

Mass Spectrometry and Chromatography Explained

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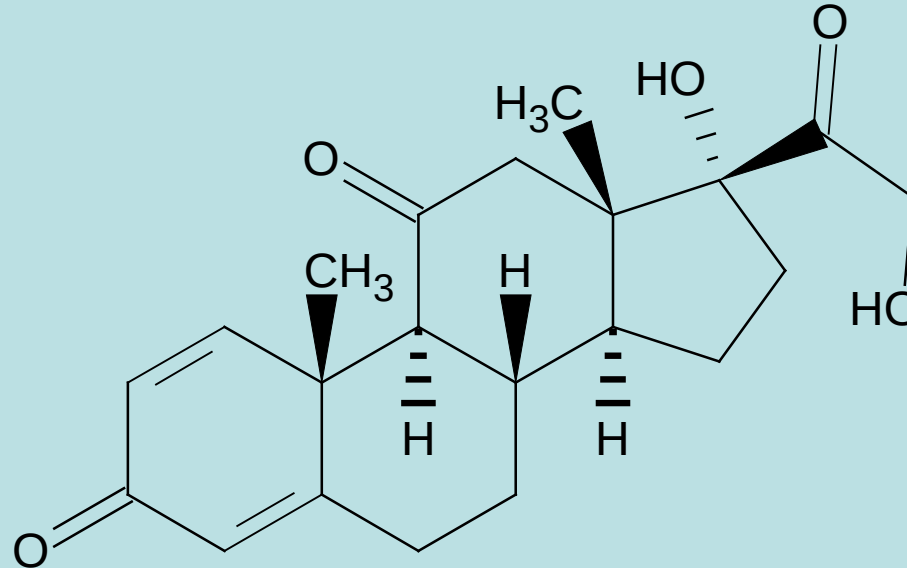
February 21st, 2018
Meeting of the House Select
Committee on North Carolina River
Quality

Questions to Answer?

- What is mass spectrometry?
- What are the types of mass spectrometry
 - (MS, MS/MS, QTOF, Orbitrap)
- What is resolution in mass spectrometry?
(low resolution, high resolution, ultra-high resolution)
- What is mass accuracy?
- What is liquid and gas chromatography?
- What can be done with each mass spectrometer?; *i.e. targeted versus non-targeted work*
- *Questions I did not answer*

What is Mass Spectrometry

Prednisone



Molecular Formula = $C_{21}H_{26}O_5$
Formula Weight = 358.42814
Composition = C(70.37%) H(7.31%) O(22.32%)
Monoisotopic Mass = 358.178024 Da
Nominal Mass = 358 Da
Average Mass = 358.4281 Da



UPLC MS/MS System

UPLC - Waters Acquity

MS/MS - Micromass Quatro
Premier XE

Column - Acquity UPLC BEH C18
1.7 μ m 2.1x50 mm

Gradient separation
A 2mM Ammonium Acetate
B Methanol



HPLC/TOFMS System

HPLC - Agilent 1100

TOFMS - Agilent LC/MSD TOF

Column - Agilent Eclipse Plus C18
3.5 μ m 3.0x50 mm
custom packed

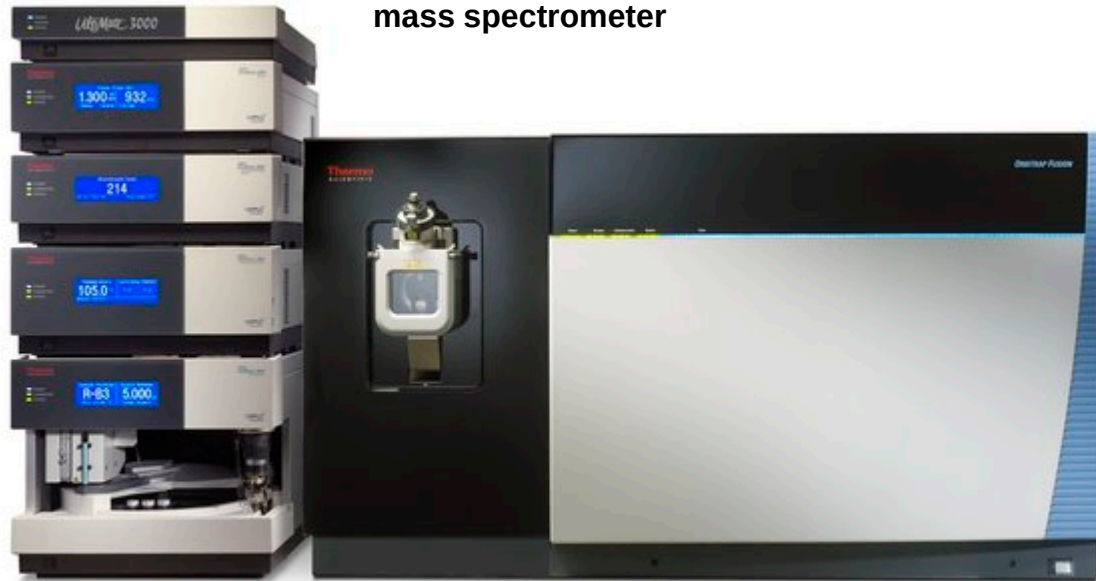
Gradient separation
A 2mM Ammonium Acetate
B Methanol

