Dra. Ildenize Cunha
State University of Campinas (UNICAMP)

Mass Spectrometry: a pioneering and renewed tool for petrochemical analysis
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?

Introduction of sample

Ionization source
- MALDI
- EI
- CI
- ESI
- APCI
- APPI
- DART
- DESI
- EASI

analyzer of m/z

High Vacuum

Detector

Direct way
- HPLC
- GC

MCP e⁻ Multiplier

B
Q
TOF
Íon Trap 3D
Linear Trap
Orbitrap
ICR
1897 J. J. Thomson e\- discovery

1912 First MS Thomson

1942 First Commercial MS

1953 Quadrupole and Trap 3D Paul & Steinwedel

1956 First GC/MS

1958 First Commercial TOF

1958 First Commercial Quadrupole

1959 First Comercial MS

1968 Linear Trap 2D

1968 First Commercial Quadrupole

1974 First LC/MS and FT-ICR description

1984 Linear Trap 2D

1987 MALDI Karas & Hillenkamp

1988 ESI by John Fenn

2000 Macromolecules Spectrum > 10^6 Da

2005 Orbitrap Makarov

Ultra High resolution analyzers

Timeline
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.

~ 30% aromatic hydrocarbons

~ 70% saturated hydrocarbons

~ 5% NSO

~ 15% resins and asphaltenes
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.
Composition

Resolution
Able to separate 2 ions that have approximate mass

Accuracy
Could be evaluated from the error

Important for correct assignment of molecular formulas

$$Error(ppm) = \frac{m_{exp} - m_{theo}}{m_{theo}} \times 10^6$$
Comparison between high and low resolution

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

**Low resolution:**
Samples with contaminants but only one peak
$R_p \ 400,000@m/z400$

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_{16}S
9. C_{33}H_{16}S
10. C_{33}H_{17}S
11. C_{30}H_{21}S
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

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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,§ Marco N. Eberlin,⋆† and Débora A. Azevedo⋆§

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*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.
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. Schmidt¹, Marcos A. Pudenzi¹, Jandyson M. Santos¹, Eugen Damoc², Eduard Denisov², Alexander Makarov², Marcos N. Eberlin¹

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PRESENTATION ON ASMS American Society for Mass Spectrometry Conference - 2014.
Ultra high resolution - $R_p$ 400,000

Besides having the accurate mass we can get...
Petroleomics by FT-MS

Applied to

EXPLORATION
- ORIGIN
- MATURATION
- BIODEGRADATION

PRODUCTION
- DEPOSITS
- EMULSIONS

REFINING
- CORROSION
- PRODUCT QUALITY
MS Fingerprinting

What is FINGERPRINT?
Human Fingerprint ⇔ MS- fingerprinting

Obtaining spectra

diagnostic ions

Analytical characterization of the sample profile
Can we use direct insertion MS fingerprinting to classify crude Oils samples?
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*,†

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‡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. VL-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 \(N,N'-\text{di-sec-butyl}-p\)-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

Biodiesel Oxidation Monitored by Ambient Desorption/Ionization Mass Spectrometry

Adriana T. Godoy,† Gustavo G. Pereira,‡ Lucas L. Ferreira,† Ildenize B. S. Cunha,†
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Research Article

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

Gustavo G. Pereira†,§, Rosana M. Alberici‡,§, Gabriel D. Fernandes†, Ildenize B. S. Cunha‡,
Marcos N. Eberlin§, M. C. Dobarganes§, Romeu J. Daroda§ and Daniel Barrera-Arellano†

† Fats and Oils Laboratory, Faculty of Food Engineering, University of Campinas – UNICAMP, Campinas, SP, Brazil
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§ Instituto de la Grasa (CSIC), Avda Padre García Tejero, Sevilla, Spain
EASI(+-)‐MS profiles of fresh soybean biodiesel and after different periods of accelerated oxidation (110°C and 10 L/h).

Oxidative stability of soybean biodiesel was 9.6 h
Appearance of secondary compounds

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

Biodiesel in inadequate conditions
Conclusion

Asphaltenes

HC

High MW HC

Emulsifiers

Distillates

Structures

Polar

~5% Polar Species

~70% Hydrocarbons

~30% Aromatics

FTICR

GCxGC/MS

LECO

MegaOrbitrap

MALDI TOF Bruker

SYNAPT TWIM-MS Waters
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