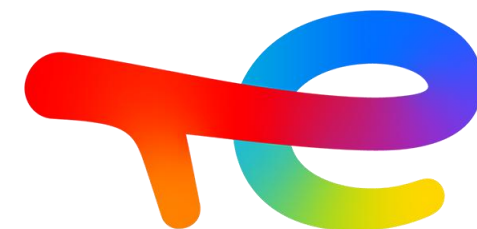


*Xperience Tour Normandy*



**TotalEnergies**

## **ELEM-SPOT:**

Selective detection and multi-element quantification (C, H, N, O, S) in gas chromatography

Titziana Orlando



# ELEM-SPOT

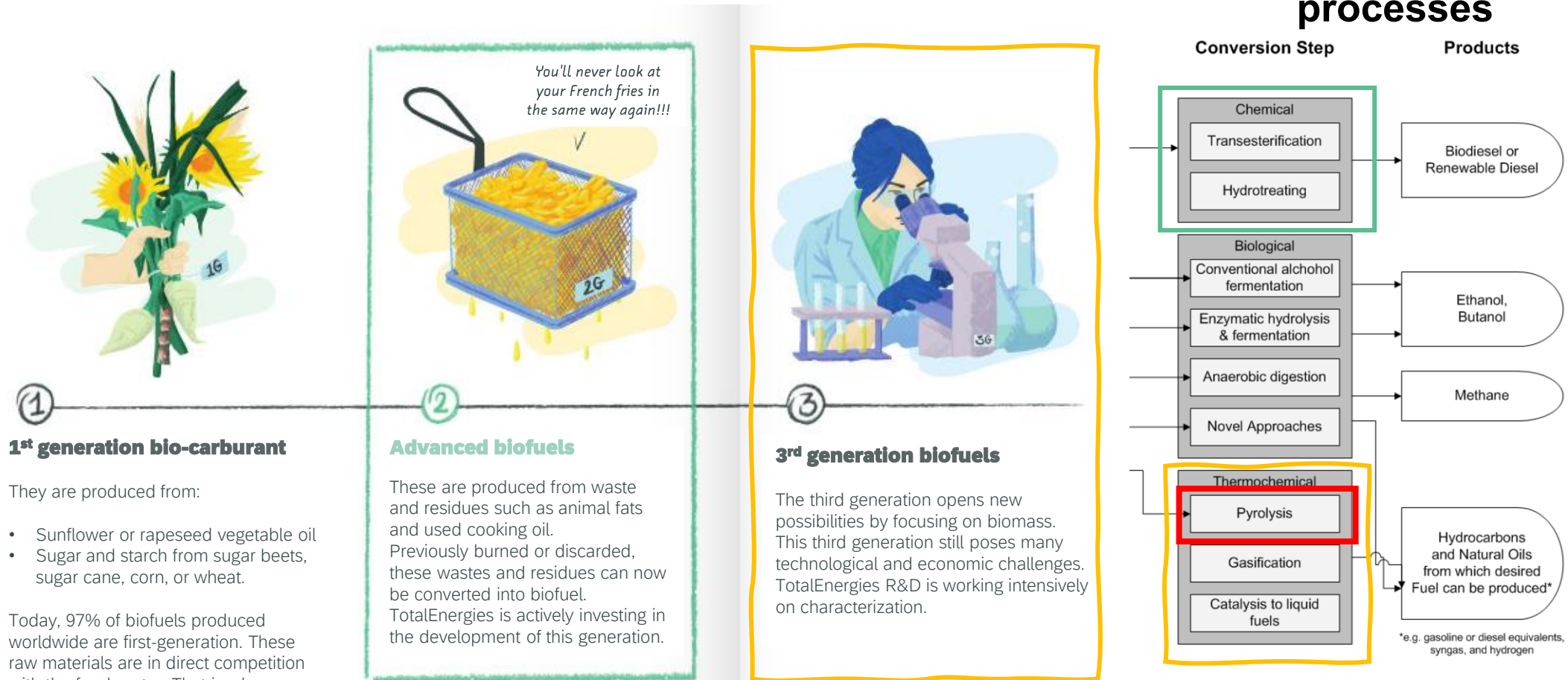


Universidad de Oviedo

# CONTEXT: European Renewable Energy Directive

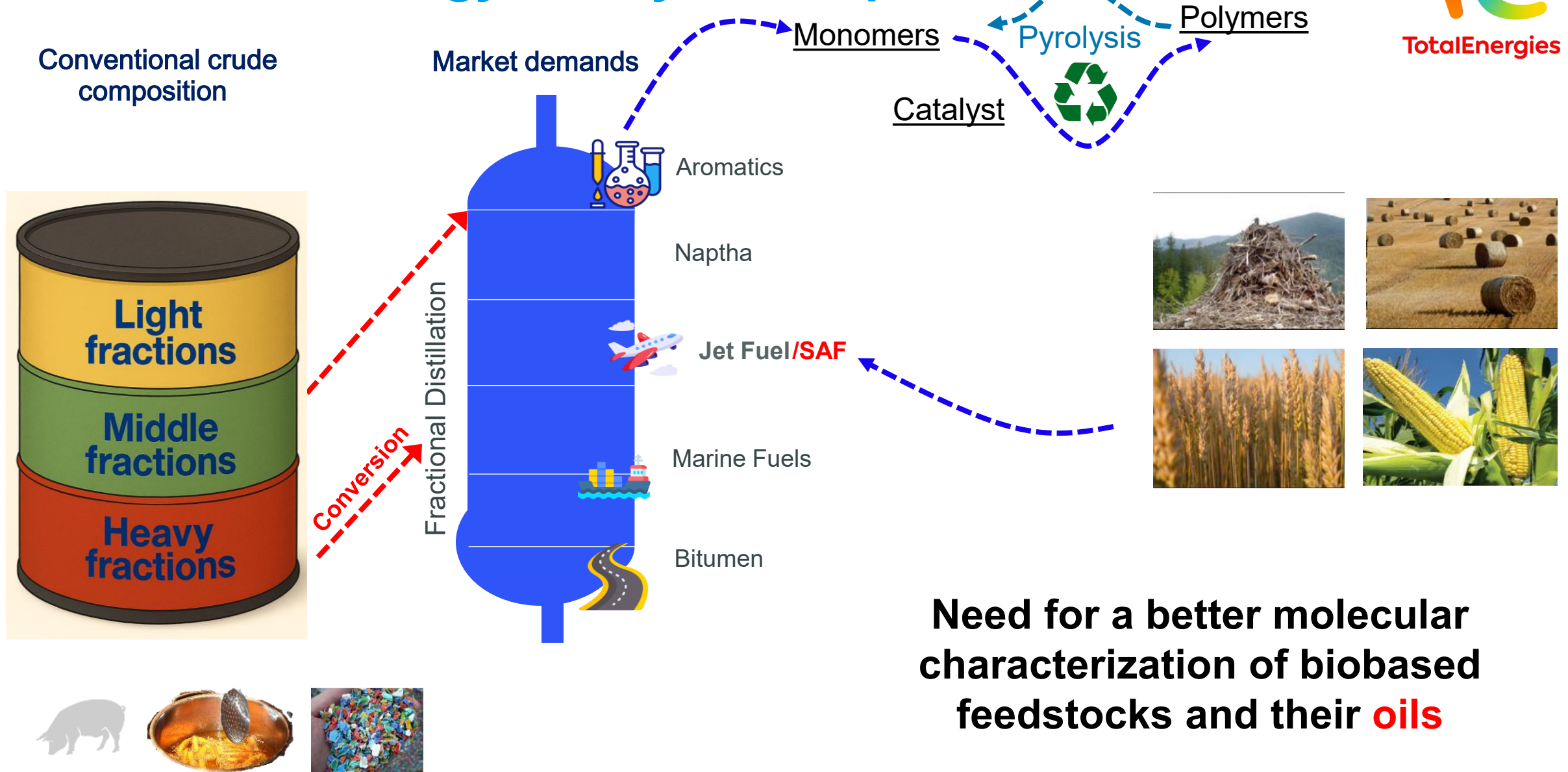
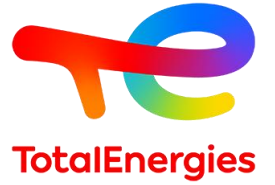
- The directive update (RED II & III) sets rules for the EU to achieve **14% renewables target by 2030**. Among other measures, it introduces a target for advanced biofuels (5.5%)

