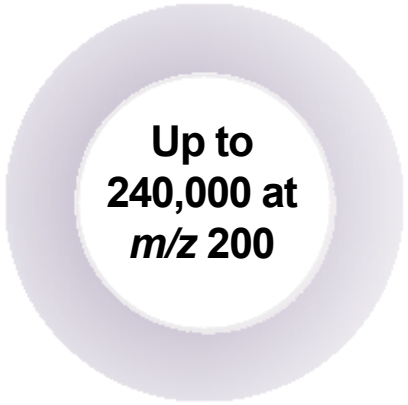
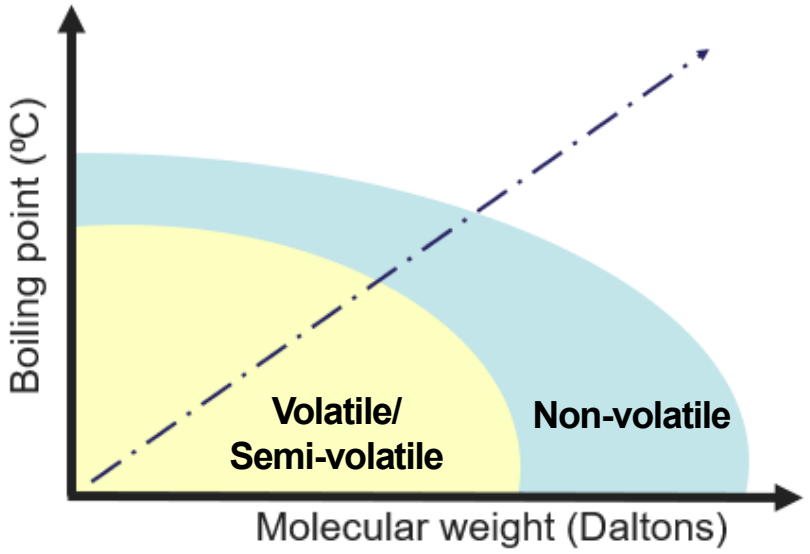
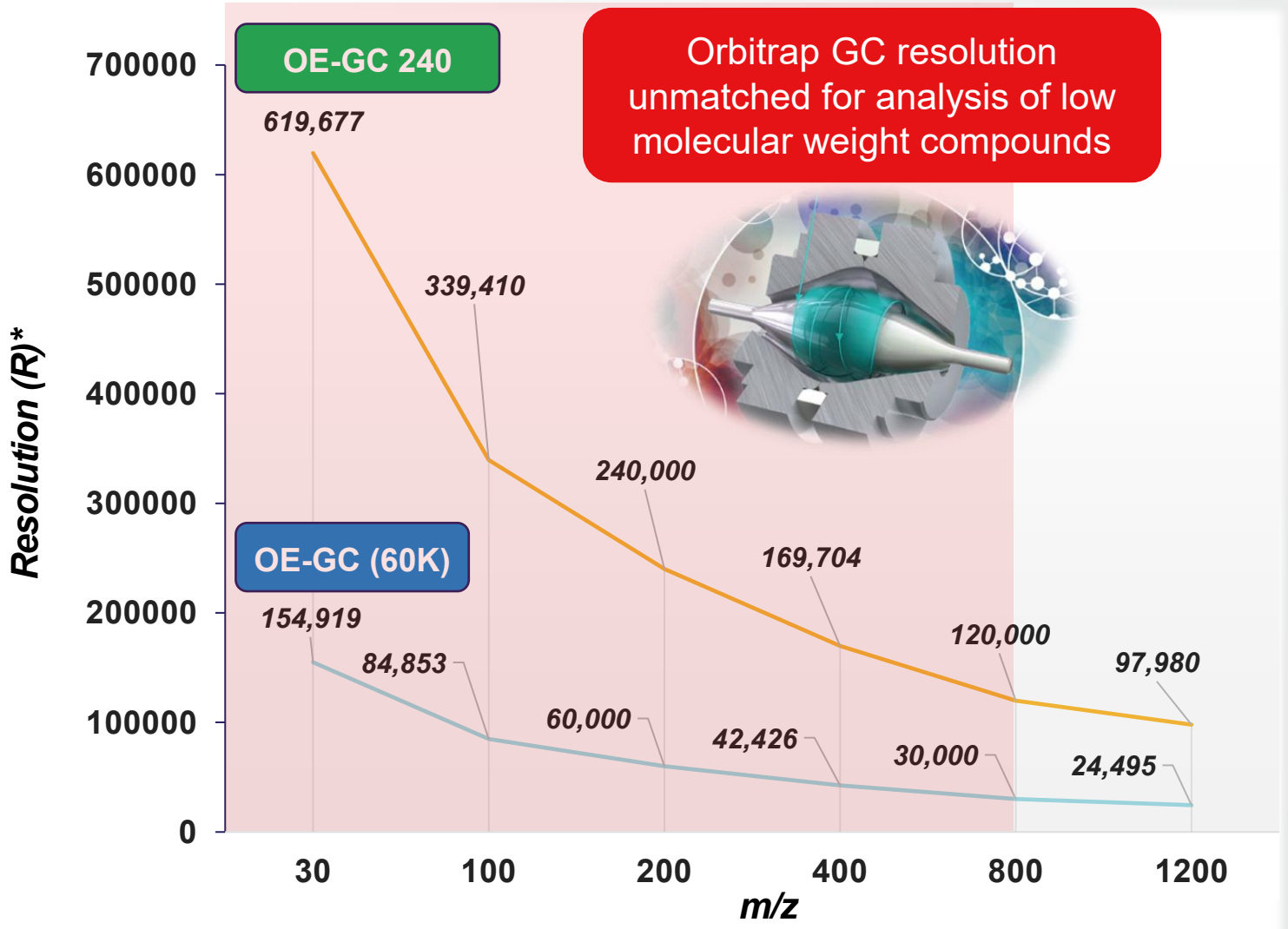
Priority and unknown compound identification in industrial stack particulate