- Chevy
- Low resolution
- Nominal mass
- Inexpensive/common

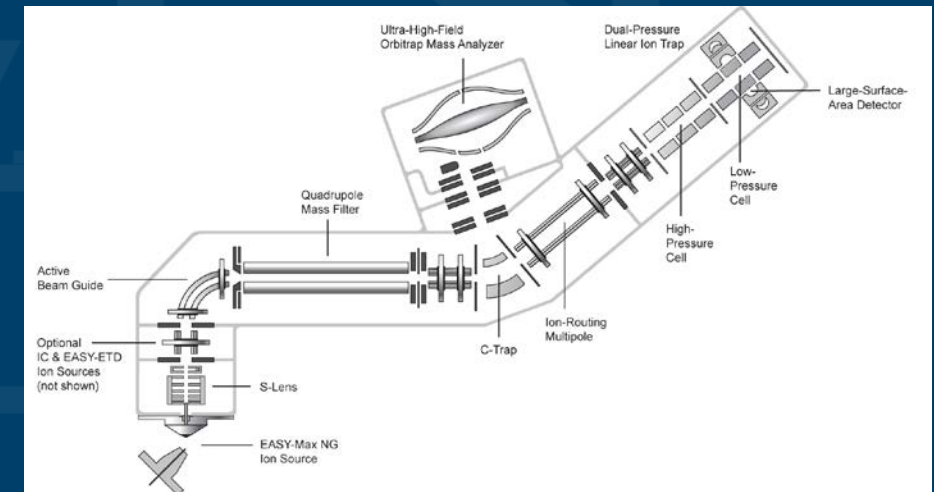
- Cadillac
- High resolution
- Exact mass
- More expensive/becoming more common

Figure 2. Picture of the (a) UPLC/MS/MS and (b) LC/TOFMS systems used

The Thermo Scientific™ Orbitrap Fusion™ Tribrid™ mass spectrometer



- Tesla
- Ultra-high resolution
- Exact Mass/ Fine isotope structure
- Significantly more expensive;
uncommon



What is resolution?

Resolution in mass spectrometry is the ability to differentiate a detected ion from any other

- Triple Quad or MS/MS 500-5,000 resolution
- TOF or QTOF ~25,000 resolution
- Orbitrap >250,000 resolution