## Biomass conversion processes



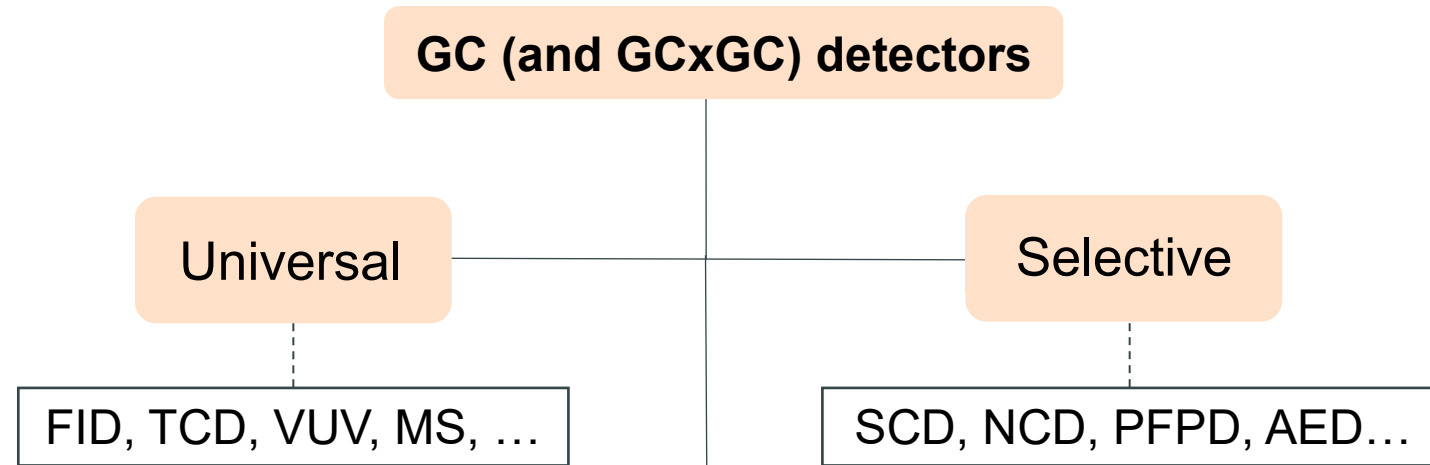
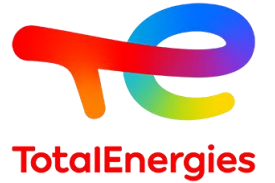
**Analytical developments are strongly required**

# CONTEXT: Energy & Polymer map



Need for a better molecular characterization of biobased feedstocks and their **oils**

# ELEM-SPOT: Pushing the boundaries of GC detection



Development of a **single detector** able to provide:

- Universal response (C and H)
- Selective response (N, S, O)
- Compound Independent calibration
- Structural compound elucidation



