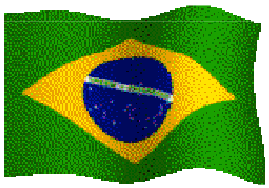
2nd World Congress on
Petrochemistry and Chemical Engineering

Dra. Ildenize Cunha

State University of Campinas (UNICAMP)



Mass Spectrometry: a pioneering and renewed tool for petrochemical analysis

(382 não lidos) - cunhaibs | Google Tradutor | :::THOMSON MASS SPEC

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ThoMSon
Thomson Mass Spectrometry Laboratory

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MENU
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- INSTRUMENTATION
- PUBLICATIONS
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ThoMSon news

Workshop Petroleômica no ThoMSon

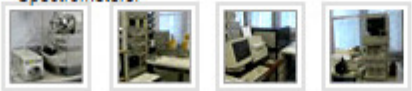
more information [+]

- Petroleômica MS Teses: Deu no JU!
- Entrevista Waters : Assita!
- Extra Extra! EASI na midia!
- Thomson e os Embriões: Deu na Fapesp!
- Eberlin fala sobre a Ciência e o Design
- ThoMSon é Capa do Journal of Lipid



Instrumentation

The ThoMSon MS Laboratory posses a very well-suited set of the most advanced Mass Spectrometers.







More Info [+]



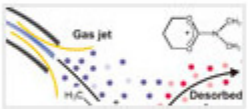
Visit the Brazilian Mass Spectrometry Society BrMASS homepage.

more information [+]



See a picture and contact information of our present and past students.

more information [+]



See a list and description of the major Research Areas of the ThoMSon Lab.

more information [+]

ThoMSon



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THOMSON

MS PUBLIC GRAPHICS

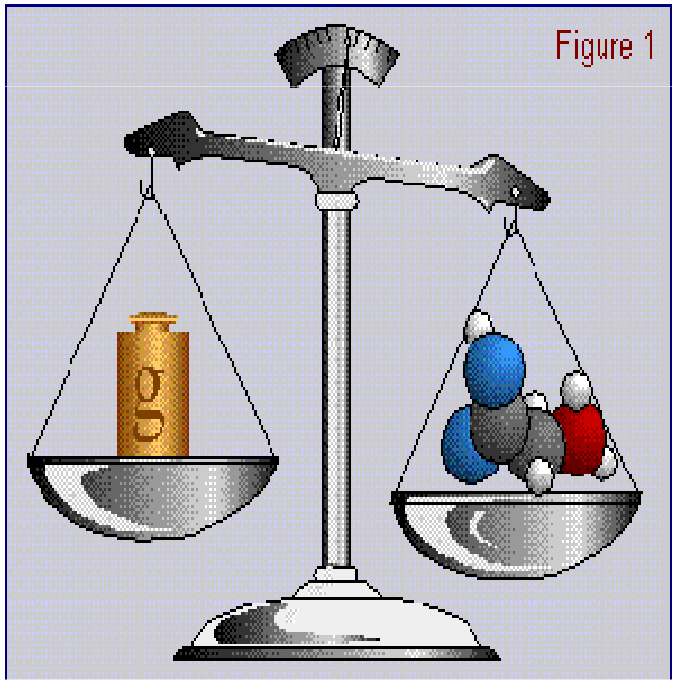
MOR

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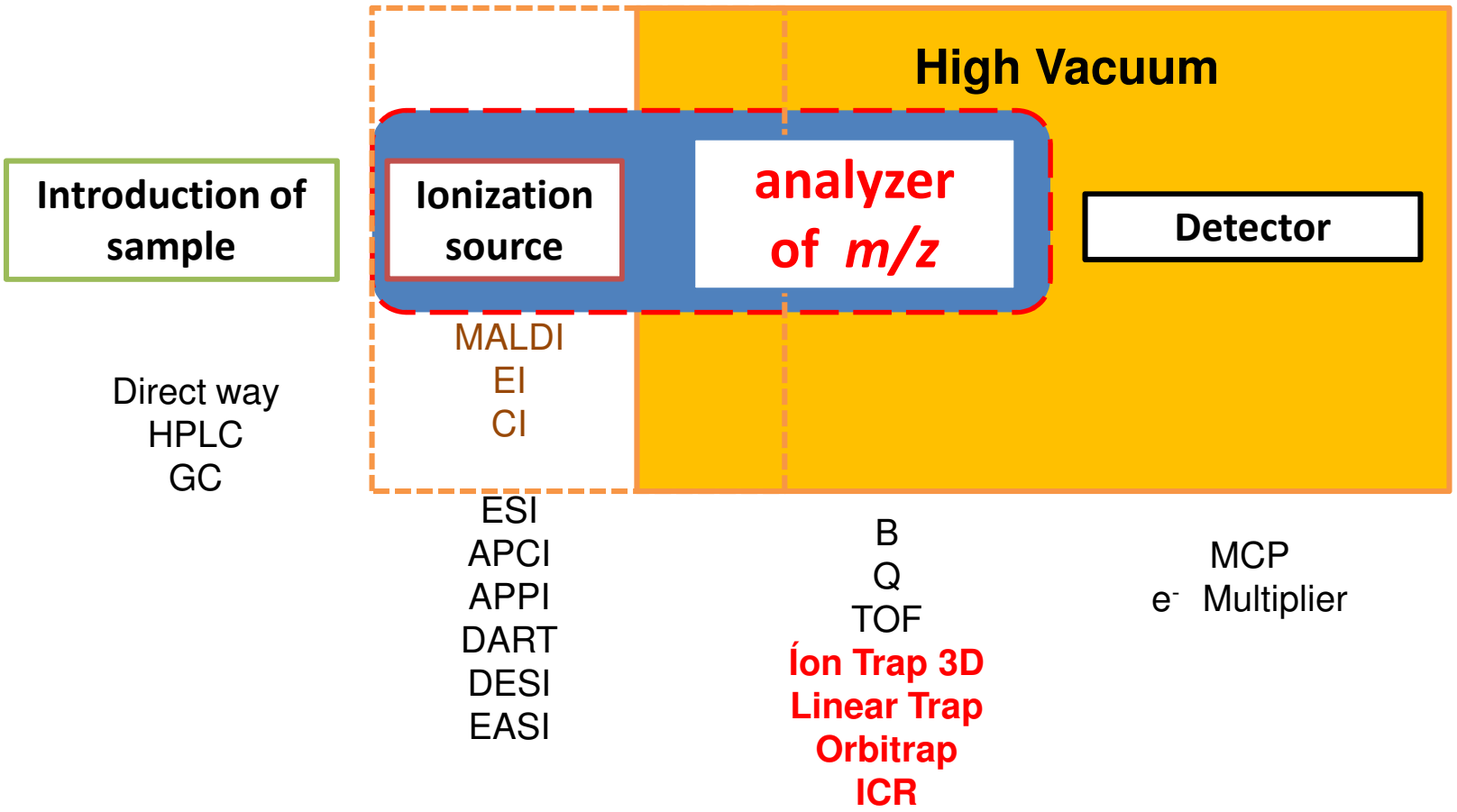
Phone: +55 19 3521.3073 | 3521.3049

Mass Spectrometry (MS)

Analytical technique in which atoms or molecules of a sample are ionized, separated according to their *m/z ratios* and then detected and quantitate.



How does a MS system Work?

