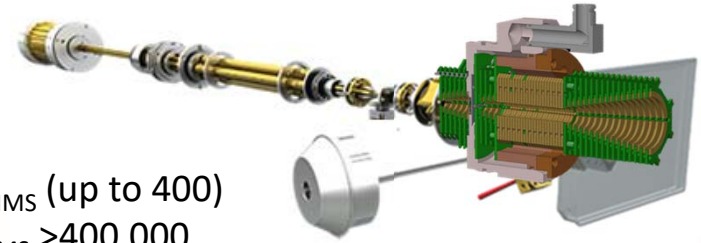
Samples

Pantanal National Park, Brazil

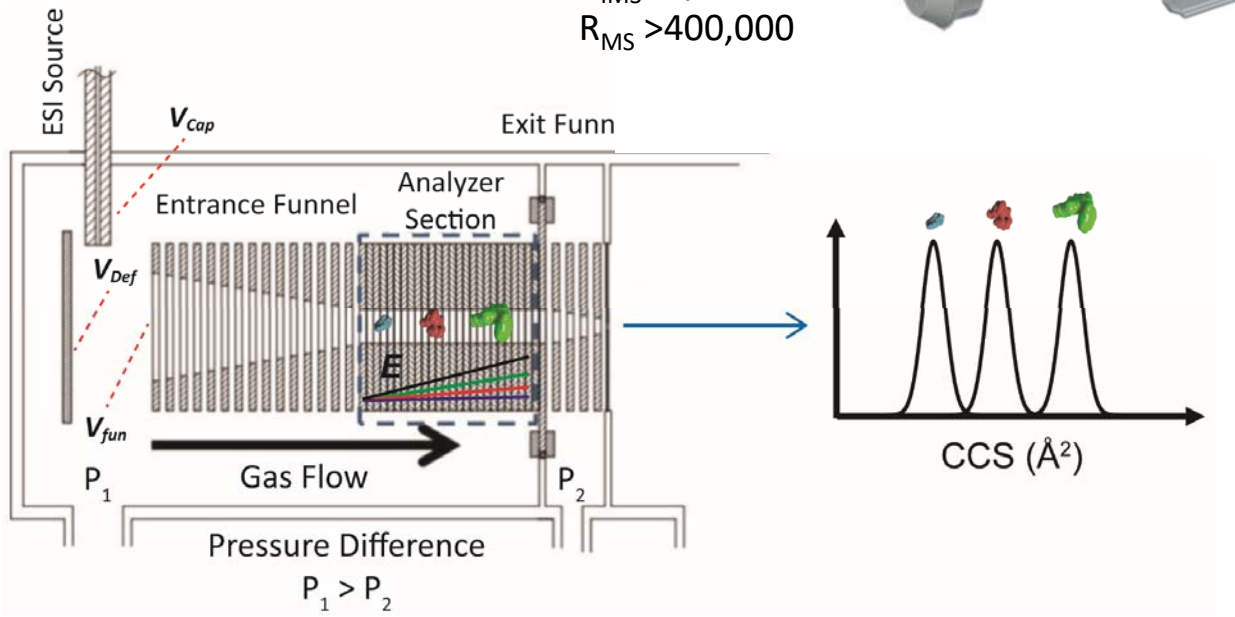
TIMS-FT-ICR MS 7T Solarix



Trapped Ion Mobility Spectrometry



R_{IMS} (up to 400)
R_{MS} >400,000



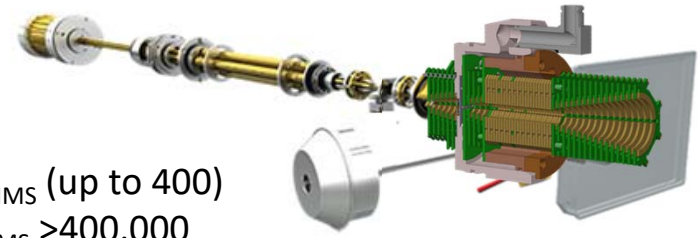
$$k = \frac{v_g}{E} = \frac{A}{(v_{elution} - v_{out})}$$

- Nonlinear stepping scan function
- Mobility spectra calibrated using Tuning Mix

FT-ICR MS/MS: quadrupole isolation-CID 15-20 eV.