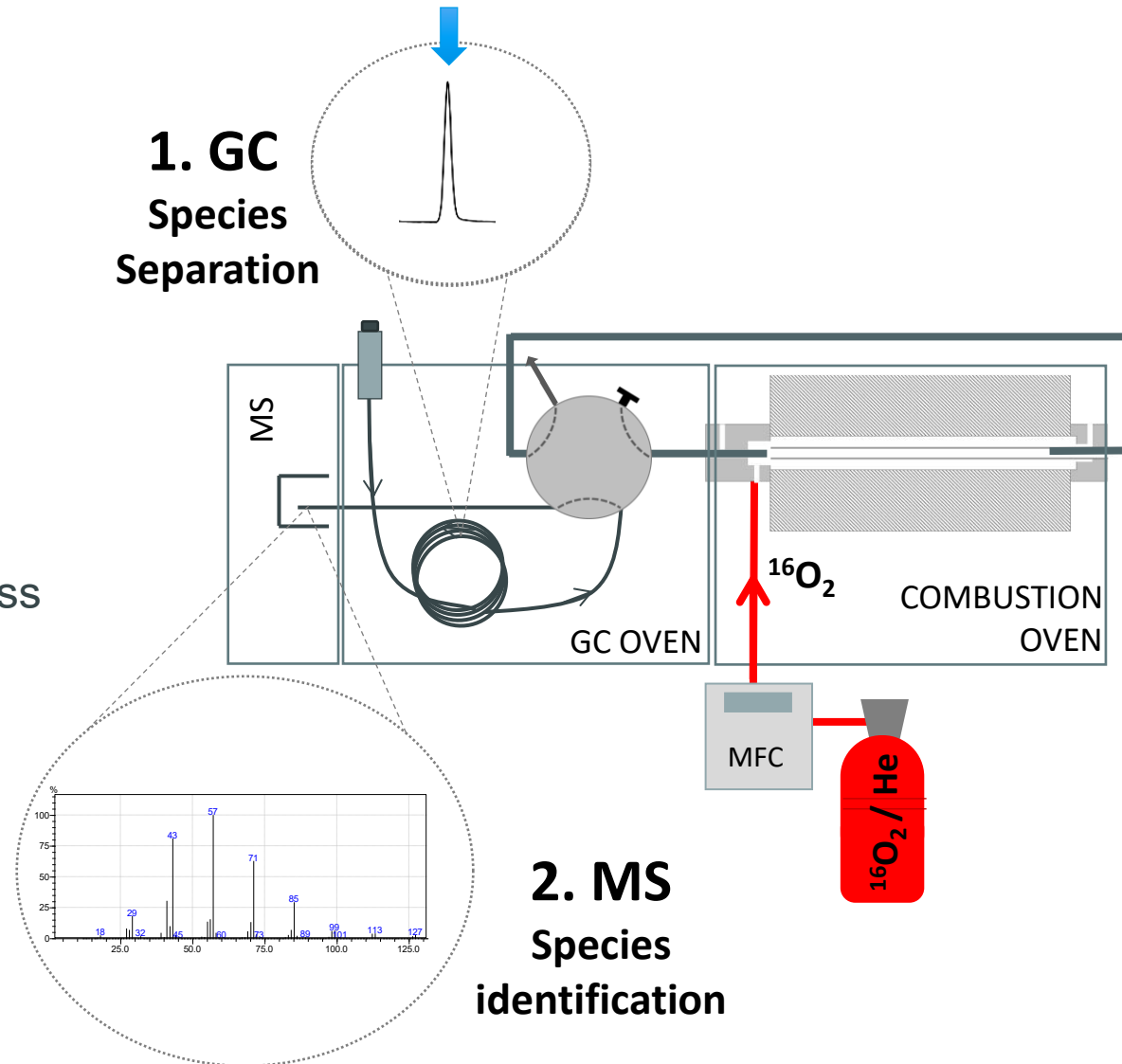
# ELEM-SPOT

# ELEM-SPOT: GC-MS

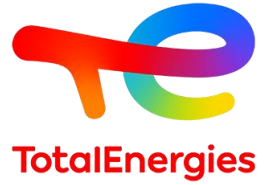
- By bypassing the combustion oven

→ classical GC-MS

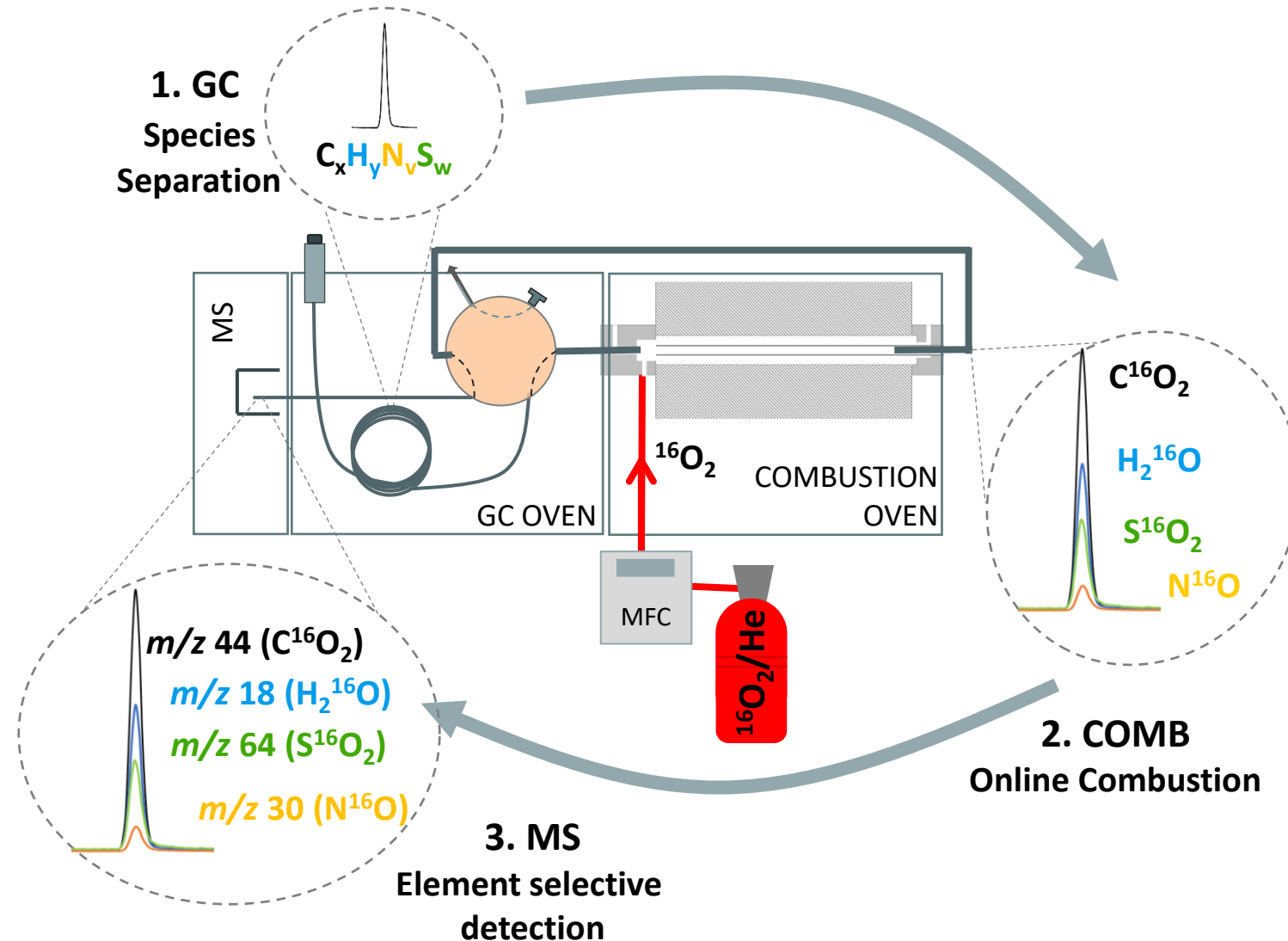
- Keep the structural elucidation power of mass spectrometry thus allowing **compound identification**



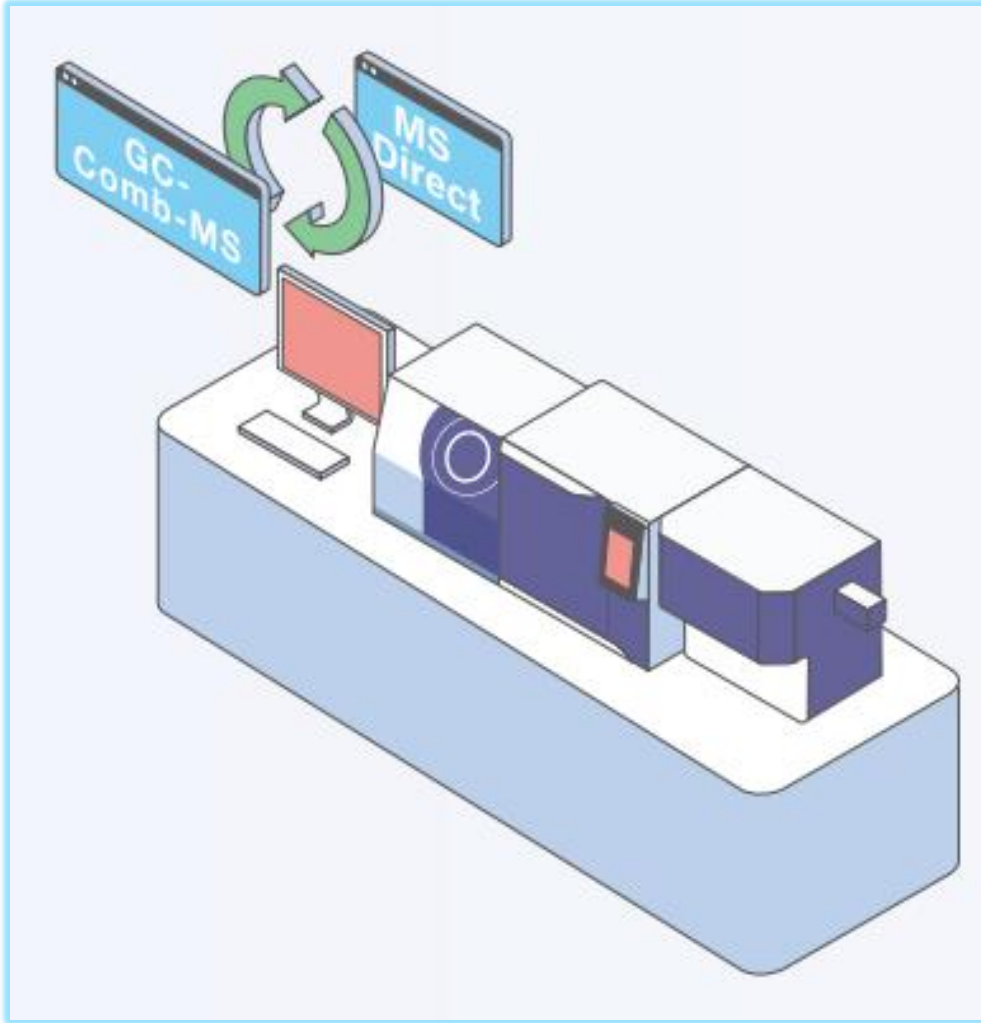
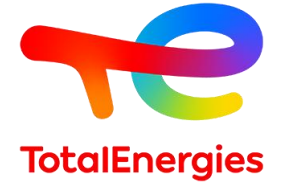
# ELEM-SPOT: GC-COMB-MS – N, S, C, H quantification



- Just by **switching** the valve, it becomes a powerful element selective and equimolar system
- Allows sensitive, selective and robust quantification of **N**, **S**, **C** and **H** present in each individual chromatographic peak



# ELEM-SPOT: Pushing the boundaries of GC detection



Just by **switching a valve** it can be operated in two modes

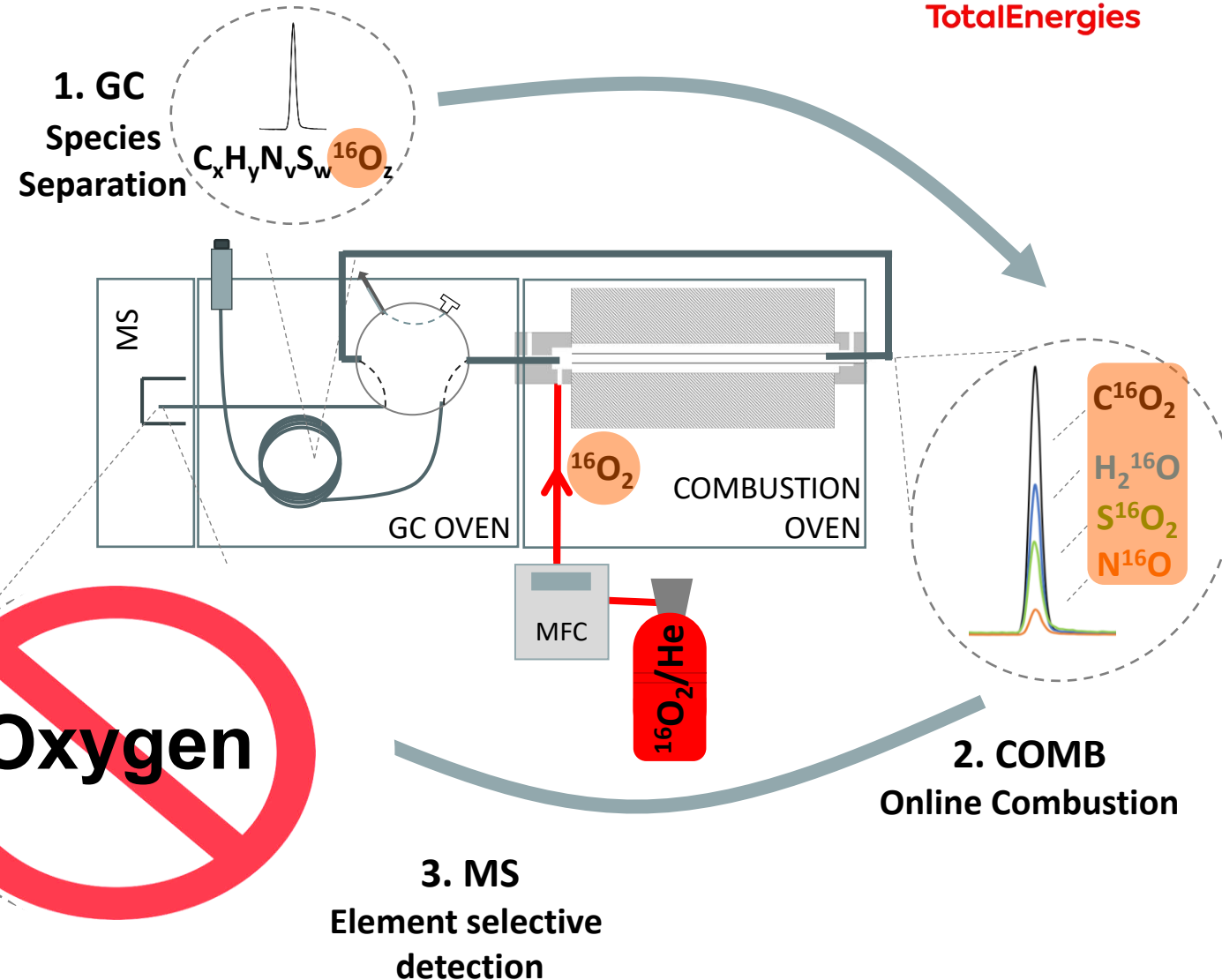
**GC-MS** → structural compound elucidation

