

**ThermoFisher**  
SCIENTIFIC

## **Resolving the food authenticity challenges – using advanced isotopic ratio and Thermo Scientific™ Orbitrap™ high resolution mass spectrometry tools in practice**

Michal Godula  
Thermo Fisher Scientific

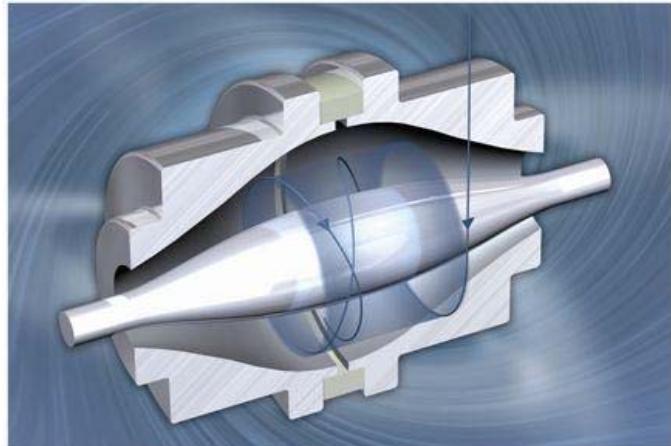
The world leader in serving science

# Food Authentication Challenges

- Chemically identical foods or identical chemical entities
- Unique marker compounds rarely found - more often small analytical differences (isotopic patterns)
- Large natural variability based on climatic conditions, fertilizers used, variety, processing.....
- Techniques must be able to distinguish small differences
- Databases of authentic foods must be available to understand natural variability



# Meet the Orbitrap™: The Performance Leader Since 2006



Unmatched ultrahigh resolution,  
accurate mass performance

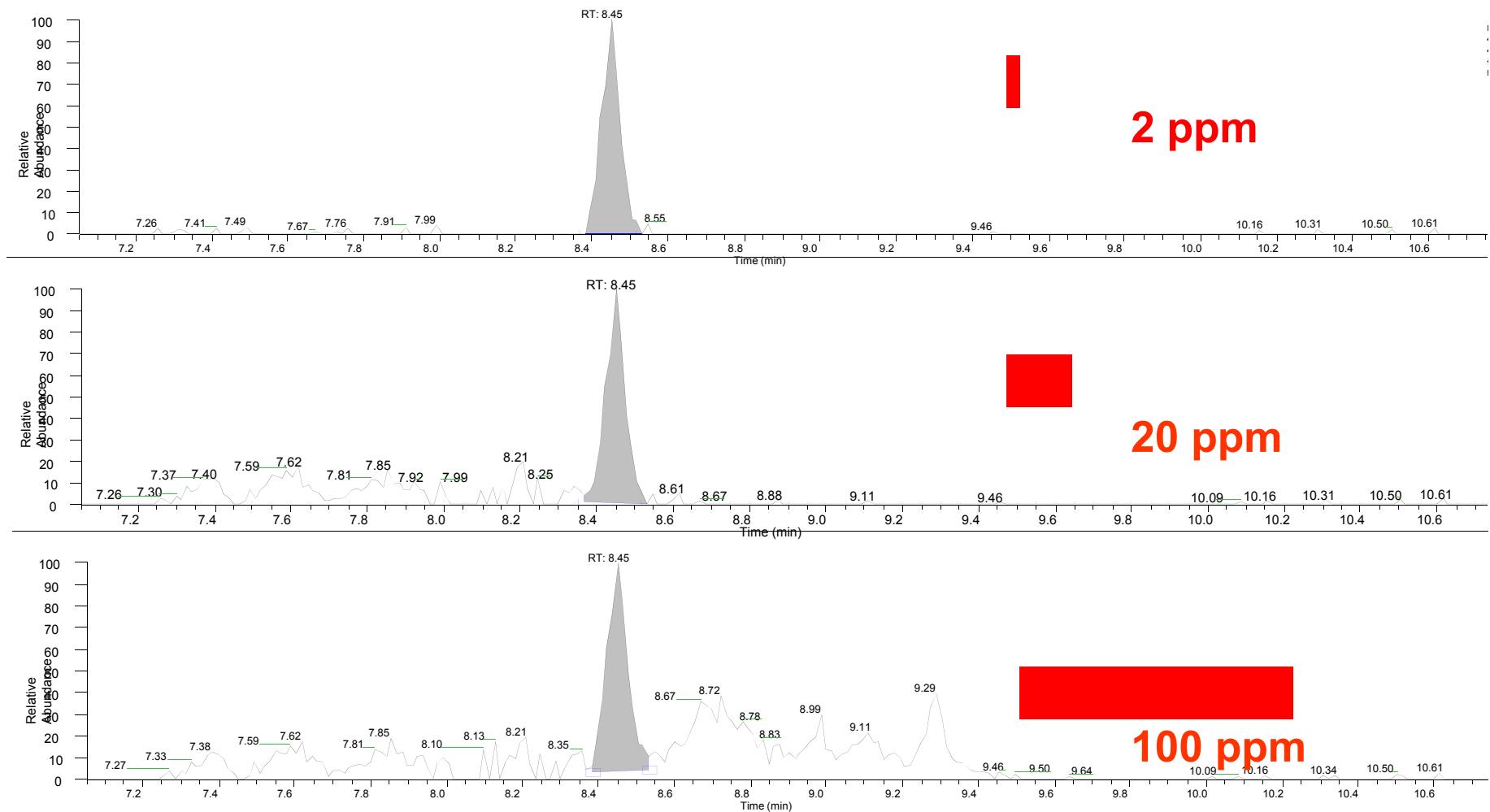
## ● What Orbitrap provides?

- Fundamental difference to other HRAM instruments
- Parameter measured is **frequency**, not time/voltage/etc
- Resolution for more accurate  $m/z$  determination
- Less prone to ambient conditions changes
- Stability within <1-2 ppm during several days
- No need for lock mass in “routine work”
- Small footprint
- Easy setup

## ● Which applications?

- Accurate identification, structural analysis, and quantification of organic molecules, lipids, carbohydrates, peptides & proteins in complex mixtures

# Selectivity Increases With Higher Mass Accuracy

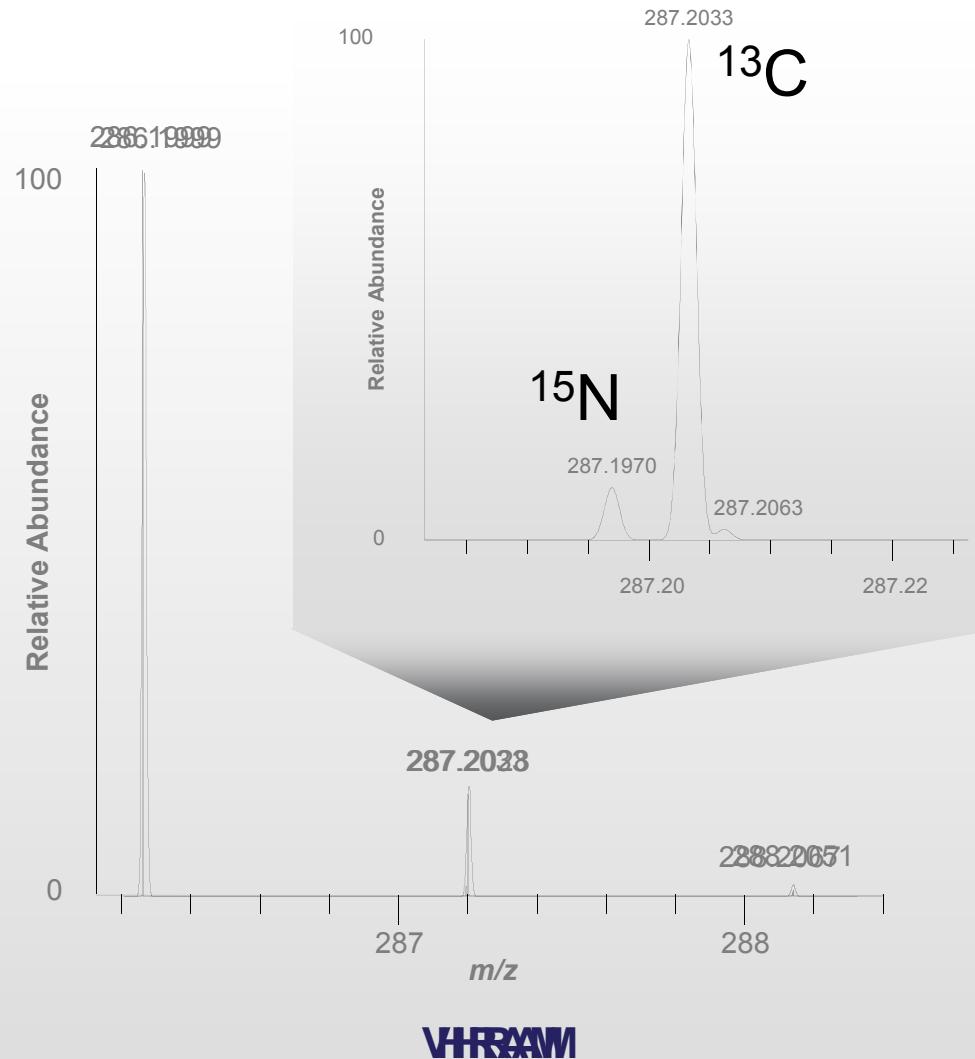


# Elemental Composition Confirmation

- Accurate mass and fragmentation are not the only tools available to us
- Accurate mass gives us access to elemental composition
- Very high resolutions bring even more power to our ability to determine correct elemental composition



