

# Mass Accuracy and Mass Resolution in TOF MS

*October 2011*

# What will we discuss?

- What is mass resolution and mass accuracy
- Why and when they are important
- How to use resolution and mass accuracy for practical analysis

# Mass resolution

What is it?

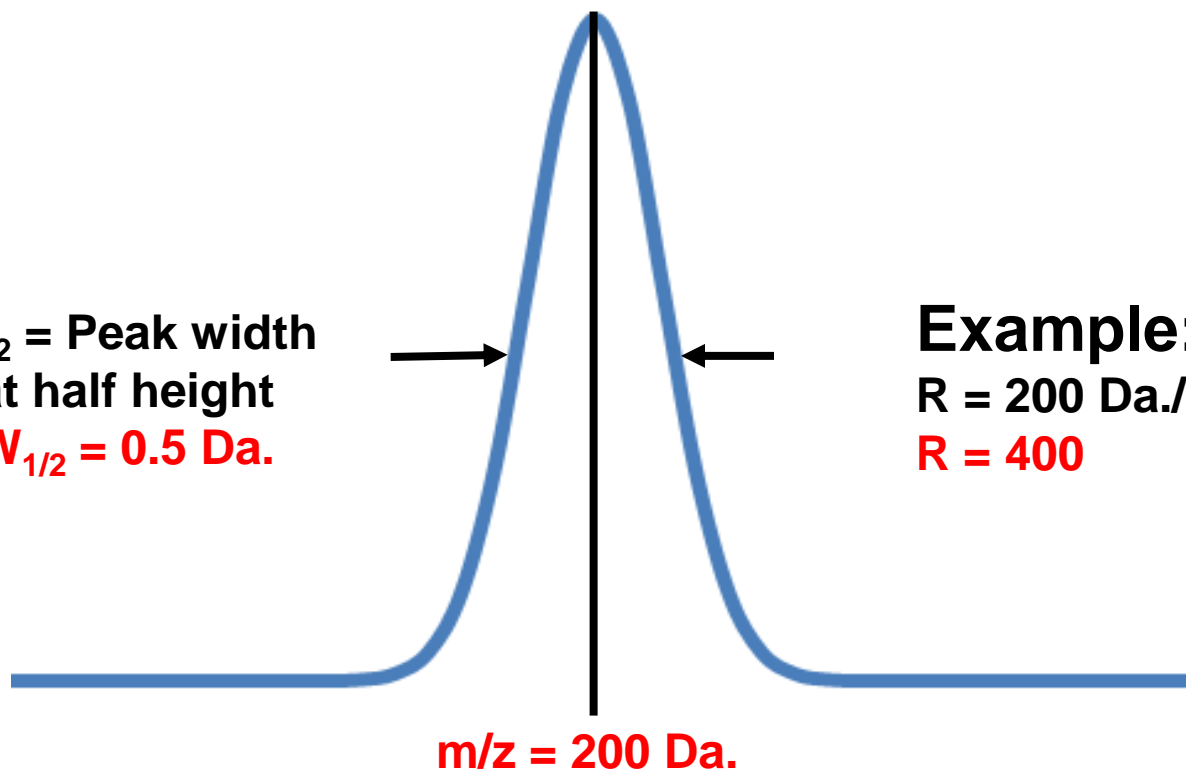
**Definition:**

**Mass resolution = (ion mass)/(mass peak width)**

$$R = (m/z) / W_{1/2}$$

$W_{1/2}$  = Peak width  
at half height  
 $W_{1/2} = 0.5 \text{ Da.}$

**Example:**  
 $R = 200 \text{ Da.}/0.5 \text{ Da.}$   
 $R = 400$



# Mass resolution

Older definition – peaks of equal heights

## Definition:

Mass resolution = (ion mass)/(mass peak separation)

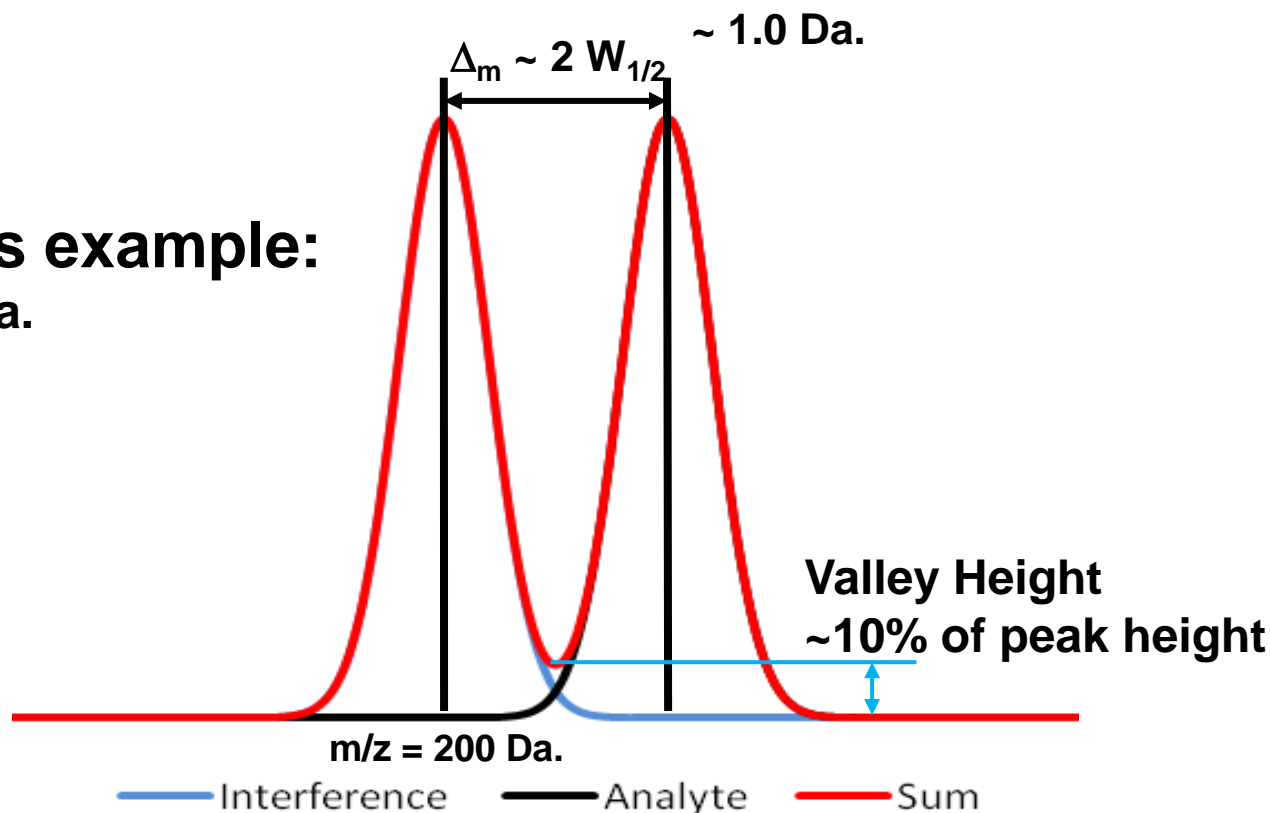
$$R = (m/z) / \Delta_m$$

From previous example:

$$R = 200 \text{ Da.} / 1.0 \text{ Da.}$$

$$R_{10\%} = 200$$

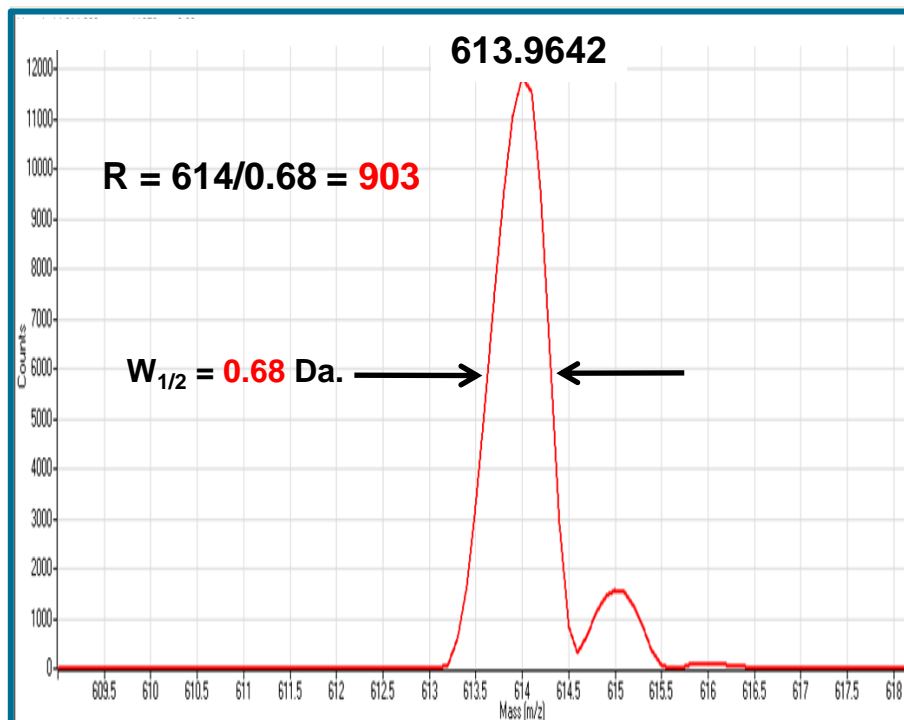
$$R_{W_{1/2}} = 400$$



# Resolving power & mass accuracy

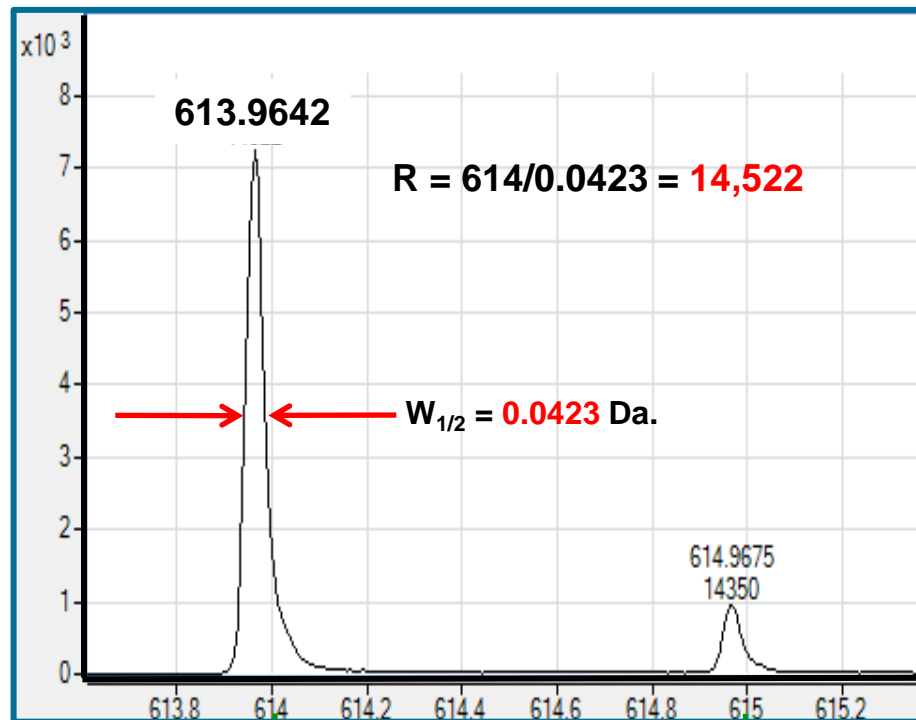
$m/z = 613.964203$

SQ, TQ, IT



1 Da.

TOF, Q-TOF

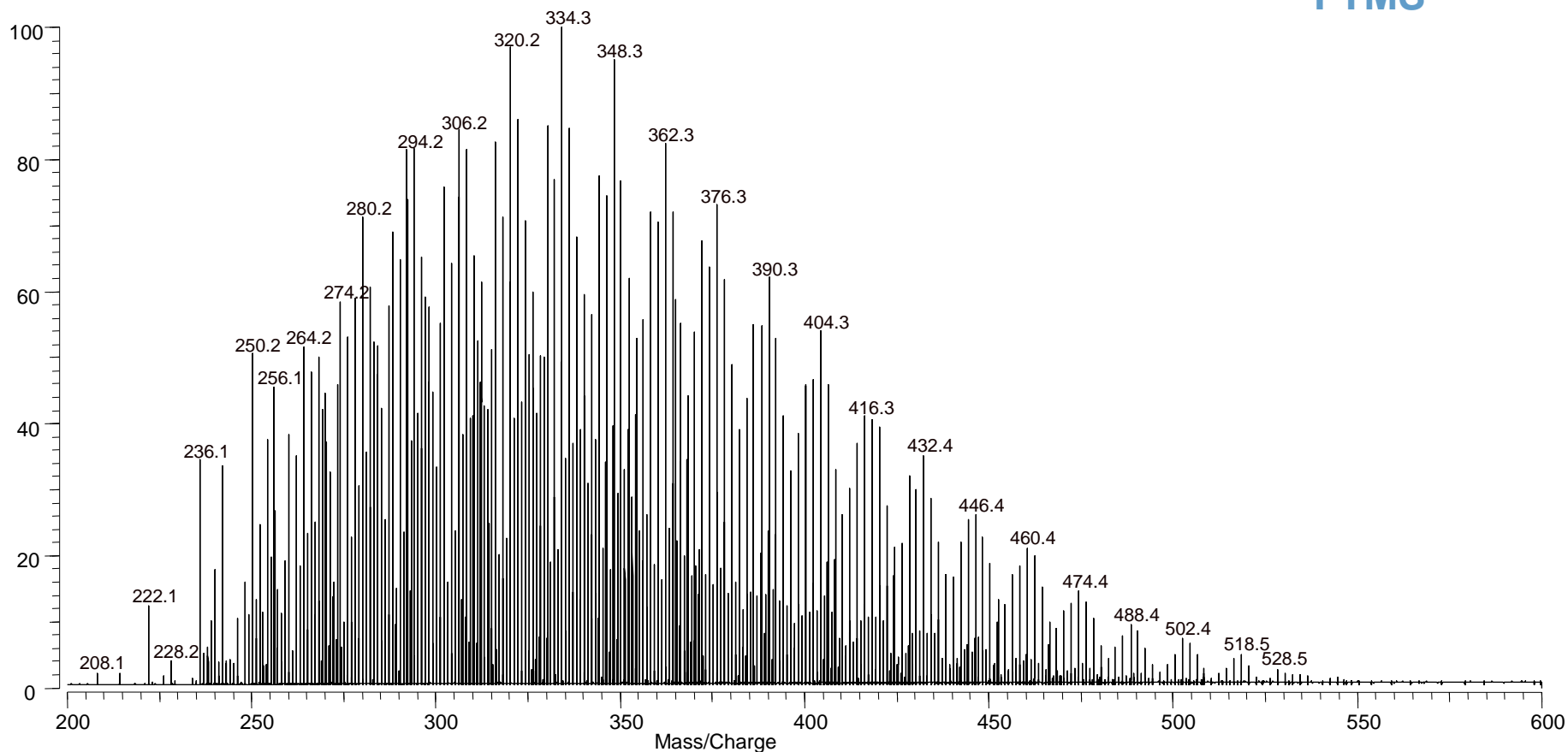


1 Da.

# Why is resolution important?

Complex sample or matrix

Crude Oil  
FTMS

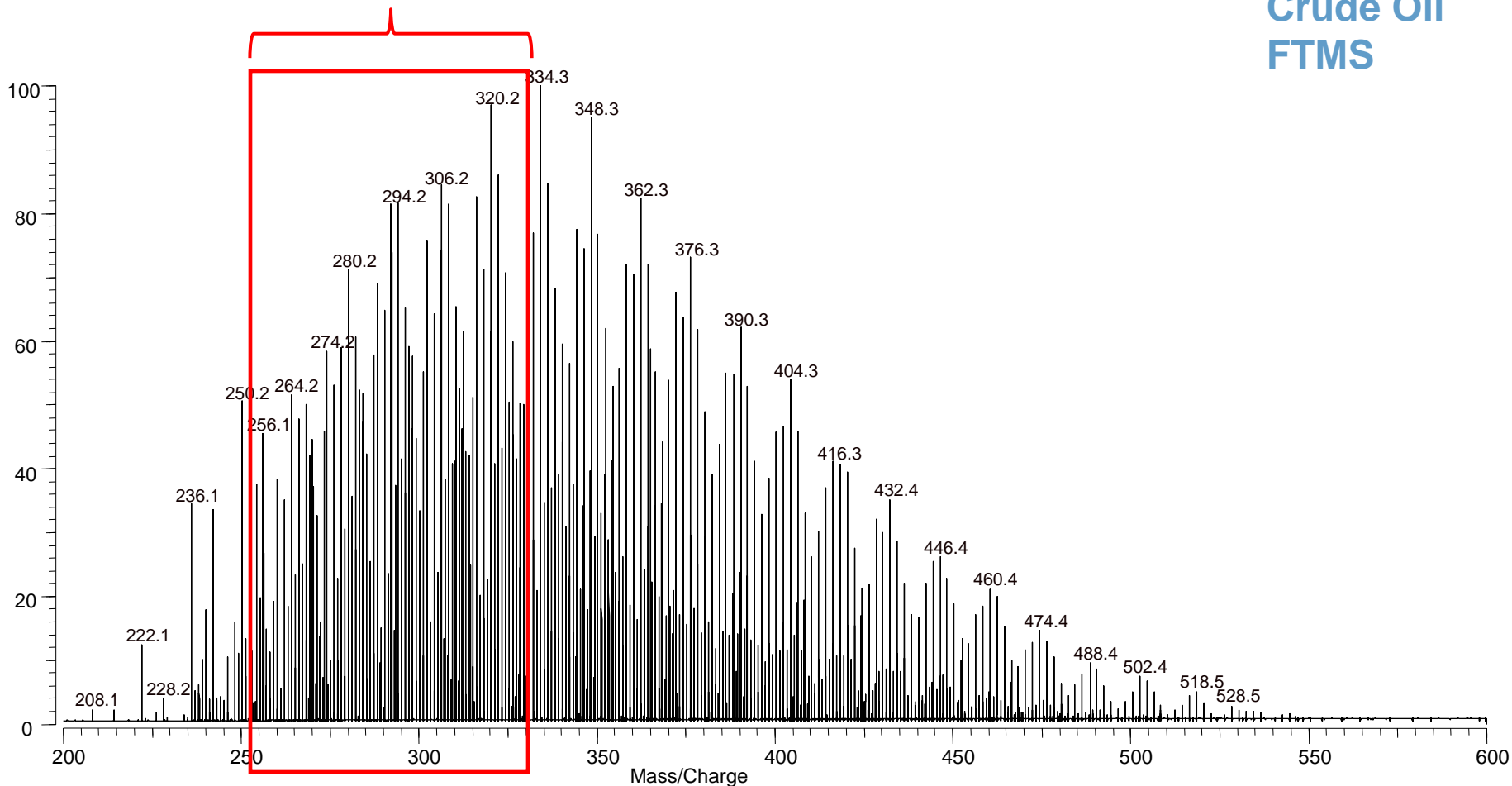


# Why is resolution important?

Complex sample or matrix – take a closer look

$m/z$  200 - 600  $m/z = 250 - 325$

Crude Oil  
FTMS



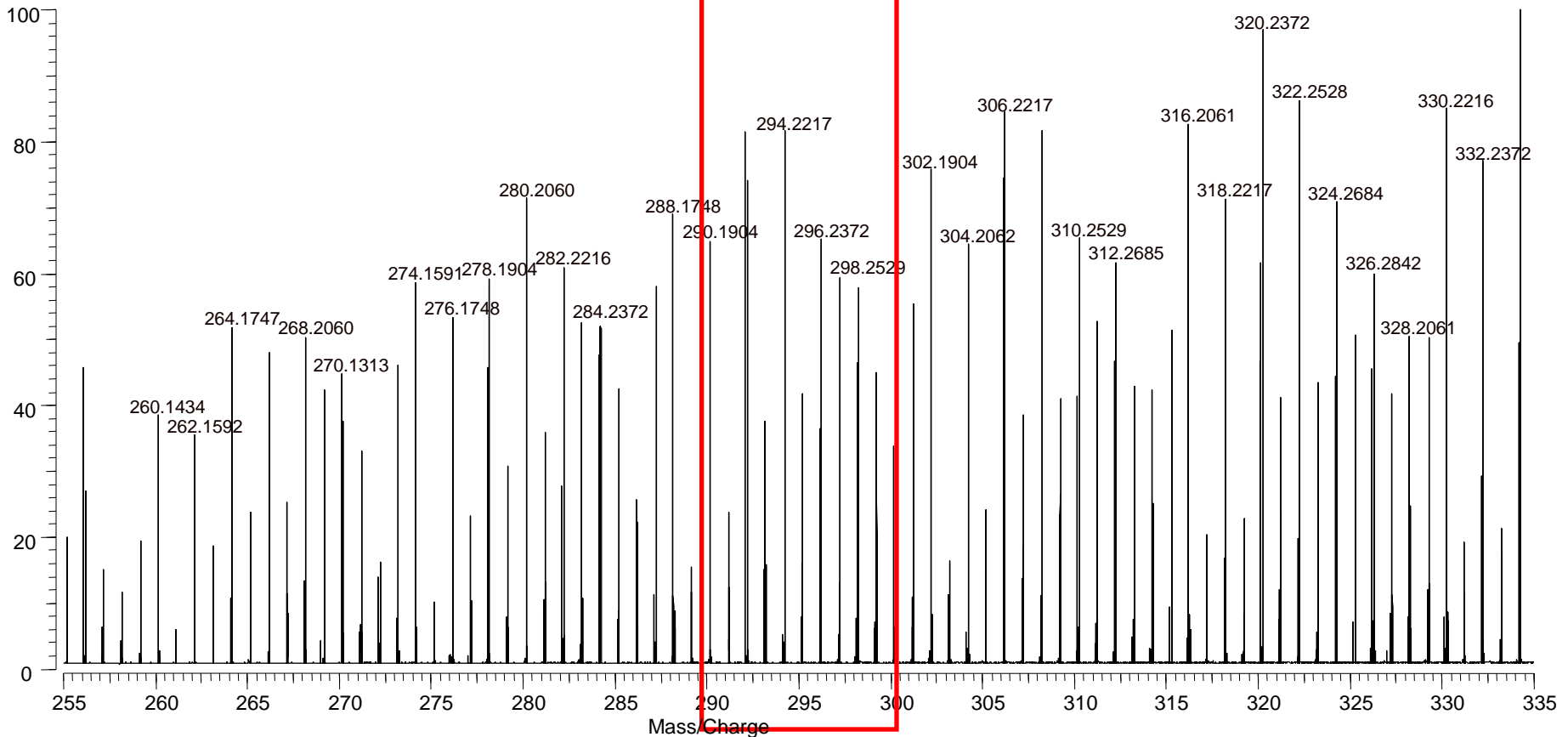
# Why is resolution important?