**GC-COMB-MS** → equimolar quantification

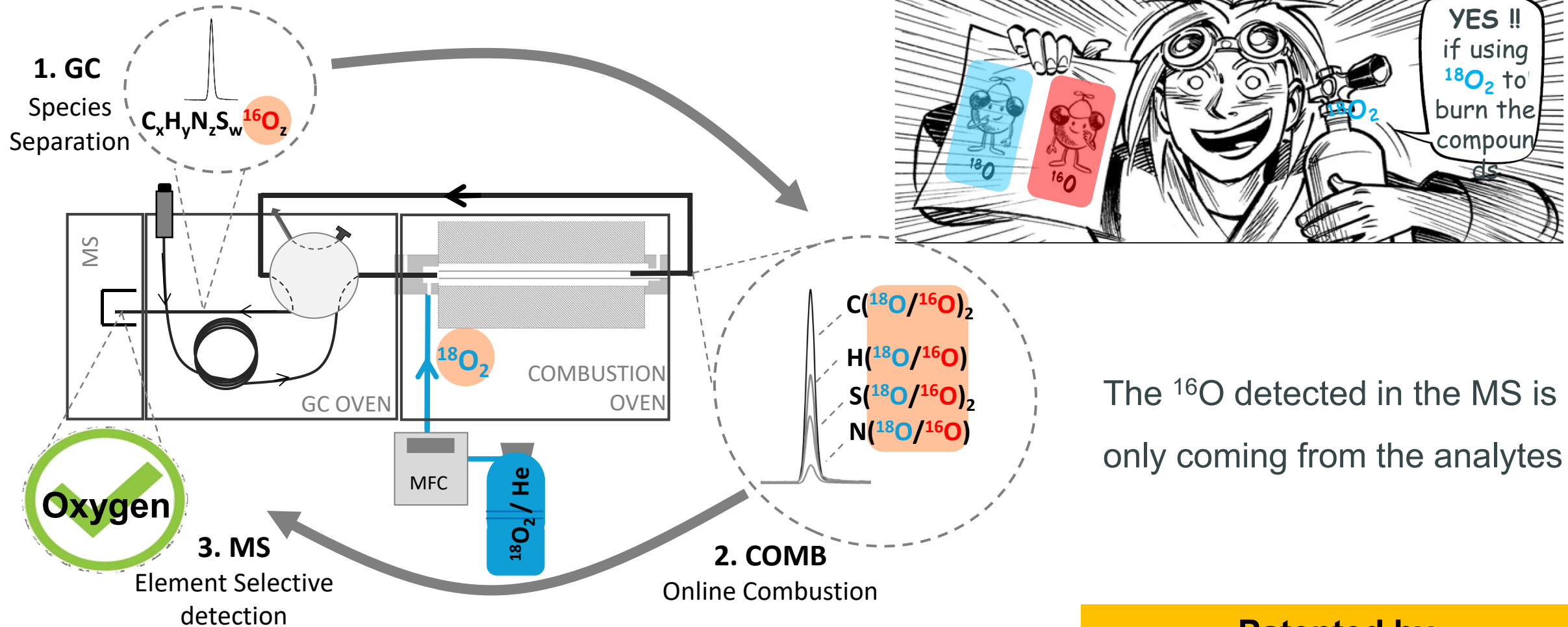


# ELEM-SPOT: GC-COMB-MS – O quantification

- Oxygen quantification **impossible** when using  $^{16}\text{O}_2$  as combustion gas !!
- Cannot distinguish the  $^{16}\text{O}$  detected that is coming from the analytes or from the combustion gas



# ELEM-SPOT: GC-COMB-MS – O quantification

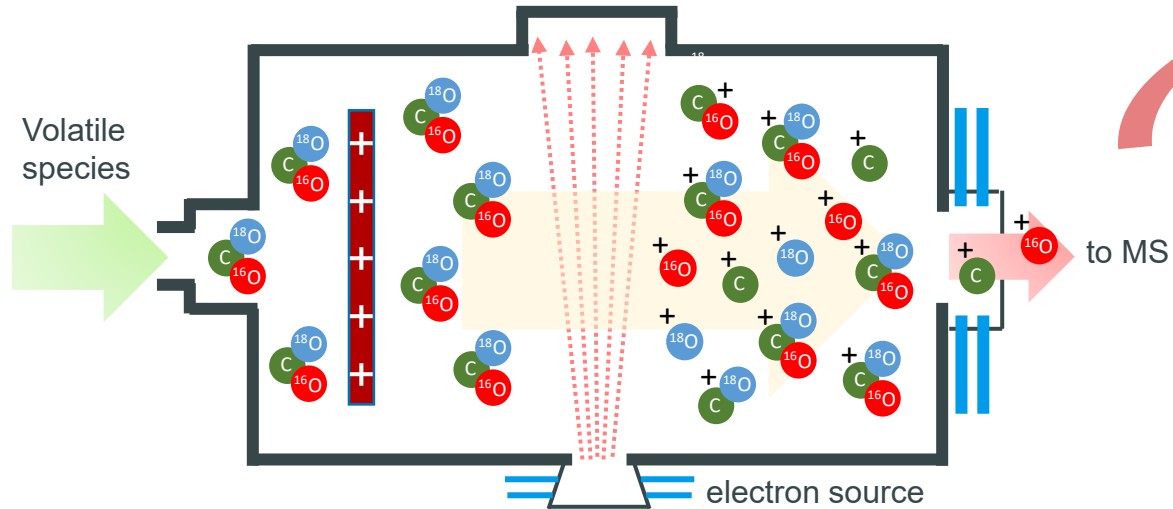


The  $^{16}O$  detected in the MS is only coming from the analytes

Under exclusive license with  
SHIMADZU Corp.