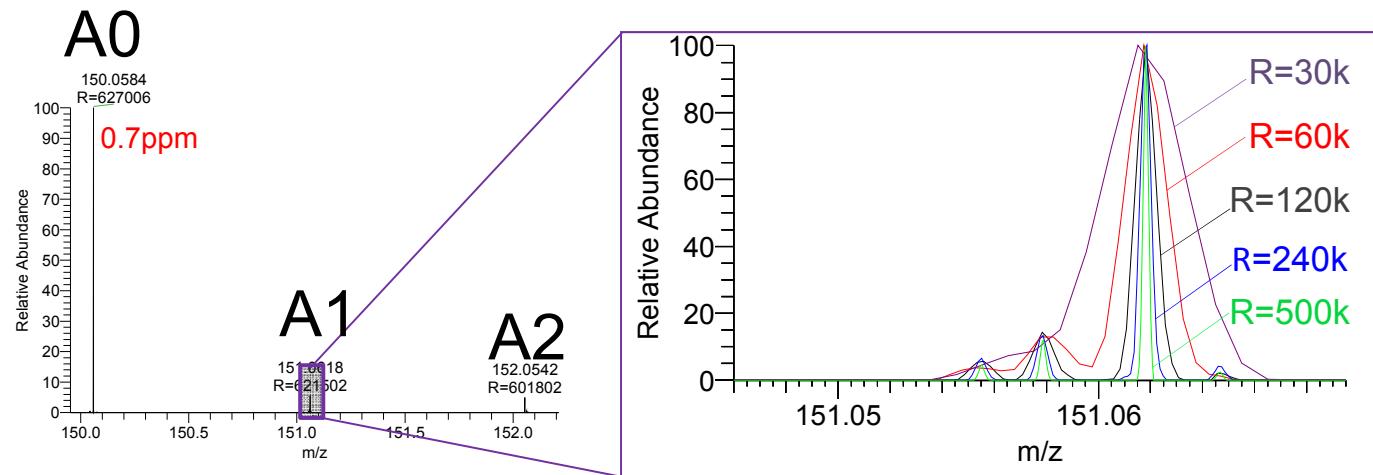
— or —



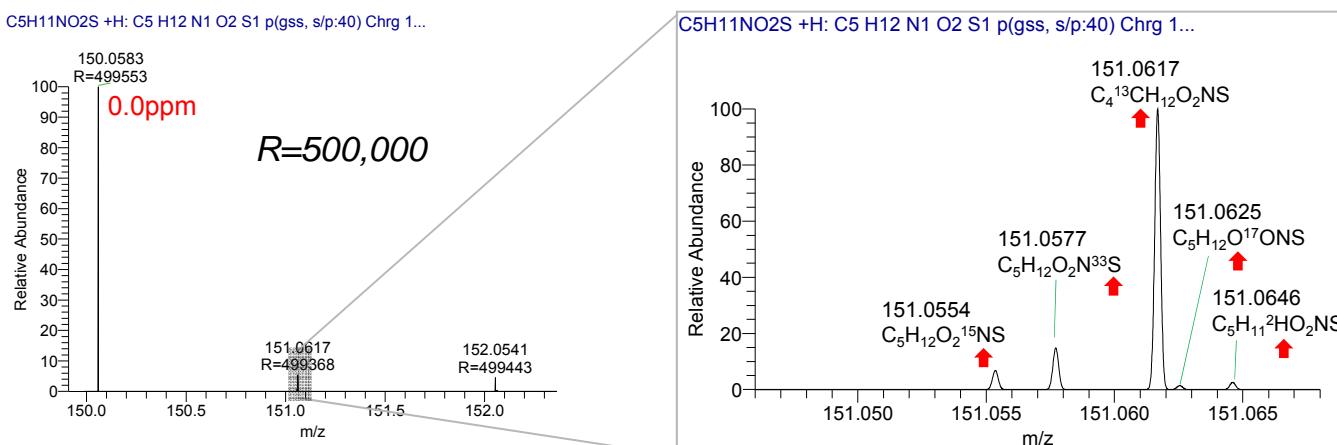
# High Resolution Essential for Fine Isotopic Pattern Determination

- L-Methionine  $C_5H_{11}NO_2S$  (+ mode)