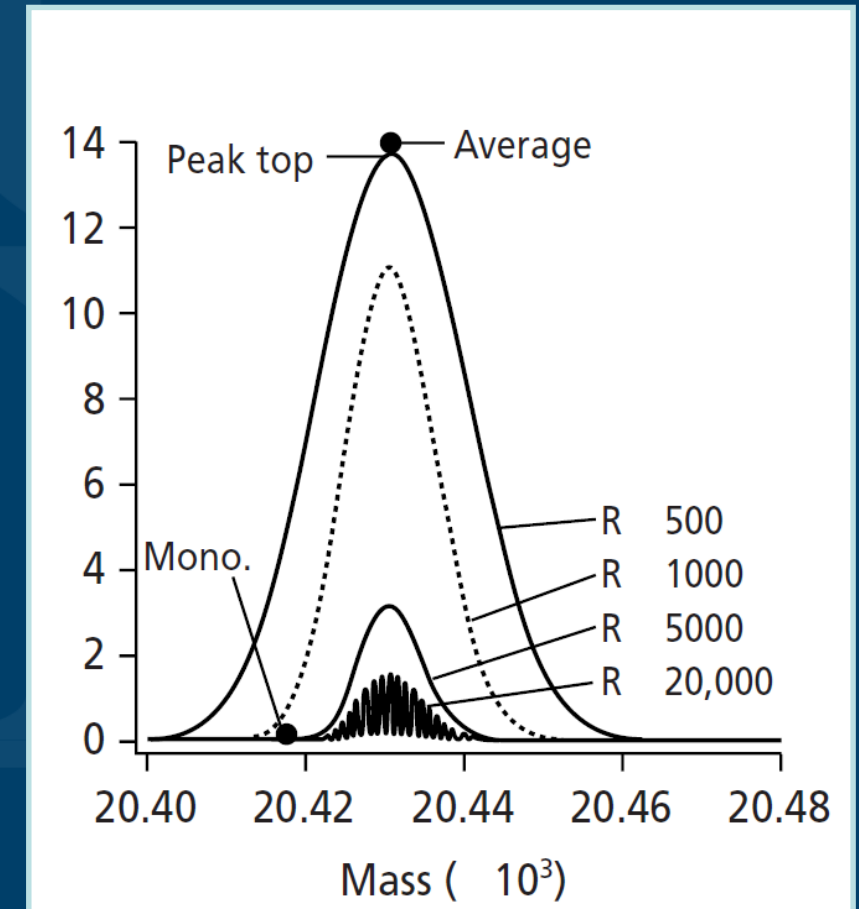
Lab scale



Bathroom Scale



Scales example.



From Balough, LCGC 2004

What is Mass Accuracy?

Mass Accuracy (Tune)