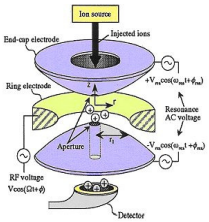


Timeline



1897
J. J. Thomson
e- discovery

1912
First MS
Thomson

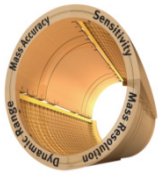


1942
First Comercial MS

1953
Quadrupole and Trap 3D
Paul & Steinwedel

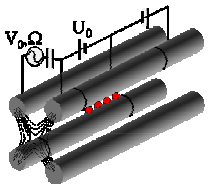
1956
First GC/MS

1958
First Comercial TOF



1974 First LC/MS
and FT-ICR description

1984
Linear Trap 2D



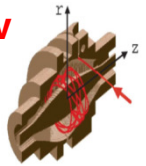
1968
First Comercial Quadrupole

1987
MALDI
Karas & Hillenkamp

1988
ESI by John Fenn

2000
Macromolecules
Spectrum> 10^6 Da

2005
Orbitrap
Makarov



Ultra High
resolution
analyzers



Joseph John Thomson
1906 Nobel Prize for Physics



Francis William Aston
1922 Nobel Prize for Chemistry



Wolfgang Paul
1989 Nobel Prize for Physics

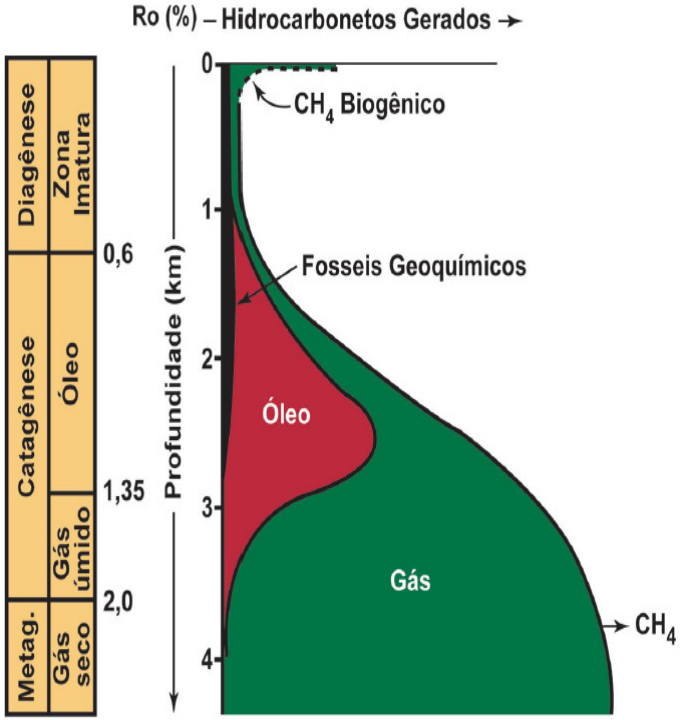


John Bennet Fenn
2002 Nobel Prize for Chemistry

complex mixture analysis



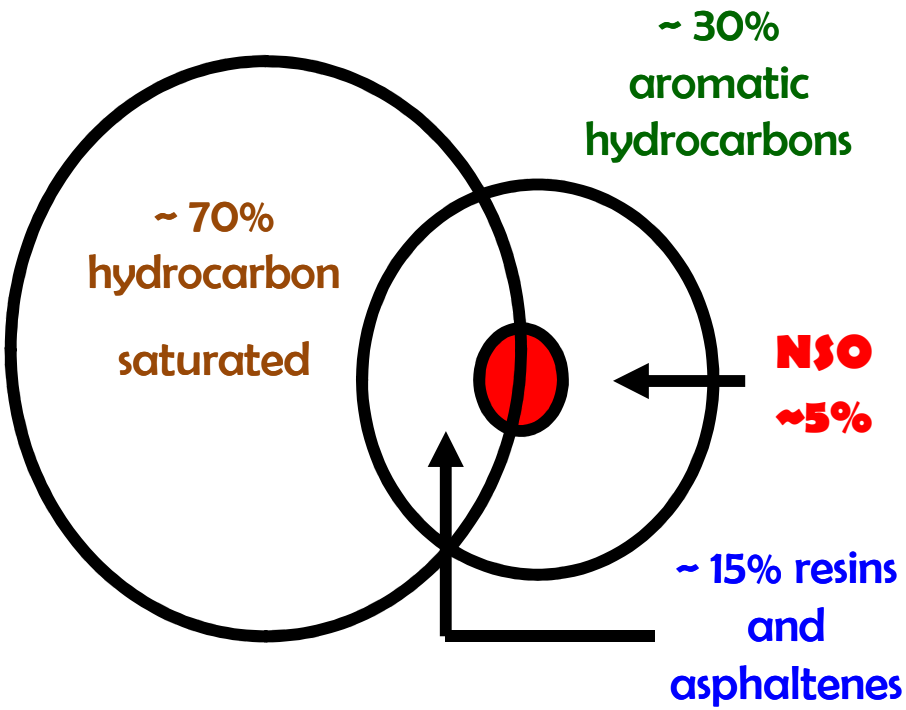
- **OIL OF FOSSIL ORIGIN.**
  - Complex chemical composition
  - Millions of years to be formed in sedimentary rocks.
  - Became the main source of energy in the modern world.

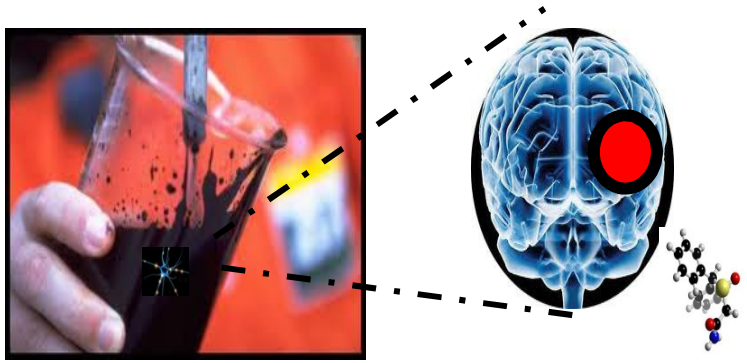




Polar compounds in crude oils

- Complex combination of hydrocarbons (aliphatic, alicyclic and aromatic) and may also contain small quantities of a class as polar compounds containing heteroatoms such as nitrogen, oxygen and sulfur.





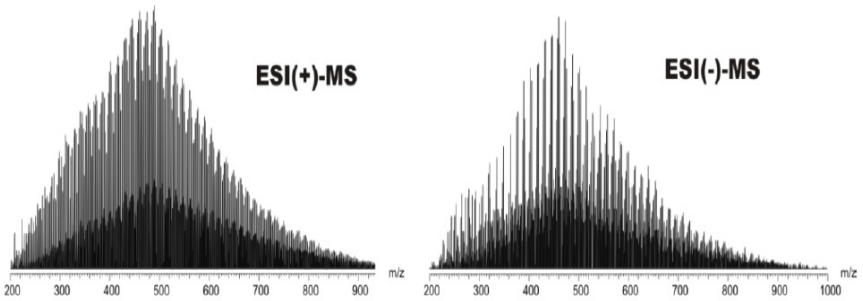
Petroleomic and its MS approaches.

Petroleomic is, in the broadest sense, the study of all the components present on oil and how these components affect the properties and reactivity of a specific oil.