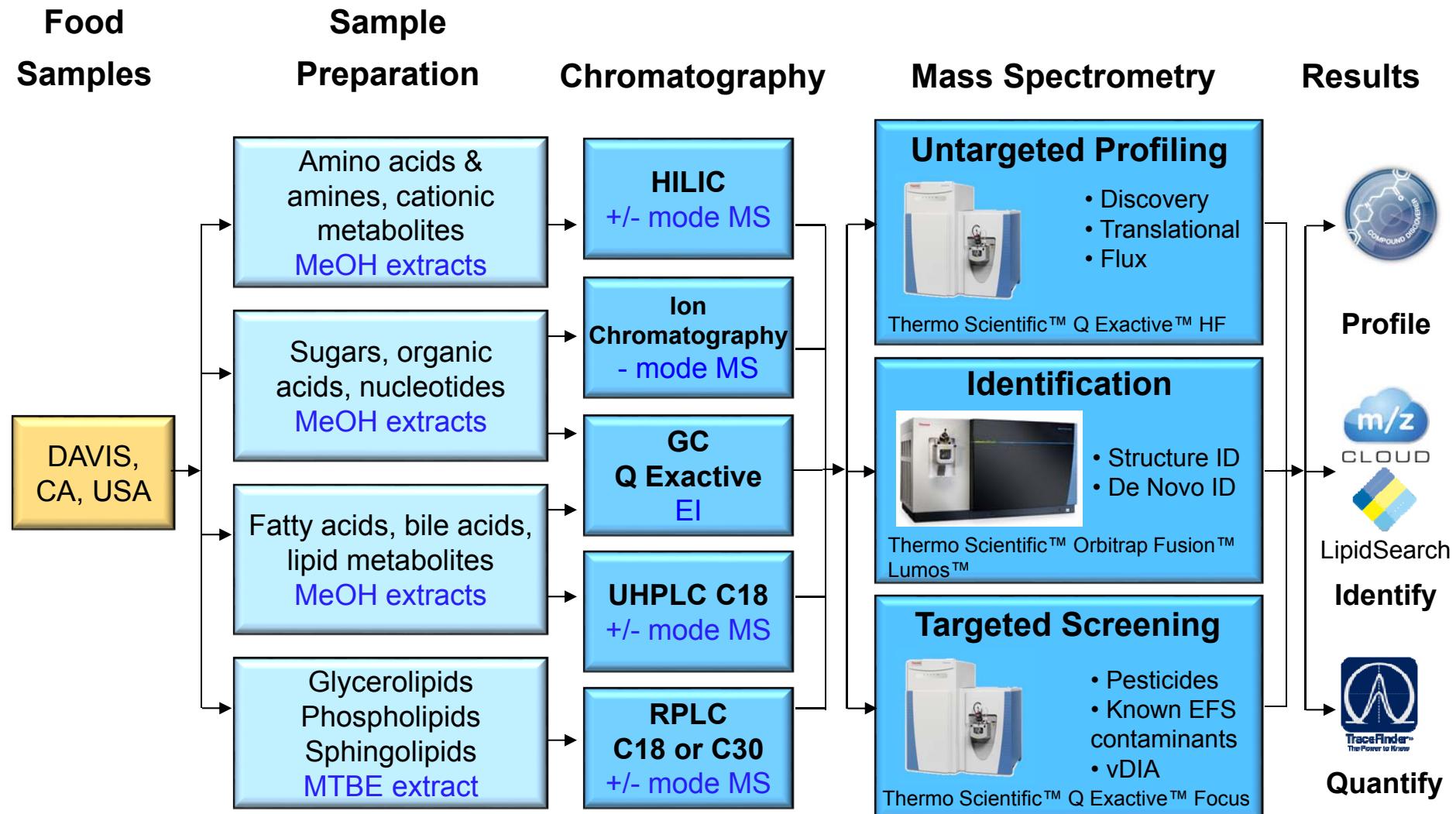
*Observed*



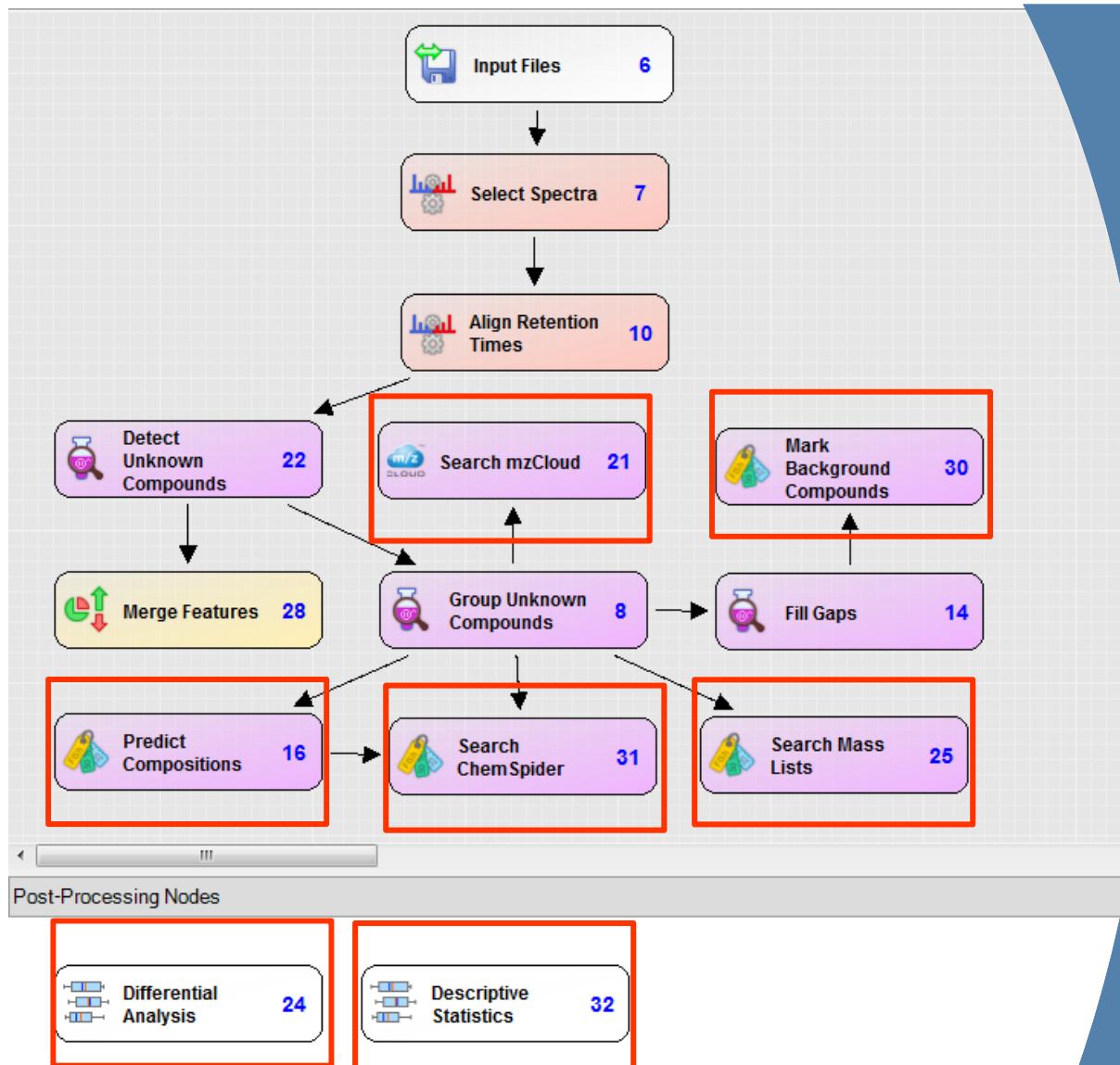
*Simulated*



# Comprehensive Workflow for Food Metabolomics

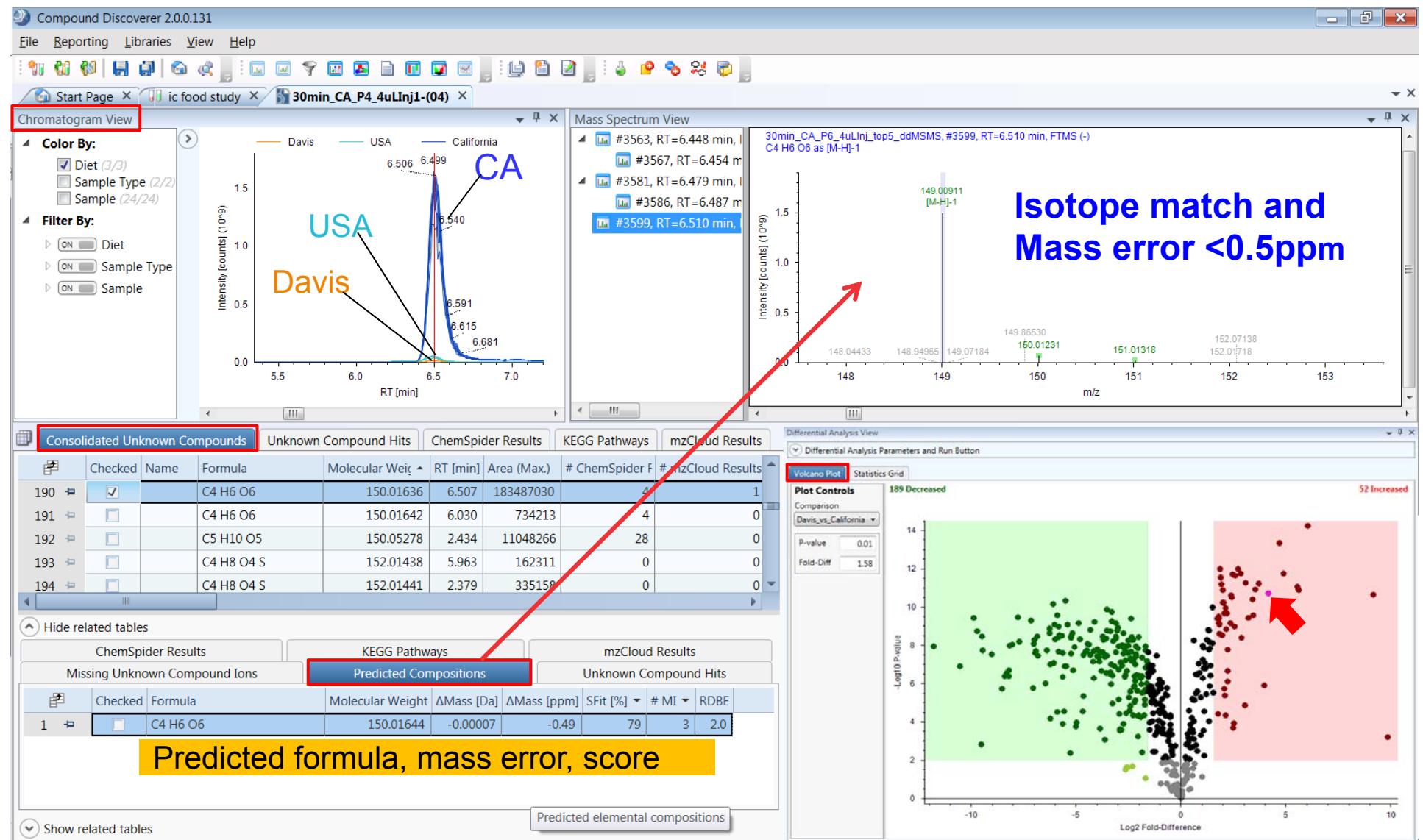


# Compound Discoverer 2.0: Unknown Workflow

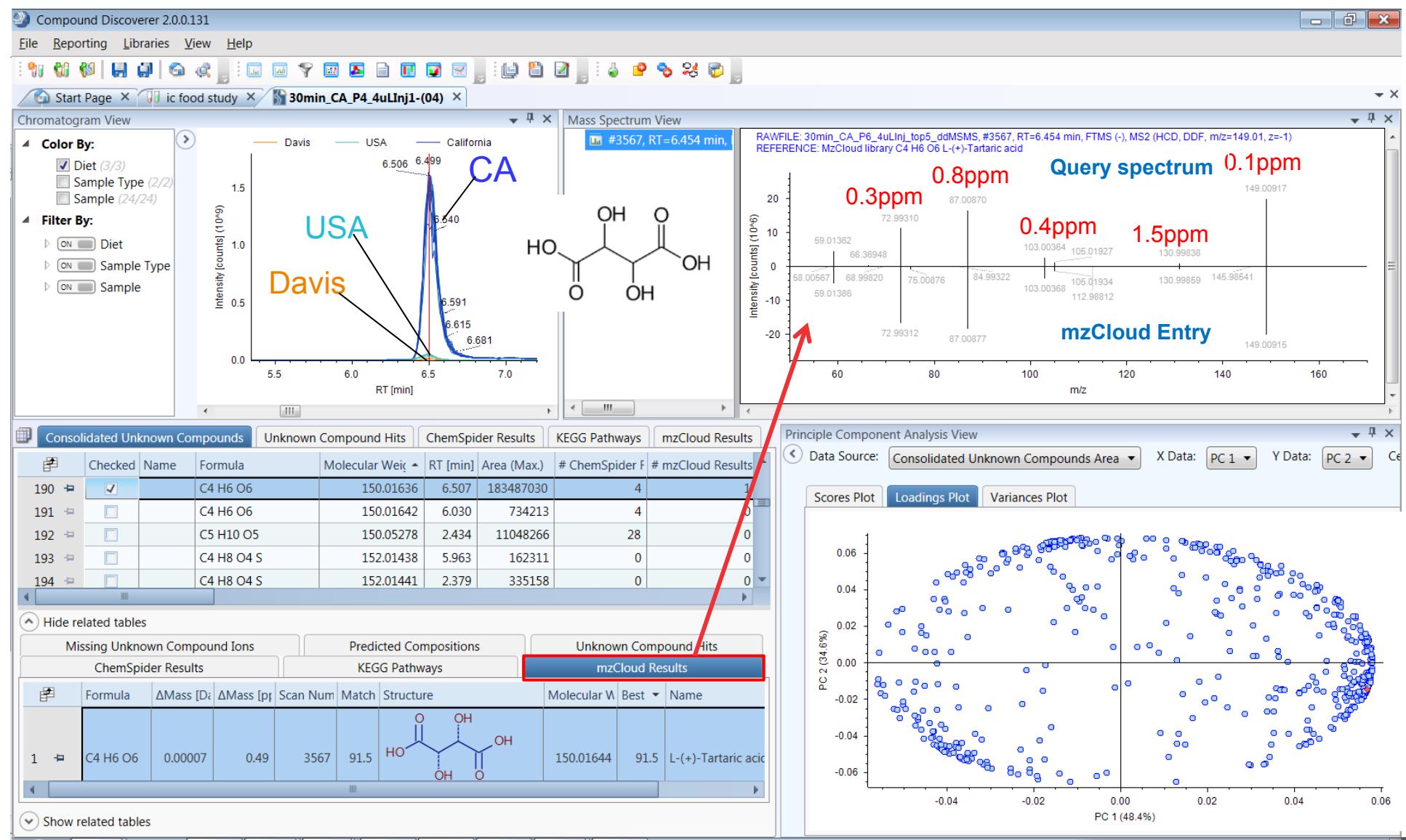


- Powerful and flexible node based workflow
- Batch searching against mzCloud™, ChemSpider databases
- Mass list search
- Unknown elemental composition
- Differential analysis