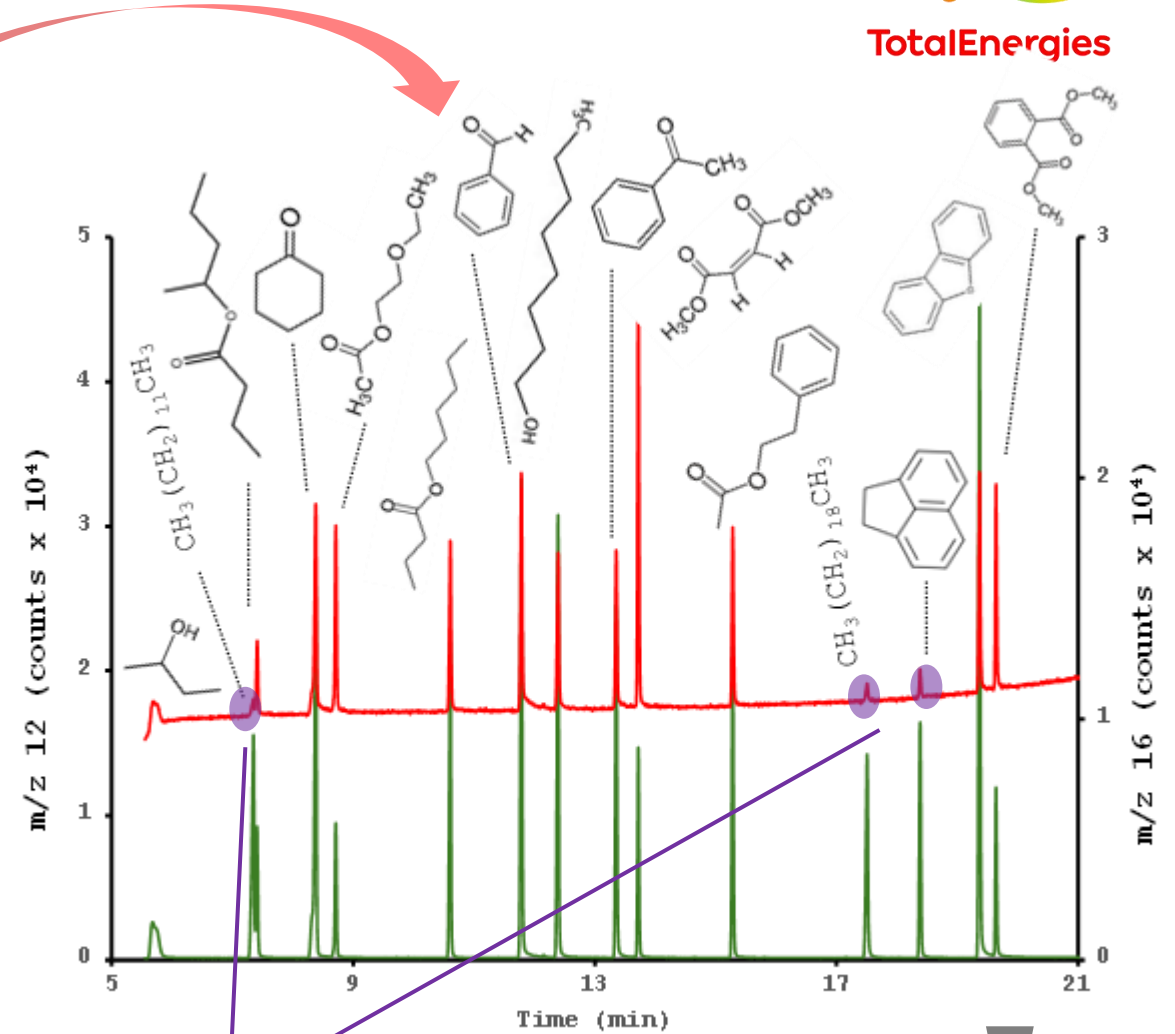
Patented by  
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Univ. Oviedo

# ELEM-SPOT: GC-COMB-MS – O quantification



Signal at **m/z 16** is directly related to the original amount of O in the analytes

However, non-oxygenated compounds also produce an unspecific **signal at m/z 16** due to the presence of  $^{16}\text{O}_2$  in the  $^{18}\text{O}_2$  gas bottle used for the combustion