Profile

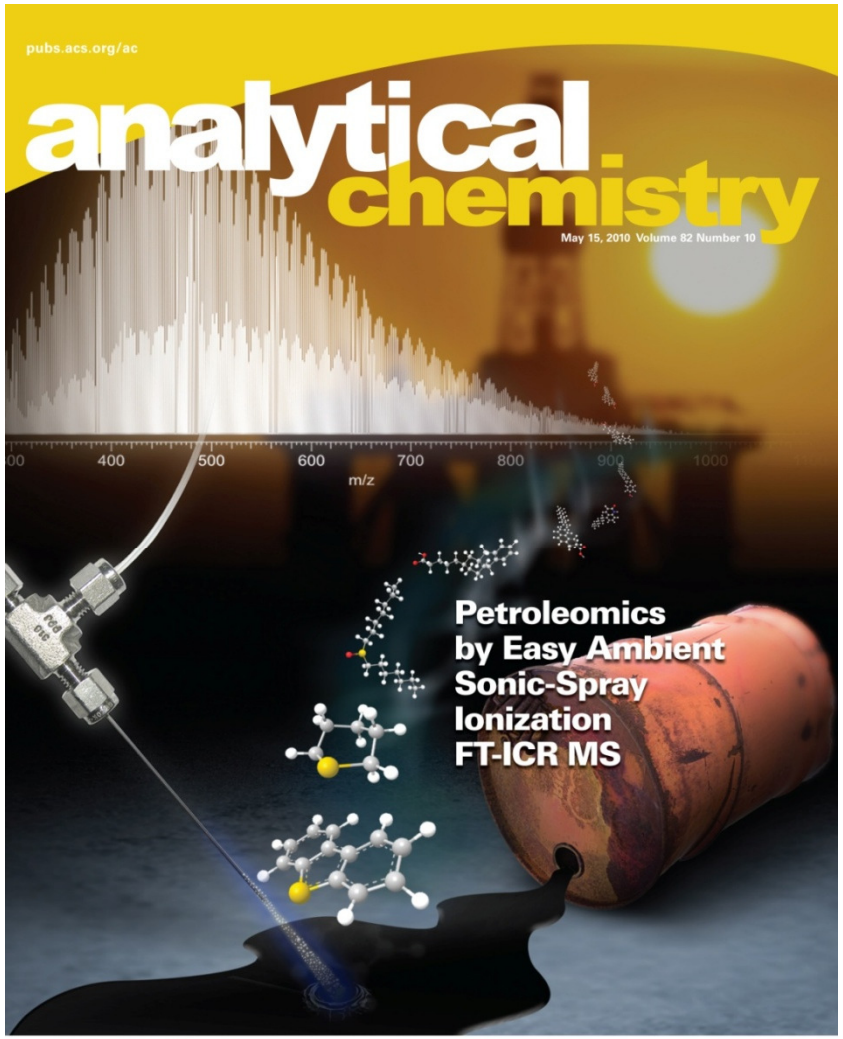






PetroMS





Petroleomics by MS

↓

Composition

↓

Properties

Analytical Chemistry **2010**, 82, 3990-3996



Resolution

Able to separate 2 ions that have approximate mass

Accuracy

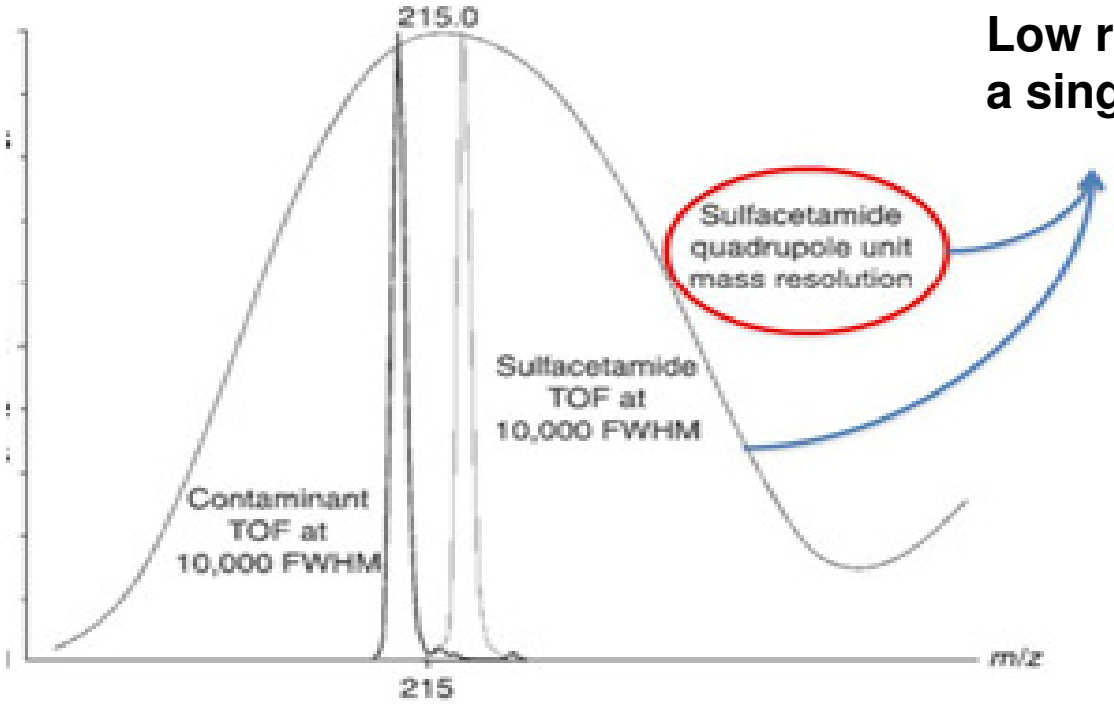
Could be evaluated from the error

$$Error(ppm) = \frac{m_{\exp} - m_{theo}}{m_{theo}} \times 10^6$$

Important for correct assignment of molecular formulas

Resolution

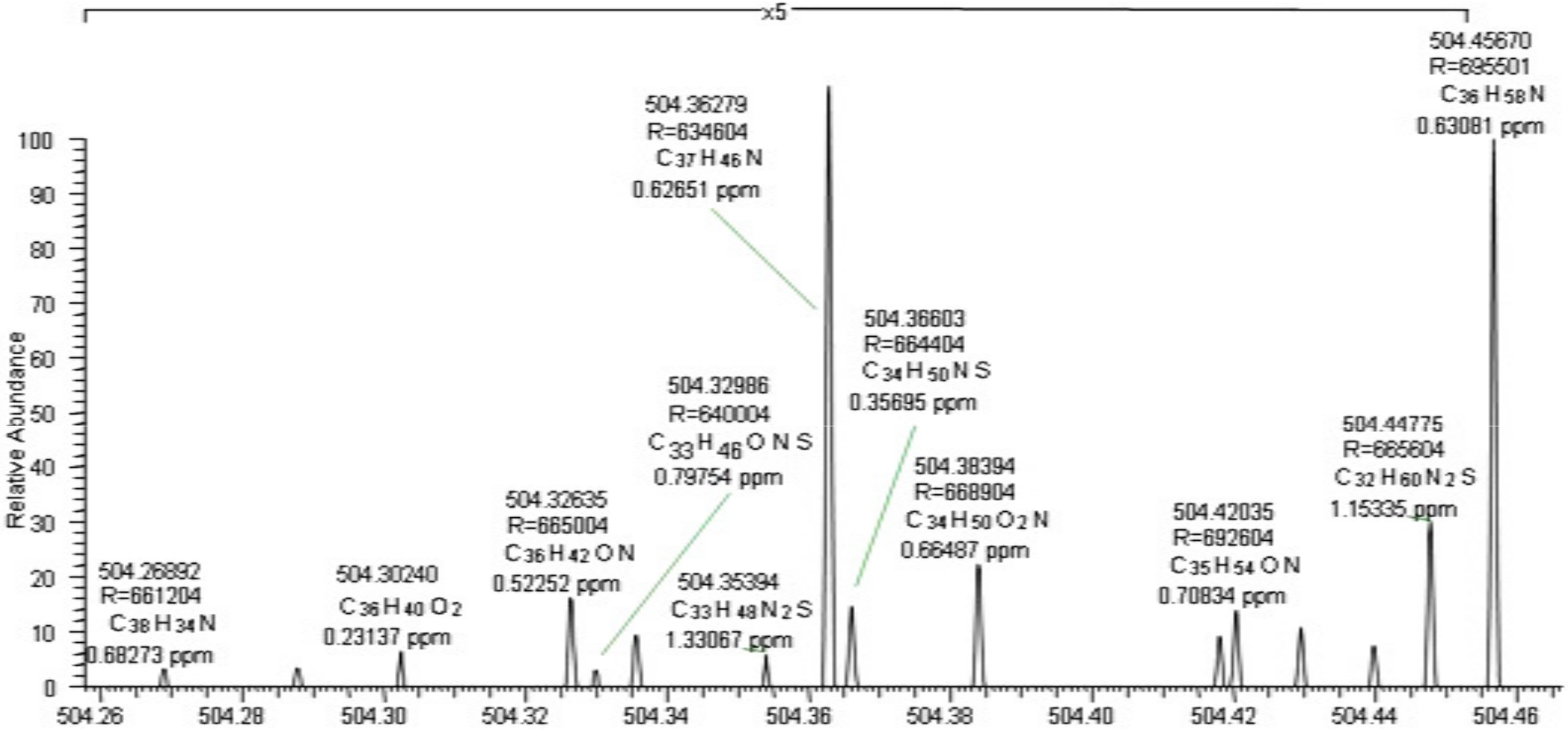
Comparison between high and low resolution



Low resolution:
a single peak

High resolution:
Samples with contaminants can be shown with two peaks

Low resolution:
Samples with contaminants but only one peak





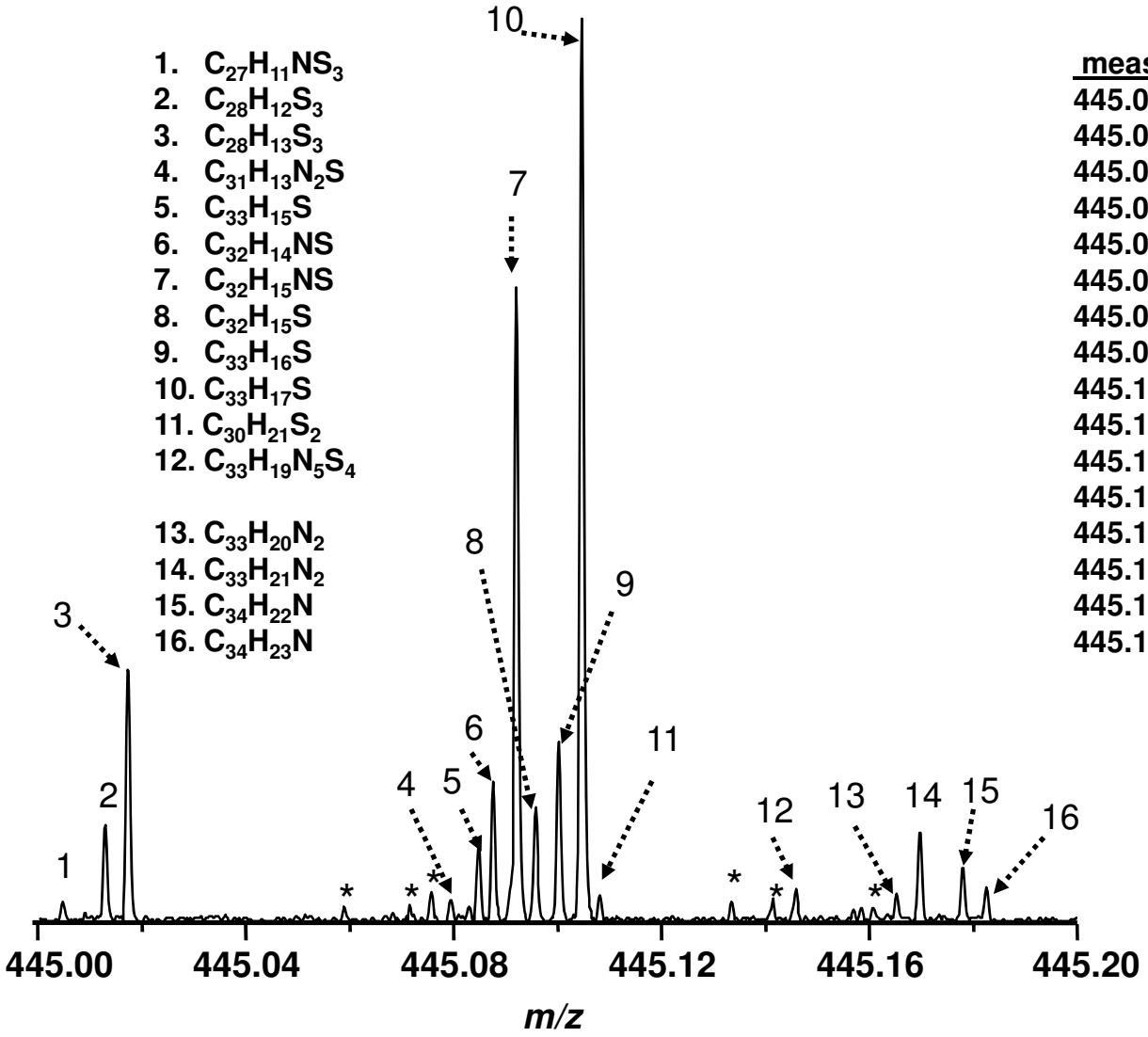
R_p 400,000@*m/z*400
Accuracy 1ppm or less