# Compound Discoverer: Comprehensive Data Review

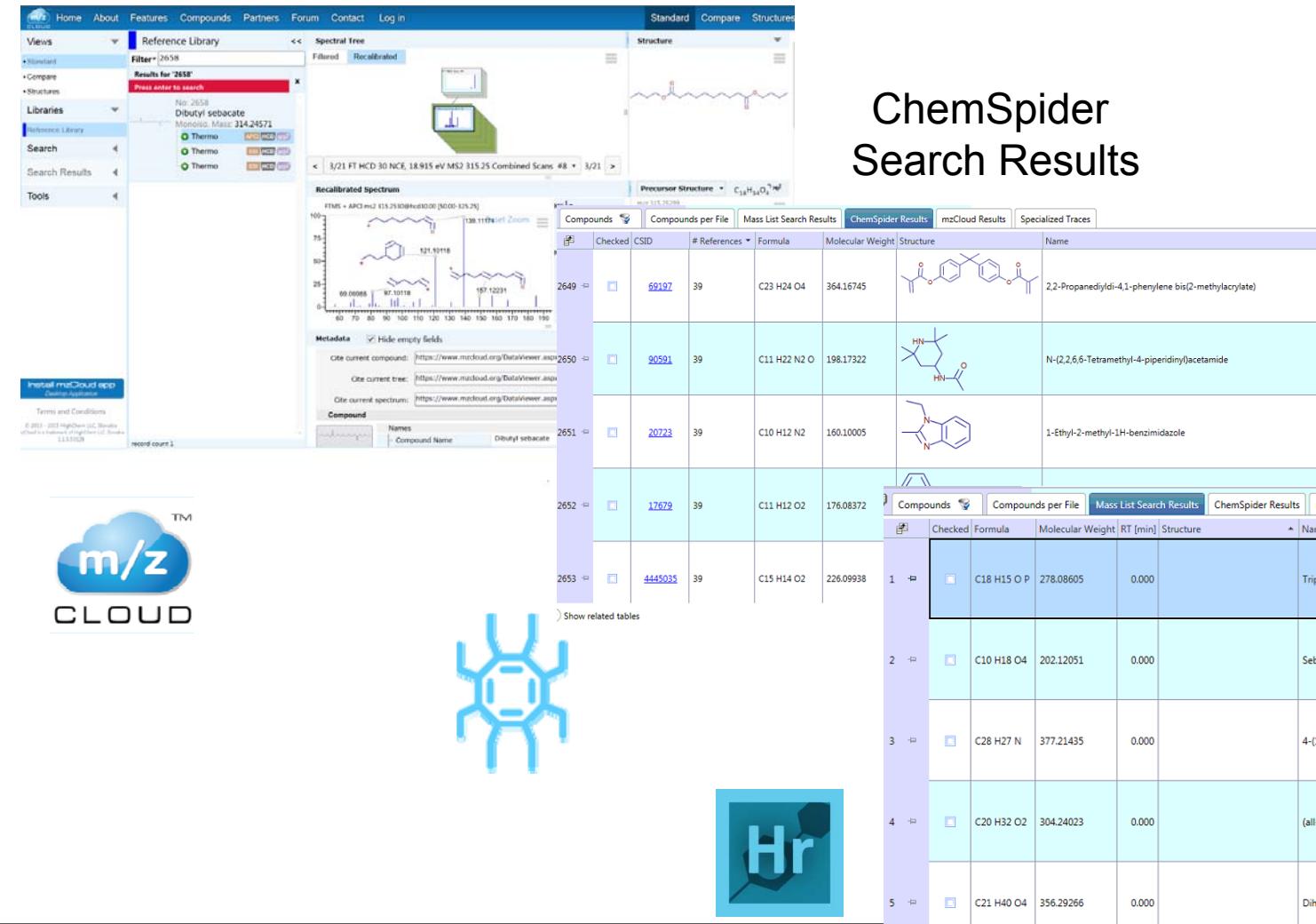


# Automated ID Using mzCloud: Tartaric Acid (grapes)



# Parallel Identification Through Multiple Reference Sources

## mzCloud Library Spectrum

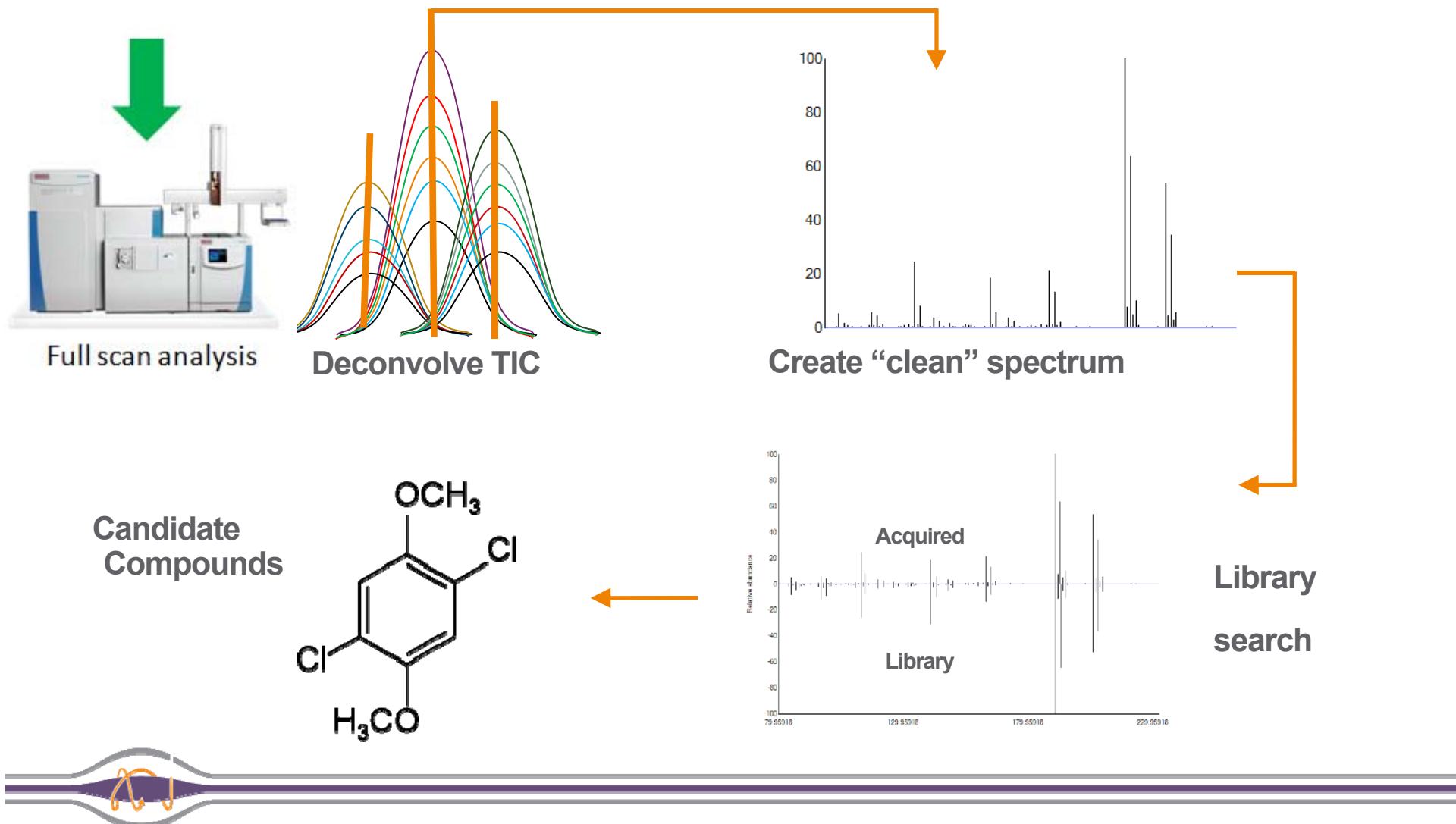


# ChemSpider Search Results

# Local Library Results

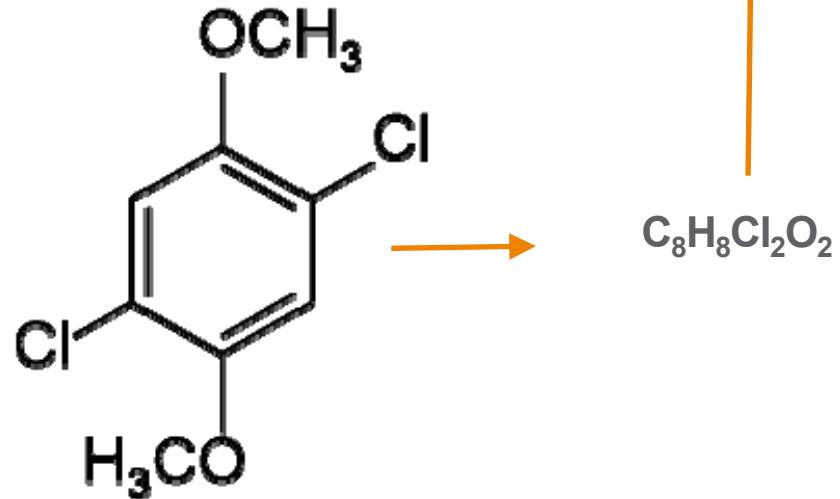


# Peak Detection and Candidate Matching with GC Orbitrap EI



# High Resolution Filtering

Candidate Compounds



Subset  
formulae

Acq m/z	Fragment ID	Theo m/z	Mass Error (ppm)
147.9477	$\text{C}_5\text{Cl}_2\text{H}_2\text{O}$	147.9477	0.20277
148.9369	$\text{C}_5\text{Cl}[37]\text{CIHO}$	148.9369	0.2679
149.9448	$\text{C}_5\text{Cl}[37]\text{ClH}_2\text{O}$	149.9448	0.06602
151.9419	$\text{C}_5[37]\text{Cl}_2\text{H}_2\text{O}$	151.9418	0.72528
154.9895	$\text{C}_7\text{ClH}_4\text{O}_2$	154.9894	0.38712
155.9974	$\text{C}_7\text{ClH}_5\text{O}_2$	155.9973	0.89745
157.9943	$\text{C}_7[37]\text{ClH}_5\text{O}_2$	157.9943	0.25381
159.9479	$\text{C}_6\text{Cl}_2\text{H}_2\text{O}$	159.9477	0.87529
161.9446	$\text{C}_6\text{Cl}[37]\text{ClH}_2\text{O}$	161.9448	0.80213
162.9711	$\text{C}_6\text{Cl}_2\text{H}_5\text{O}$	162.9712	0.36816
163.9745	$\text{C}_5[13]\text{CCl}_2\text{H}_5\text{O}$	163.9745	0.3342
164.9682	$\text{C}_6\text{Cl}[37]\text{ClH}_5\text{O}$	164.9682	0.24186
165.9716	$\text{C}_5\text{CCl}[37]\text{ClH}_5\text{O}$	165.9716	0.02832