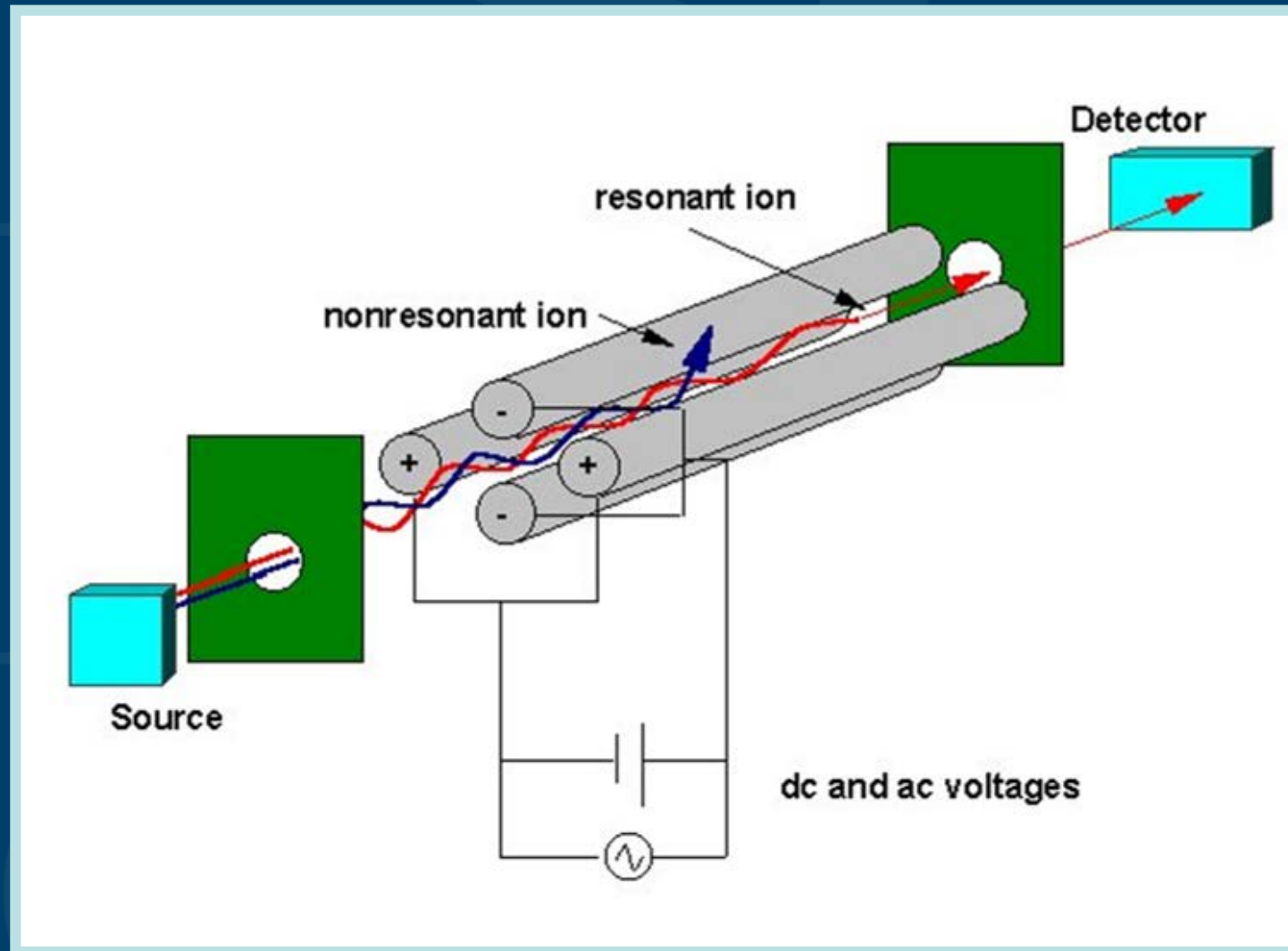
$$1633.9498 - 1633.9395 = 0.0103$$

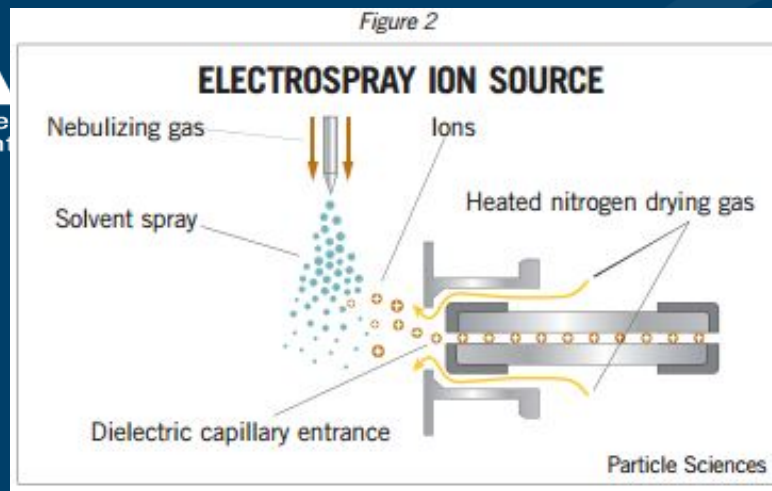
$$0.0103 / 1633.9498 \times 10^6 = 6.3 \text{ ppm}$$

True mass	400.0000
Measured mass	400.0020
Difference	0.0020 or 2 mmu
Error	$\frac{0.002}{400} \times 10^6 = 5 \text{ ppm}$

LCGC North America Vol 22 Number 2 February 2004 MS The Practical Art
Michael Balough "Debating Resolution and Mass Accuracy"