Resolution and Accuracy

The Importance of Ultra High-Resolution

1. $C_{27}H_{11}NS_3$
2. $C_{28}H_{12}S_3$
3. $C_{28}H_{13}S_3$
4. $C_{31}H_{13}N_2S$
5. $C_{33}H_{15}S$
6. $C_{32}H_{14}NS$
7. $C_{32}H_{15}NS$
8. $C_{32}H_{15}S$
9. $C_{33}H_{16}S$
10. $C_{33}H_{17}S$
11. $C_{30}H_{21}S_2$
12. $C_{33}H_{19}N_5S_4$

13. $C_{33}H_{20}N_2$
14. $C_{33}H_{21}N_2$
15. $C_{34}H_{22}N$
16. $C_{34}H_{23}N$



m/z measured	m/z Calculated
445.00485	445.00481
445.01297	445.01291
445.01741	445.01738
445.07954	445.07939
445.08487	445.08469
445.08764	445.08750
445.09214	445.09197
445.09580	445.09560
445.10024	445.10007
445.10472	445.10454
445.10809	445.10791
445.14587	445.14611
445.16525	445.16545
445.16979	445.16992
445.17799	445.17803
445.18258	445.18250

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Article

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Assessing Biodegradation in the Llanos Orientales Crude Oils by Electrospray Ionization Ultrahigh Resolution and Accuracy Fourier Transform Mass Spectrometry and Chemometric Analysis

Boniek G. Vaz,*[,†,‡] Renzo C. Silva,*[,§] Clécio F. Klitzke,[†] Rosineide C. Simas,[†] Heliara D. Lopes Nascimento,[†] Rosana C. L. Pereira,[†,∥] Diego F. Garcia,[⊥] Marcos N. Eberlin,*[,†] and Débora A. Azevedo*[,§]

[†]Laboratório ThoMSon de Espectrometria de Massas, Universidade Estadual de Campinas, Instituto de Química, Campinas, SP, 13083-970, Brazil

[‡]Universidade Federal de Goiás, Instituto de Química, Campus Samambaia, Goiânia, GO, 74001-970, Brazil

[§]Universidade Federal do Rio de Janeiro, Instituto de Química, Ilha do Fundão, Rio de Janeiro, RJ, 21949-900, Brazil

[∥]Petroleo Brasileiro S/A – Petrobras, CENPES, Rio de Janeiro, RJ, 21941-901, Brazil

[⊥]Instituto Colombiano del Petróleo, ICP/ECOPETROL, Bucaramanga, Colombia

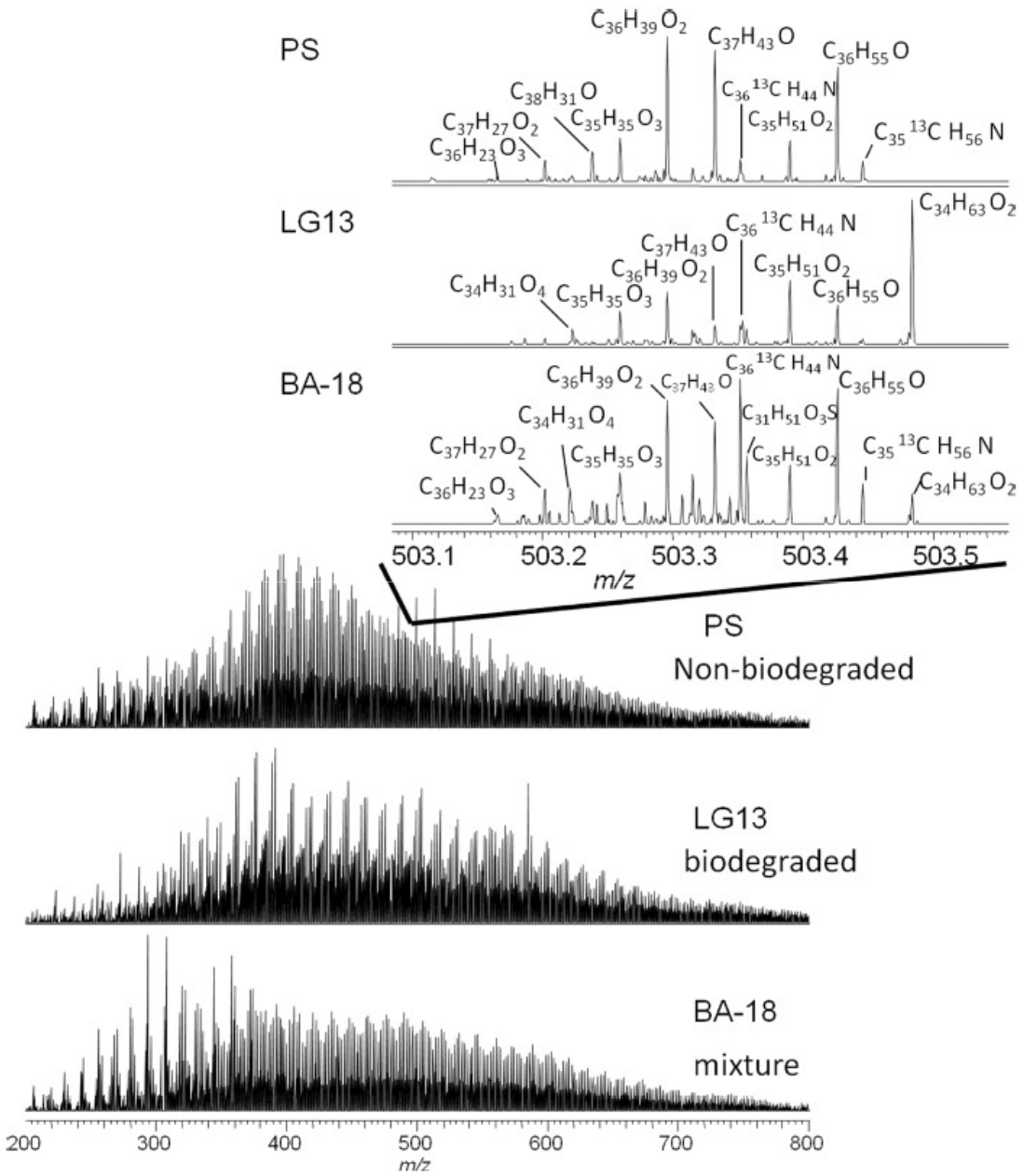


Figure 1. ESI(−) FT-ICR MS of non-biodegraded (PS), biodegraded (LG13), and mixture (BA-18) crude oils.

CLASS DISTRIBUTION CHANGES IN CRUDE OILS

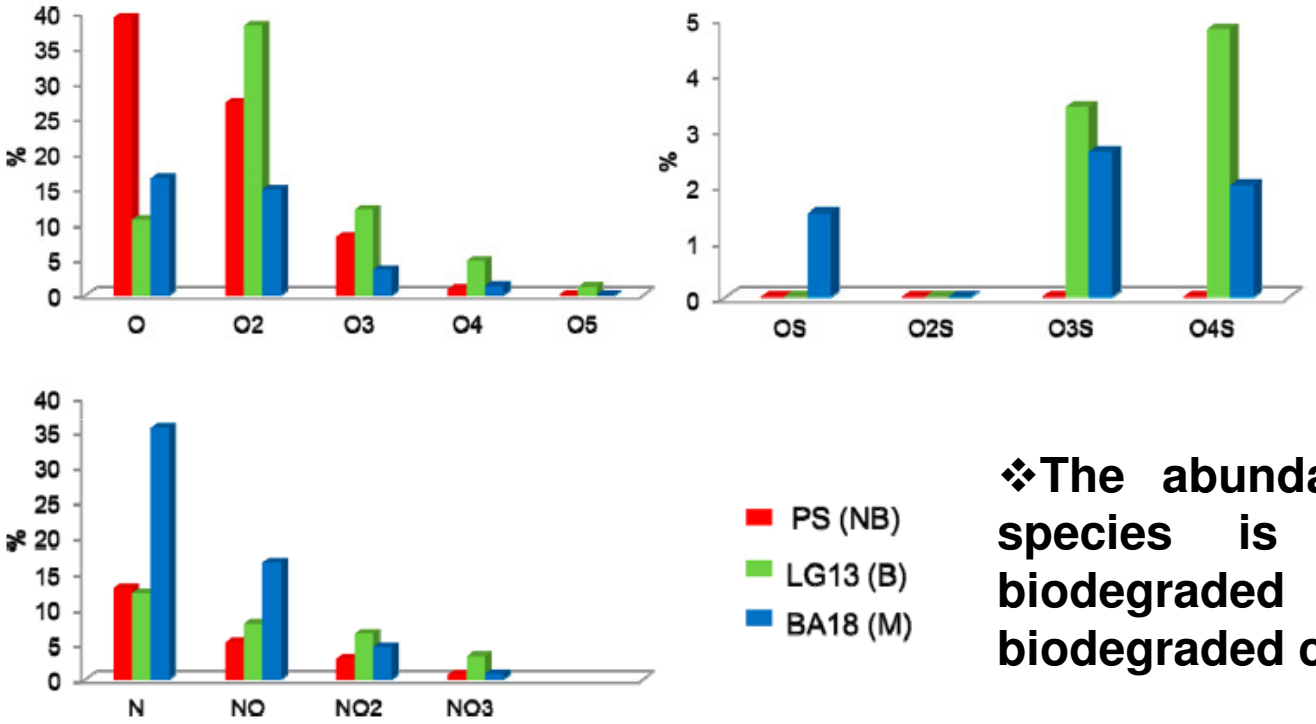


Figure 2. Class distribution changes in crude oils as revealed by ESI(−) FT-ICR MS.