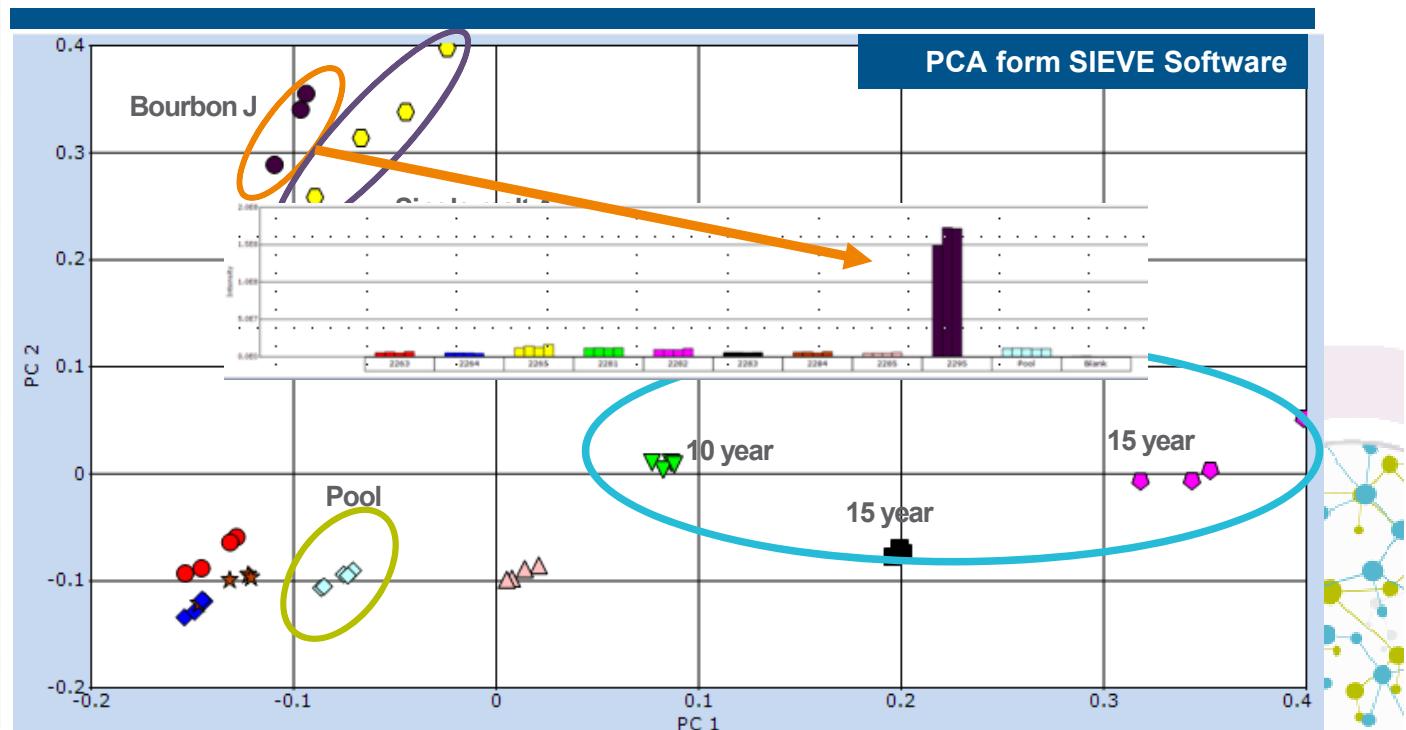
$$\text{HRF Score} = \frac{\sum (\text{m/z} * \text{Intensity})_{\text{explained}}}{\sum (\text{m/z} * \text{Intensity})_{\text{observed}}} \times 100\%$$



## Whiskey profiling using Q Exactive GC

### Principle component analysis

- Clear differences apparent
- Bourbon J well separated from single malts
- Except Single malt A more like bourbon than other single malts



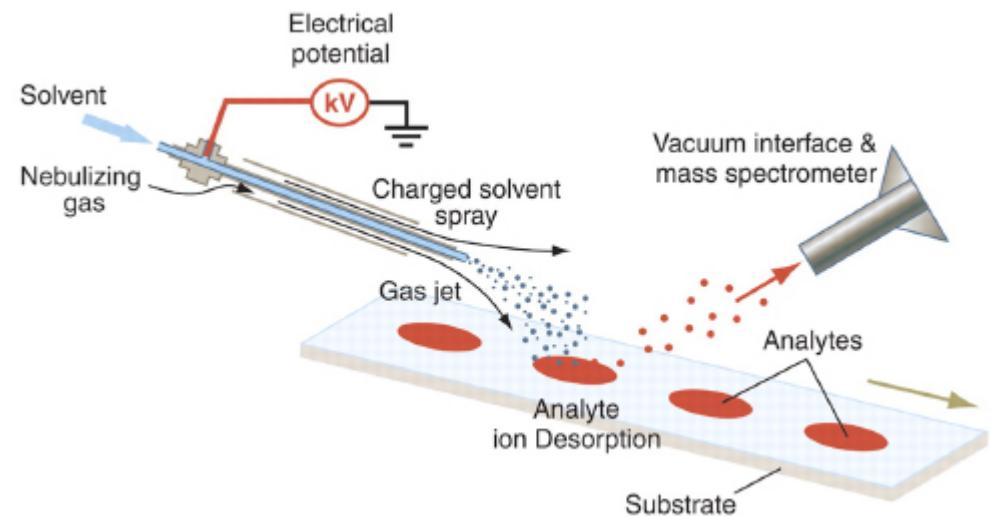
# Ambient Ionisation Sources Coupled to Thermo Scientific Orbitrap MS



