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Simultaneous Analysis of Full Scan Method 625 Semi-Volatiles and MRM Method 608 Pesticides by GCMSMS in a Single Extract

William Lipps
Analytical & Measuring Instrument Division
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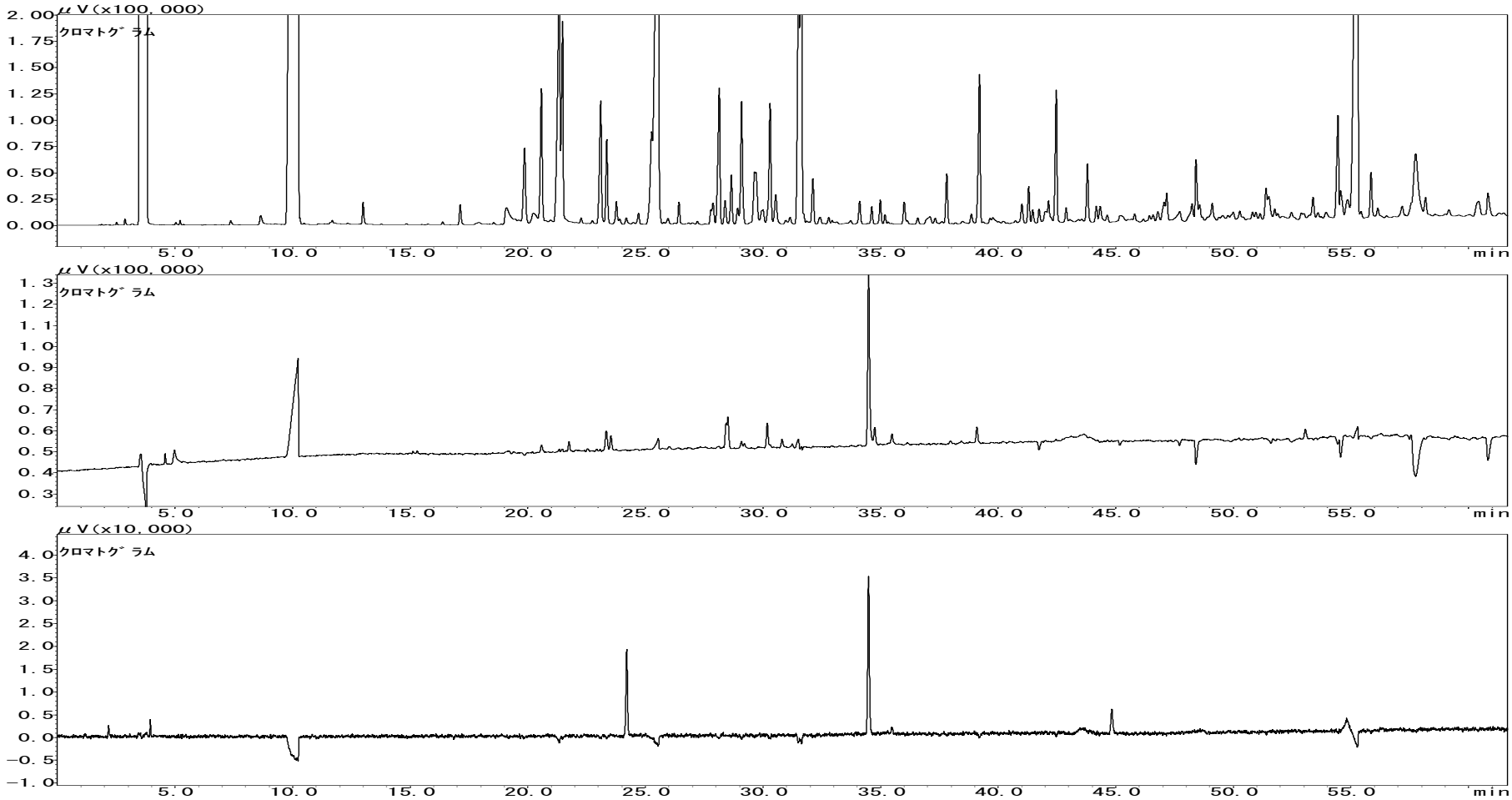
Pesticide and Semi-volatile analysis requires two extractions and two analyses