Experimental

Trapped Ion Mobility Spectrometry



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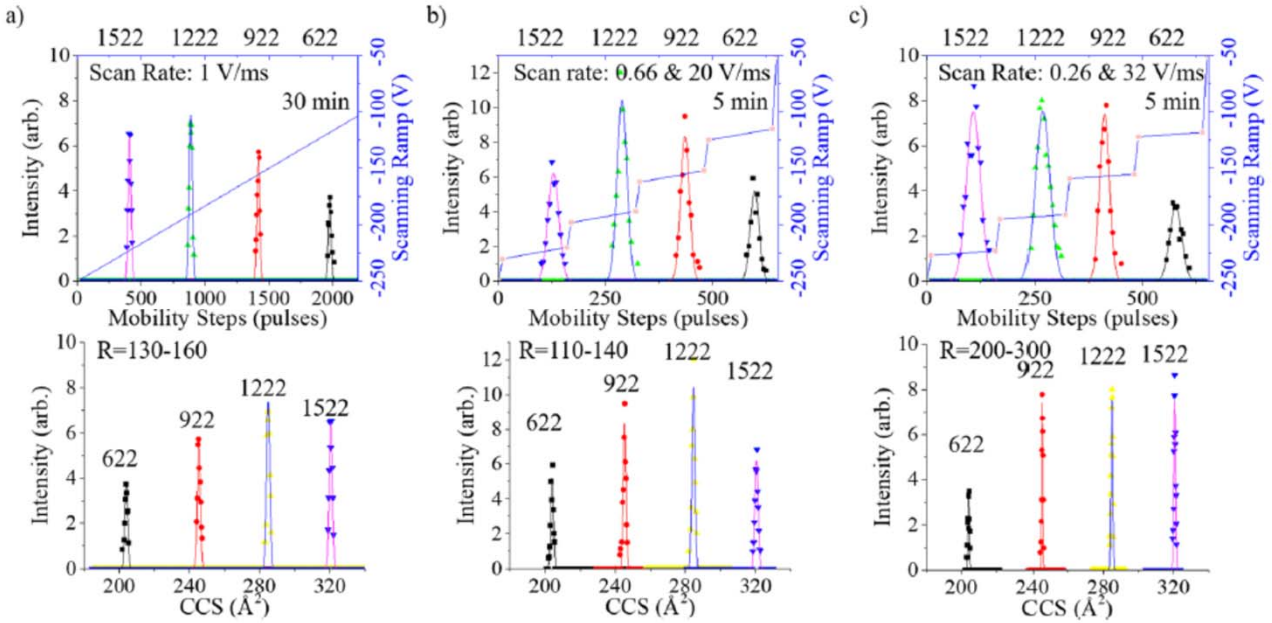
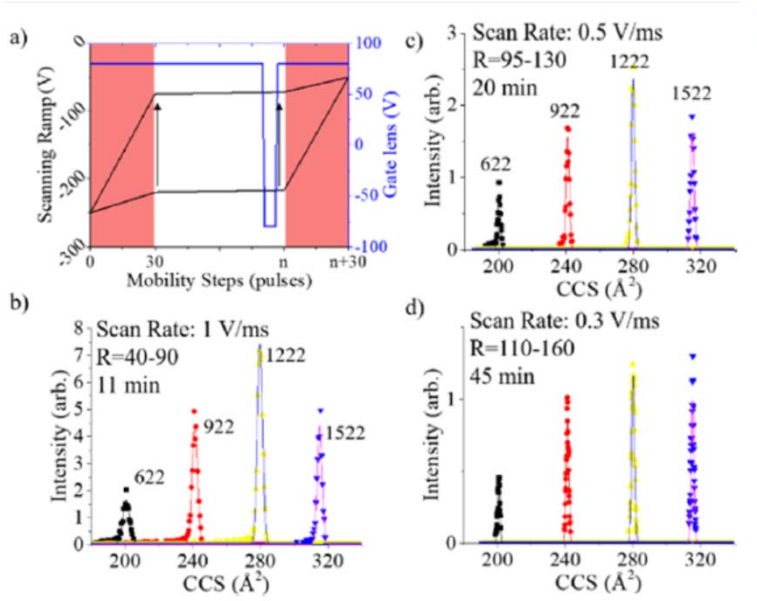
R_{MS} >400,000

Non linear scan functions TIMS-FT-ICR MS

Targeted





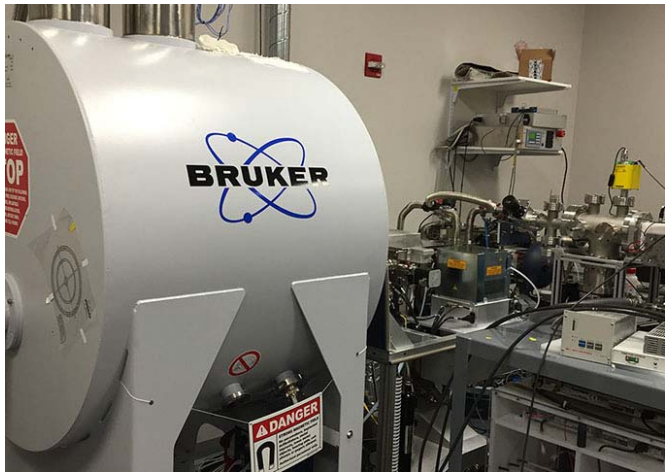
P. Benigni; J. Porter; M. Ridgeway; M. Park; F. Fernandez-Lima*. "Increasing analytical separation and duty cycle with non-linear analytical mobility scan functions in TIMS-FT-ICR MS". Anal Chem. 2018, 90 (4), 2446–2450.