❖**The abundance of O2-species is greater in biodegraded than non-biodegraded crude oils.**

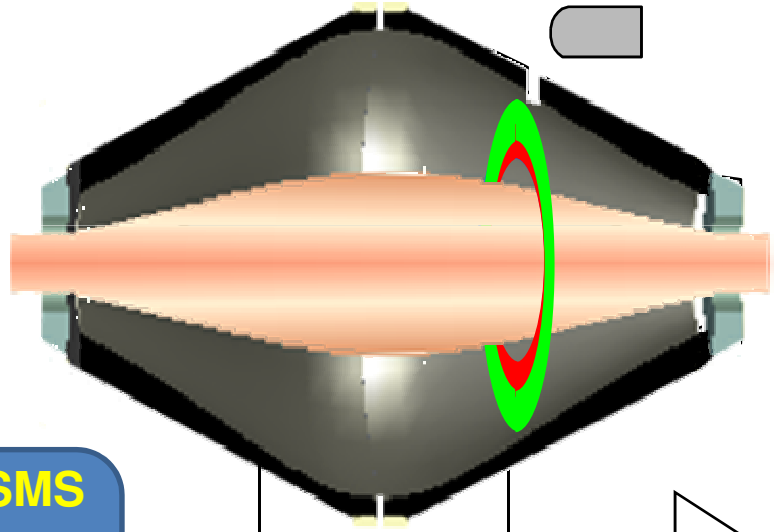
❖**The abundance of O2-species increases as the degree of biodegradation increases**

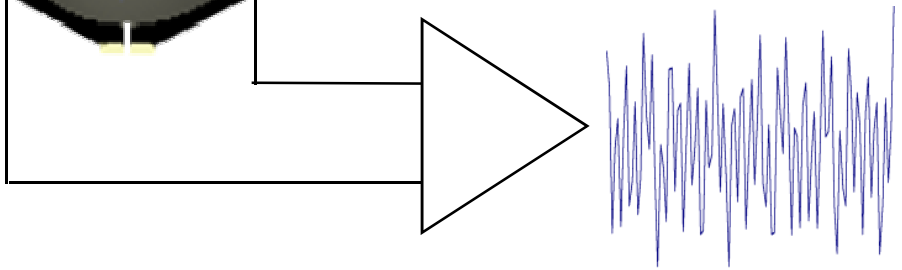
Direct Analysis of Crude Oil using Orbitrap Mass Spectrometry with Resolving Powers above 1,000,000

Eduardo M. Schmidt[1], Marcos A. Pudenzi[1], Jandyson M. Santos[1], Eugen Damoc[2], Eduard Denisov[2], Alexander Makarov[2], Marcos N. Eberlin[1]

[1]ThoMSon Mass Spectrometry Laboratory, Campinas, Brazil;

[2]Thermo Fisher Scientific, Bremen, Germany



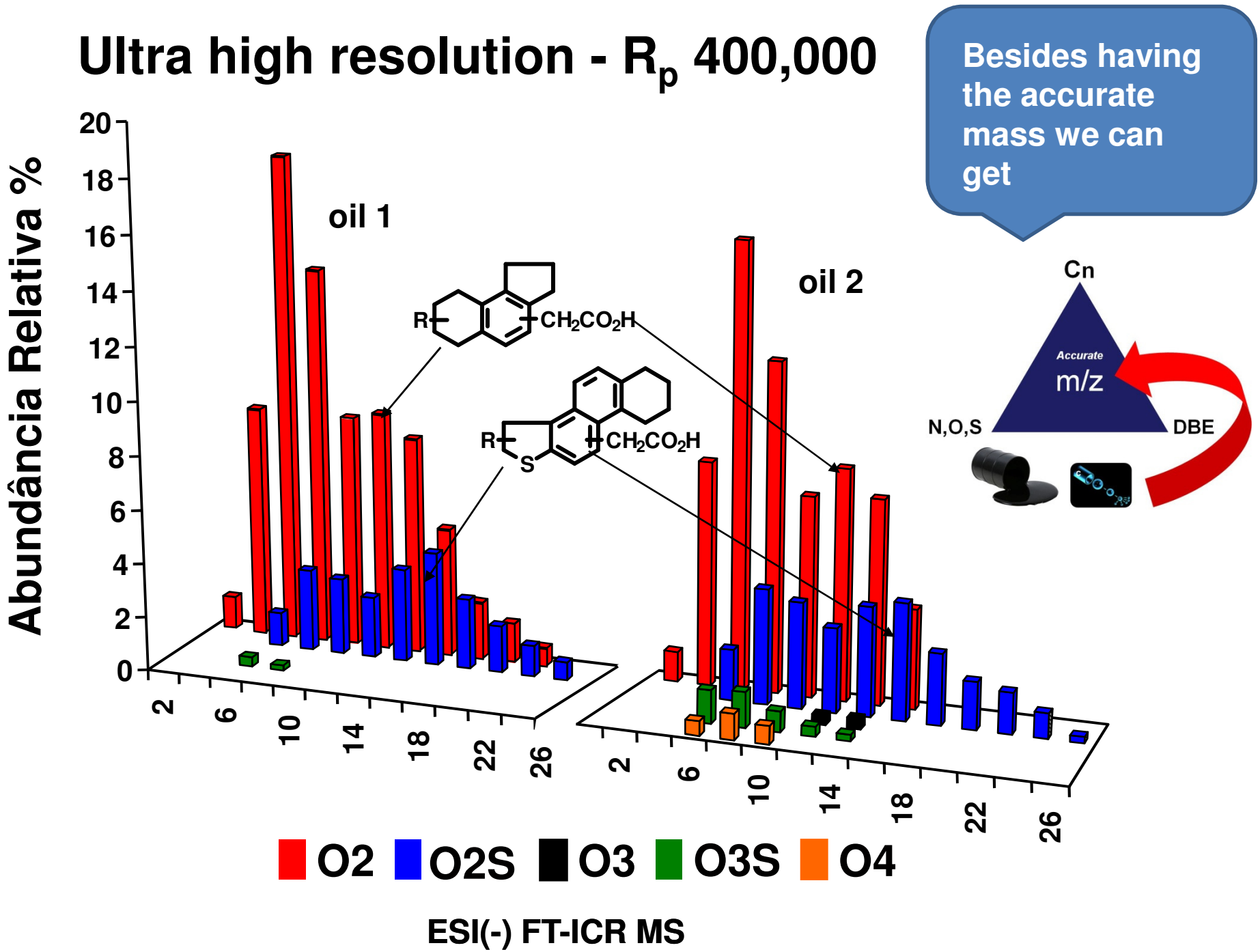


PRESENTATION ON ASMS American Society for Mass Spectrometry Conference - 2014.