HRAM for Volatile / Semi-volatile analysis

Resolving Power







**Resolution defined as full width half maximum at 200 m/z*

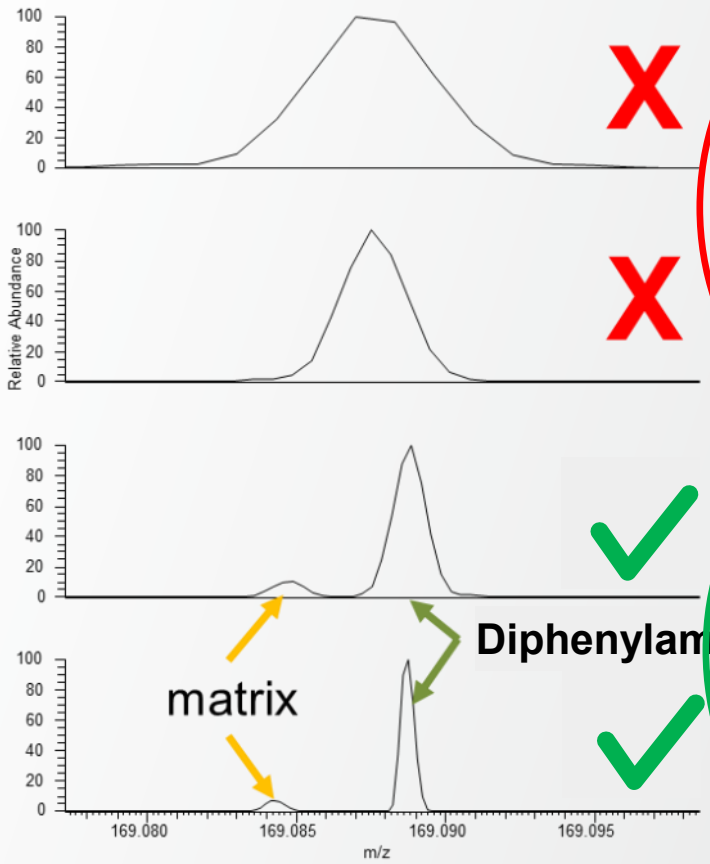
Resolution and Mass accuracy:

Why is it important?

- **Selectivity**:
  - Matrix interference is greatly reduced
  - Avoid interference between ions of the same compound (e.g. fine isotopic structure)

- **Accurate mass**
  - Narrow mass peak allows more accurate mass position on the m/z scale - critical for elemental composition determination of a compound
  - Resolve ions with similar m/z

Diphenylamine
$C_{12}H_{11}N$
m/z = 169.0886



R30K
169.08752
-6.38 ppm

R60K
169.08756
-6.18 ppm

R120K
169.08879
1.10 ppm

R240K
169.08870
0.56 ppm

Orbitrap Technology mass error ≤ 1 ppm

Thermo Scientific™ Compound Discoverer™ Software workflow:

Full-Scan acquisition EI

Putative identification

Multivariate statistical analysis

Molecular ion identification

Structural elucidation

GC ionization modes

Thermo Scientific™ Extractabrite ion source

Electron Ionization (EI)

- Sensitive
- Non-selective
- Hard ionization

Chemical Ionization (CI)

Positive (PCI)

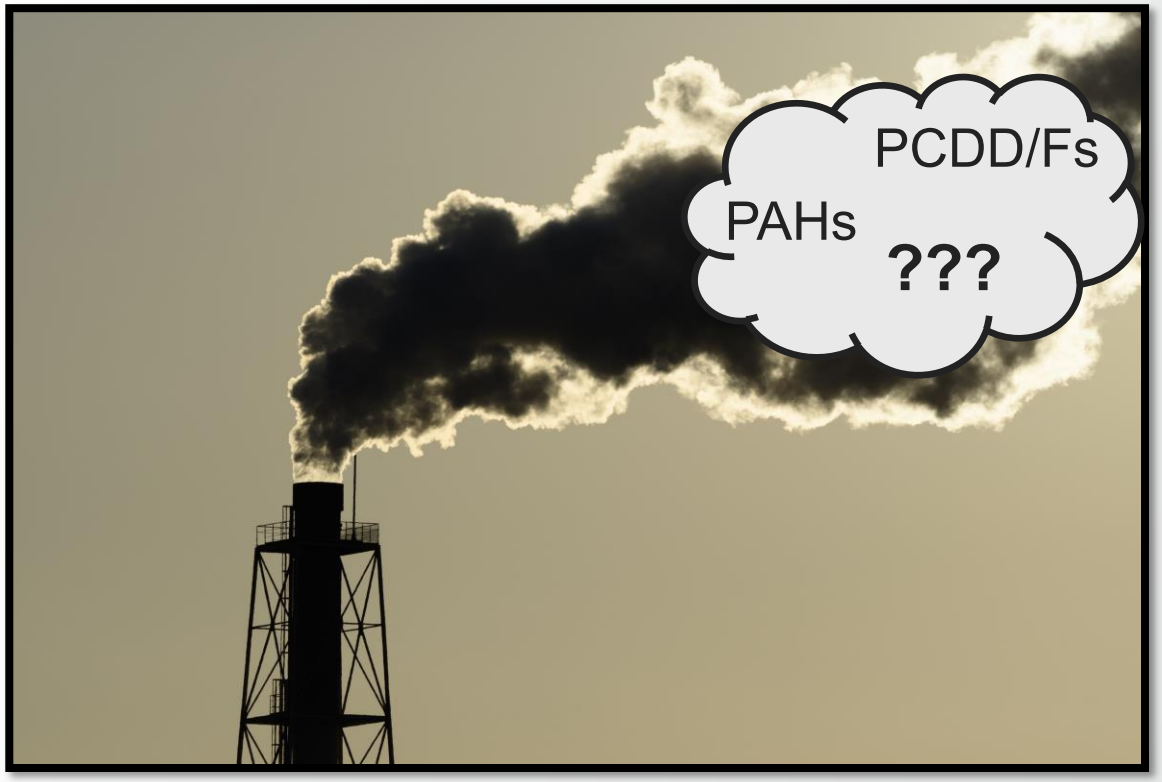
Negative (NCI)

- Reagent gas (CH_4) used to ionize analyte
  - Soft ionization
- Selective sensitivity

Thermo Scientific™ NeverVent™ technology

Monitoring of industrial stack particulate

- Needed for environmental protection
- Regulatory check for industrial operations
  - Energy
  - Waste management
  - Heavy manufacturing