Experimental

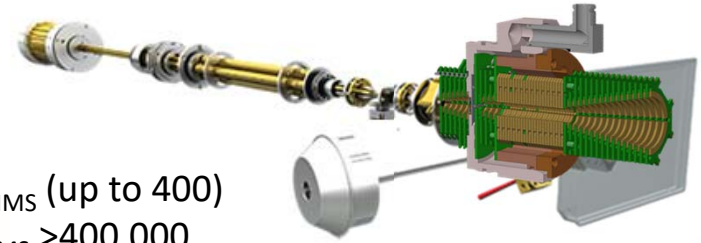
Samples

Pantanal National Park, Brazil

TIMS-FT-ICR MS 7T Solarix



Trapped Ion Mobility Spectrometry



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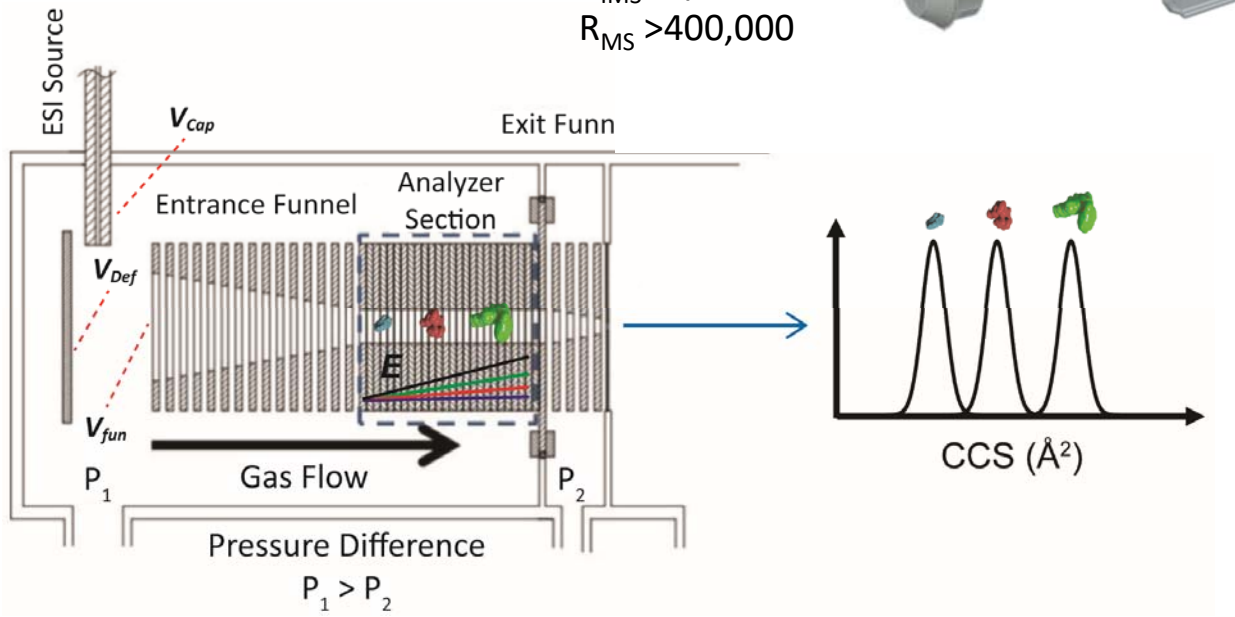


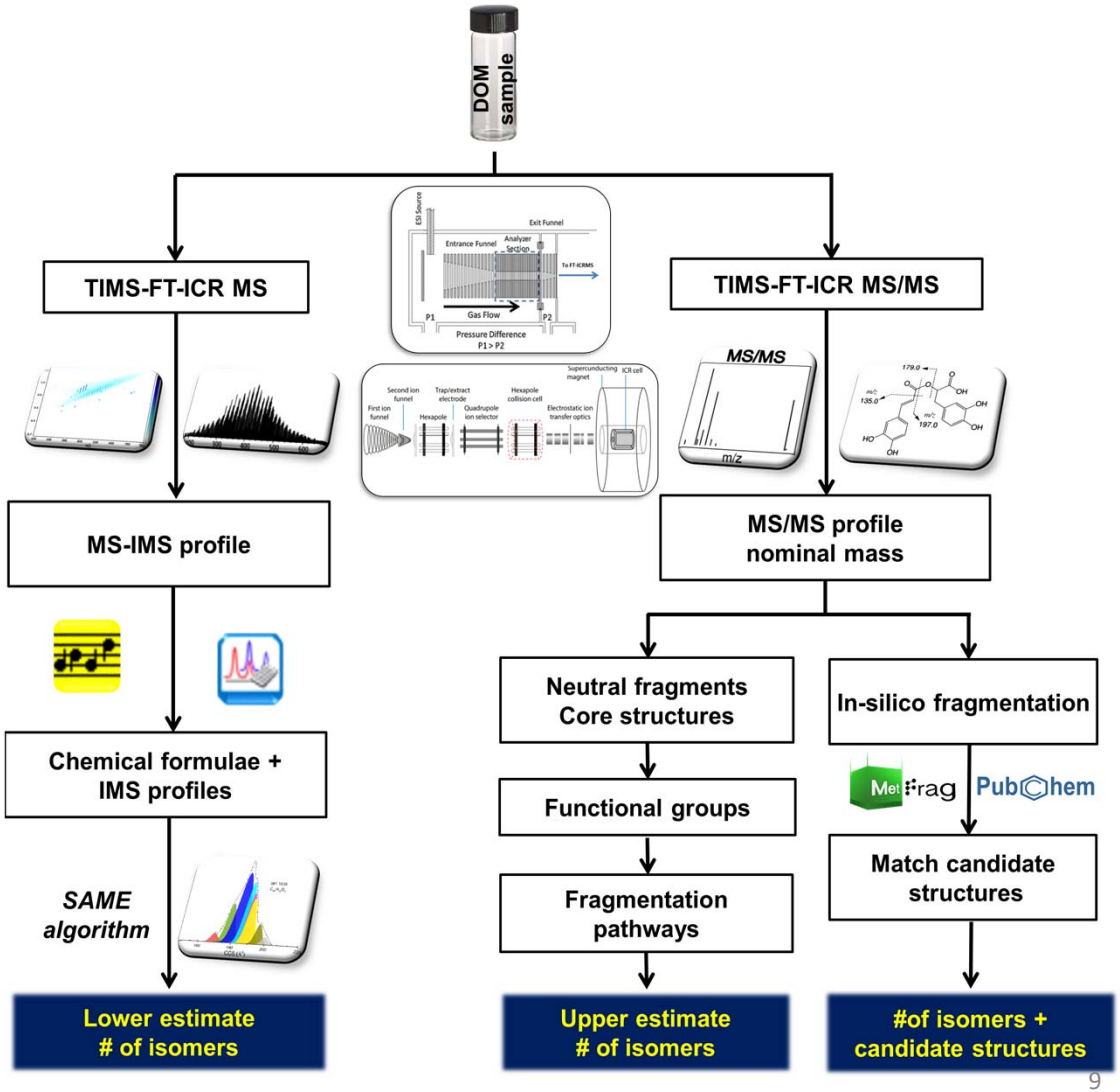
$$k = \frac{v_g}{E} = \frac{A}{(v_{elution} - v_{out})}$$