<https://phytronix.com/ltd/>

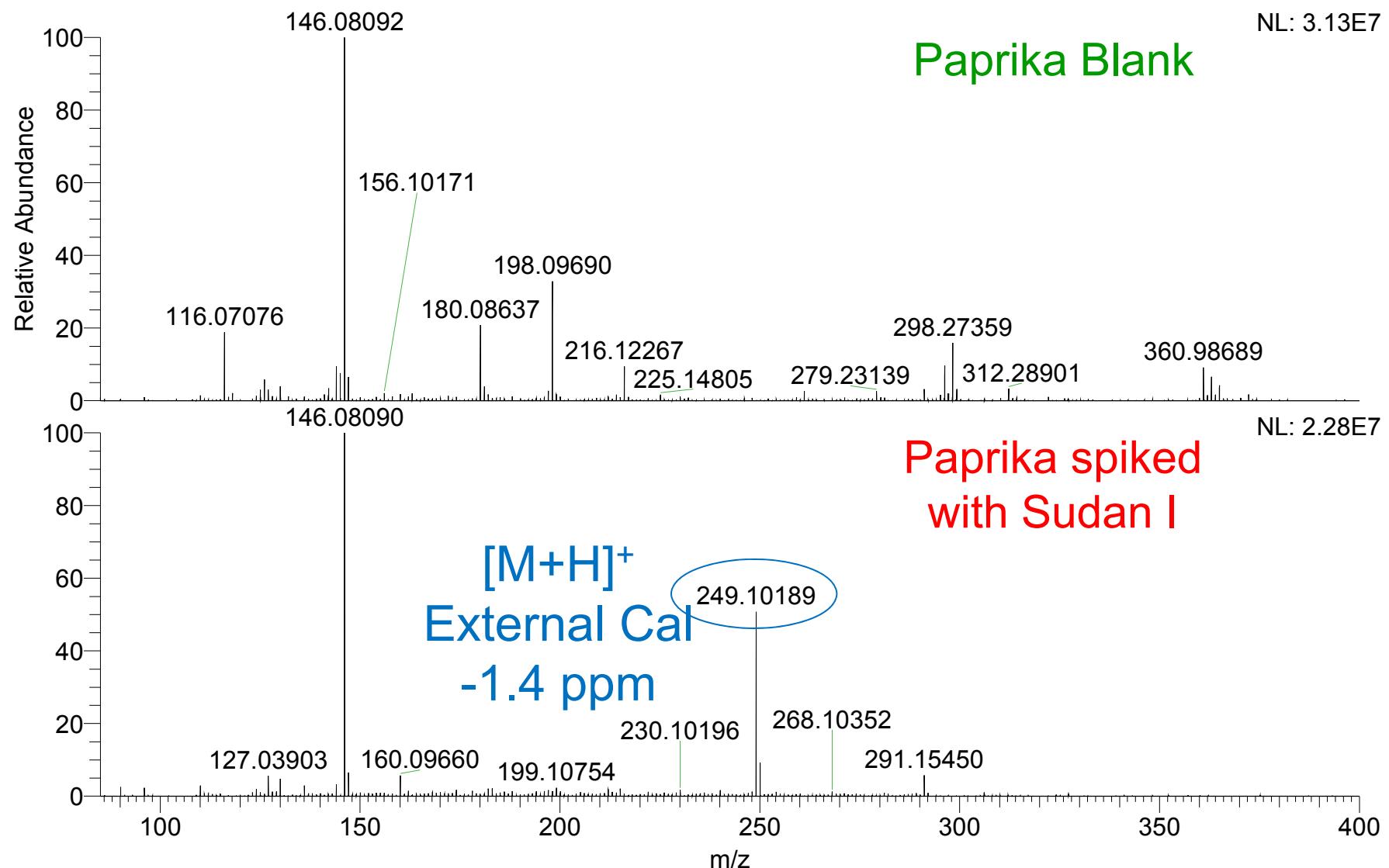


<http://www.ionsense.com/>

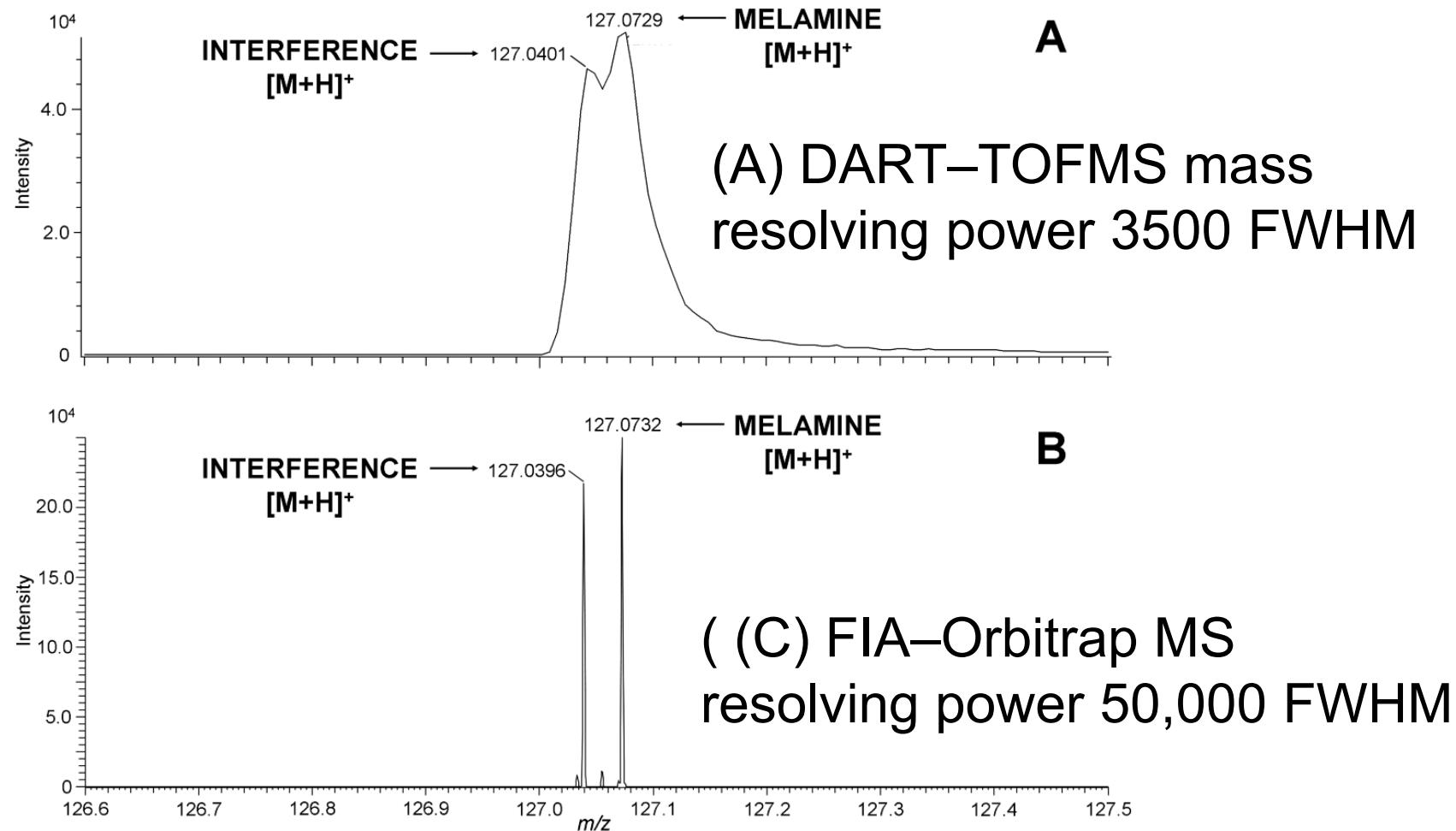


<http://www.prosolia.com/products/desi>

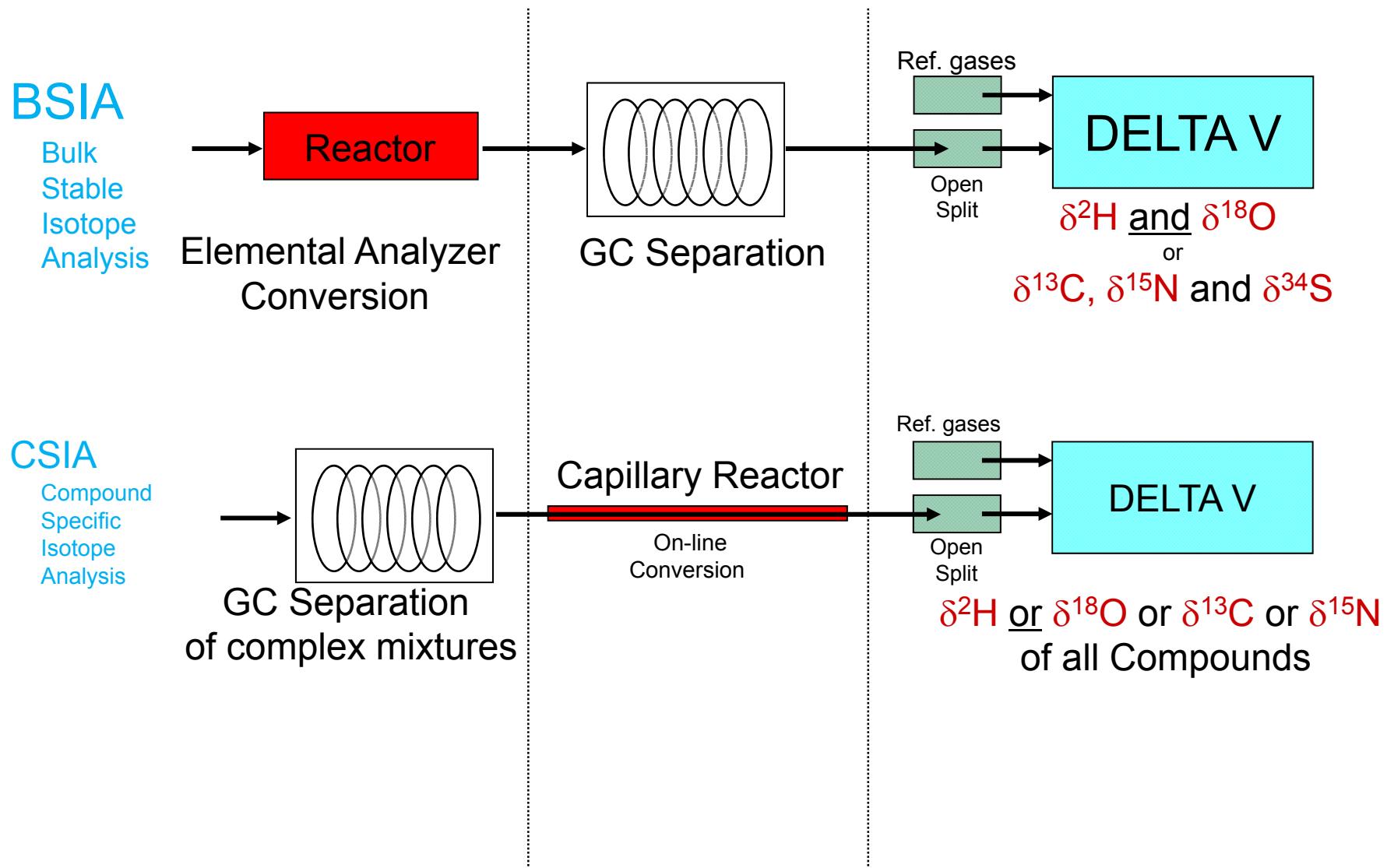
# Sudan I Powder In Paprika At 50 ppm



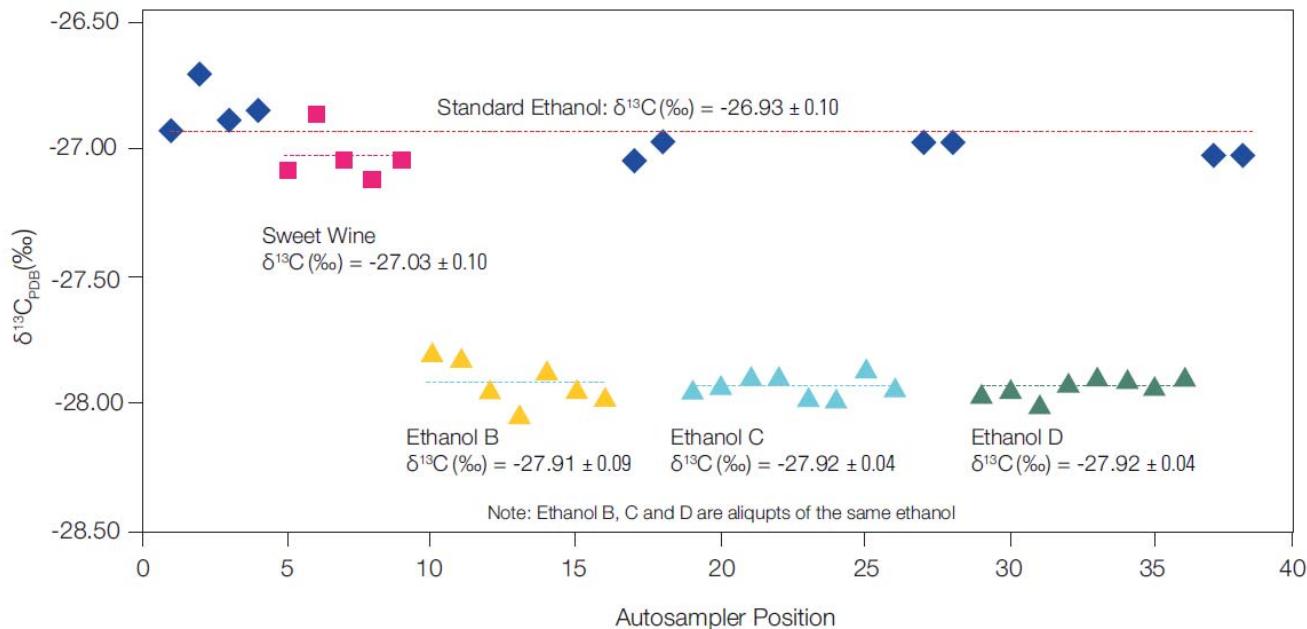
# DART- Orbitrap: Melamine In Milk At 50 mg/kg