- Emissions will be industry dependent
- High temp conditions produce several priority contaminants
  - Polyaromatic hydrocarbons (PAHs)
  - Polychlorinated dibenzodioxins/furans (PCDD/Fs)
  - Unknown pollutants will also be formed through chemical reactions/transformations under high heat conditions

Identification of Priority pollutants in stack particulate

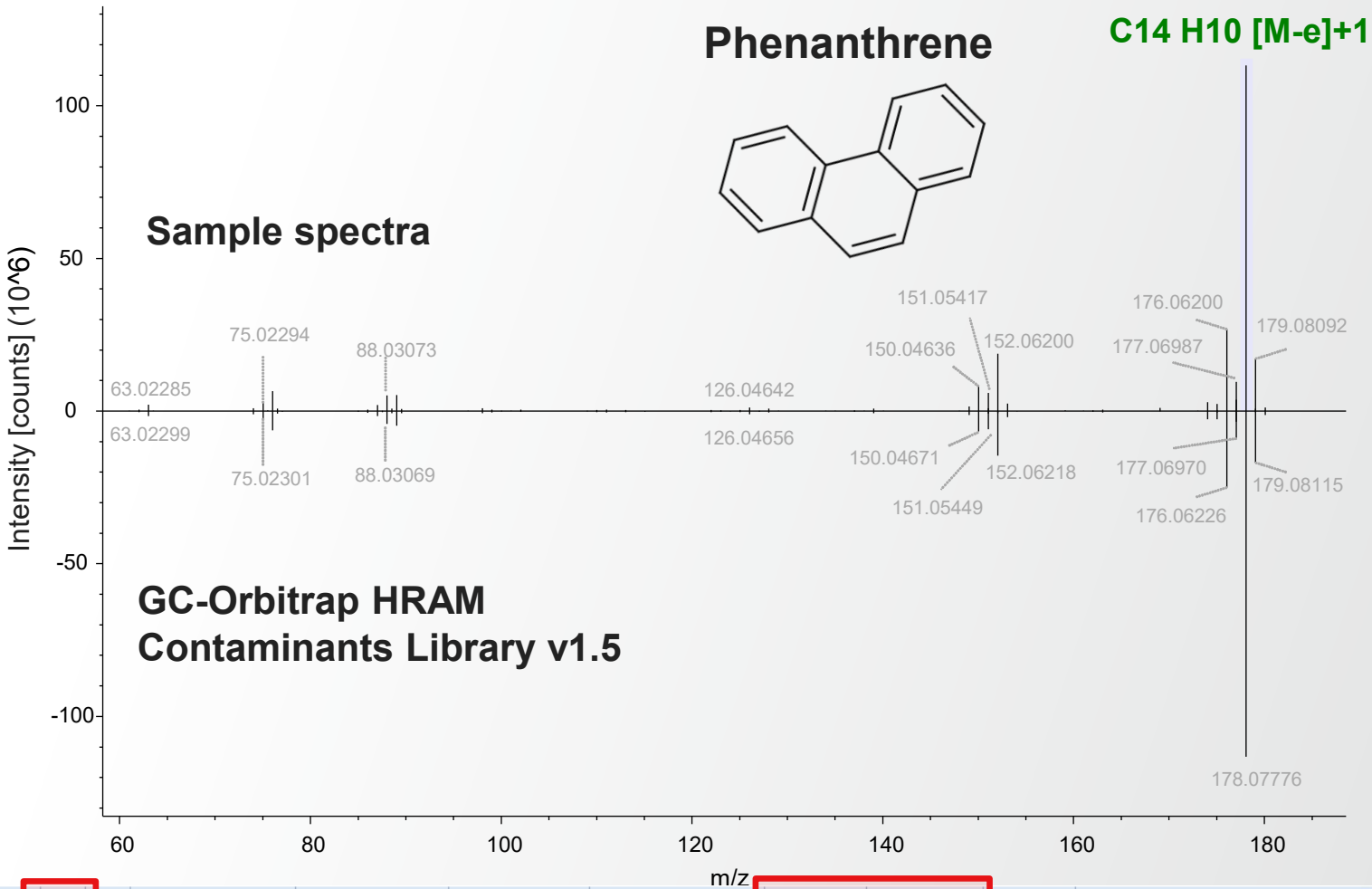
PACIFIC RIM LABORATORIES INC

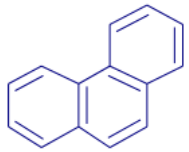
Identification through HRAM libraries with < 1 ppm mass error (ΔMass)

- Phenanthrene

Additional PAHs identified

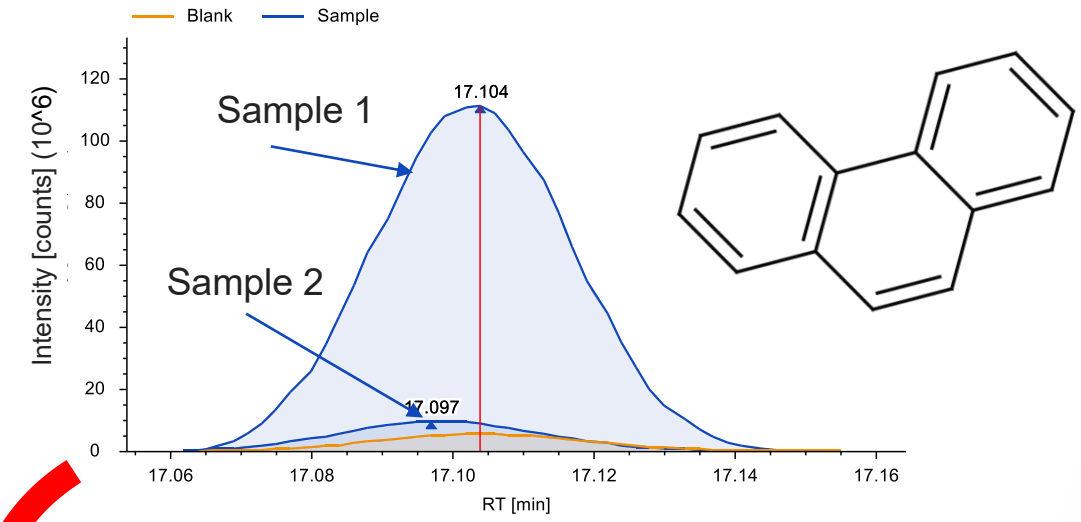
- Naphthalene (Δmass: 0.19 ppm)
- Flourene (Δmass: 0.30 ppm)
- Pyrene (Δmass: 0.36 ppm)