Complex sample or matrix – take a closer look

5X zoom →  $m/z$  255 - 335

$m/z = 290 - 300$

Crude Oil  
FTMS





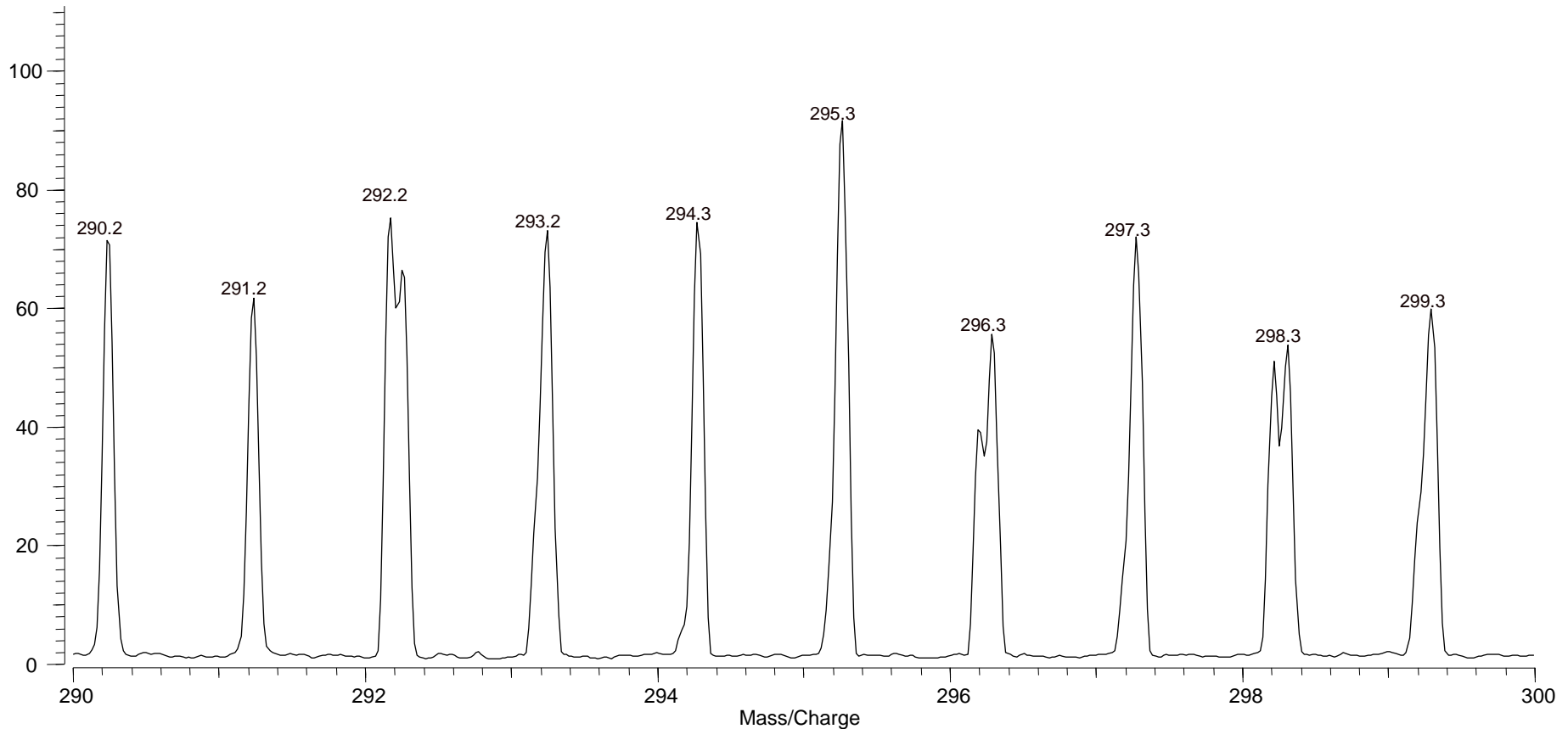
# Why is resolution important?

Complex sample or matrix – take a closer look

40X zoom →  $m/z$  290 - 300

Resolution → 5000

Crude Oil  
FTMS



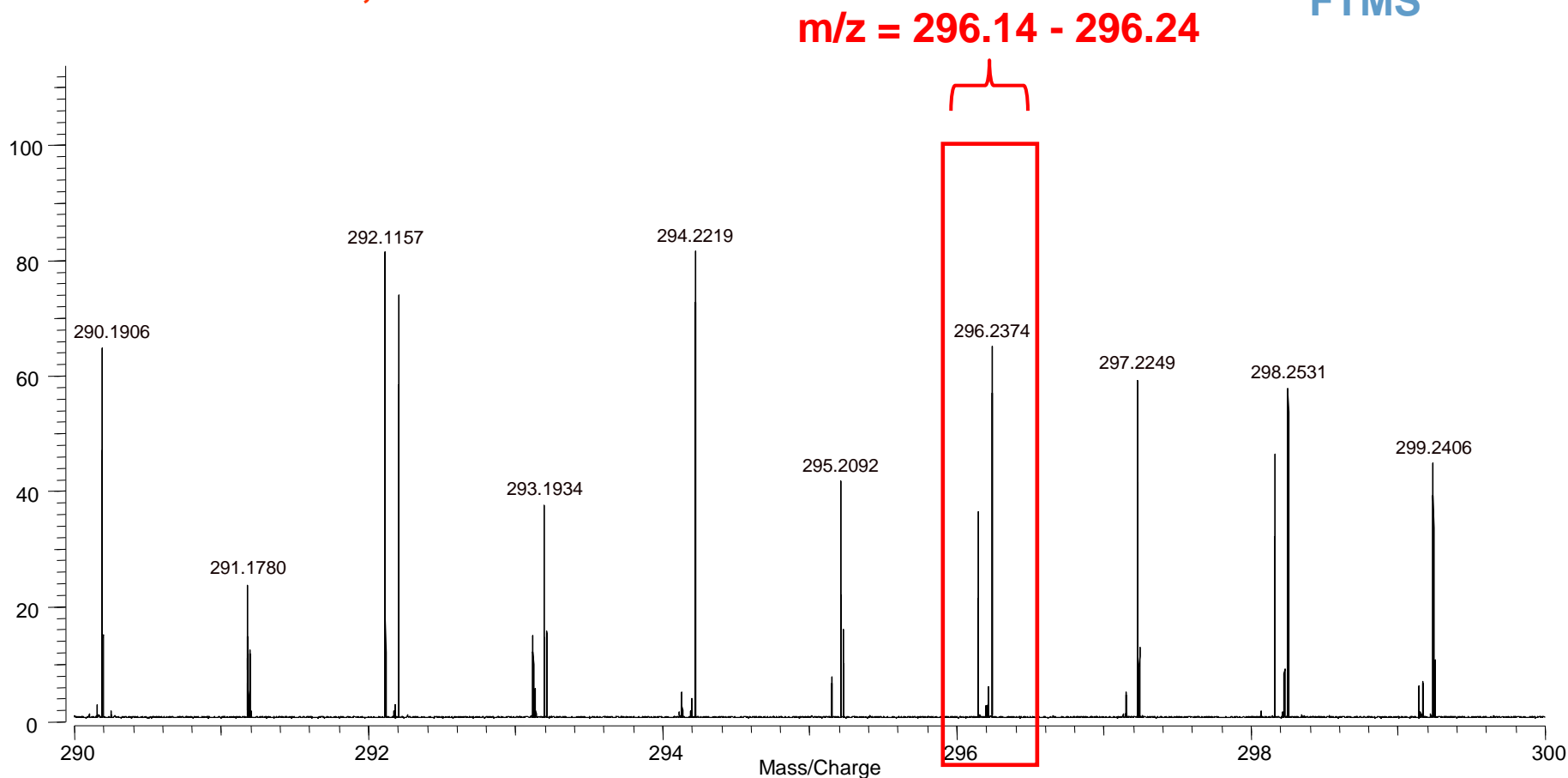
# Why is resolution important?