Single Quad MS





MS/MS or Triple Quad

- MRM or transition
- Parent to daughter

Ex. PFOA 413-369
 413-169

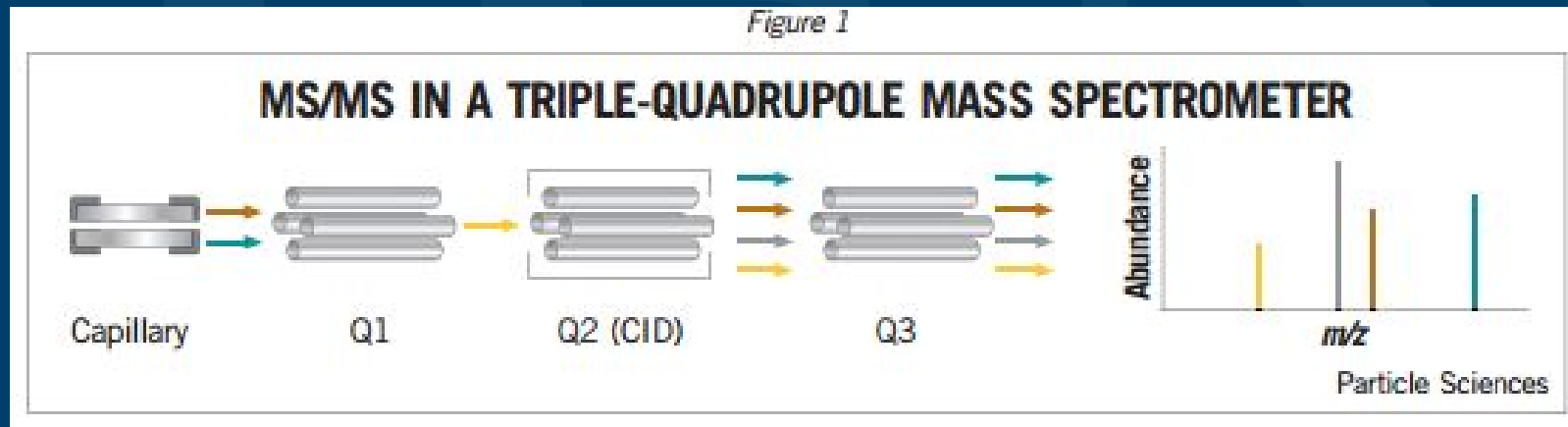