# Stable Isotope Ratio MS



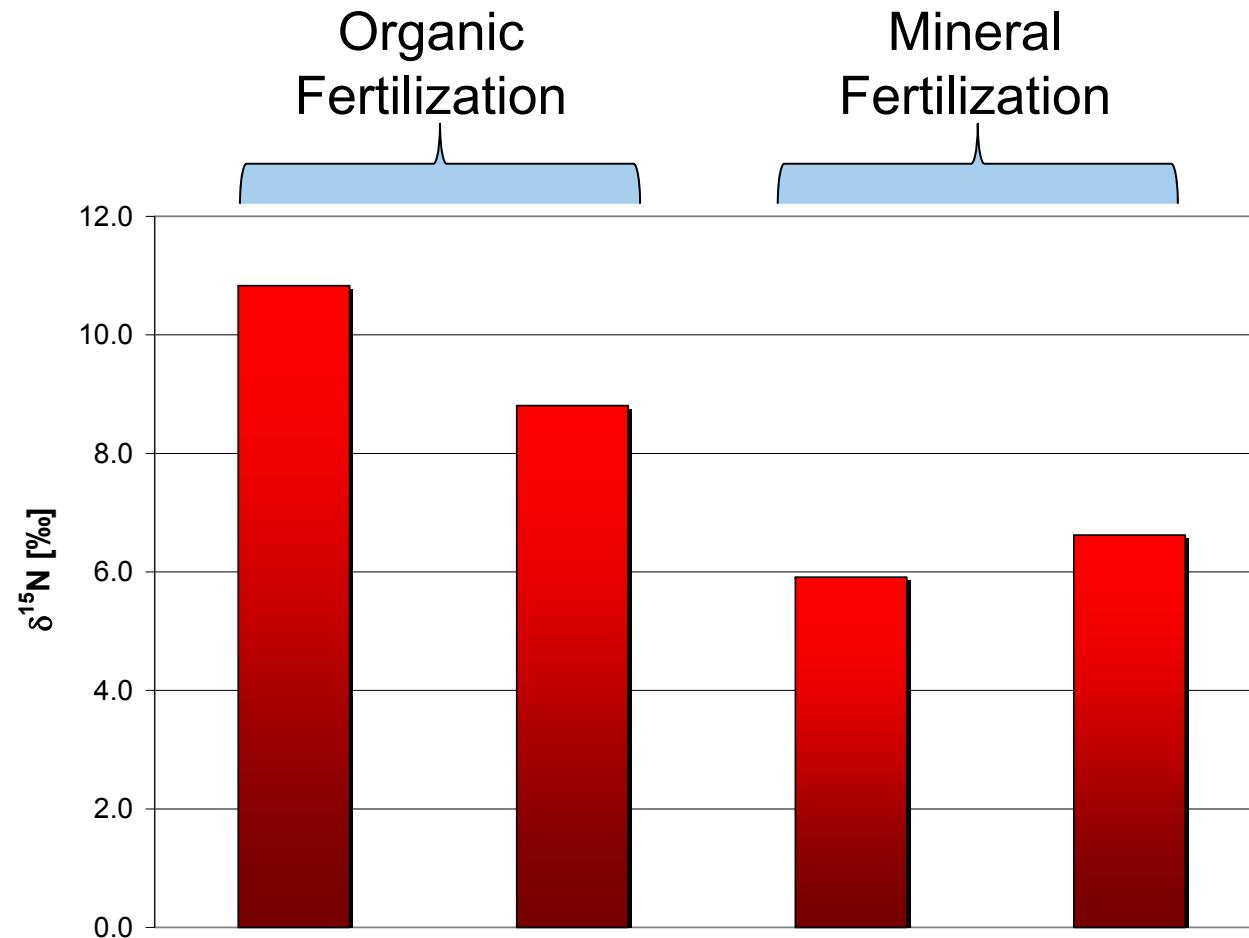
# EA IsoLink™ IRMS: C analysis Of Ethanol



- $\delta^{13}\text{C}$  can be used to determine if wines have been adulterated with sugar
  - See Applications note AN30147

## EA-IRMS: $\delta^{15}\text{N}$ In Tomatoes (Organic vs. Non-Organic)

Mineral fertilizer show low N values while organic fertilization by compost results in higher N values.



# EA IsoLink™ IRMS System: NEW in 2016

- The new **Thermo Scientific™ EA IsoLink™ IRMS System** is an all-in-one fully automated, modular EA–IRMS solution for all CNSOH applications.

*A modular EA-IRMS System fully software supported for CNSOH analyses*

## The EA IsoLink IRMS System includes:

**Thermo Scientific™ Flash IRMS™  
Elemental Analyzer**

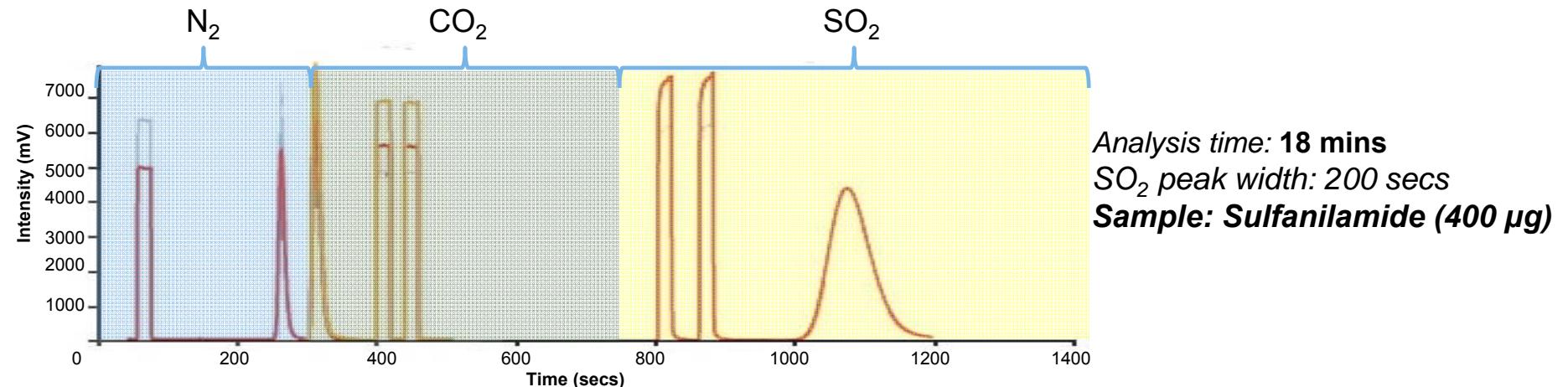
**Thermo Scientific™ ConFlo IV™  
Universal Interface**