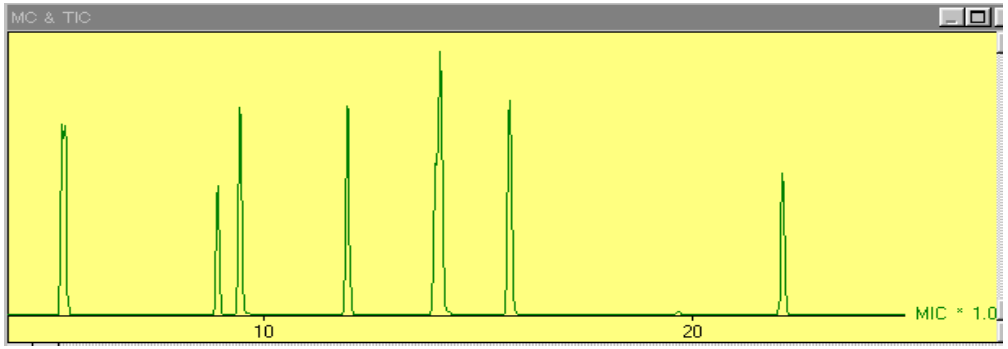
- Pesticides → 1000 ml → $MeCL_2$ → Hexane
  - 608
  - 8080

- Semi-Volatiles → 1000 ml → $MeCL_2$
  - 625
  - 8270

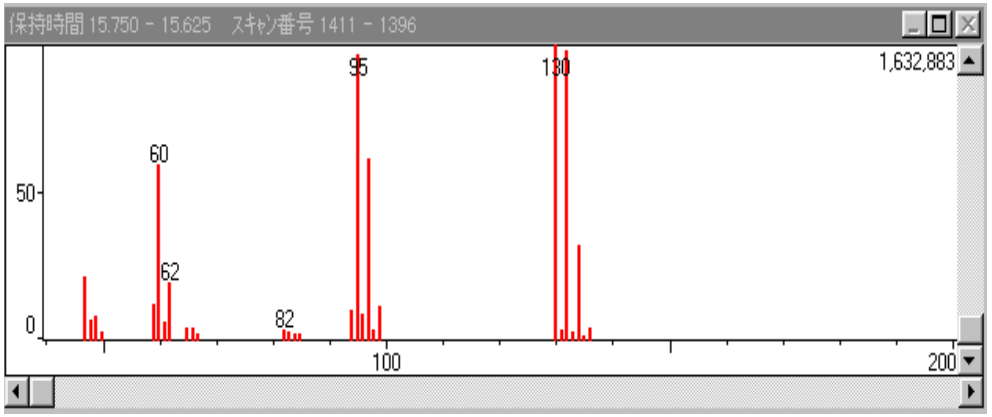
Pesticide requires GC-ECD with dual column or multiple detectors for confirmation