Structure	Name	CAS Num	Formula	Total Score	HRF Score	RHRF Score	SI	RSI	Elements Found[%]	Molecular Weight	Theo. Mol. Mass	Observed Mol. Mass	ΔMass [Da]	ΔMass [ppm]	M+ found	Library
	Phenanthrene	85-01-8	C14 H10	97.8	97.4	98.0	939	941	100.0	178.07825	178.07770	178.07761	-0.00010	-0.54	Yes	gc-orbitrap contaminants library_v1.5

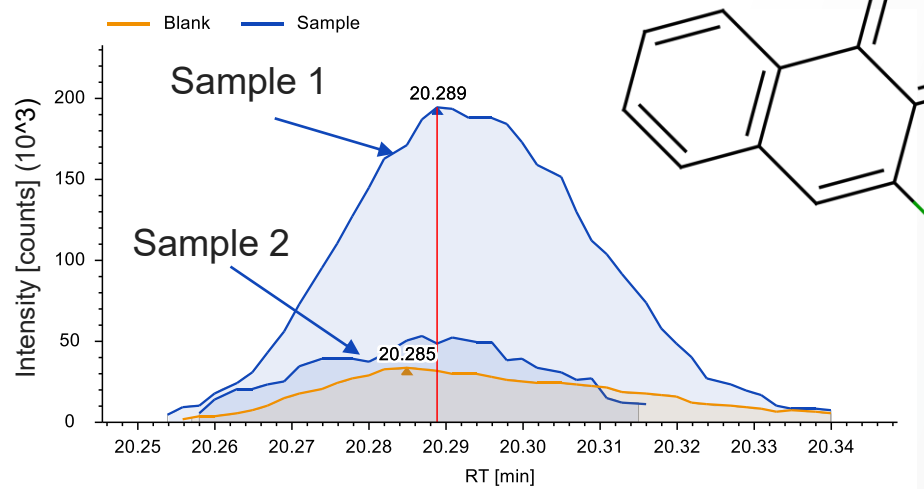
Identification of chlorinated-PAH analogs