- Nonlinear stepping scan function
- Mobility spectra calibrated using Tuning Mix

FT-ICR MS/MS: quadrupole isolation-CID 15-20 eV.

Analytical workflow

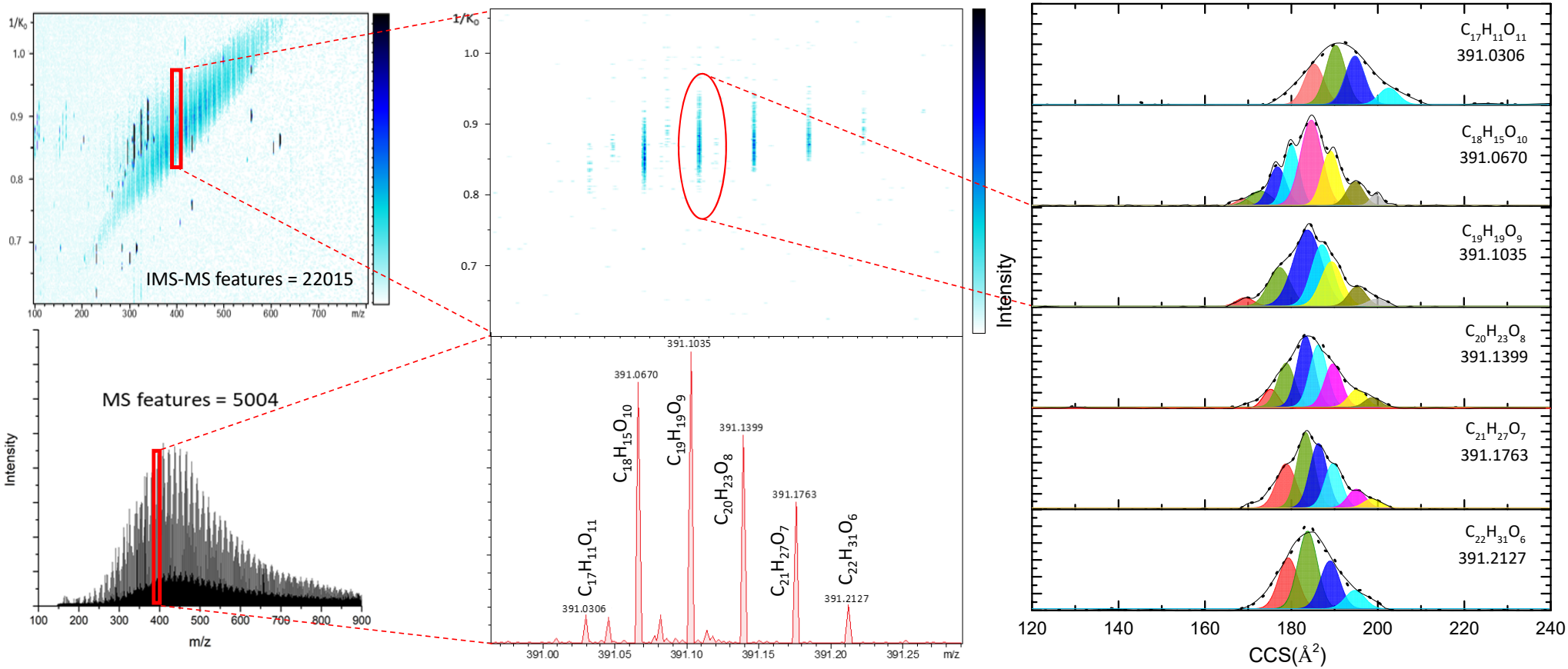
How can TIMS-FT-ICR MS help to understand the isomeric diversity of DOM?