Complex sample or matrix – take a closer look

40X zoom →  $m/z$  290 - 300

Resolution → 237,000

Crude Oil  
FTMS



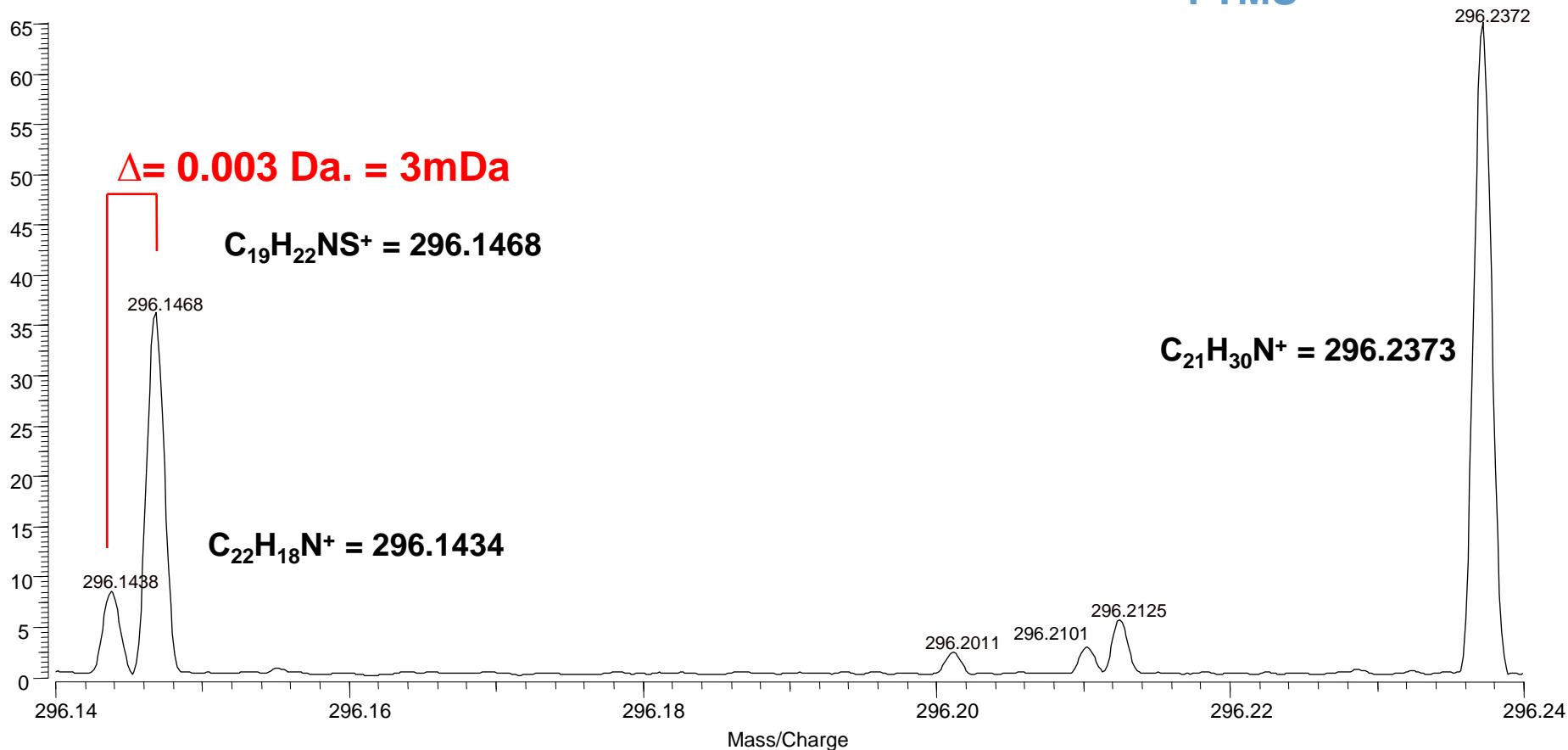
# Why is resolution important?

Complex sample or matrix – take a closer look

4000X zoom →  $m/z$  295.14 - 295.24

Resolution → 237,000

Crude Oil  
FTMS

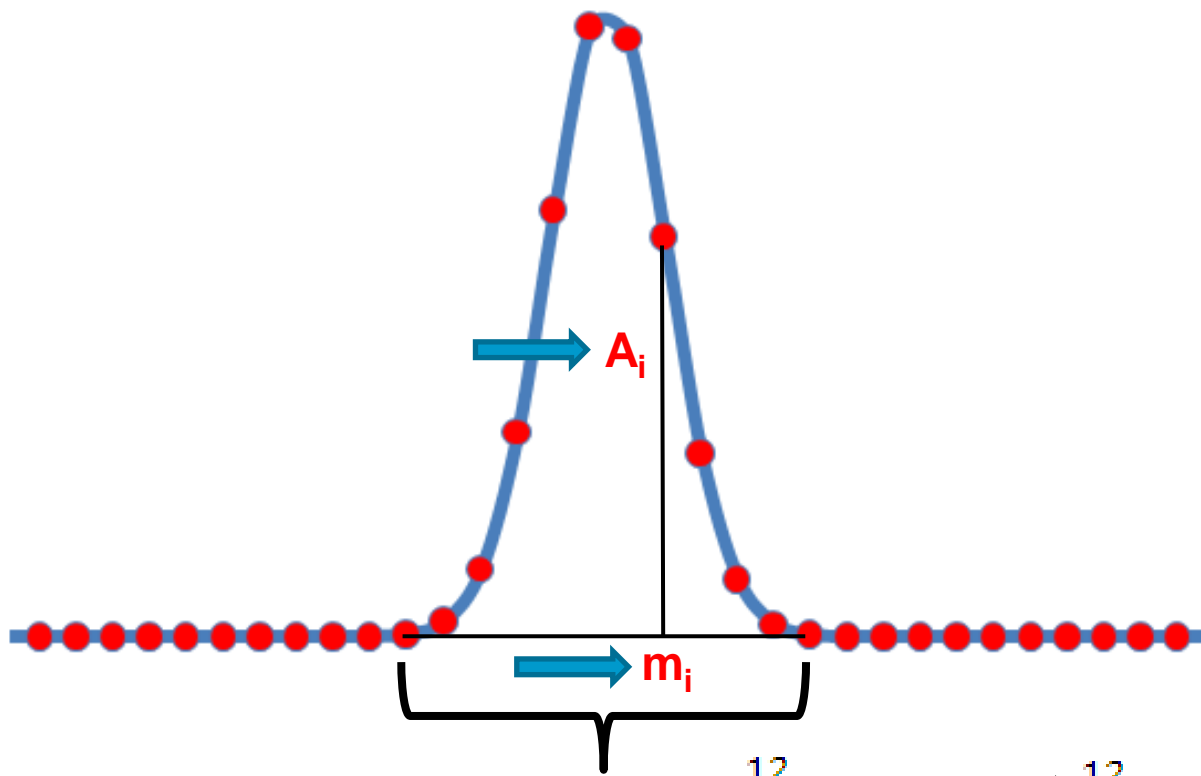


# How much resolution is required?

- The resolution required to solve a given analytical problem depends on the sample and matrix
- Sample preparation reduces potential chemical interferences and therefore the resolution requirements
- Most applications require a resolution of 10,000
- For some sample/matrix combinations however, there may never be enough resolution

# How the mass determined - mass centroid

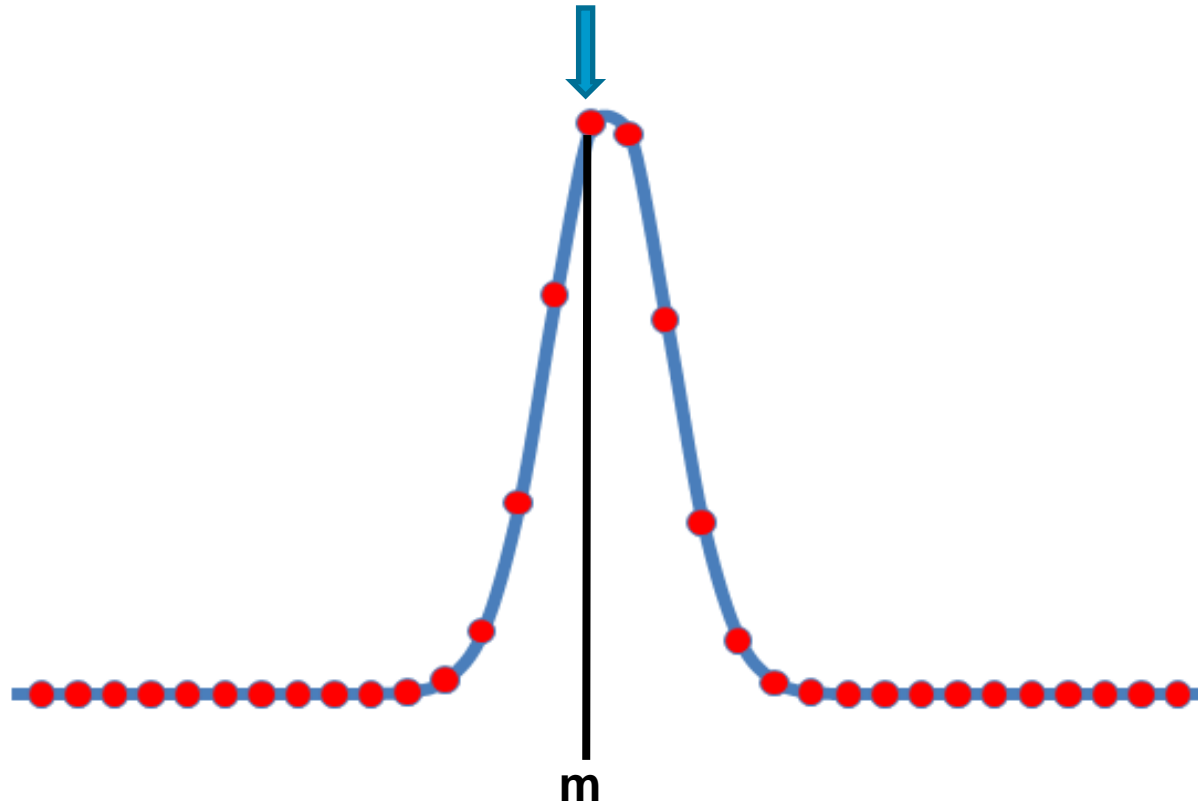
Definition: – “center of mass” of the peak = 1<sup>st</sup> moment



$$\text{Mass centroid} = \bar{m} = \frac{\sum_{i=0}^{12} m_i A_i}{\sum_{i=0}^{12} A_i}$$

# Mass centroid

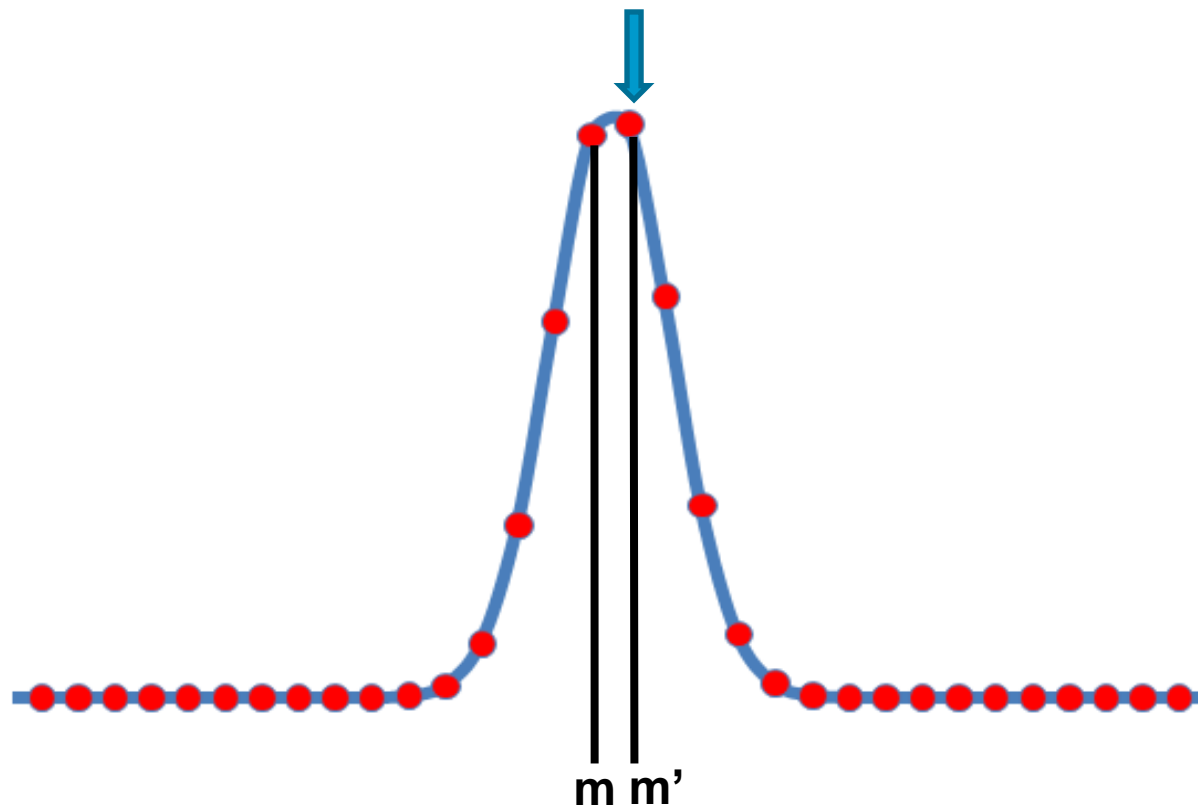
Why centroid and not apex?