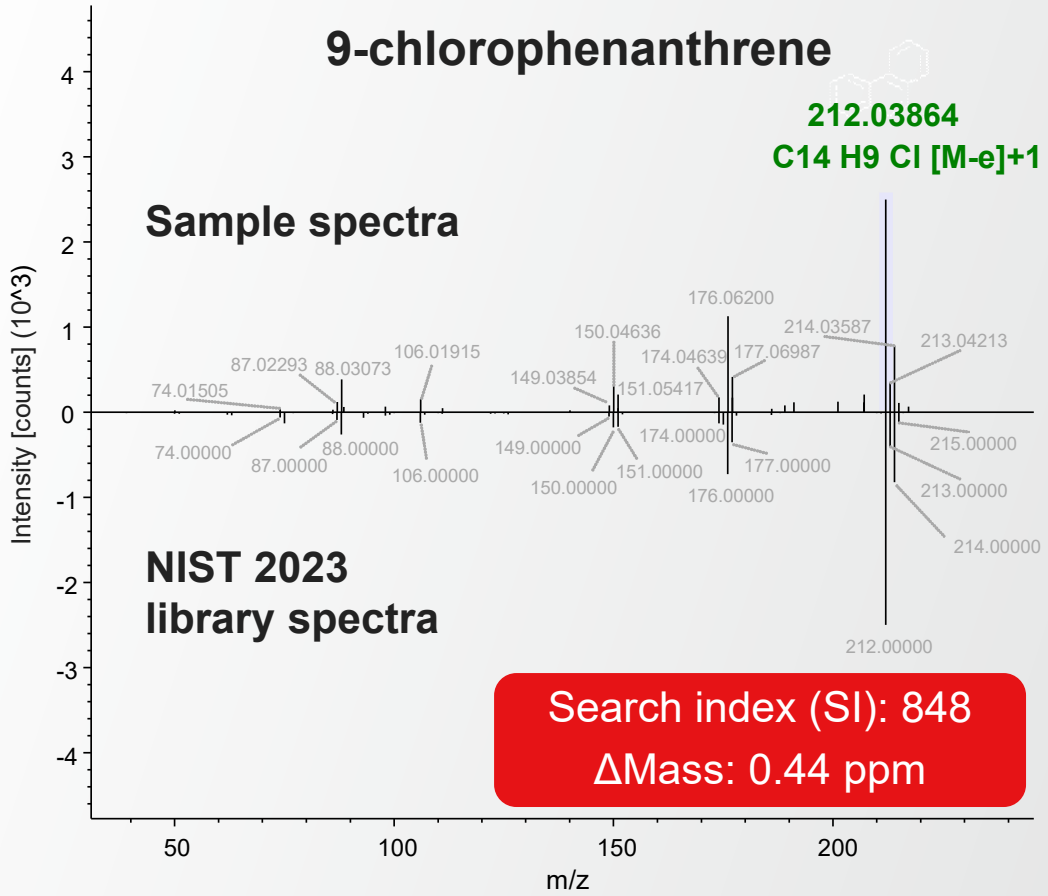
EI workflow with NIST 2023 library



Heat

+ Cl_2



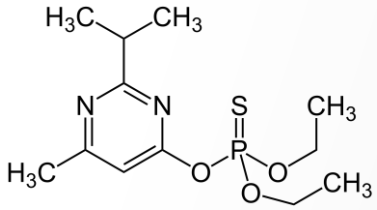


Search index (SI): 848

ΔMass: 0.44 ppm

1-chloropyrene and several monochlorinated anthracene analogues also identified

GC ionization modes - Diazinon

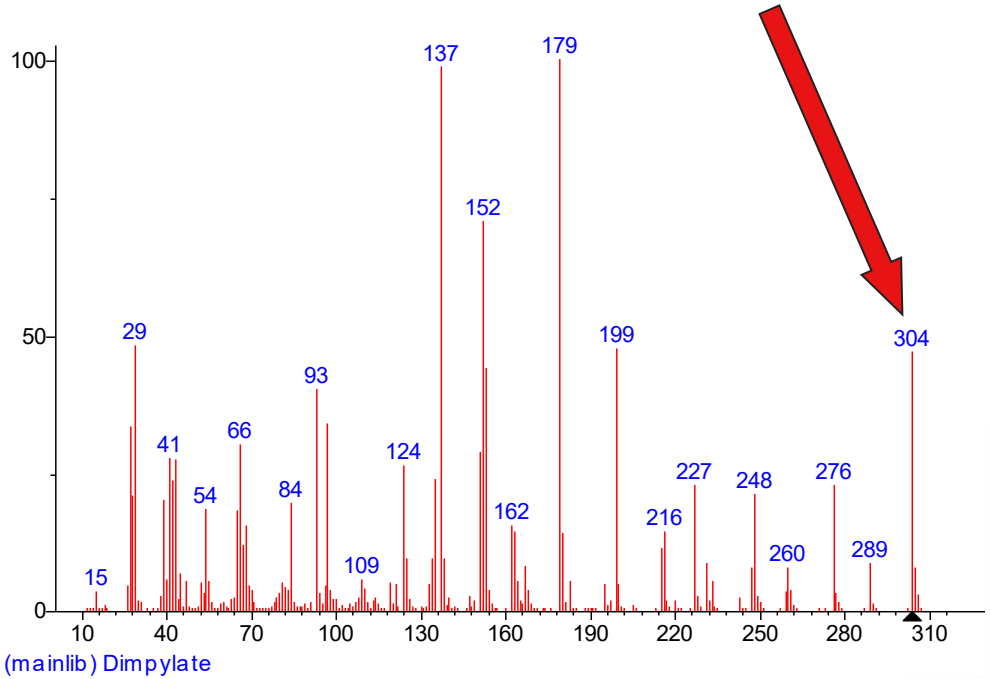


Electron Ionization

$$AB + e^- \rightarrow A^+ + B + 2e^-$$

$$AB + e^- \rightarrow AB^+ + 2e^-$$

Molecular ion (M) = 304



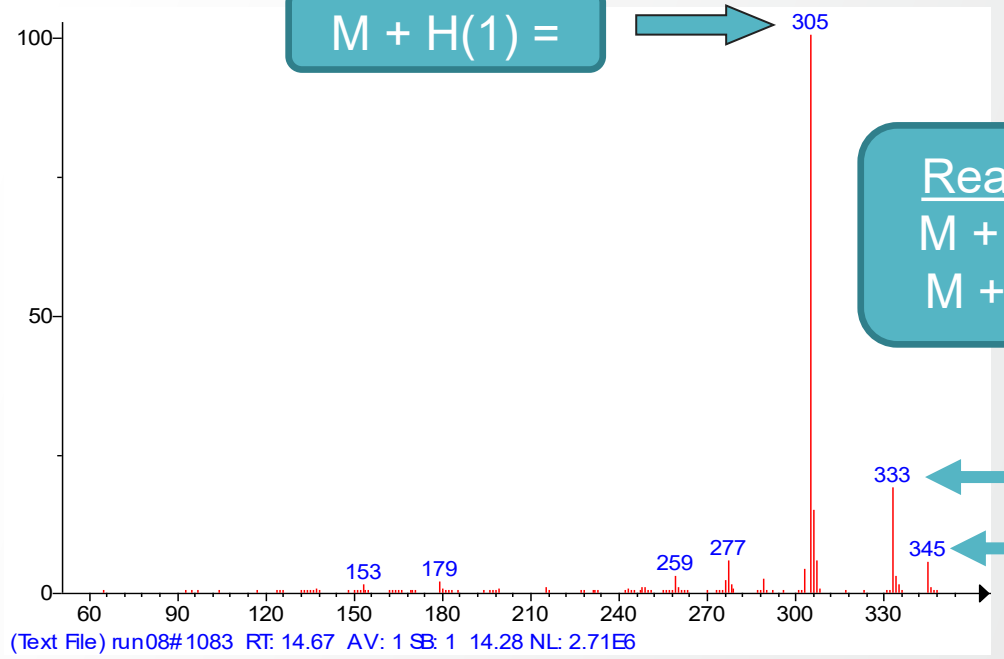
Positive Chemical Ionization

CH_5^+ , $C_2H_5^+$, $C_3H_5^+$

Reagent gas (CH_4) ionized to produce several charged species

$$M + CH_5^+ \rightarrow [M+H]^+ + CH_4$$

M + H(1) =



Reagent adduct ions

M + $C_2H_5^+$ (29) = 333

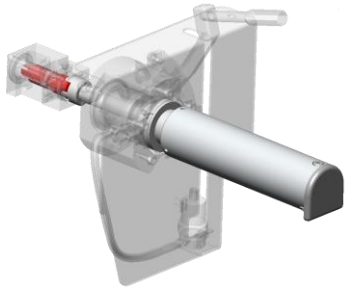
M + $C_3H_5^+$ (41) = 345

Chlorinated-PAH isomers

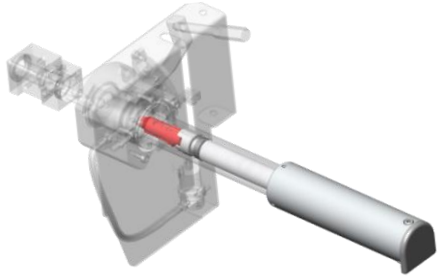
Structural isomers identified using molecular ion in CI workflow