TIMS-FT-ICR MS

More than 3,000 chemical components identified

6-10 isomers per chemical formula

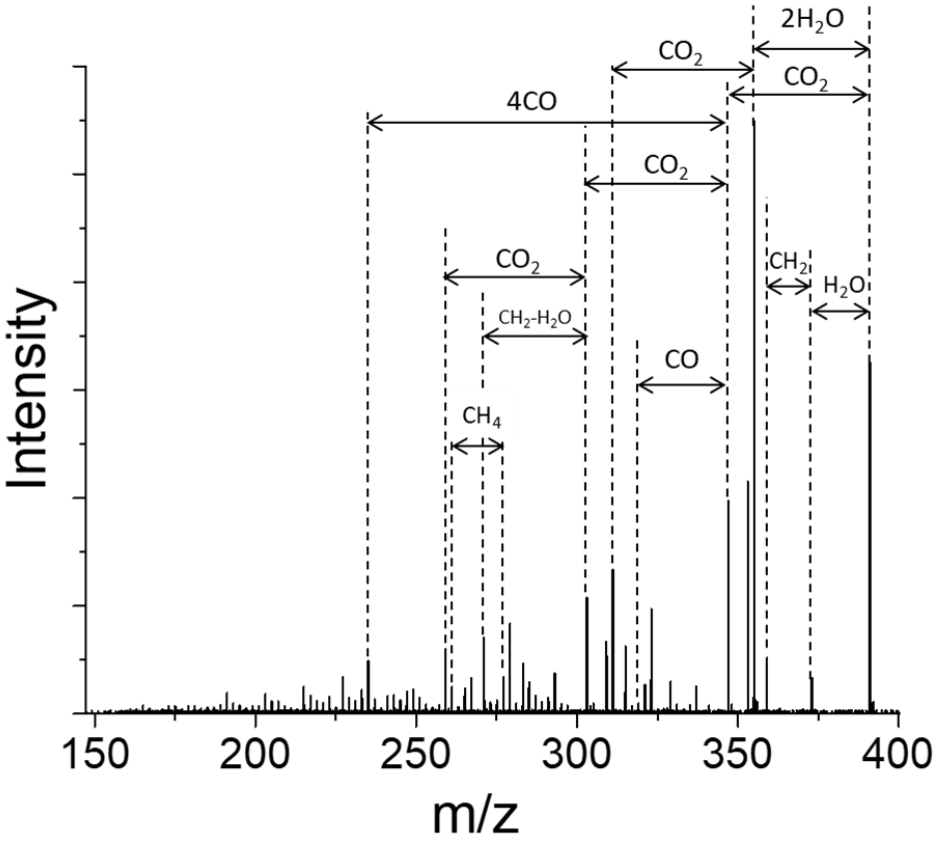


2D IMS-MS and MS projection at m/z 391

IMS projection at nominal mass m/z 391

D. Leyva, L. Valadares, J. Porter, J. Wolff, R. Jaffè and F. Fernandez-Lima, *Faraday Discussions*, 2019, DOI: 10.1039/C8FD00221E.

FT-ICR MS/MS



FT-ICR MS/MS (q-CID) profile of precursor ion 391 m/z

- Neutral losses associated with functional groups and precursor ion.
- The number of pathways could provide an estimate of the number of structural isomers.