**Thermo Scientific™ Isotope Ratio  
Mass Spectrometer**

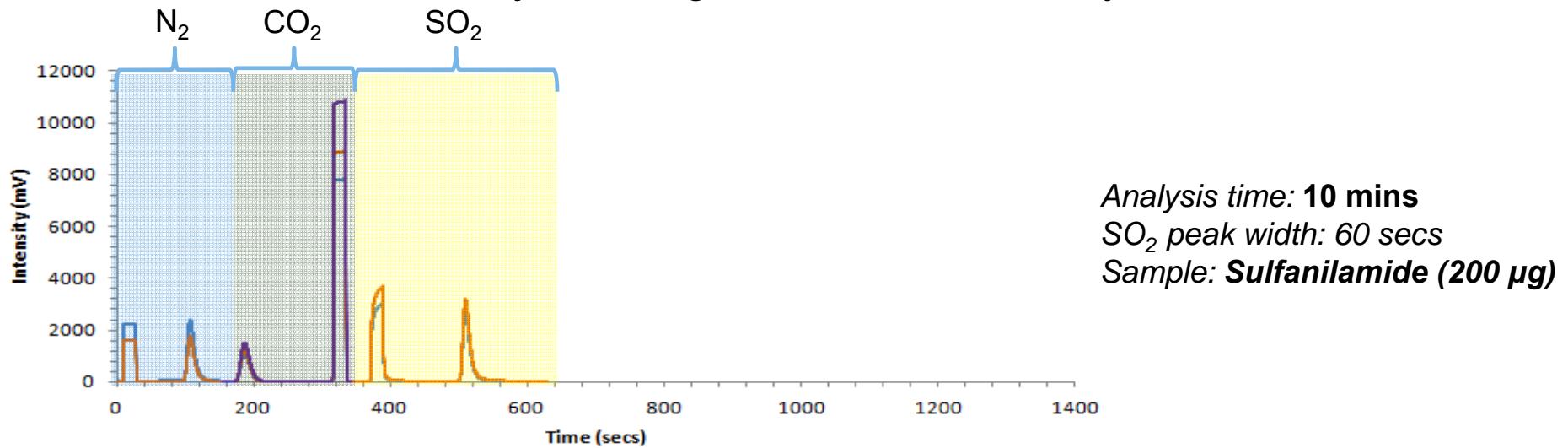


# EA IsoLink IRMS System: Temperature Ramped GC

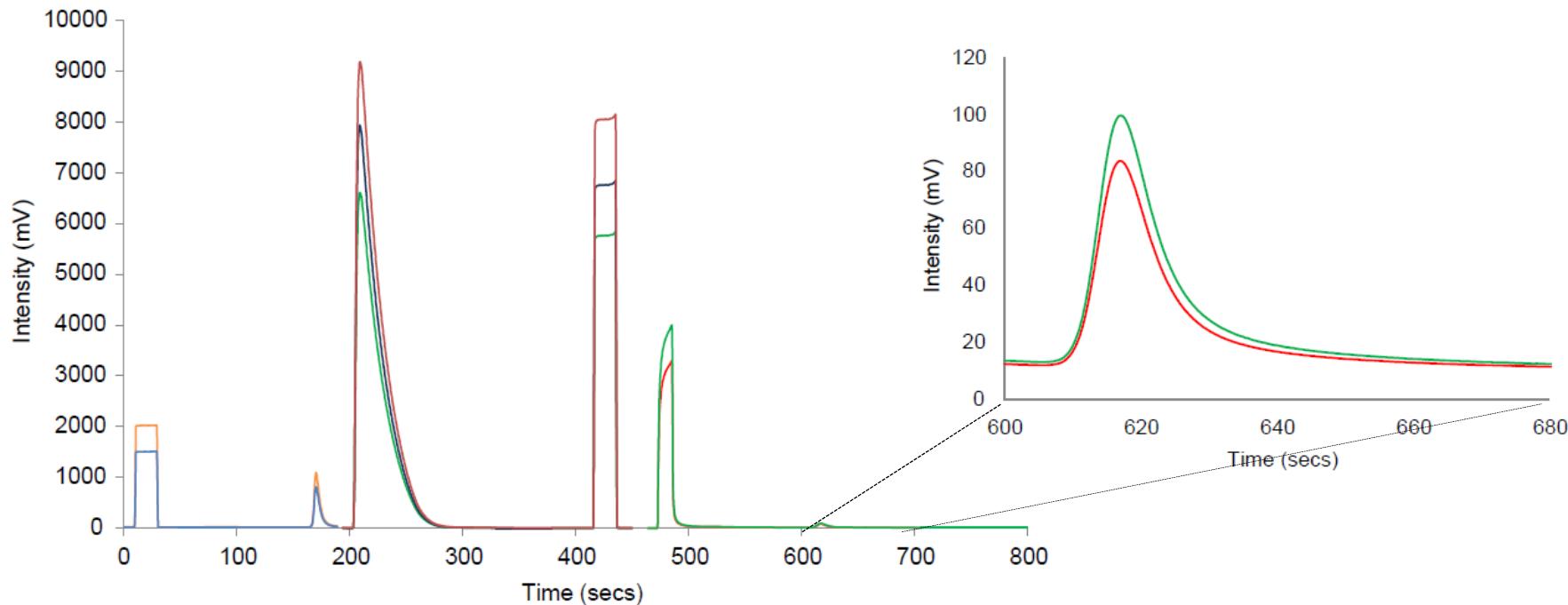
## NCS Analysis using Flash HT Plus System



## NCS Analysis using EA IsoLink IRMS System



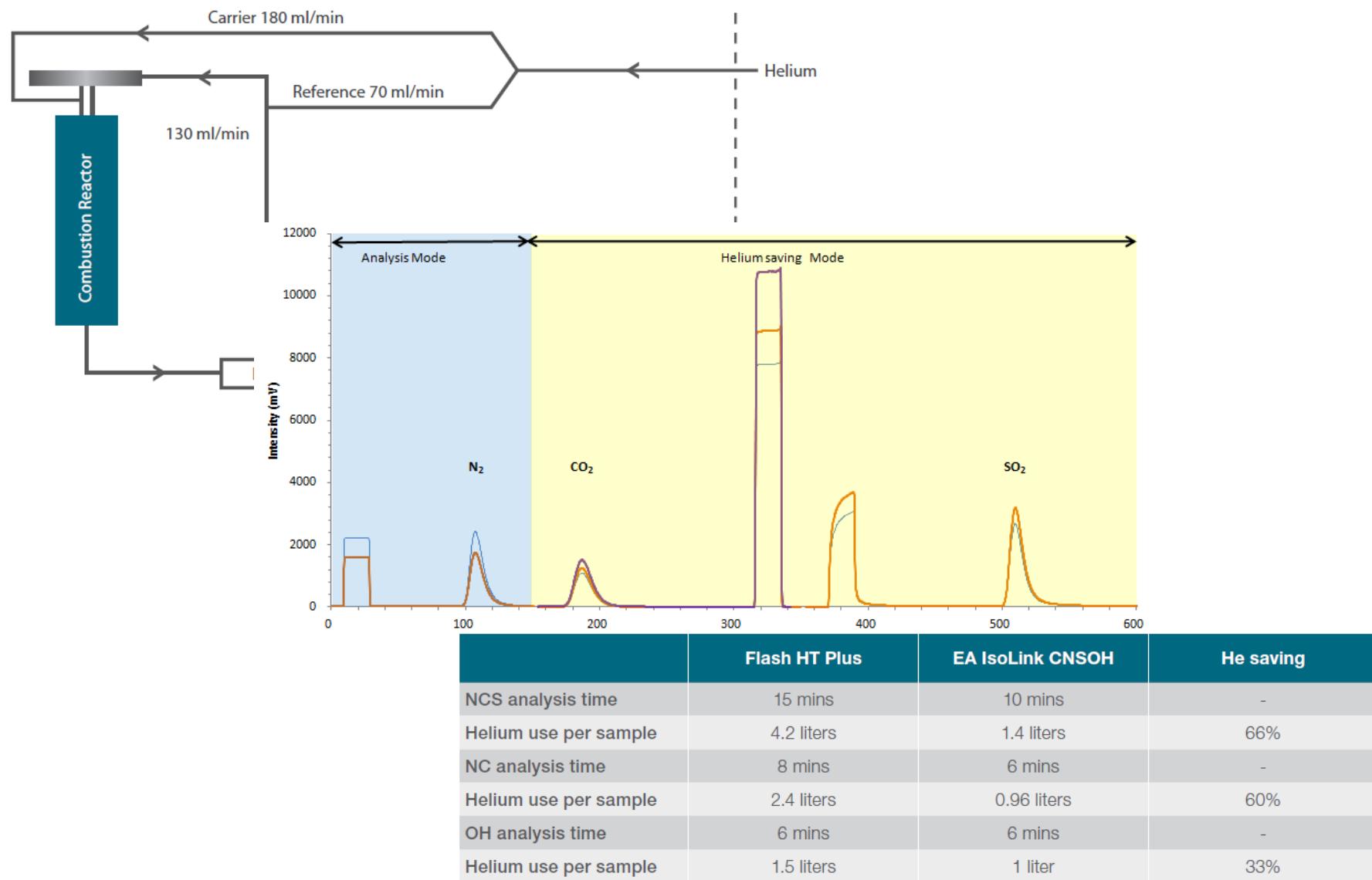
# Analyze High C/S Ratio Samples In One Run

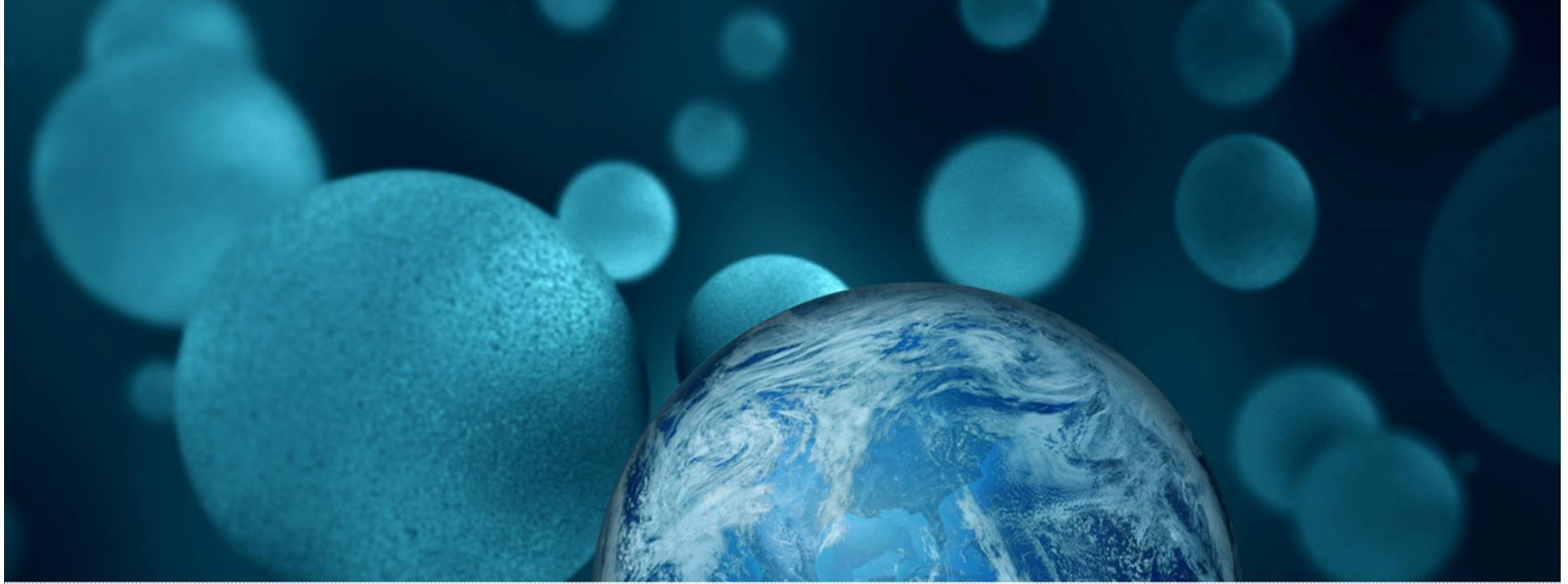


Sample	Weight (mg)	wt% C	wt% N	wt% S	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\mu\text{g C}$	$\mu\text{g N}$	$\mu\text{g S}$	ppm S	C/S Ratio
Spruce	12.69 (11.72–14.24)	54.954 $\pm$ 1.086	0.088 $\pm$ 0.003	0.007 $\pm$ 0.0002	-24.10 $\pm$ 0.06	3.20 $\pm$ 0.23	5.92 $\pm$ 0.26	7036.48	11.14	0.89	70	7905
Iroko	15.63 (15.00–16.07)	32.018 $\pm$ 0.814	0.123 $\pm$ 0.01	0.005 $\pm$ 0.0005	-26.43 $\pm$ 0.04	10.13 $\pm$ 0.32	6.36 $\pm$ 0.27	5004.75	19.20	0.71	70	7048

- Analyzing small amounts (< 20 µg) has become much simpler and more reliable...

# EA IsoLink IRMS System: Lowest Helium Usage





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Thank you!  
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