Electron impact (EI) → **Chemical ionization (CI)**

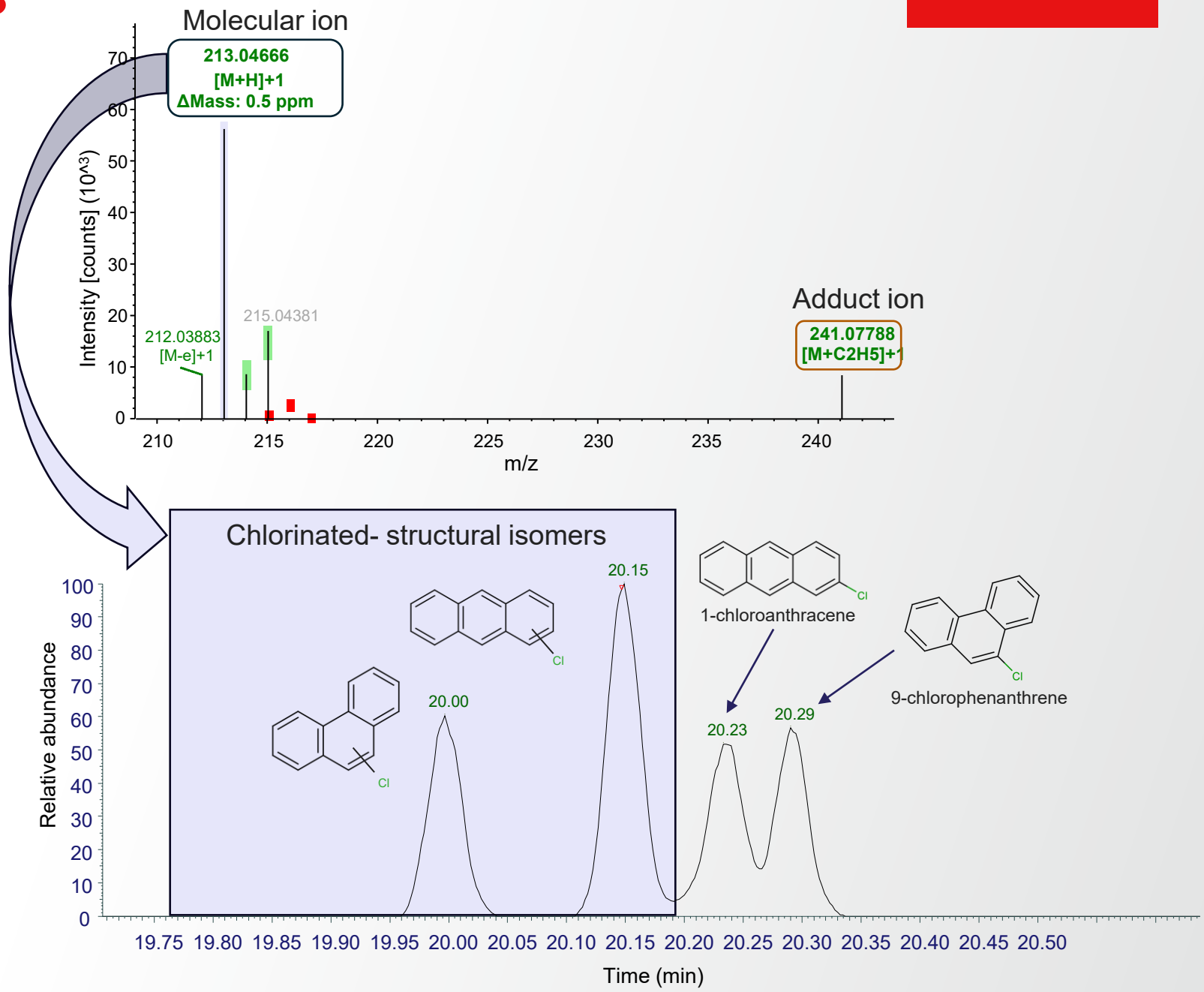
NeverVent™ technology



Step 1. Insert removal tool



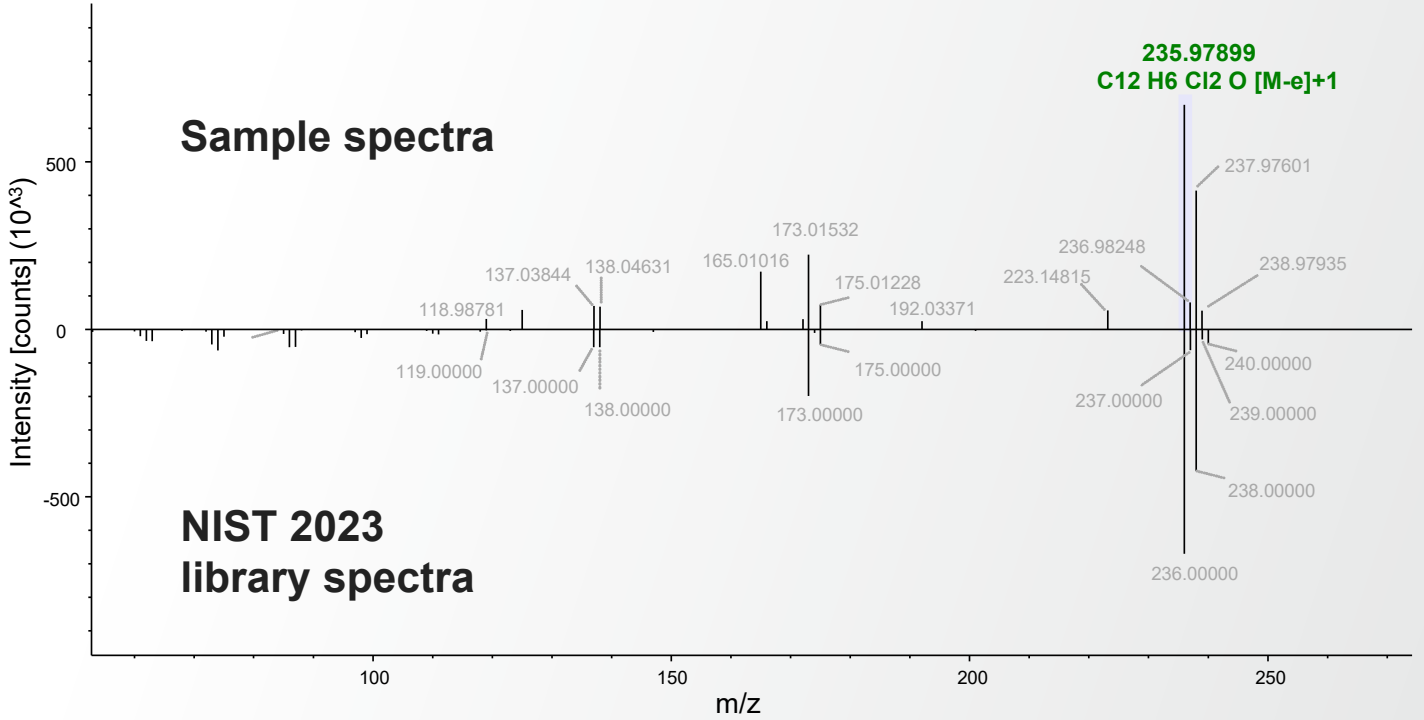
Step 2. Remove source



Identification of halogenated POPs

PCDFs

- Incineration byproduct from organochlorine compounds.
- Several matches to 2,8-dichlorodibenzofuran were identified from NIST with Δmass = 0.2 ppm
  - Indicates several congeners are present