Core fragment **Neutral fragments**

$[C_{19}H_{20}O_9\text{-}H]^-$ **Precursor ion**

$[C_{10}H_9O_2]^- + \{5CH_2; CO; 3CO_2\}$

$[C_{12}H_7O_2]^- + \{2CH_3; O_2; CH_4; H_2O; 4CO\}$

$[C_{13}H_{11}O]^- + \{CH_4; 2H_2O; 4CO, CO_2\}$

⋮ ⋮

$[C_{10}H_3O_5]^- + \{7CH_2; O; H_2O; 2CO\}$

$[C_{13}H_5O_5]^- + \{2CH_2; 2CH_4; H_2O; CO; CO_2\}$

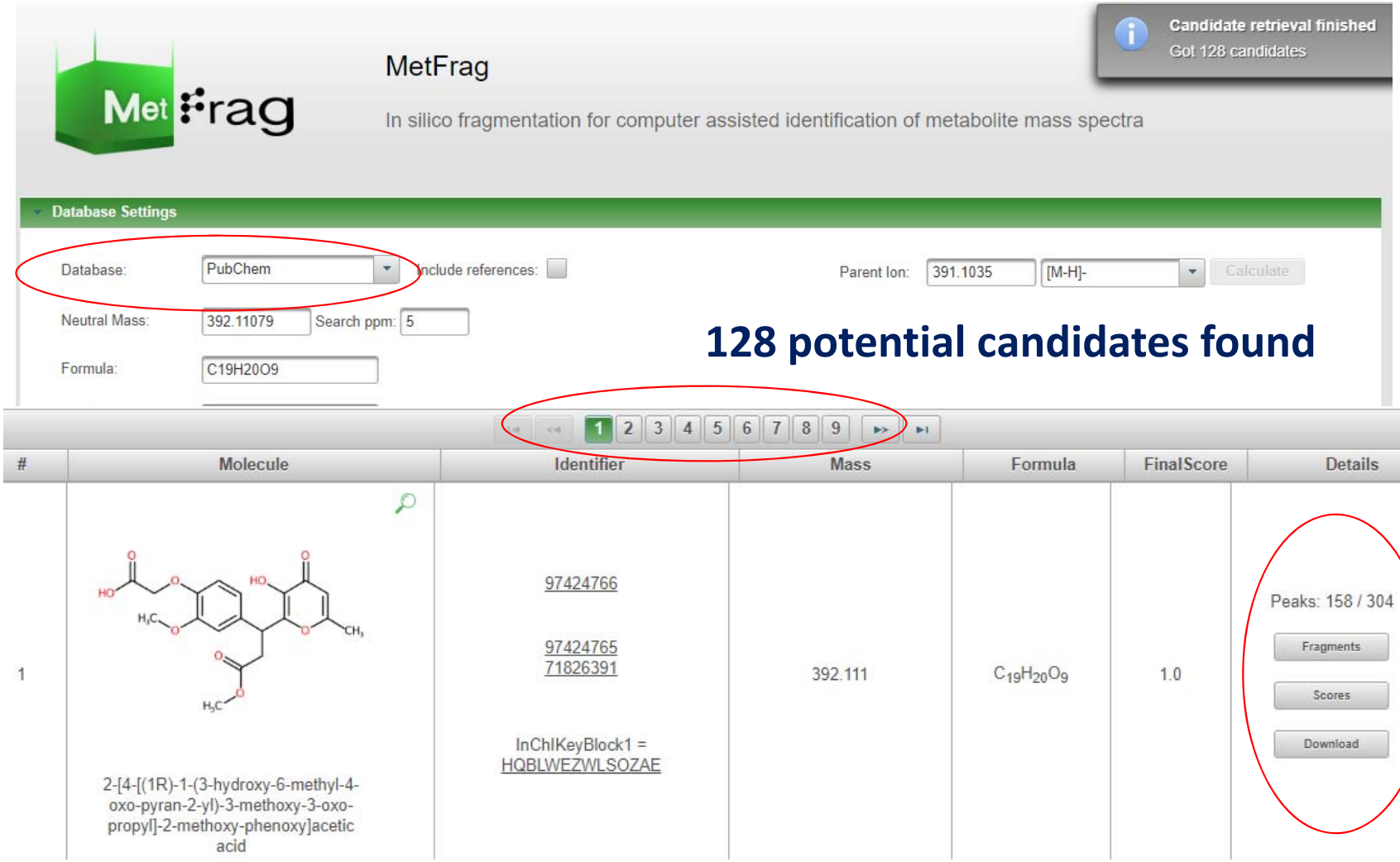
FT-ICR MS/MS (q-CID) of precursor ion 391 m/z

Potential neutral losses							Core fragment m/z	Number of pathways
CH_2	CH_3	O	CH_4	H_2O	CO	CO_2		
5	-	1	-	-	-	3		
2	-	-	1	1	4	1		
3	-	-	1	-	1	3		
1	2	-	-	1	4	1		
2	2	-	-	-	1	3		
4	-	-	-	1	2	2		
4	-	2	-	1	4	-		
-	-	-	2	1	6	-		
5	-	2	-	-	1	2		
-	2	1	1	-	4	1		
1	-	1	2	-	4	1		
5	-	3	-	-	2	1	173.0607 $C_{11}H_9O_2$	23
5	-	4	-	-	3	-		
1	-	-	2	-	3	2		
2	2	1	-	-	2	2		
3	-	1	1	-	2	2		
3	-	2	1	-	3	1		
2	2	2	-	-	3	1		
1	2	1	-	1	5	-		
2	-	1	1	1	5	-		
-	2	-	1	-	3	2		
3	-	-	-	2	5	-		
4	-	1	-	1	3	1		

Precursor ion m/z	Core Fragment m/z	Structural isomers
391.1031 $C_{19}H_{19}O_9$	161.0607 $C_{10}H_9O_2$	13
	163.0763 $C_{10}H_{11}O_2$	7
	165.0192 $C_8H_5O_4$	3
	165.056 $C_9H_9O_3$	2
	167.0349 $C_8H_7O_4$	1
	171.0814 $C_{12}H_{11}O$	23
	173.0607 $C_{11}H_9O_2$	23
	175.0400 $C_{10}H_7O_3$	15
	183.0450 $C_{12}H_7O_2$	40
	183.0814 $C_{13}H_{11}O$	25
	185.0607 $C_{12}H_9O_2$	29
	187.0400 $C_{11}H_7O_3$	25
	201.0192 $C_{11}H_5O_4$	25
	202.9984 $C_{10}H_3O_5$	15
	205.0140 $C_{10}H_5O_5$	7
	241.0140 $C_{13}H_5O_5$	7