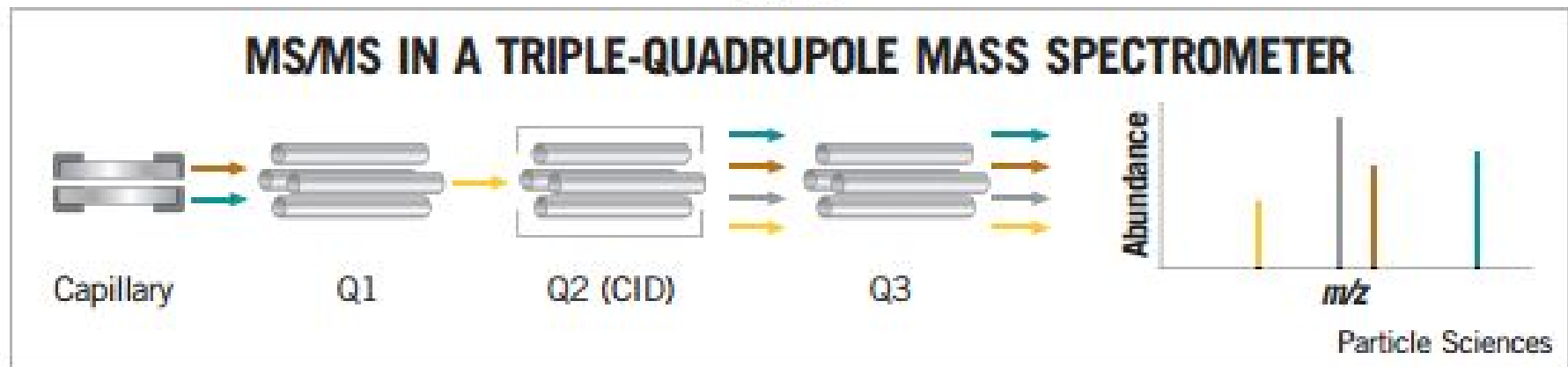
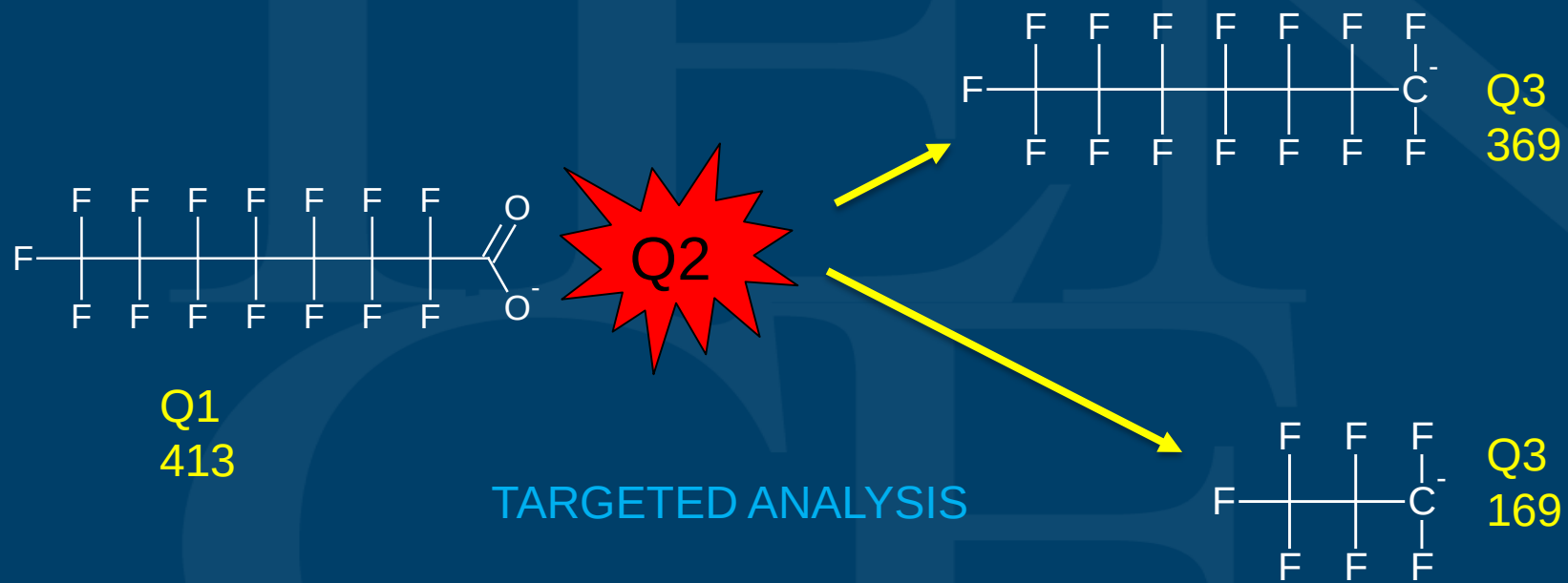
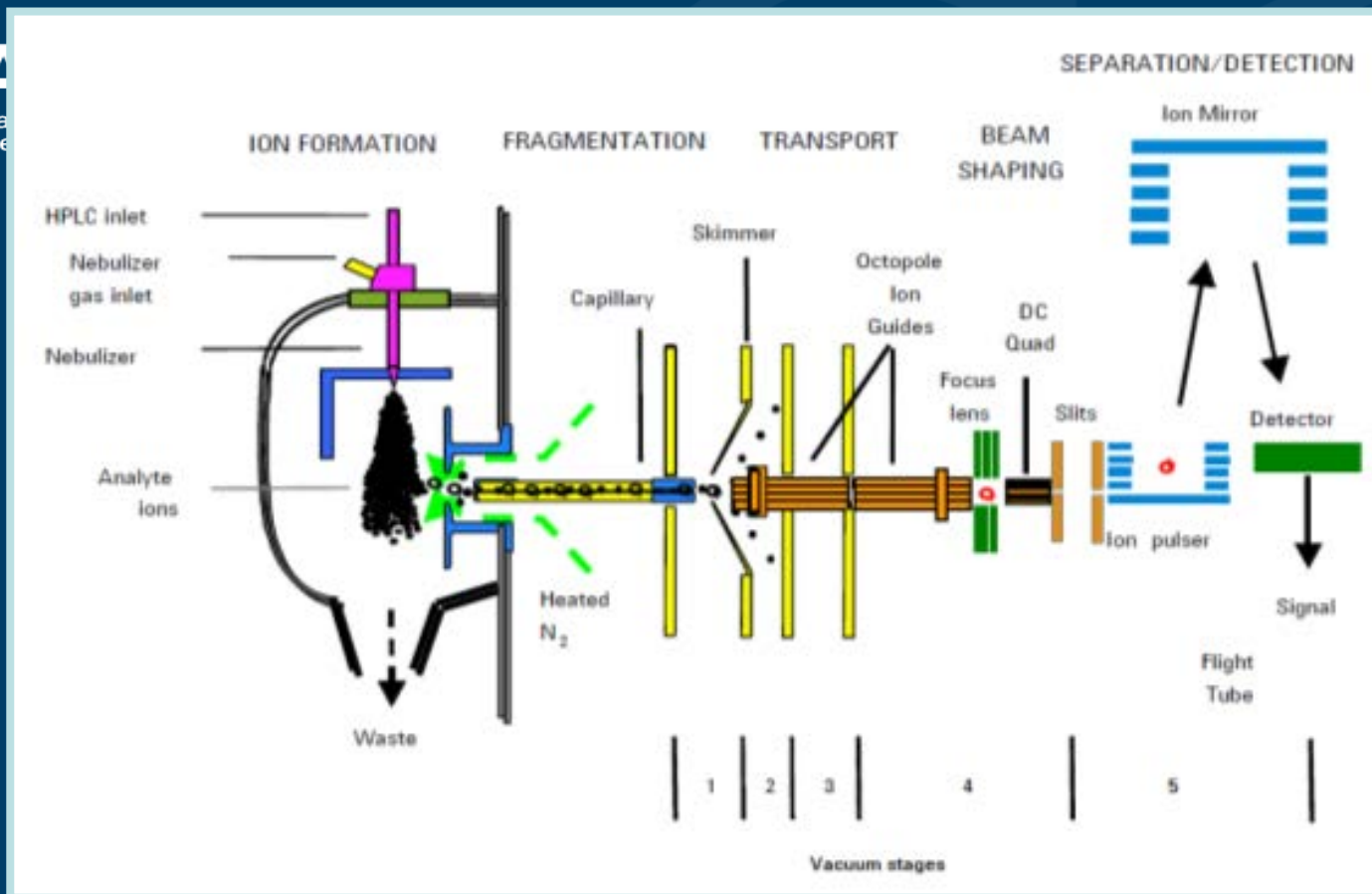