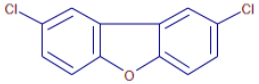


GC EI Compounds | Input Files | Study Information

	Checked	Tags	Name	Calc. MW	RT [min]	Reference m/z	Avg TIC	NIST Lib Hit Formula	NIST Theo. Mol. Mass	NIST Observed Mol. Mass	Total Score	HRF Score	SI	Calculated RI	RI Delta	Area		
1	☑		Dibenzofuran	168.05743	12.245	168.05688	6275958	C12 H8 O	168.05697	168.05688	89.3	85.2	759	1748		6.03e5	6.95e6	8.11e6
2	☑		Dibenzofuran, 2,8-dichloro-	235.97954	18.252	137.03844	2218612	C12 H6 Cl2 O	235.97902	235.97899	92.7	91.8	801	2176		4.63e3	7.49e5	1.09e5
3	☑		Dibenzofuran, 2,8-dichloro-	235.97954	18.408	235.97899	806303	C12 H6 Cl2 O	235.97902	235.97899	93.1	93.1	793	2188			1.48e6	7.83e3
4	☑		Dibenzofuran, 2,8-dichloro-	235.97954	18.561	110.01509	2111152	C12 H6 Cl2 O	235.97902	235.97899	90.7	84.6	843	2200		1.84e3	7.77e4	7.00e3

Hide Related Tables

GC EI Compounds per File | NIST Library Search Results

Check	Structure	Name	CAS Num	Formula	Total Score	HRF Score	RHRF Score	SI	RSI	Elements Found[%]	Theo. Mol. Mass	Observed Mol. Mas:	ΔMass [Da]	ΔMass [ppm]	M+ found	Library
☐		Dibenzofuran, 2,8-dichloro-	5409-83-6	C12 H6 Cl	93.1	93.1	96.5	793	876	100.0	235.97902	235.97899	-0.00003	-0.14	Yes	mainlib

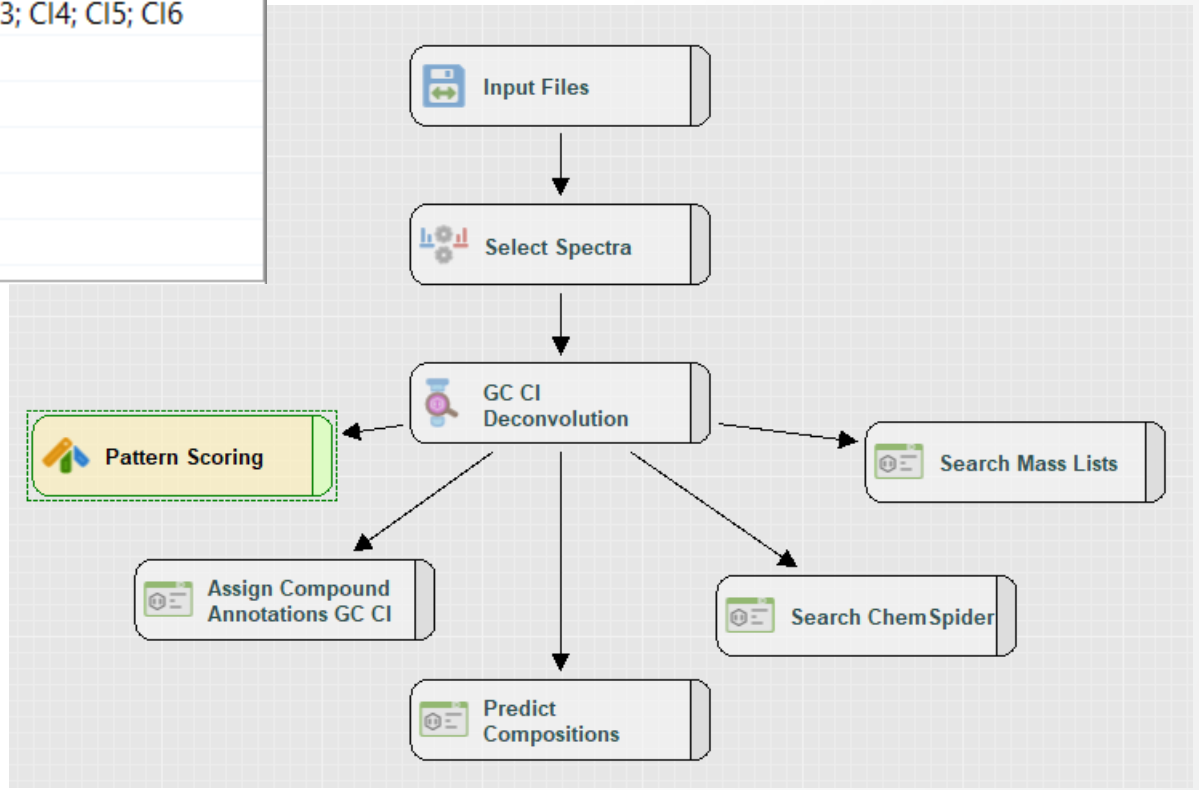
Pattern scoring with chemical ionization

Isotopic pattern matching

Parameters of 'Pattern Scoring'