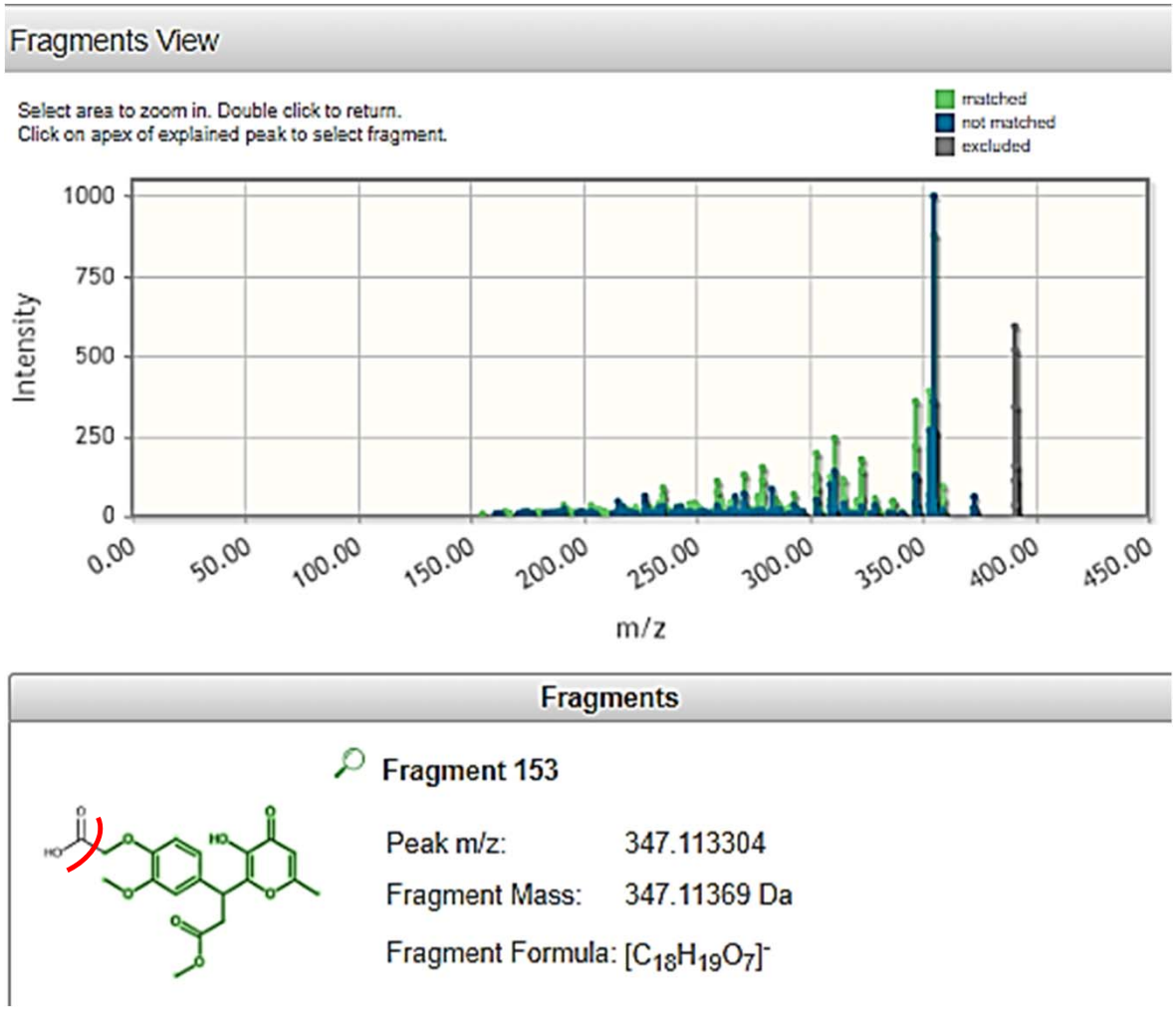
Rapid upper estimate of 260 structural isomers

In-silico fragmentation



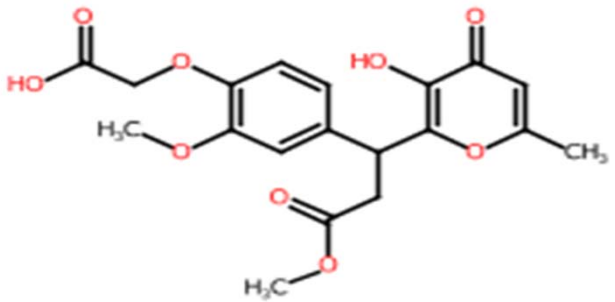
Journal of Cheminformatics,2016, 8:3

In-silico fragmentation



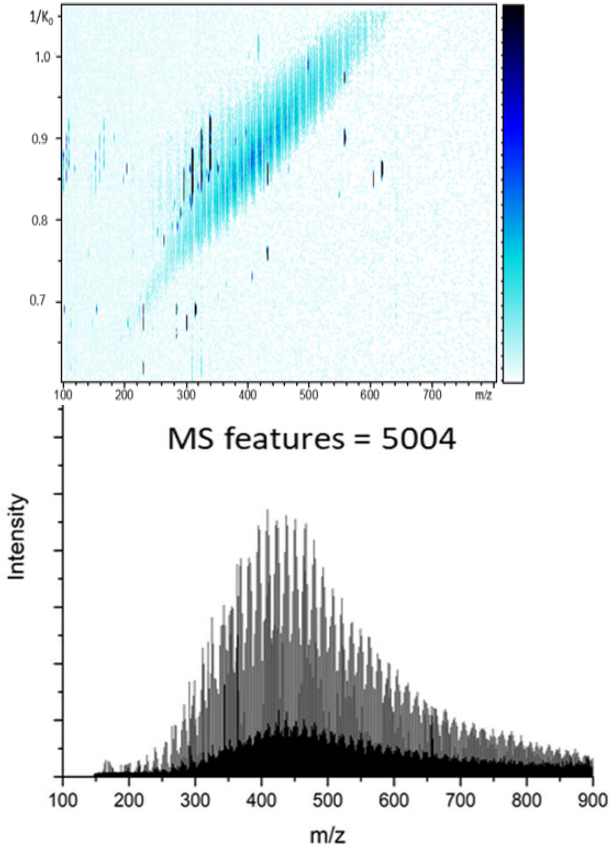
96 candidate structures based on accurate masses of precursor and fragments.