ThoMSon Mass Spectrometry Laboratory

Thermo SCIENTIFIC

Ultra high resolution - R_p 400,000



PETROBRAS

Petroleomics by FT-MS

Applied to

EXPLORATION

- ORIGIN
- MATURATION
- BIODEGRADATION

PRODUCTION

- DEPOSITS
- EMULSIONS

REFINING

- CORROSION
- PRODUCT QUALITY





MS Fingerprinting

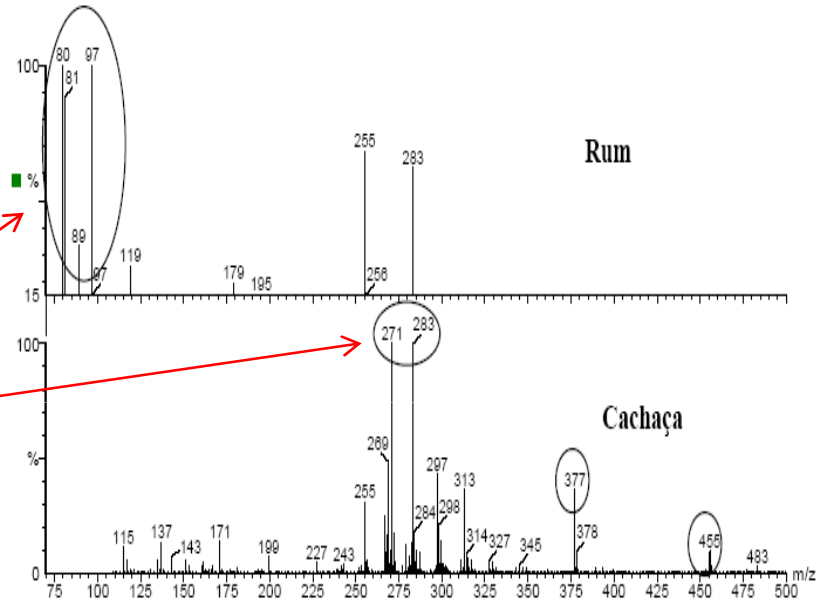
What is FINGERPRINT?



https://www.google.nr/search?hl=pt-BR&site=imghp&tbm=isch&source=hp&biw=1366&bih=667&q=cara+de+dúvida+bebê&oq=cara+de+dúvida&gs_l=img.1.1.0l4.6576.1

Human Fingerprint ⟺ *MS- fingerprinting*

diagnostic ions



Obtaining spectra

Analytical characterization of the sample profile

Can we use direct insertion MS fingerprinting to classify crude Oils samples?



energy&fuels

Article

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Gasoline, Kerosene, and Diesel Fingerprinting via Polar Markers

Renato Haddad,[†,§] Thaís Regiani,[†] Clécio F. Klitzke,[†] Gustavo B. Sanvido,[†] Yuri E. Corilo,[†] Daniella V. Augusti,[‡] Vânya M. D. Pasa,[‡] Rita C. C. Pereira,[‡] Wanderson Romão,[†] Boniek G. Vaz,[†] Rodinei Augusti,[‡] and Marcos N. Eberlin*[,†]

[†]ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, University of Campinas (UNICAMP), 13083-970 Campinas, São Paulo (SP), Brazil

[‡]Department of Chemistry, Federal University of Minas Gerais (UFMG), 31270-901 Belo Horizonte, Minas Gerais (MG), Brazil

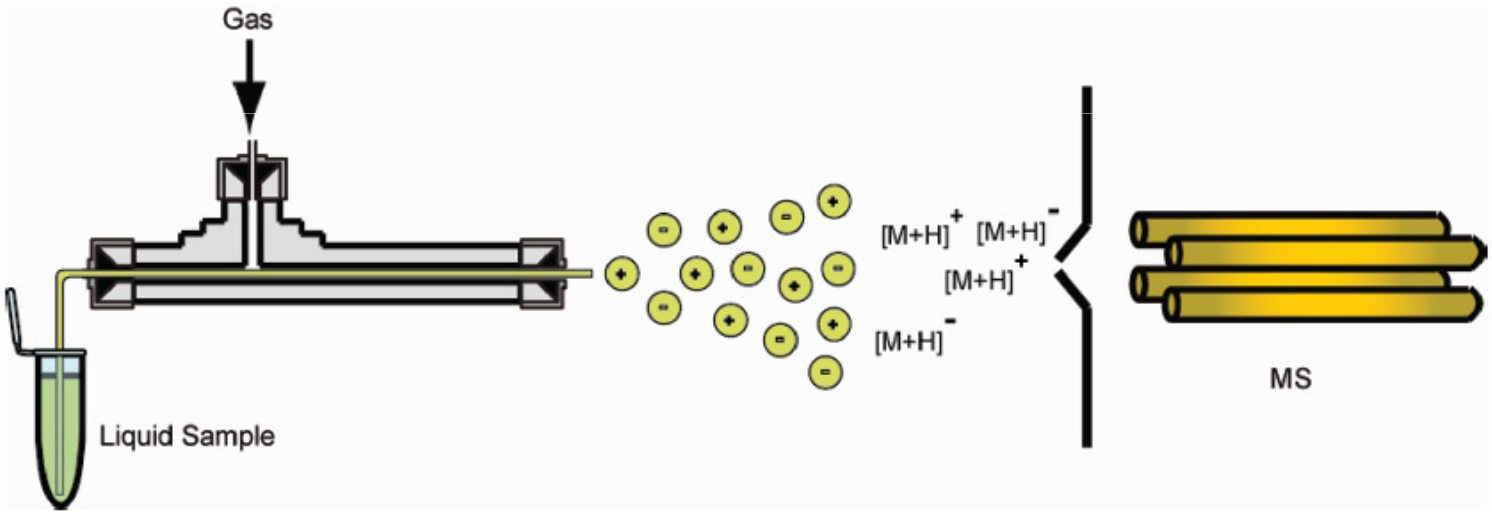


Figure 1. V-EASI-MS setup used for the analysis of diluted methanolic solutions of crude oil distillates.

Low resolution

only to see the profile

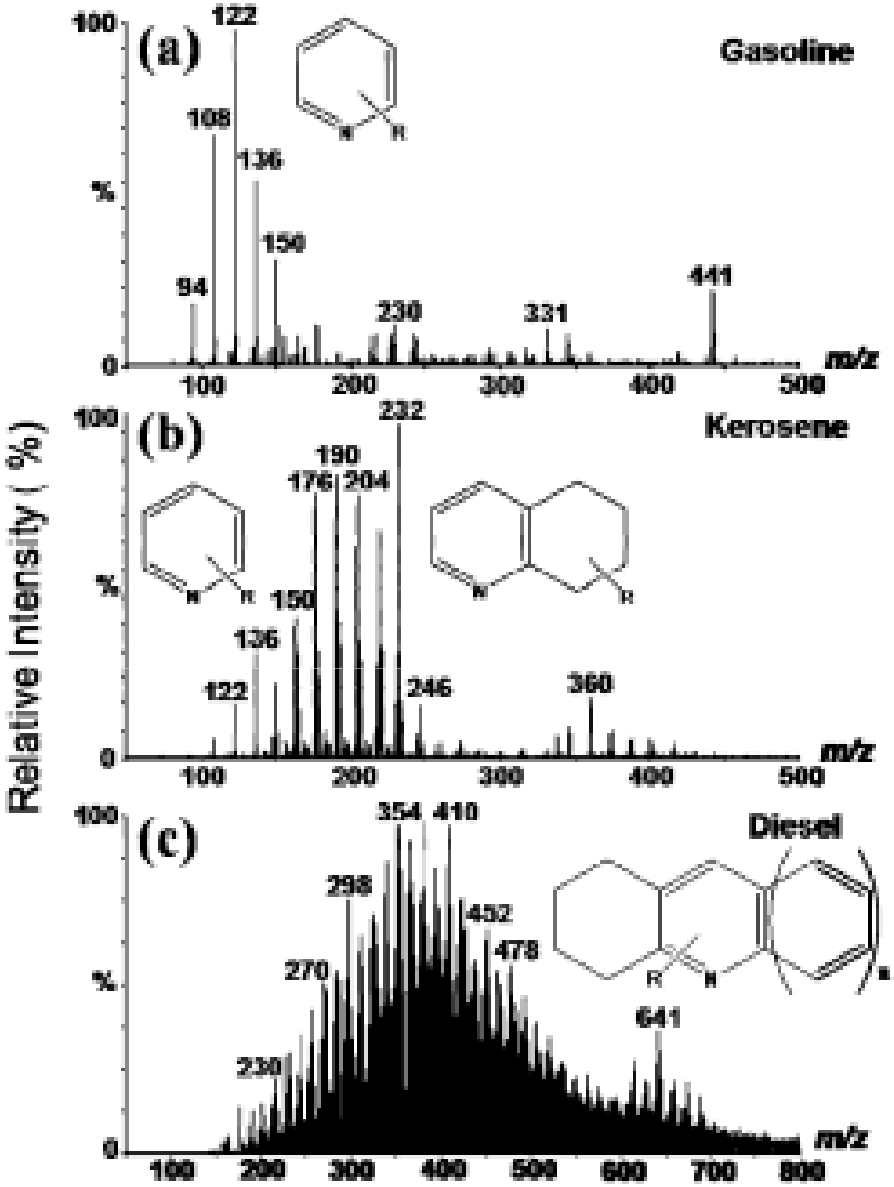


Figure 2. V_L-EASI(+)-MS of fresh methanolic solutions of (a) gasoline, (b) kerosene, and (c) diesel.