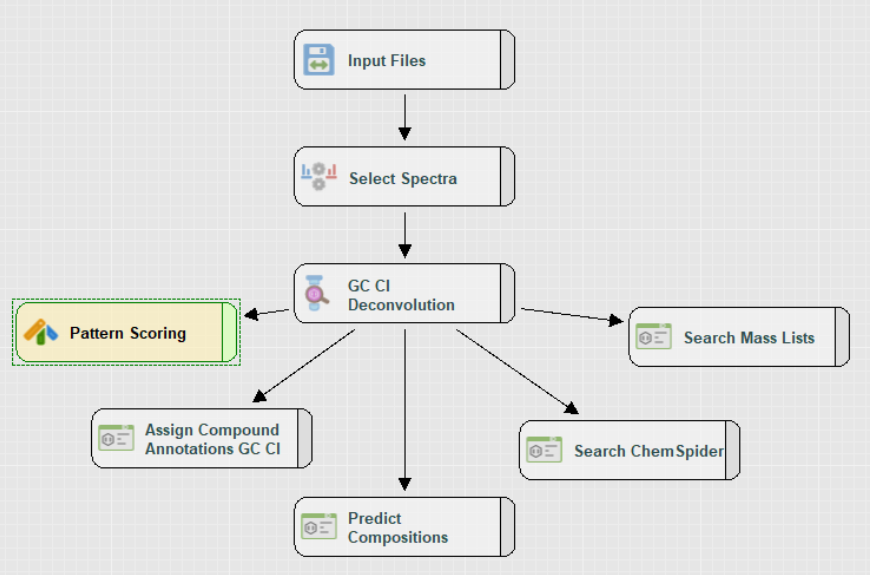
Show Advanced Parameters

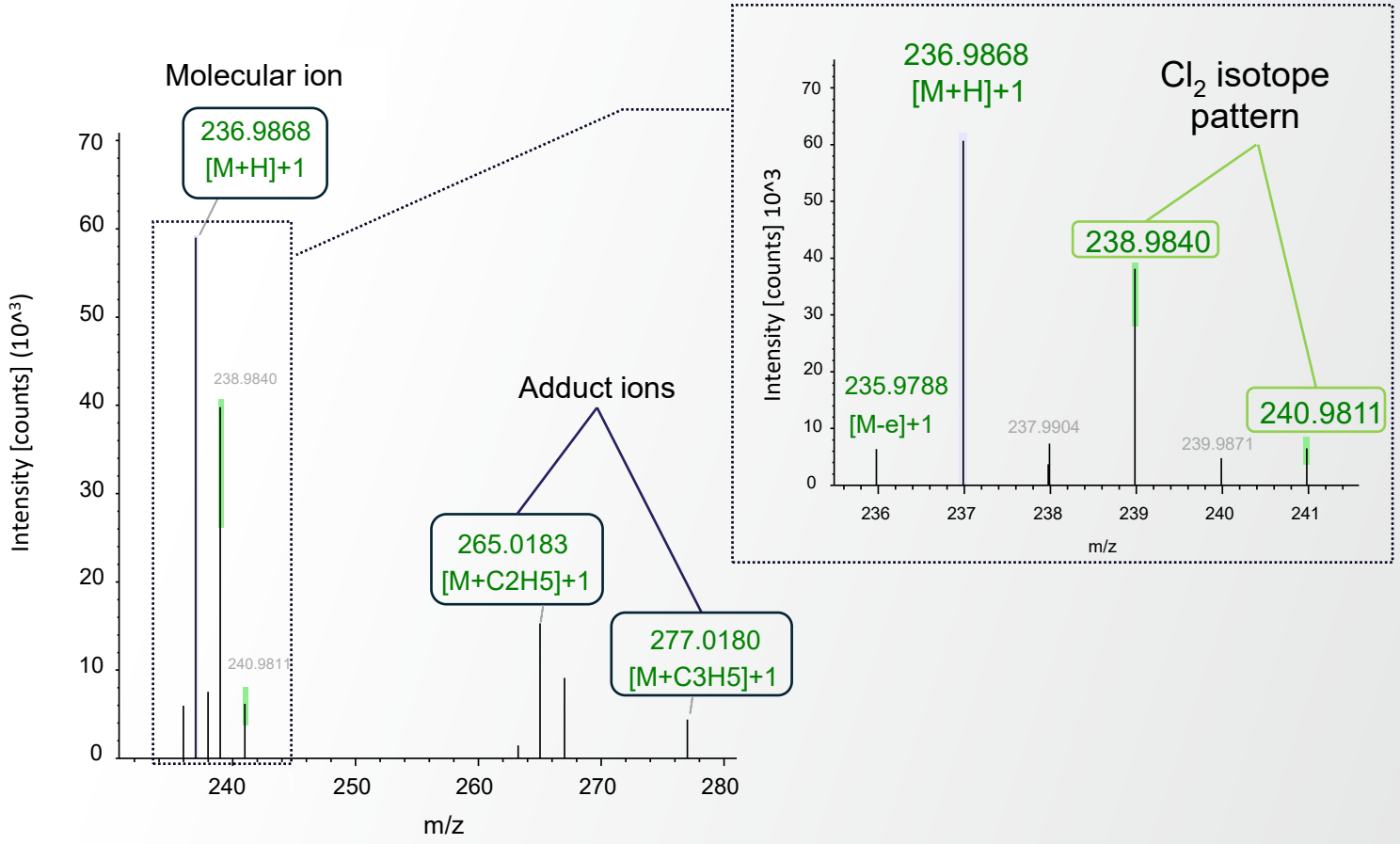
1. General Settings	
Isotope Patterns	Cl; Cl2; Cl3; Cl4; Cl5; Cl6
Mass Tolerance	5 ppm
Intensity Tolerance [%]	30
SN Threshold	3
Min. Spectral Fit [%]	0
Preferred Ions	[M+H]+1



Pattern scoring with chemical ionization

Isotopic pattern matching





Structure Proposals | GC CI Compounds per File | Predicted Compositions | ChemSpider Results | Mass List Search Results | Matched Patterns

	Tags	Checked	Name	SFit [%]	Pattern Cov.	# Matched Iso.	Study File ID
1		☐	Cl3	37	85.25	2	F2
2		☑	Cl2	92	100.00	3	F2

Sfit (pattern similarity) score: 92%

Pattern Coverage (intensity similarity) scores: 100 %

In summary

- Mass resolution of Orbitrap technology advantageous for identification of volatile and semi-volatile compounds

- EI fragmentation provides a unique and reliable fingerprint for identification through spectral libraries
  - MS2 in most cases is not needed.
  - Identification of several priority pollutants (PAHs, PCDFs) at sub ppm mass accuracy reduces the number of potential chemical annotations helping aid compound identification

- NeverVent technology provides rapid switching between complimentary ionization techniques of EI and CI for confirmation of molecular ion

- Use of EI and CI data together in CD software and its various nodes provides high accuracy and surety in compound identification

Thank you

Questions?