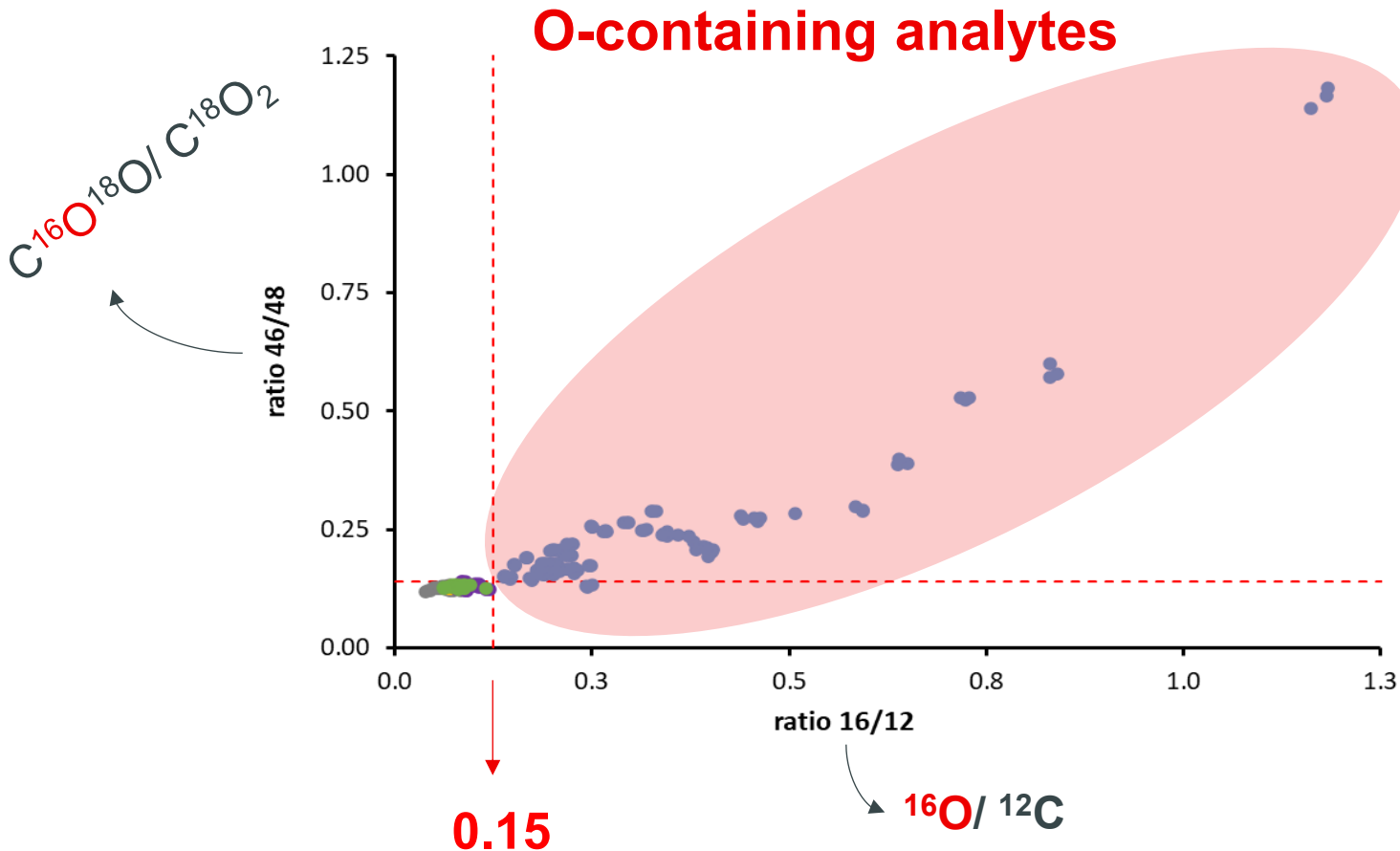
$$\frac{m/z\ 16}{m/z\ 12} = 0.15$$

$^{18}\text{O}_2$  95%  
 $^{16}\text{O}_2$  5%

$^{18}\text{O}_2/\text{He}$

# ELEM-SPOT: GC-COMB-MS – O quantification

## Oxygenated molecules discrimination



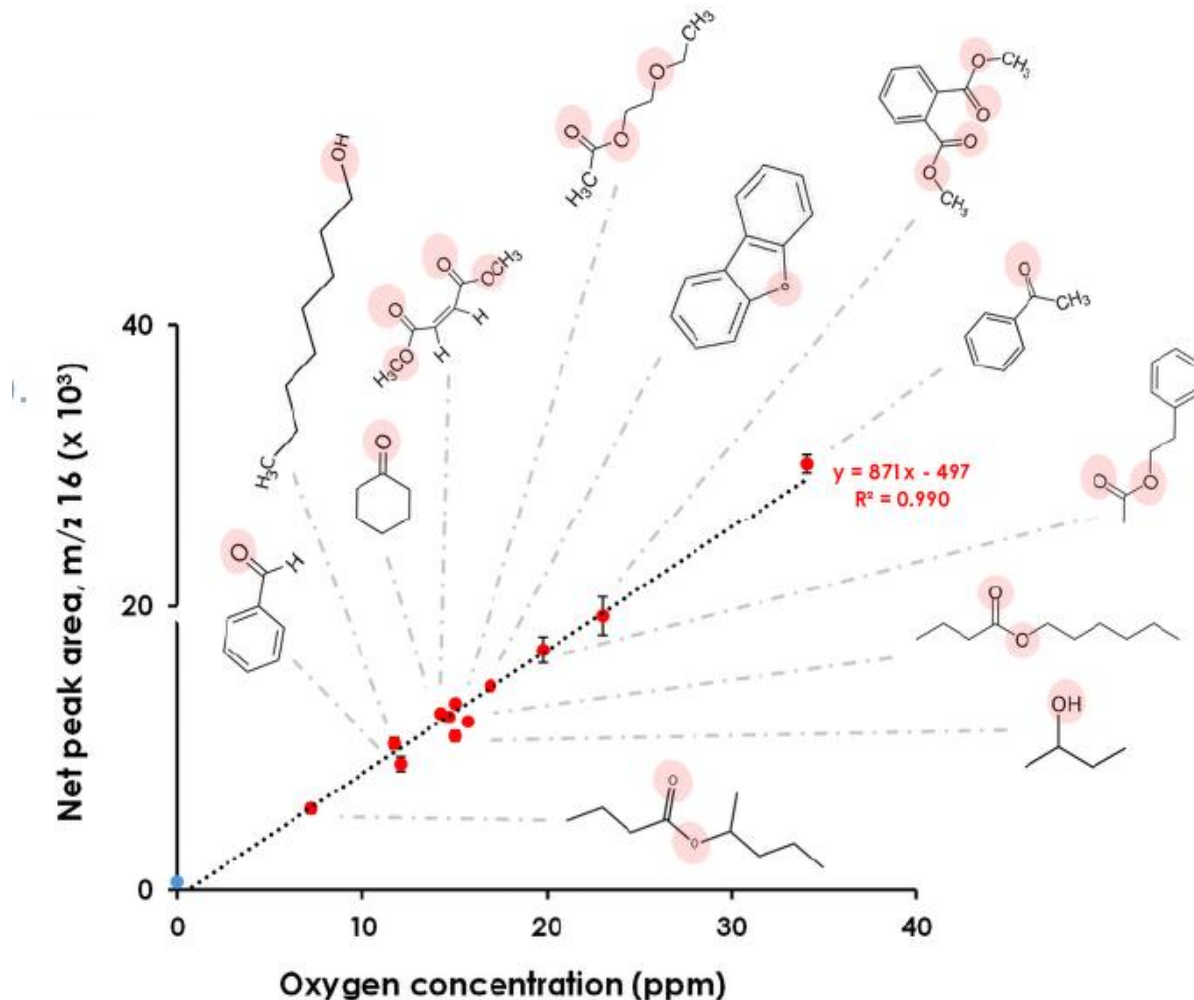
200 compounds processed:

- 93 non-O containing molecules
- 107 O-containing molecules (4 to 37 ppm O)

**Discrimination of the oxygenated molecules**

# ELEM-SPOT: GC-COMB-MS – O quantification

## Linearity and equimolarity



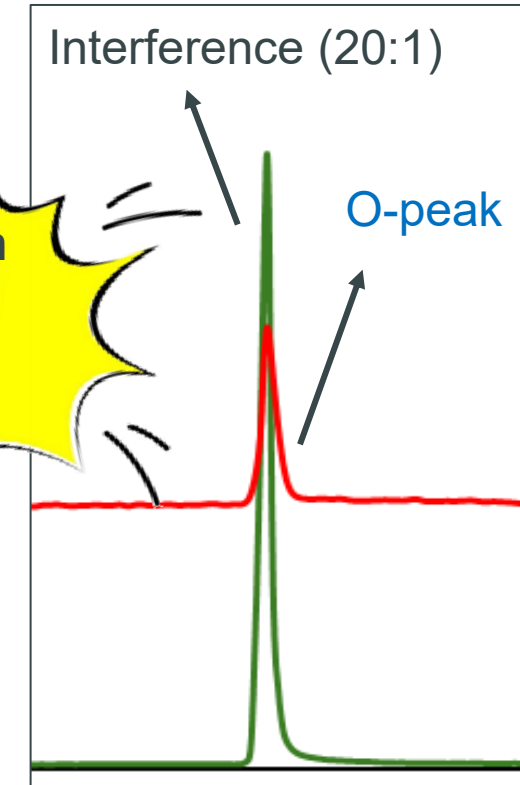
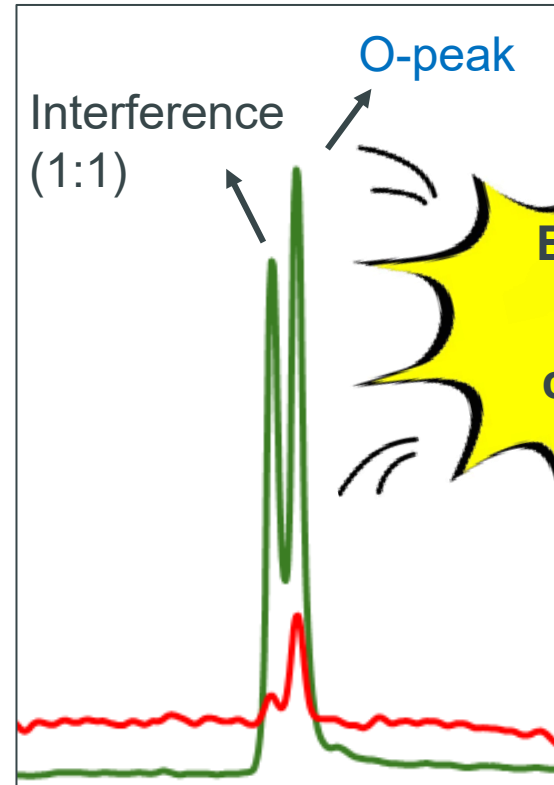
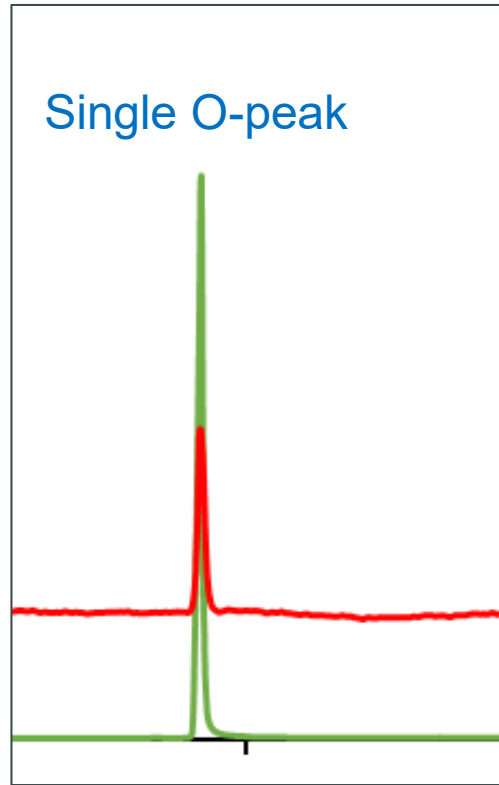
12 O-containing compounds from different oxygenated chemicals family in various O concentration have **very similar response factor**

This open the door to quantification **without using specific standards** → helpfull in complex matrices

# ELEM-SPOT: GC-COMB-MS – O quantification

## Limit of detection

m/z 12  
m/z 16



Even with  
matrix  
coelution

**Lowest LOD for O ever published for a GC detector !!**

# ELEM-SPOT: GC-COMB-MS – O quantification

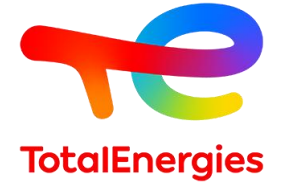
## Accuracy

| FAME compound                  | SRM 2772                      | GC-Combustion-MS          |
|--------------------------------|-------------------------------|---------------------------|
|                                | Certified, mg g <sup>-1</sup> | Found, mg g <sup>-1</sup> |
| Methyl palmitate (C16:0)       | 107 ± 2                       | 110 ± 2                   |
| Methyl stearate (C18:0)        | 43.0 ± 2.7                    | 43.9 ± 3.8                |
| Methyl oleate (C18:1, n-9)     | 247.3 ± 6.2                   | 249 ± 10**                |
| Methyl vaccinate (C18:1, n-7)  |                               |                           |
| Methyl linoleate (C18:2, n-6)  | 523 ± 17                      | 521 ± 7                   |
| Methyl linolenate (C18:3, n-3) | 69.3 ± 2.6*                   | 68.6 ± 3.3                |