*Small changes in amplitude can change where the apex is located*

# Mass centroid

Why centroid and not apex?



*Variation in mass measurement equals the mass spacing of data points  
Centroid mass accuracy is greater than a single point measurement*

# Exact mass and accurate mass

- **Accurate mass** is the experimentally measured mass value
- **Exact mass** is the calculated mass based on adding up the masses of each atom in the molecule
- **Atomic mass** of each element is determined relative to Carbon having a mass of exactly 12.0000
- **Mass defect** is the difference between the mass of the individual components of the nucleus alone, and the mass of the bound nucleus



# Mass error

- Mass error = (exact mass) – (accurate mass)
- Mass error in parts per million (ppm) =

$$\frac{\text{(mass error)}}{\text{(exact mass)}} \times 10^6$$

# Accurate mass makes mass defect important

Element	Symbol	Integer Mass	Exact Mass	Abundance	Mass Defect
Hydrogen	H	1	1.0078	99.99	0.0078
	D or $^2\text{H}$	2	2.0141	0.01	0.0141
Carbon	$^{12}\text{C}$	12	12	98.91	0
	$^{13}\text{C}$	13	13.0034	1.1	0.0034
Nitrogen	$^{14}\text{N}$	14	14.0031	99.6	0.0031
	$^{15}\text{N}$	15	15.0001	0.4	0.0001
Oxygen	$^{16}\text{O}$	16	15.9949	99.76	-0.0051
	$^{17}\text{O}$	17	16.9991	0.04	-0.0009
	$^{18}\text{O}$	18	17.9992	0.2	-0.0008
Fluorine	F	19	18.9984	100	-0.0016
Silicon	$^{28}\text{Si}$	28	27.9769	92.2	-0.0231
	$^{29}\text{Si}$	29	28.9765	4.7	-0.0235
	$^{30}\text{Si}$	30	29.9738	3.1	-0.0262
Phosphorus	P	31	30.9738	100	-0.0262
Sulfur	$^{32}\text{S}$	32	31.9721	95.02	-0.0279
	$^{33}\text{S}$	33	32.9715	0.76	-0.0285
	$^{34}\text{S}$	34	33.9679	4.22	-0.0321
Chlorine	$^{35}\text{Cl}$	35	34.9689	75.77	-0.0311
	$^{37}\text{Cl}$	37	36.9659	24.23	-0.0341
Bromine	$^{79}\text{Br}$	79	78.9183	50.5	-0.0817
	$^{81}\text{Br}$	81	80.9163	49.5	-0.0837
Iodine	I	127	126.9045	100	-0.0955

# Why is mass defect important?

Many defects are large enough to be measurable by TOF MS

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	$^{15}\text{N}$	15	15.0001	0.4	0.0001
Oxygen	$^{16}\text{O}$	16	15.9949	99.76	-0.0051
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One  $^1\text{H}$   
+ 13 ppm

One  $^{16}\text{O}$   
- 8 ppm

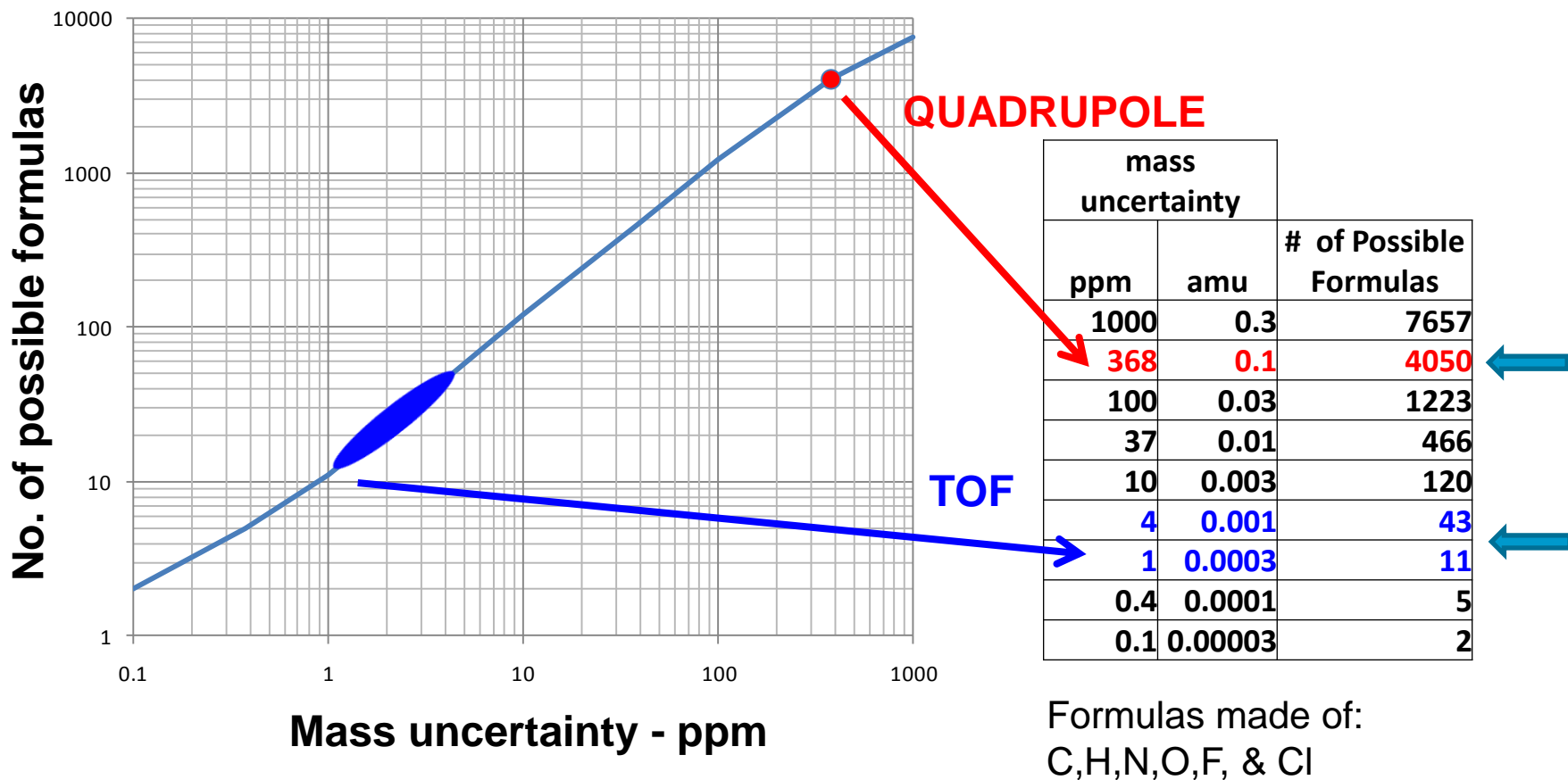
One  $^{35}\text{Cl}$   
- 51 ppm

*TOF capable of < 5 ppm measurement routinely*

# Many possible formulas with an MSD or IT

## But only a few with TOF

Possible chemical formulas for  $m/z = C_{10}F_8 = 271.98667$

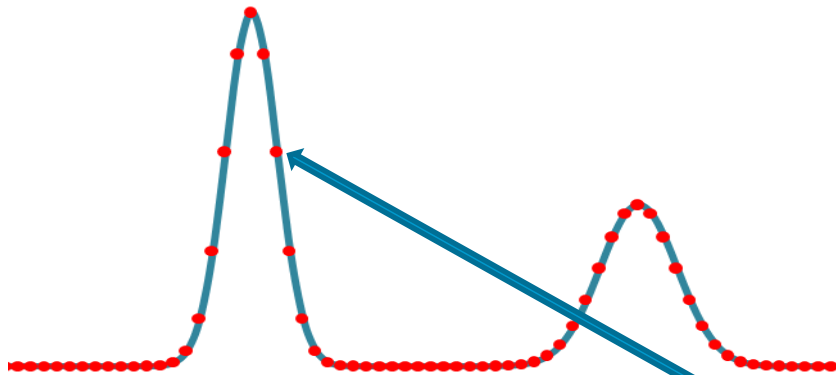


*Isotopic abundances can further reduce the number of possible formulas*

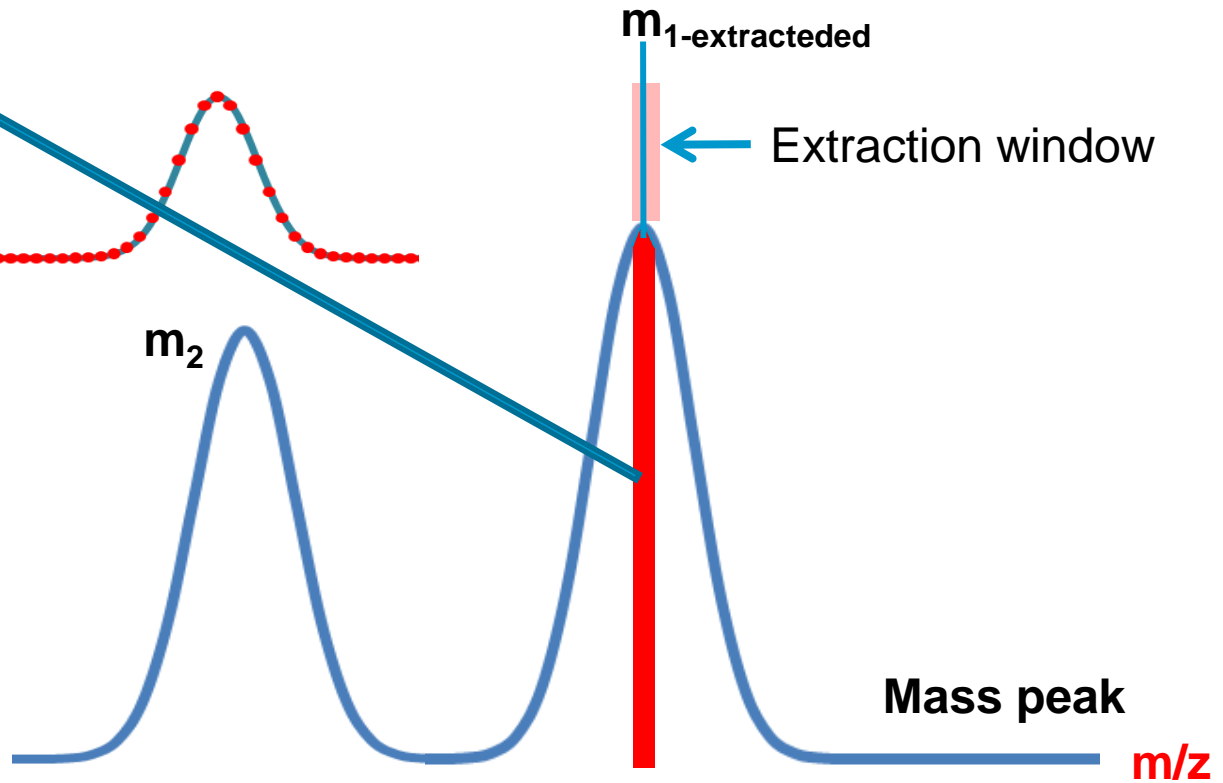
# How is accurate mass used?