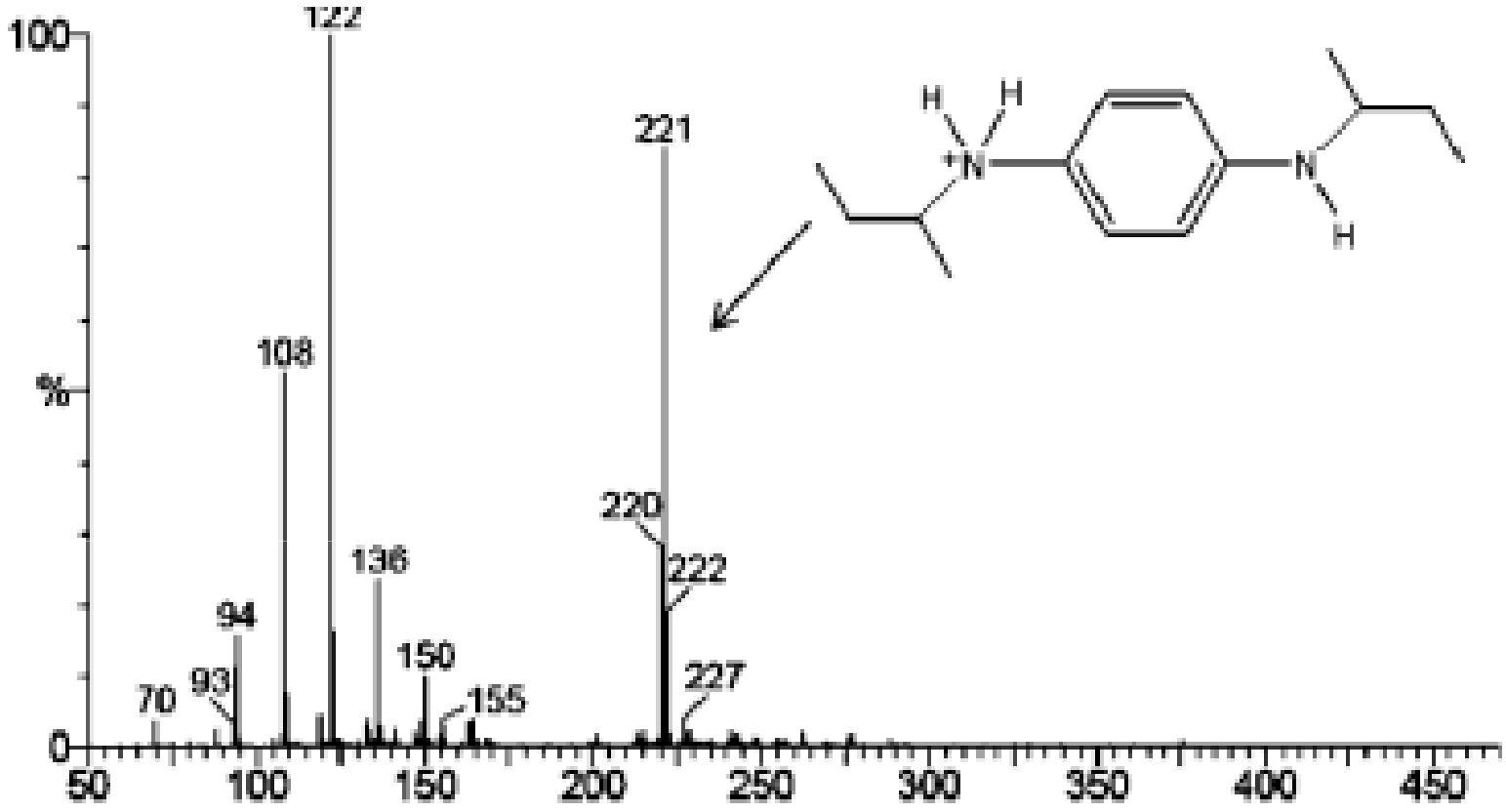


Figure 3. V-EASI(+)-MS of methanolic solutions of a gasoline sample with the detection of an "artificial marker", the antioxidant additive *N,N'*-di-*sec*-butyl-*p*-phenylenediamine.

Profile of mixtures of Gas/Diesel in different proportions

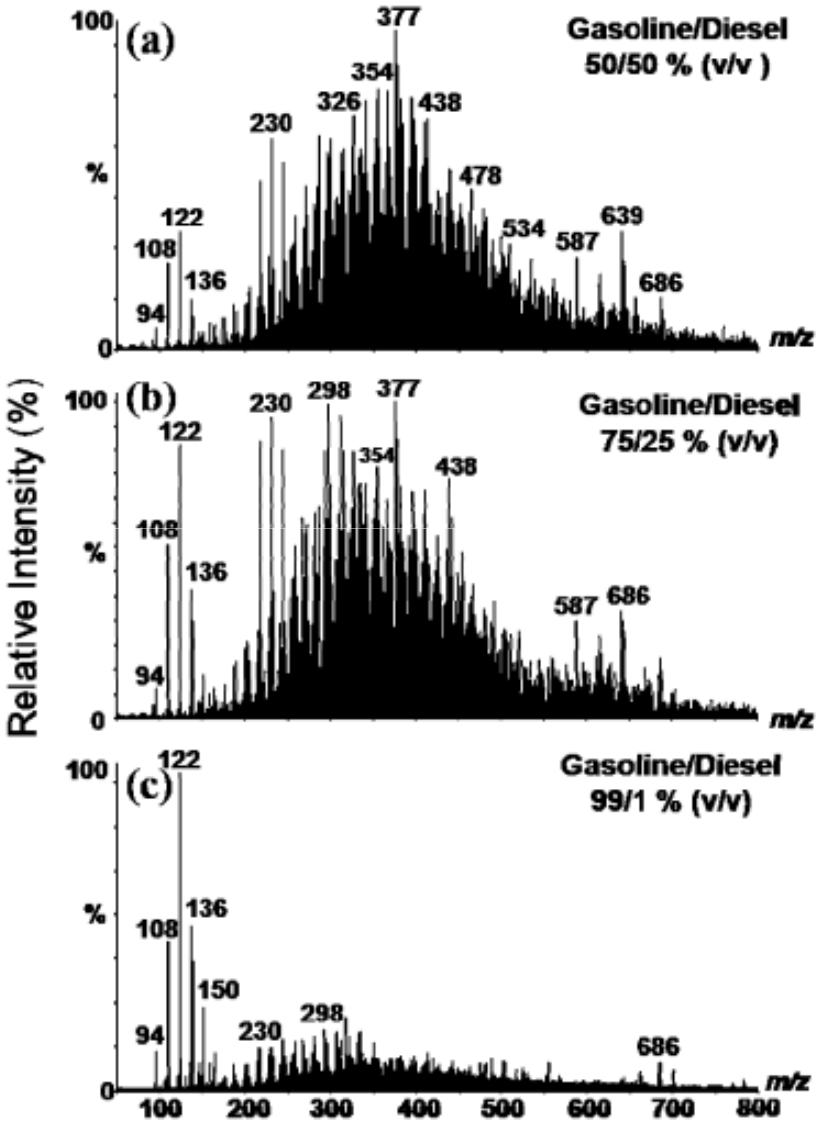


Figure 5. V-EASI(+)-MS of methanolic solutions of gasoline/diesel admixtures: (a) 50:50, (b) 75:25, and (c) 99:1 (%, v/v).

Evaluation of oxidation products in fatty acid esters

energy&fuels

Article

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Biodiesel Oxidation Monitored by Ambient Desorption/Ionization Mass Spectrometry

Adriana T. Godoy,[†] Gustavo G. Pereira,[‡] Lucas L. Ferreira,[†] Ildenize B. S. Cunha,[†] Daniel Barrera-Arellano,[‡] Romeu J. Daroda,[§] Marcos N. Eberlin,[†] and Rosana M. Alberici*[,†,§]

[†]ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, and [‡]Fats and Oils Laboratory, Faculty of Food Engineering, University of Campinas (UNICAMP), 13083-970 Campinas, São Paulo, Brazil

[§]National Institute of Metrology, Quality and Technology (INMETRO), 25250-020 Duque de Caxias, Rio de Janeiro, Brazil

Eur. J. Lipid Sci. Technol. 2014, *116*, 952–960

Research Article

Ambient sonic-spray ionization mass spectrometry for rapid monitoring of secondary oxidation products in biodiesel

Gustavo G. Pereira[1,a], Rosana M. Alberici[2,3,a], Gabriel D. Fernandes[1], Ildenize B. S. Cunha[2], Marcos N. Eberlin[2], M. C. Dobarganes[4], Romeu J. Daroda[3] and Daniel Barrera-Arellano[1]

[1] Fats and Oils Laboratory, Faculty of Food Engineering, University of Campinas – UNICAMP, Campinas, SP, Brazil