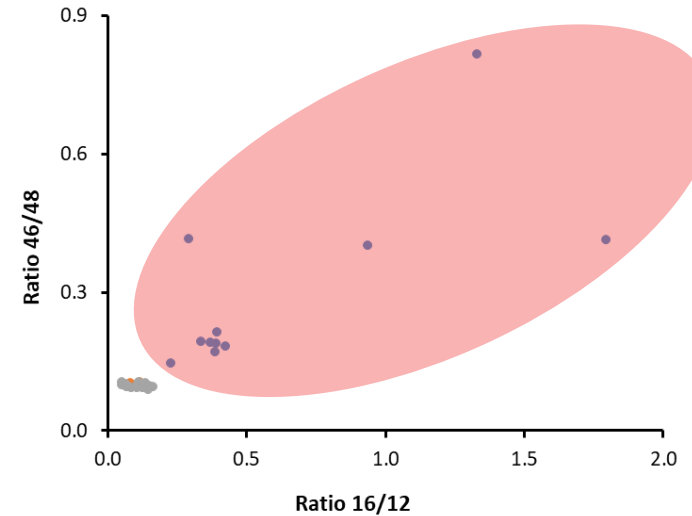
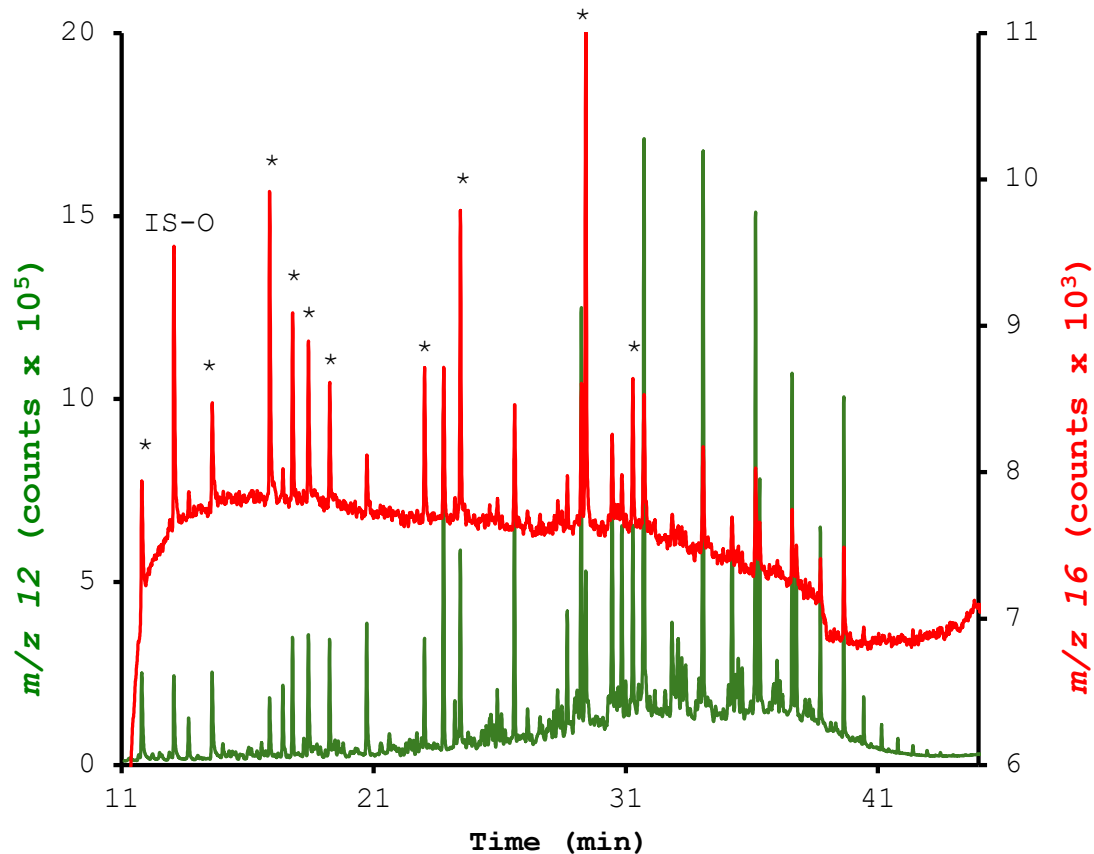
**Error < 3%**  
**Precision 1-4%**

\* reference value, \*\* sum of C18:1(n-9) and C18:1(n-7)

# ELEM-SPOT: GC-COMB-MS – O quantification



## Oxygenates spiked in a diesel



**Perfect discrimination!**

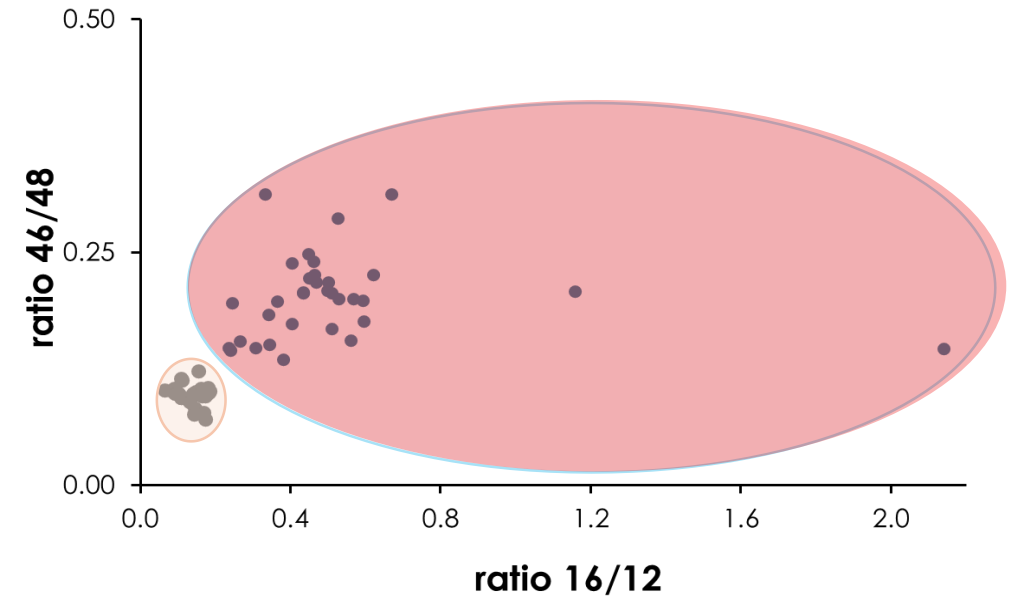
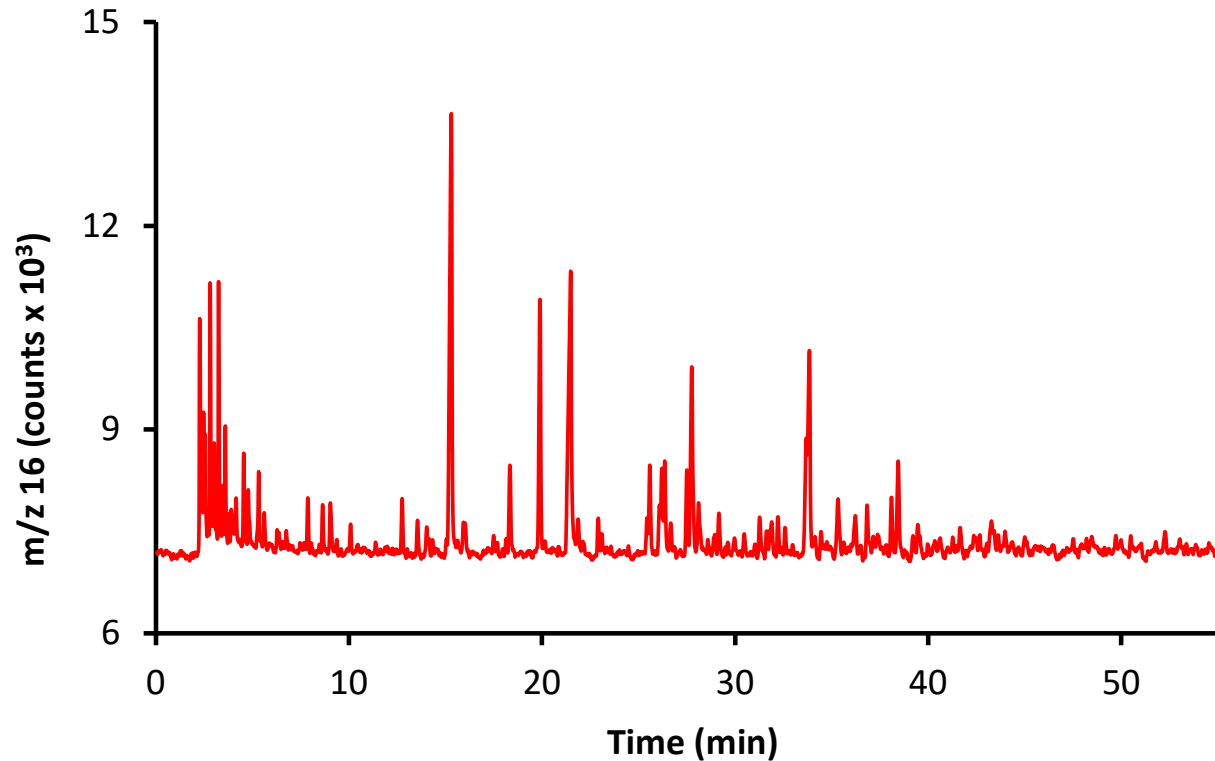
**Adequate quantification  
using a single internal  
standard!**