## Extracted ion chromatograms - EIC

Chromatogram – EIC  $m_1$



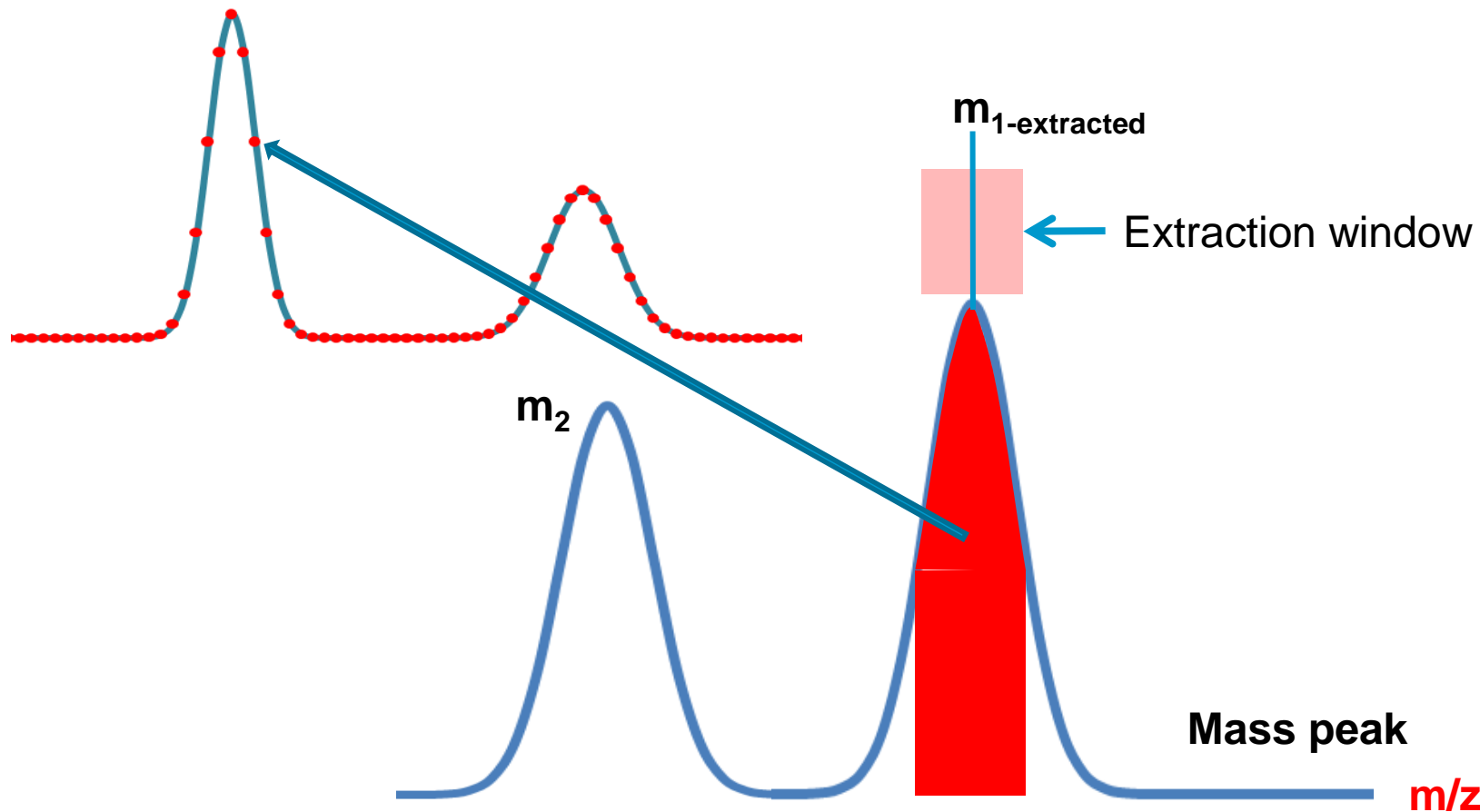
Each point of EIC represents the sum of ions in mass peak within a specified mass range



# Extraction window

Wide extraction window measures more ions = more sensitivity

Chromatogram – EIC  $m_1$

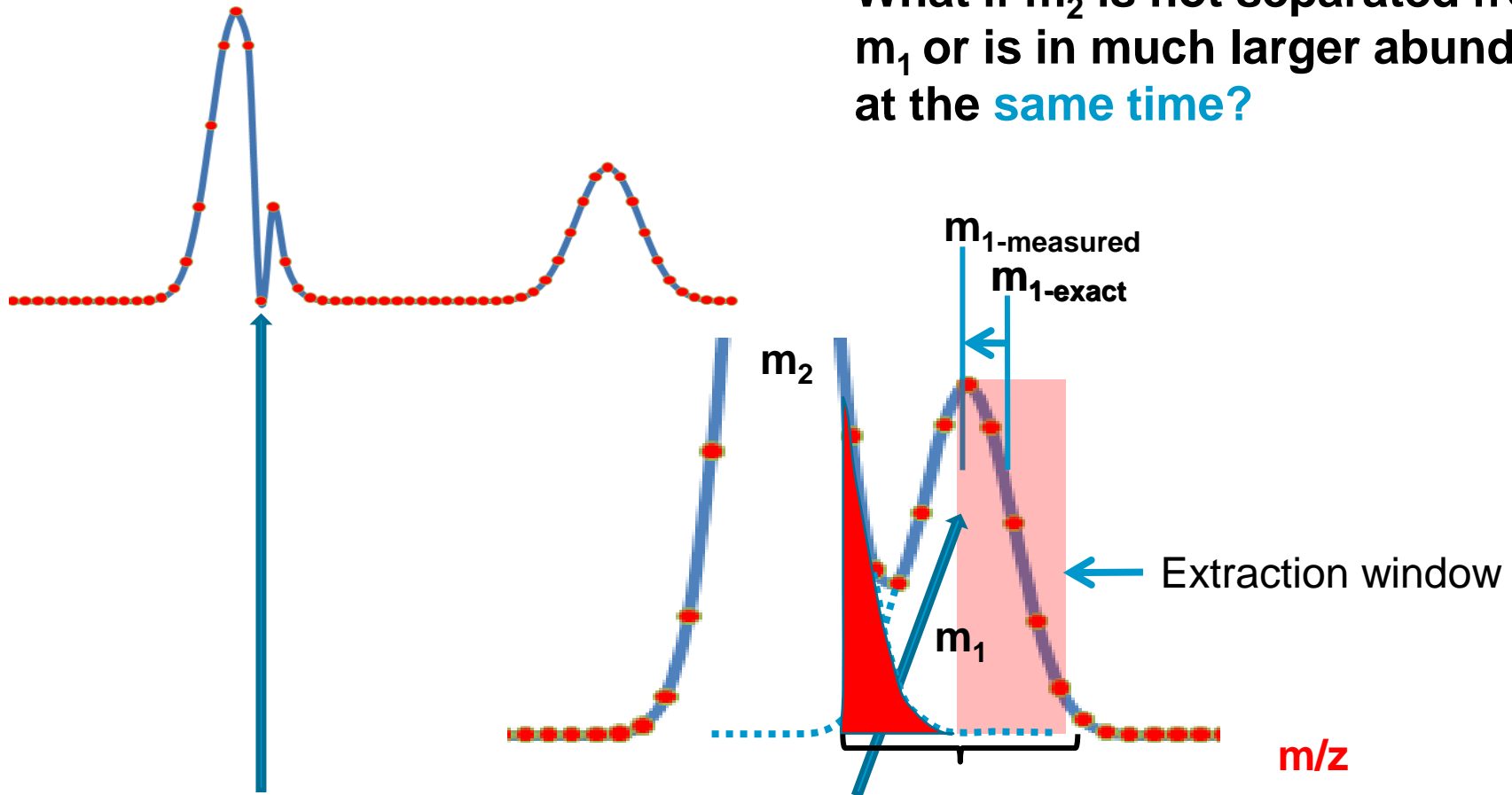


*Good results if  $m_1$  is well separated from  $m_2$  and comparable abundance*

# Why is resolution important?

Ions from  $m_2$  are added to  $m_1$  EIC thus shifting the  $m_1$  centroid

Chromatogram – EIC  $m_1$



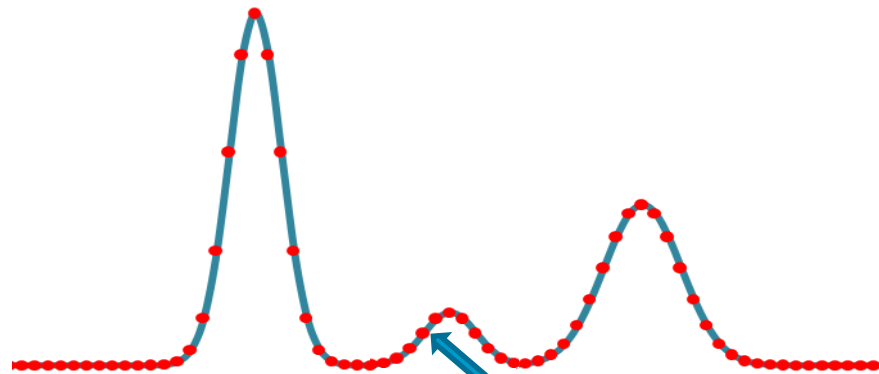
What if  $m_2$  is not separated from  $m_1$  or is in much larger abundance at the **same time**?