Candidate structure

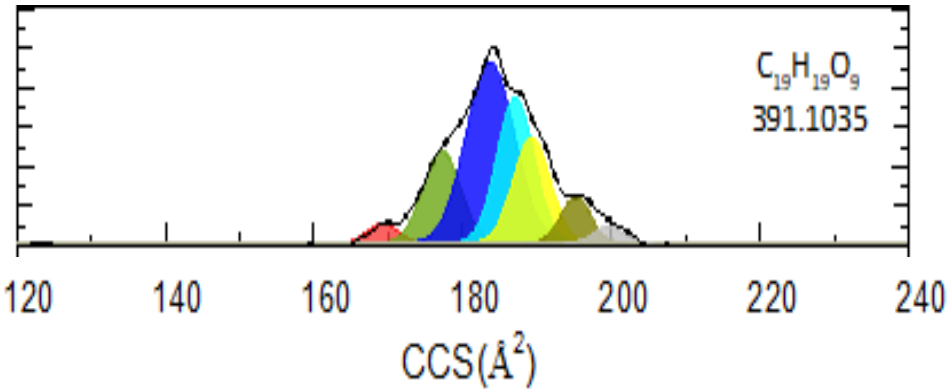


Conclusions

3,066 chemical components identified.



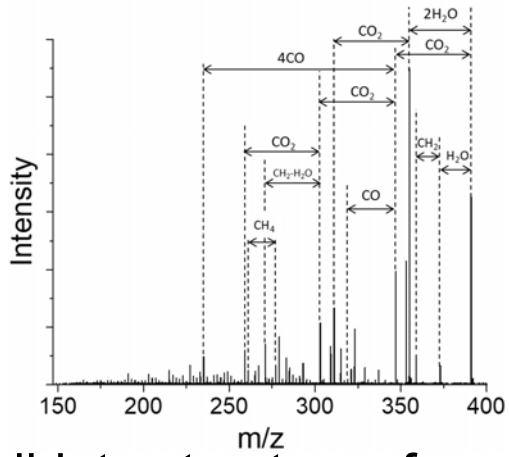
DOM Isomeric content per chemical formula based on TIMS.



Faraday Discussions, 2019, in press,

Conclusions

DOM isomeric content based on unique neutral loss fragmentation pathways/core fragments.



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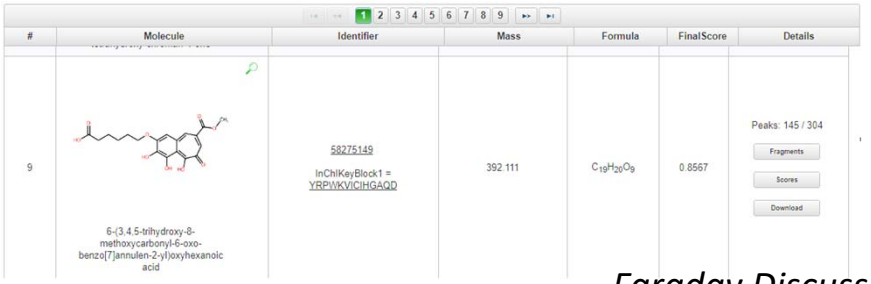
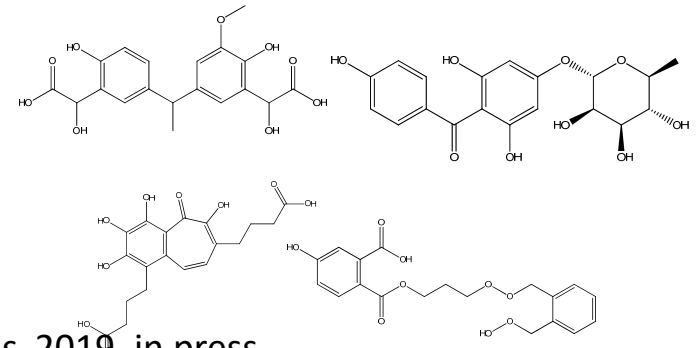
96 candidate structures from Metfrag-Pubchem





Faraday Discussions, 2019, in press,

Acknowledgements

NSF-CREST Program award HRD-1547798
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NSF Center of Research Excellence in Science and Technology

Advisor
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Kevin Jeanne Dit Fouque
Jean Haler
Graduate students
Anthony Castellanos
Jacob Porter
Yarixa Cintron
Kim Dang
Elisa Shoff
Clerment Olanrewaju
Undergraduate students
Benjamin Bokor
Shirley Hernandez

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