| O-compound<br>spiked | Recovery<br>%  |
|----------------------|----------------|
| Cyclohexanone        | 89             |
| Benzaldehyde         | 82             |
| Dimethyl maleate     | 102            |
| Pentyl butyrate      | 104            |
| Acetophenone         | 112            |
| 1-octanol            | 109            |
| Hexylbutyrate        | 103            |
| Phenethylacetate     | 107            |
| Dimethylphthalate    | 107            |
| Dibenzofurane        | 104            |
| <b>mean</b>          | <b>102 ± 9</b> |

# ELEM-SPOT: GC-COMB-MS – O quantification

## Wood pyrolysis oil

89 Chromatographic peaks detected



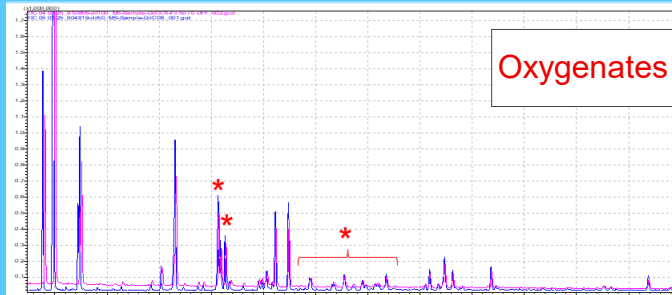
33 compounds were unambiguously identified as oxygenated molecules and quantified with generic standards !!

# What's next ??

## SAF production



Coprocessing to  
produce sustainable  
aviation fuel



ELEM-SPDT

## Composite recycling



Material recovery



10% of Oxy

Energy recovery



ELEM-SPDT

## CO<sub>2</sub> conversion



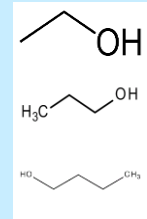
CO<sub>2</sub> to MeOH to Jet

MeOH



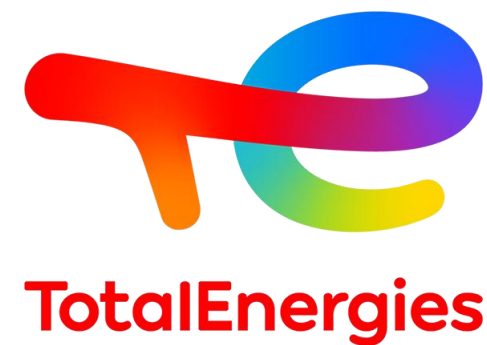
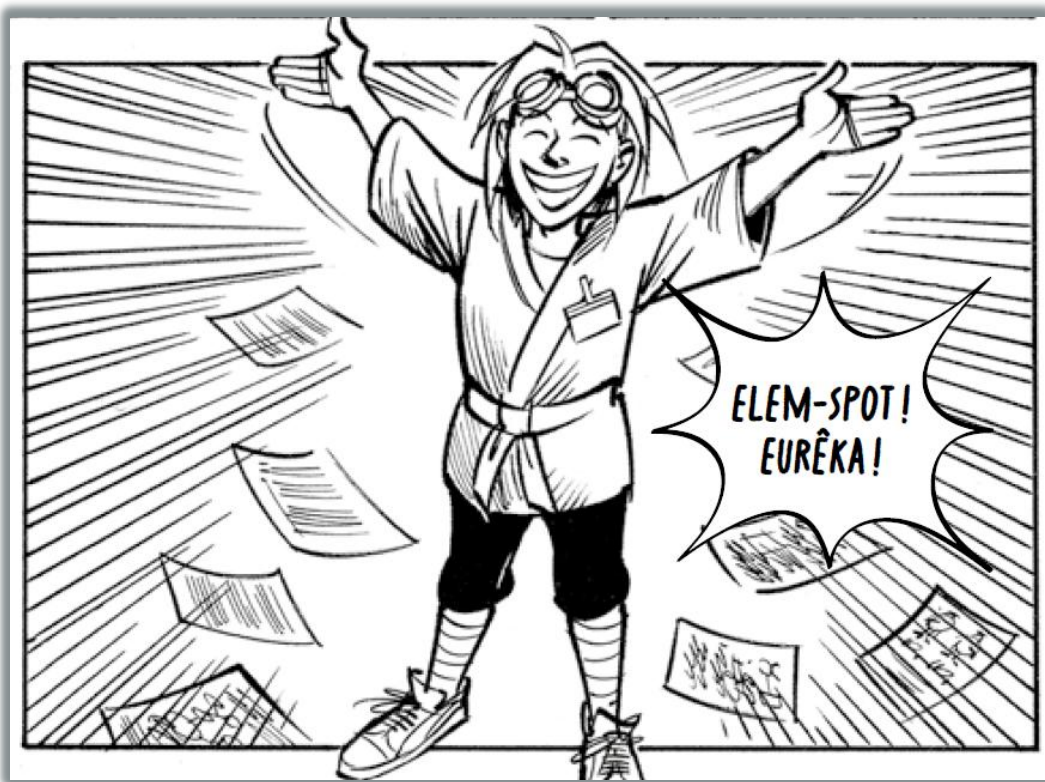
Catalyseur

CO<sub>2</sub> + H<sub>2</sub>



O-molecules

ELEM-SPDT



THANK YOU



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Laura Freije-Carrello,<sup>a</sup> Javier García-Bellido,<sup>a</sup> Laura Alonso Sobrado,<sup>a</sup> Mariella Moldovan,<sup>a</sup> Brice Bouyssiere,<sup>b</sup> Pierre Giusti<sup>b,c</sup> and Jorge Ruiz Encinar<sup>a\*</sup>

**analytical chemistry**

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**Sensitive Detection and Quantification of Oxygenated Compounds in Complex Samples Using GC-Combustion-MS**

Javier García-Bellido,<sup>#</sup> Montserrat Redondo-Velasco,<sup>#</sup> Laura Freije-Carrello, Gaëtan Burnens, Mariella Moldovan, Brice Bouyssiere, Pierre Giusti,\* and Jorge Ruiz Encinar\*

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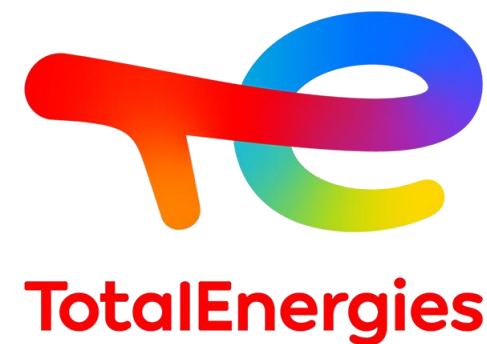
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**Potential of GC-Combustion-MS as a Powerful and Versatile Nitrogen-Selective Detector in Gas Chromatography**

Javier García-Bellido, Laura Freije-Carrello, Montserrat Redondo-Velasco, Marco Piparo, Mariosimone Zoccali, Luigi Mondello, Mariella Moldovan, Brice Bouyssiere, Pierre Giusti, and Jorge Ruiz Encinar\*

Cite This: <https://doi.org/10.1021/acs.analchem.3c01943>

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**THANK YOU**

# GC-COMBUSTION-MS for Oxygen: $m/z$ 16 correction



TotalEnergies