Figure 1



Ex. PFOA





TOFMS or QTOFMS

Targeted Analysis or
Non-targeted Analysis
Post-analysis data mining

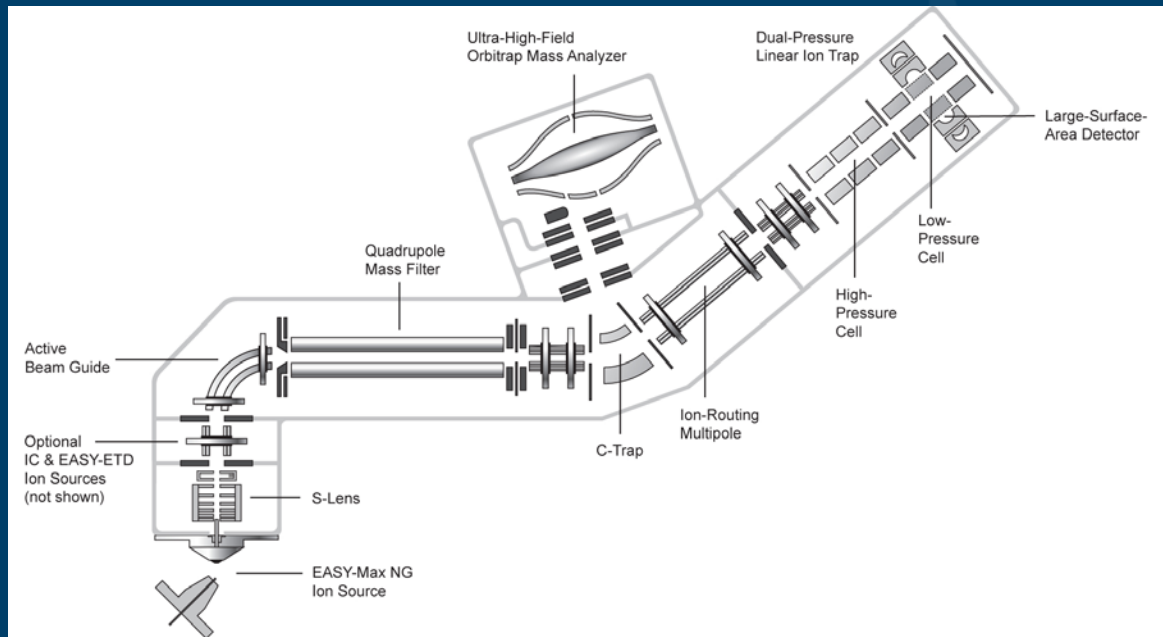
Ex. PFOA exact mass 412.9664 Da



368.9766 Da

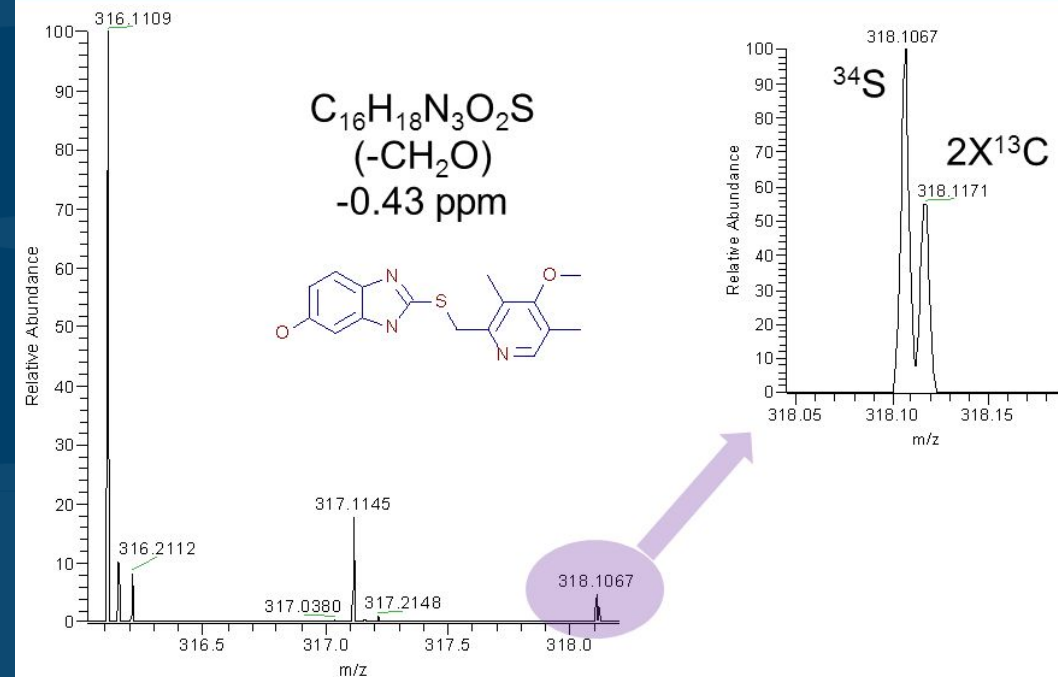


Orbitrap

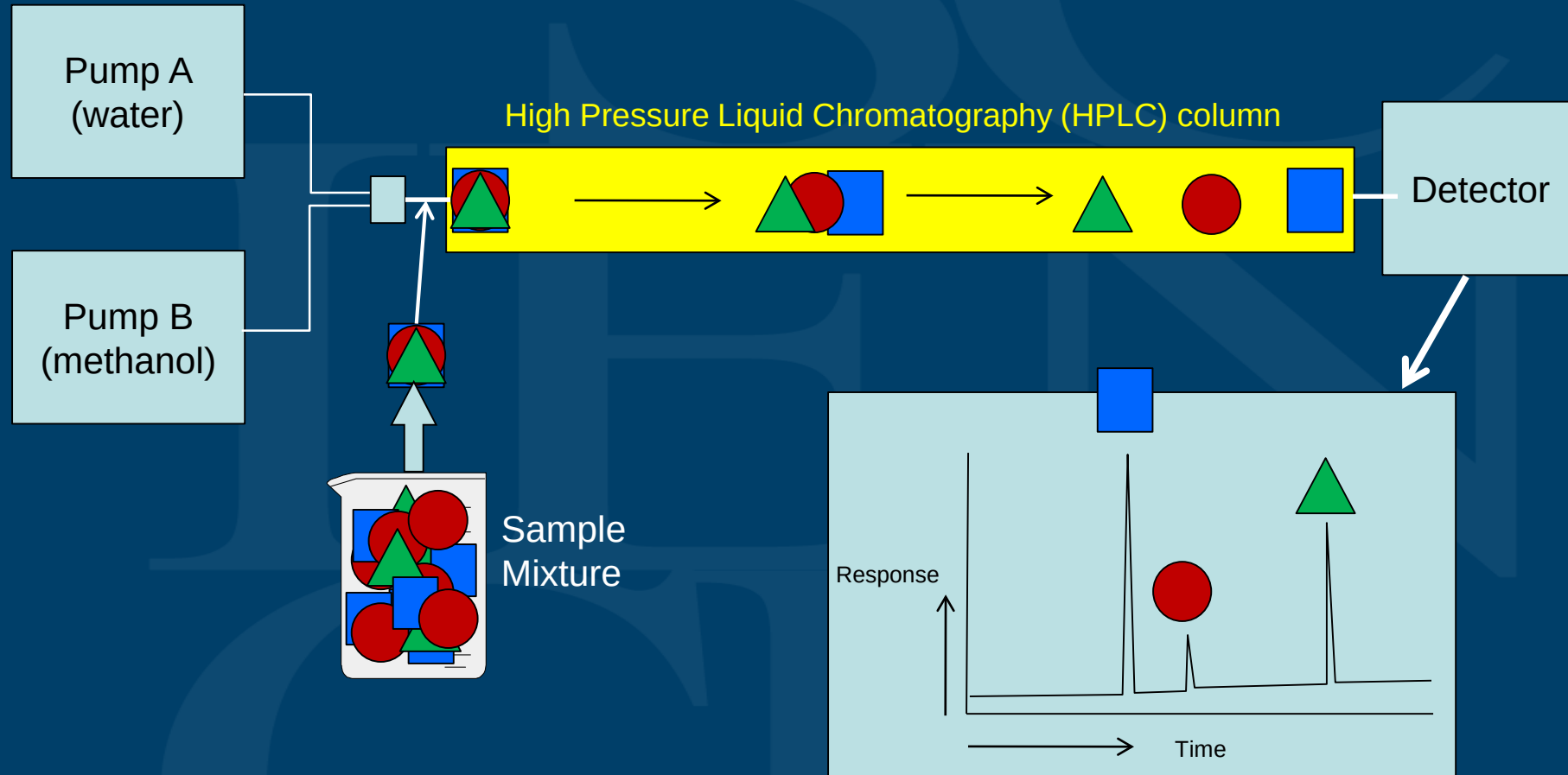


TARGETED ANALYSIS
NON TARGETED ANALYSIS
STRUCTURE ELUCIDATION
POST ANALYSIS DATA MINING

Resolution and Identification – Fine Isotope Structure



What is Liquid Chromatography; Gas Chromatography



****RT and response****

Liquid Chromatography

VS

Gas Chromatography

Non-volatile chemicals
Polar chemicals
Water soluble chemicals
Example: PFOA, GenX, Nafion BP

Volatile chemicals
Non-Polar chemicals
Water soluble chemicals
Example: Benzene, formaldehyde, HFPO

Work done in collaboration with NC DEQ summer/fall 2017 (GenX)

Targeted analysis of PFAS in water samples (MS/MS or Triple Quad analysis)
resolution 500-5000 GenX, legacy PFAS (PFOS/PFOA)

Non-targeted analysis of PFAS in water samples (TOFMS analysis) resolution 25,000
Nafion BP1, Nafion BP2, PFMOAA, PFO2HxA, PFO3OA, **other previously
undescribed analytes**

Questions?

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