*Shifted centroid changes measured ion abundance and mass accuracy*

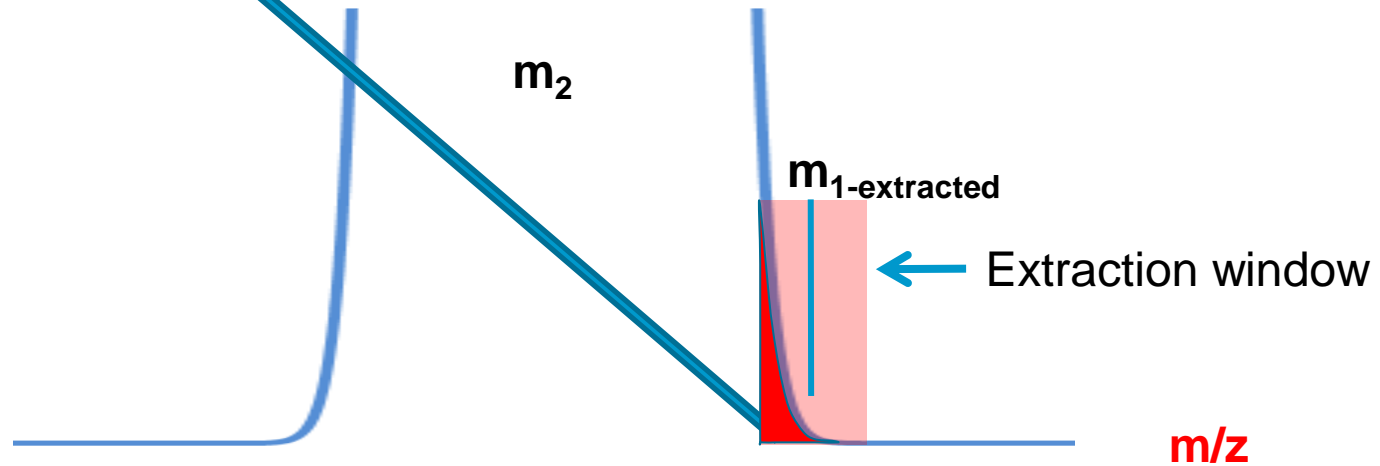
# Why is resolution important?

Wide extraction window will add in ions from adjacent mass

Chromatogram – EIC  $m_1$



What if  $m_2$  is not separated from  $m_1$  or is in much larger abundance at **different times** and **no  $m_1$**  is present?



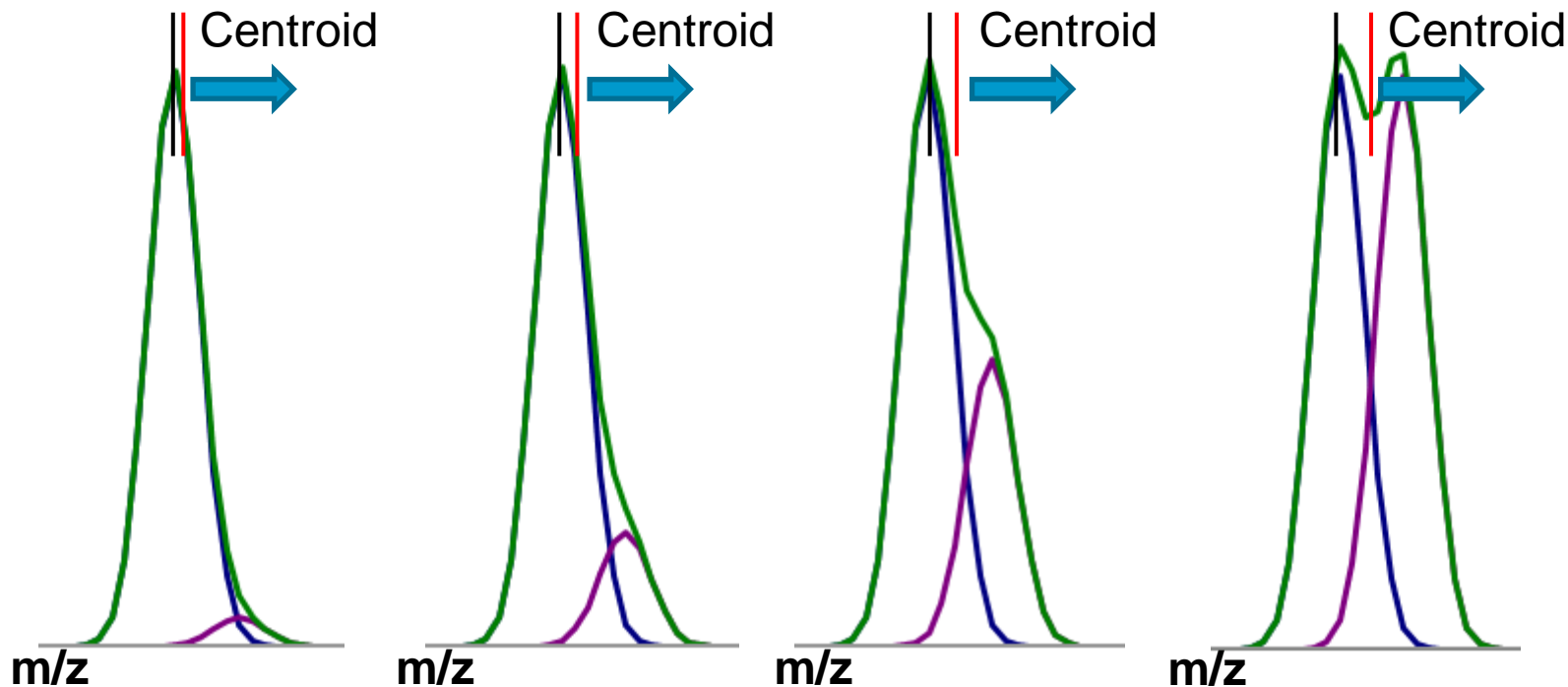
*Ions from  $m_2$  are added into  $m_1$  EIC thus displaying a false  $m_1$  response*



# Mass centroid

Relative intensity affects the result

Profile view of mass peaks

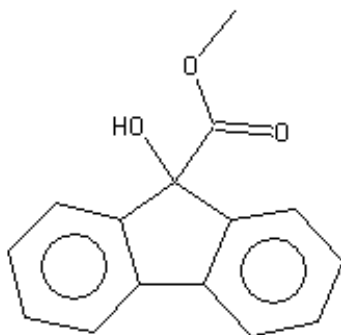


*Centroid view of mass peaks obscures this fact*

# How much resolution is enough?

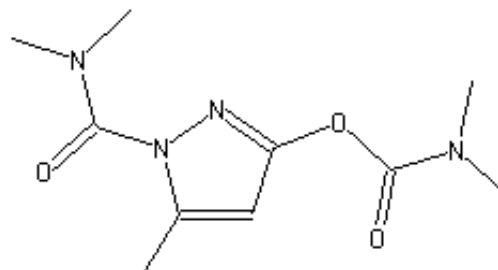
Relative intensity affects the result

Flurenol methyl ester  
 $m/z = 240.0781$   
Mass error = 1.7 ppm



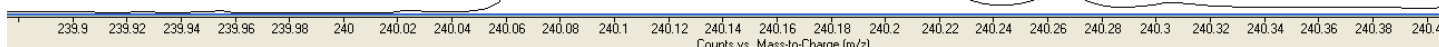
240.0785  
240.1218

Dimetilan  
 $m/z = 240.1217$   
Mass error = 0.4 ppm



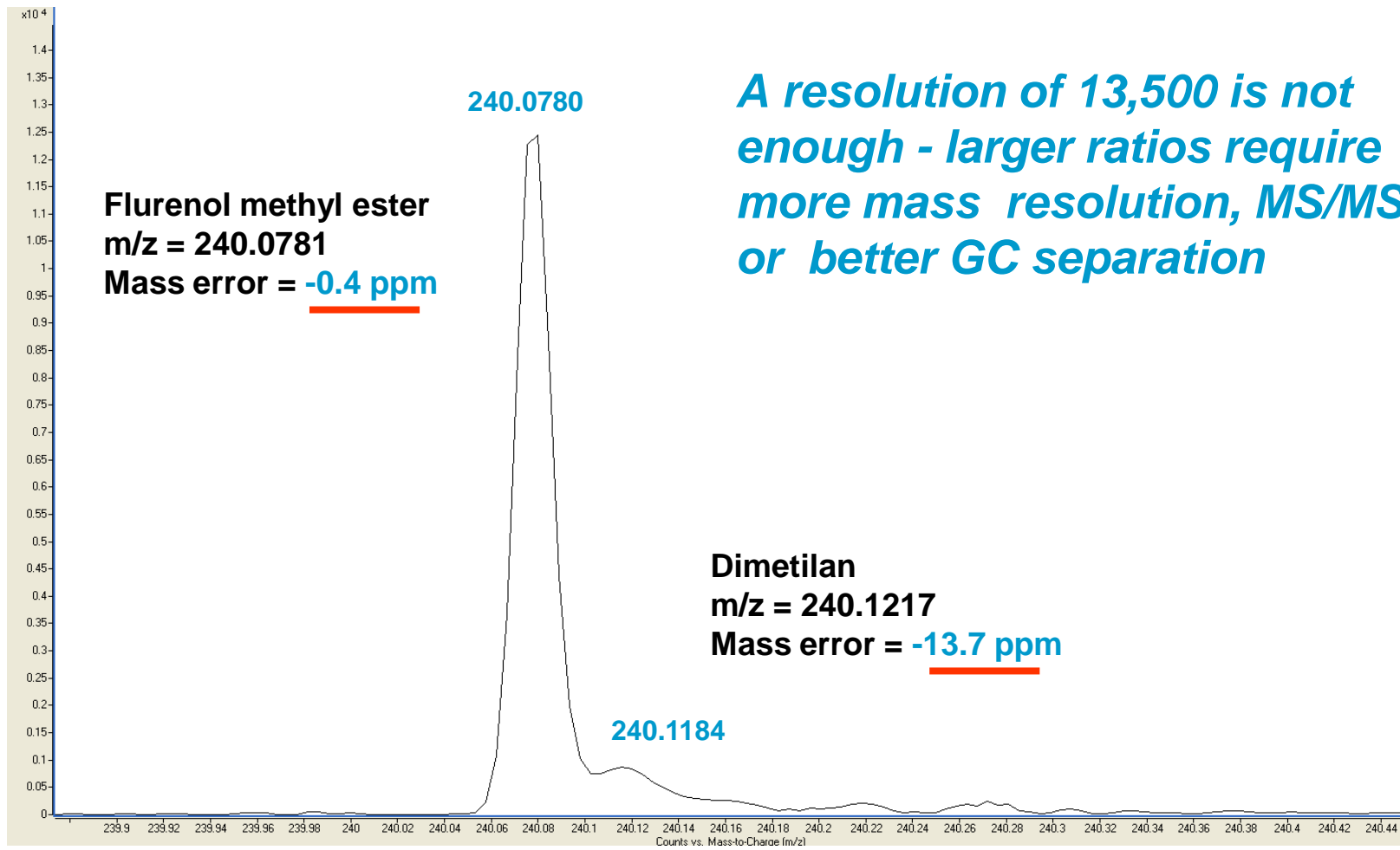
$\Delta m = 0.043$  Da.