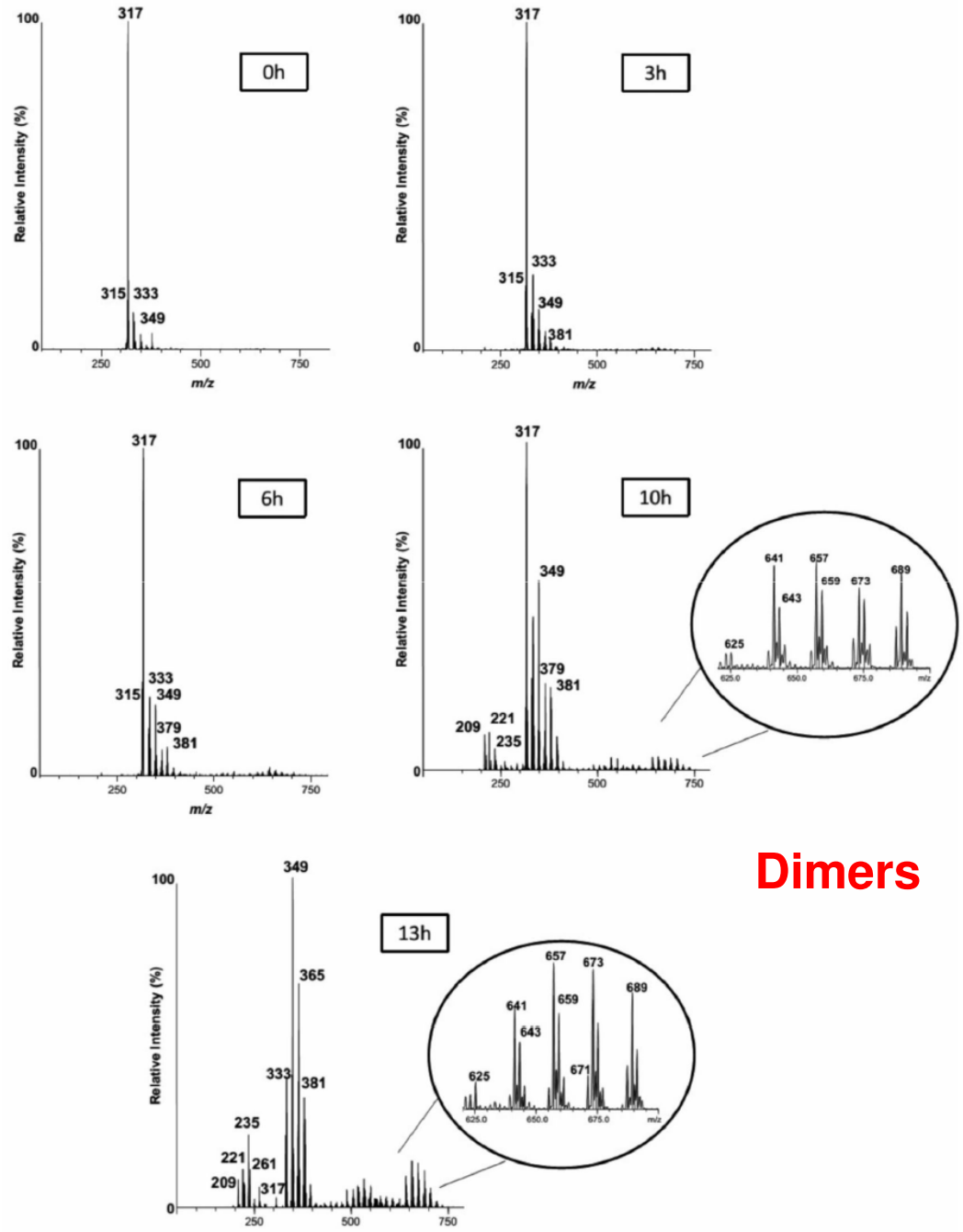
[2] ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, University of Campinas – UNICAMP, Campinas, SP, Brazil

[3] National Institute of Metrology, Quality and Technology (INMETRO), Duque de Caxias, RJ, Brazil

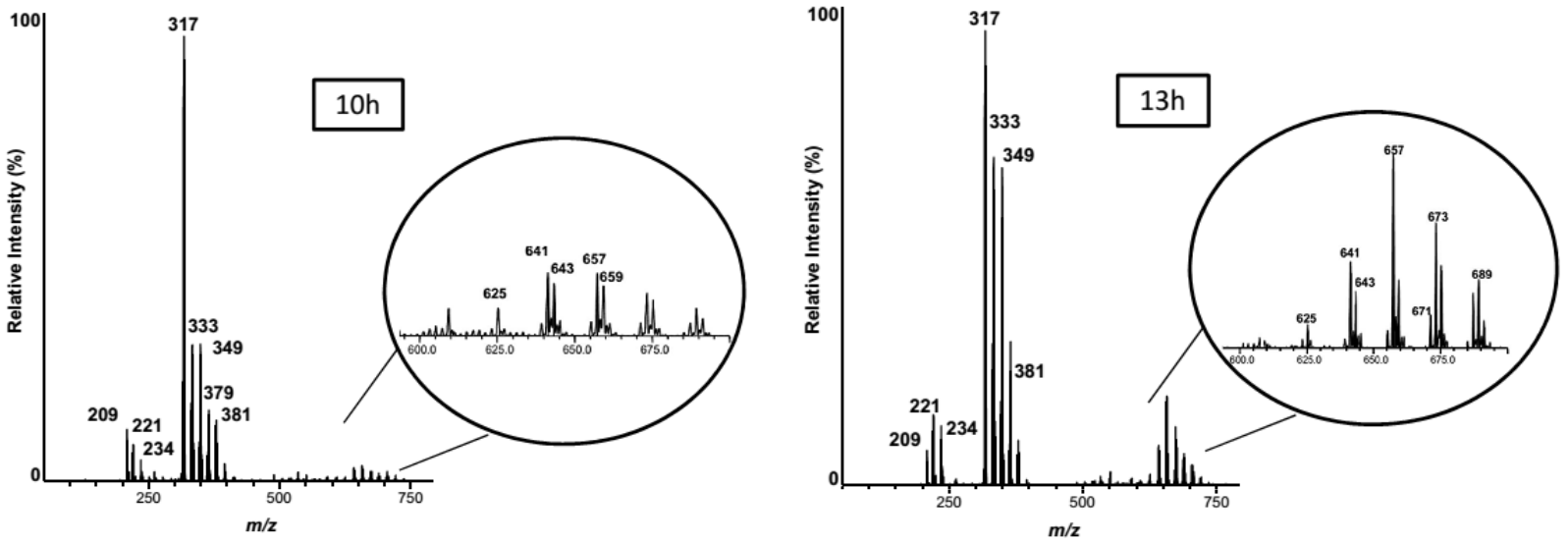
[4] Instituto de la Grasa (CSIC), Avda Padre Garcia Tejero, Sevilla, Spain

EASI(+)-MS profiles of fresh soybean biodiesel and after different periods of accelerated oxidation (110℃ and 10 L/h).

Oxidative stability of soybean biodiesel was 9.6 h



EASI-MS

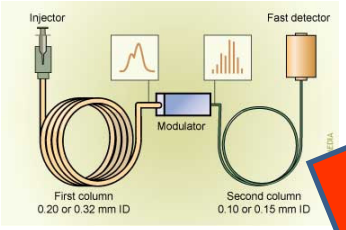


Appearance of secondary compounds

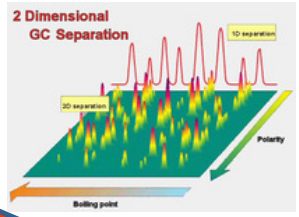
(1) Dimers
(2) Compounds from fission hydroperoxide
Markers of oxidative high degree

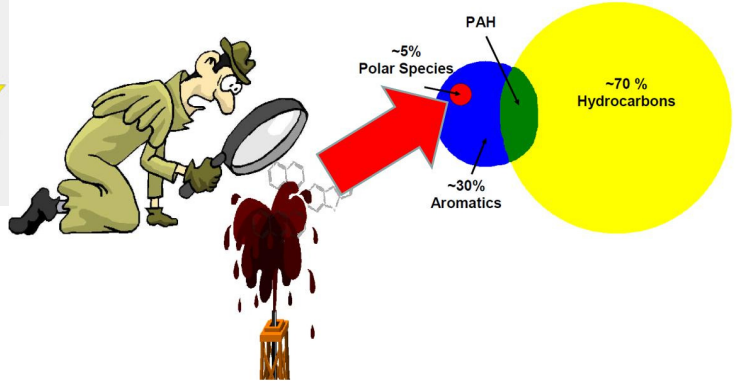
→ Biodiesel in inadequate conditions

Conclusion



GCxGC/MS
LECO





FTICR

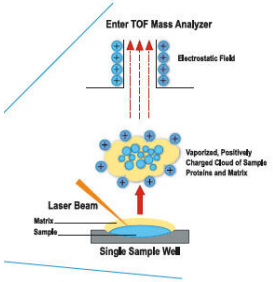


HC

Asphalthenes



Polar





MegaOrbitrap

High MW HC

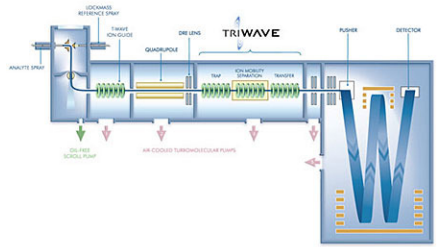
Emulsifiers

distillates

Structures



MALDI TOF Bruker



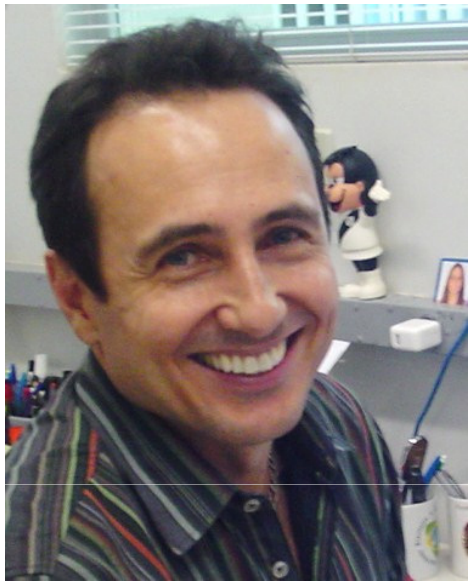


SYNAPT
TWIM-MS
Waters

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