~13,500 resolution FWHM



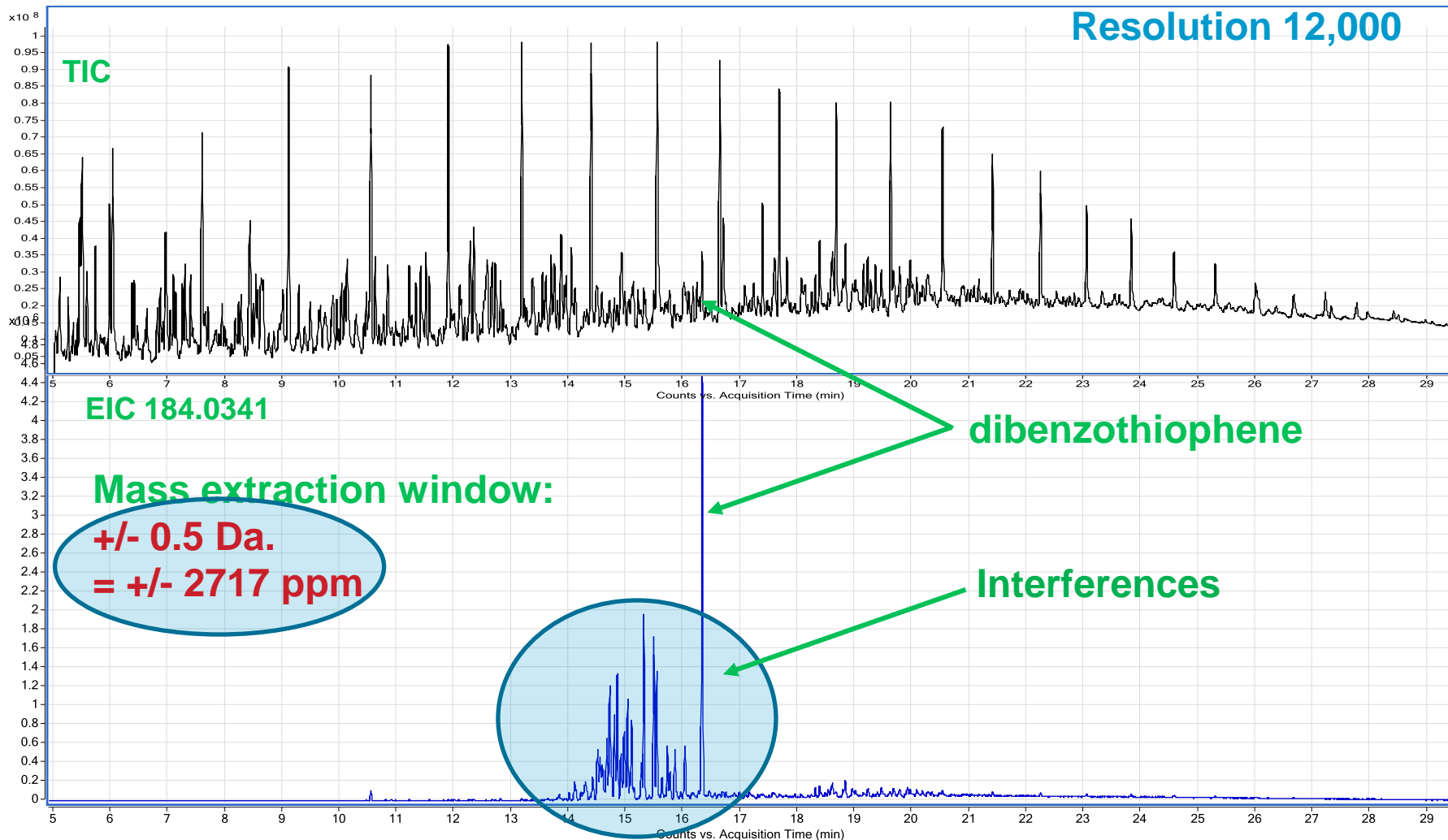
# How much resolution is enough?

Intensity Ratio = 10:1



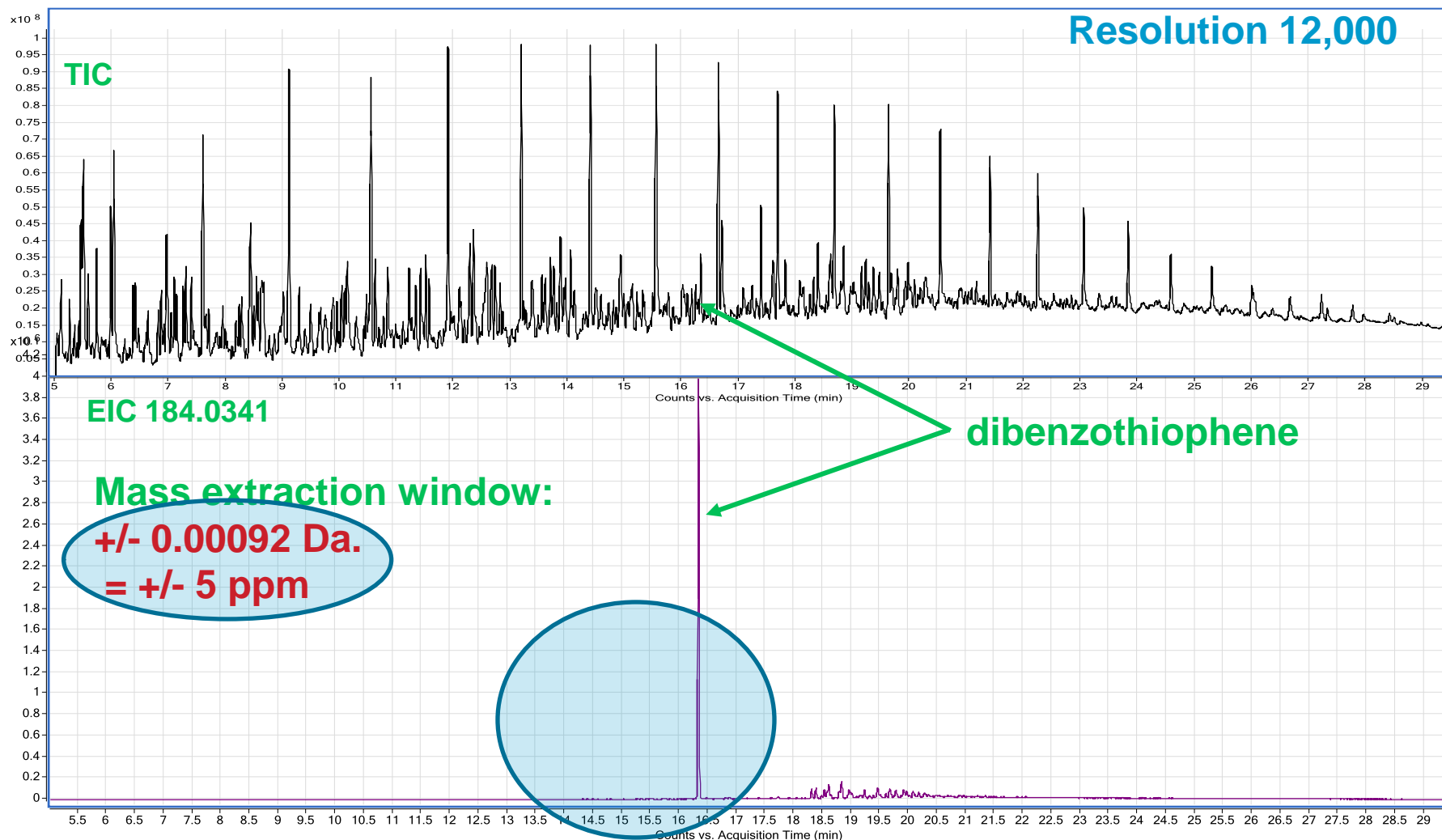
# Crude oil target analysis – target analysis

Problem: identify and quantify dibenzothiophene



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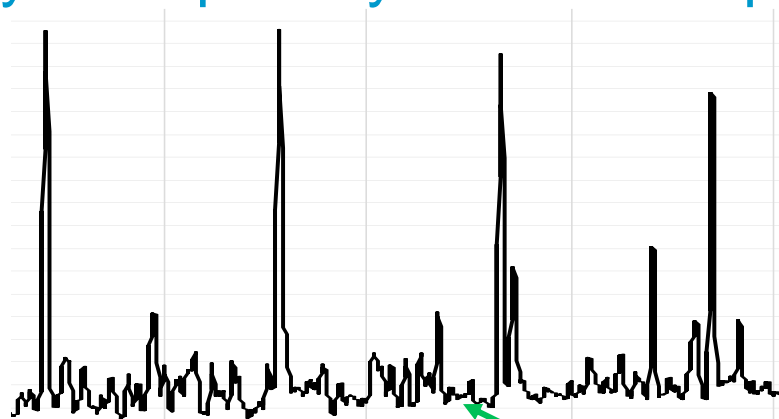


# Crude oil target analysis

Problem: identify and quantify dibenzothiophene

Resolution 12,000

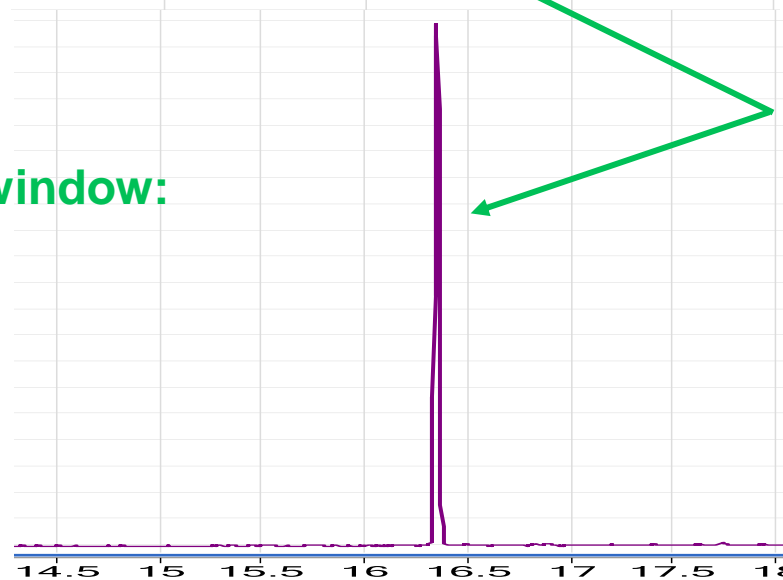
TIC



EIC 184.0341

dibenzothiophene

Mass extraction window:  
+/- 5 ppm



# Summary

- Mass accuracy (MA) is a valuable tool for target quantification and confirmation
- High resolution (HR) ensures mass accuracy over sample range – good test for adequate mass resolution
- How much resolution is required depends on sample, matrix, and their relative abundance
- TOF mass accuracy & high resolution is an important tool for solving complex analytical problems

**Thank you for your attention**