GCMS (full scan or SIM) is used for semi-volatile analysis

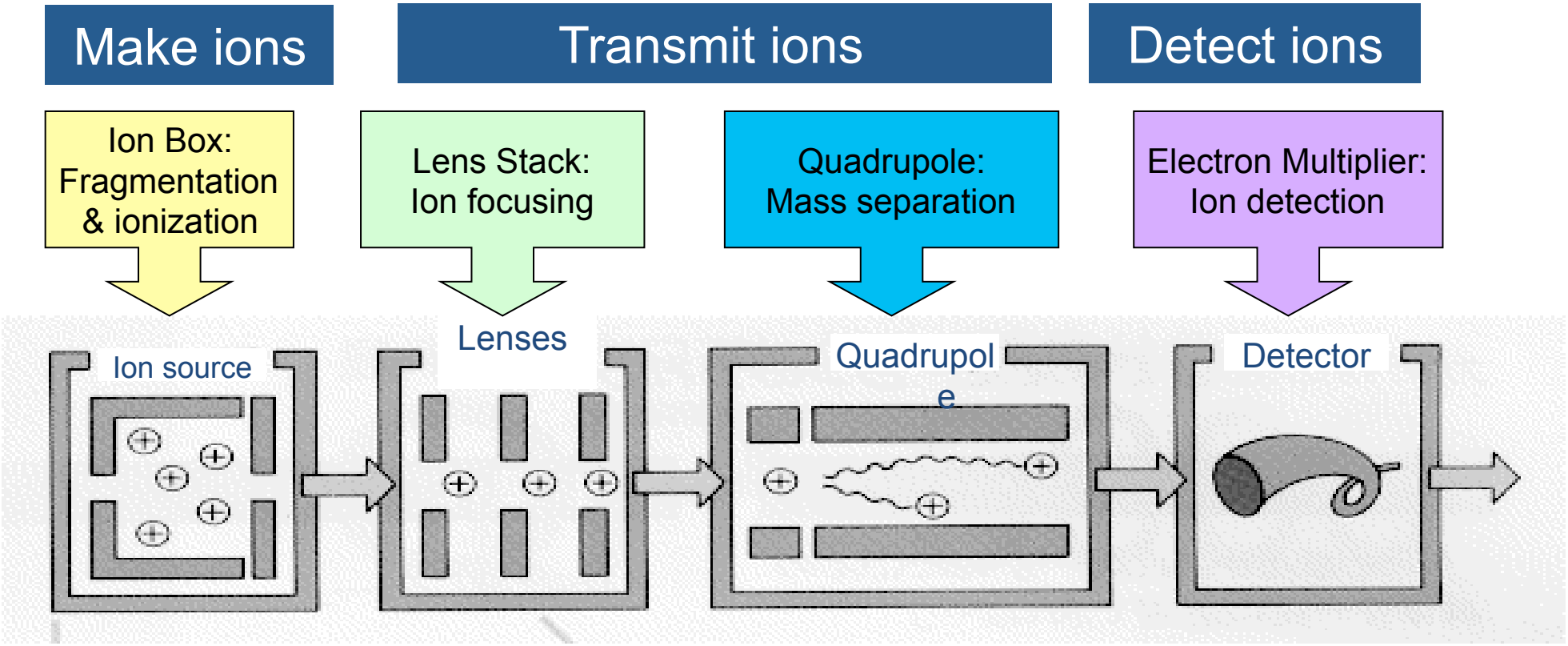


Gas Chromatograph: separation on a capillary column, identification by RT, and quantitation



Mass Spectrometer: positive identification by matching to a library

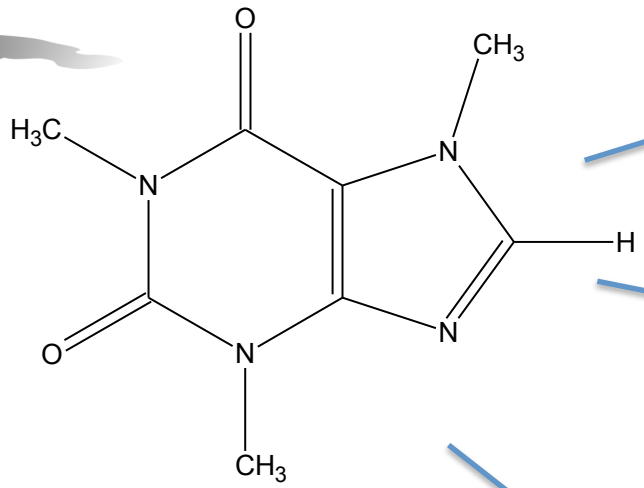
Quadrupole Mass Spectrometer



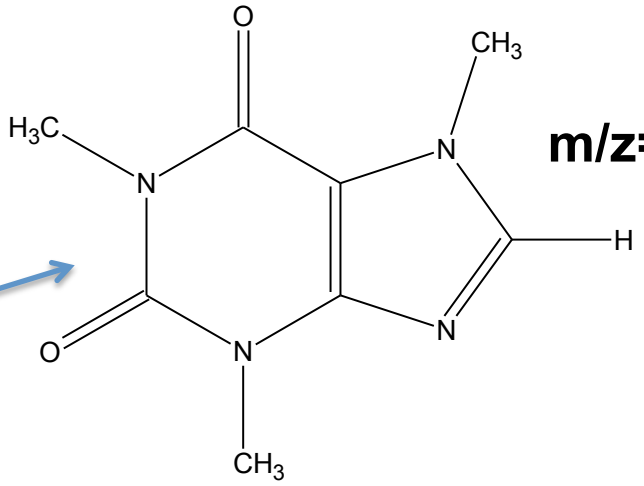
Entire mass spectrometer is under high vacuum

EI busts molecules into fragments

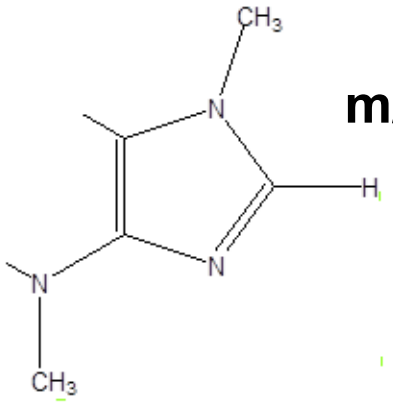
e-



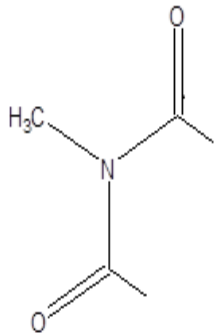
m/z=194



m/z=194

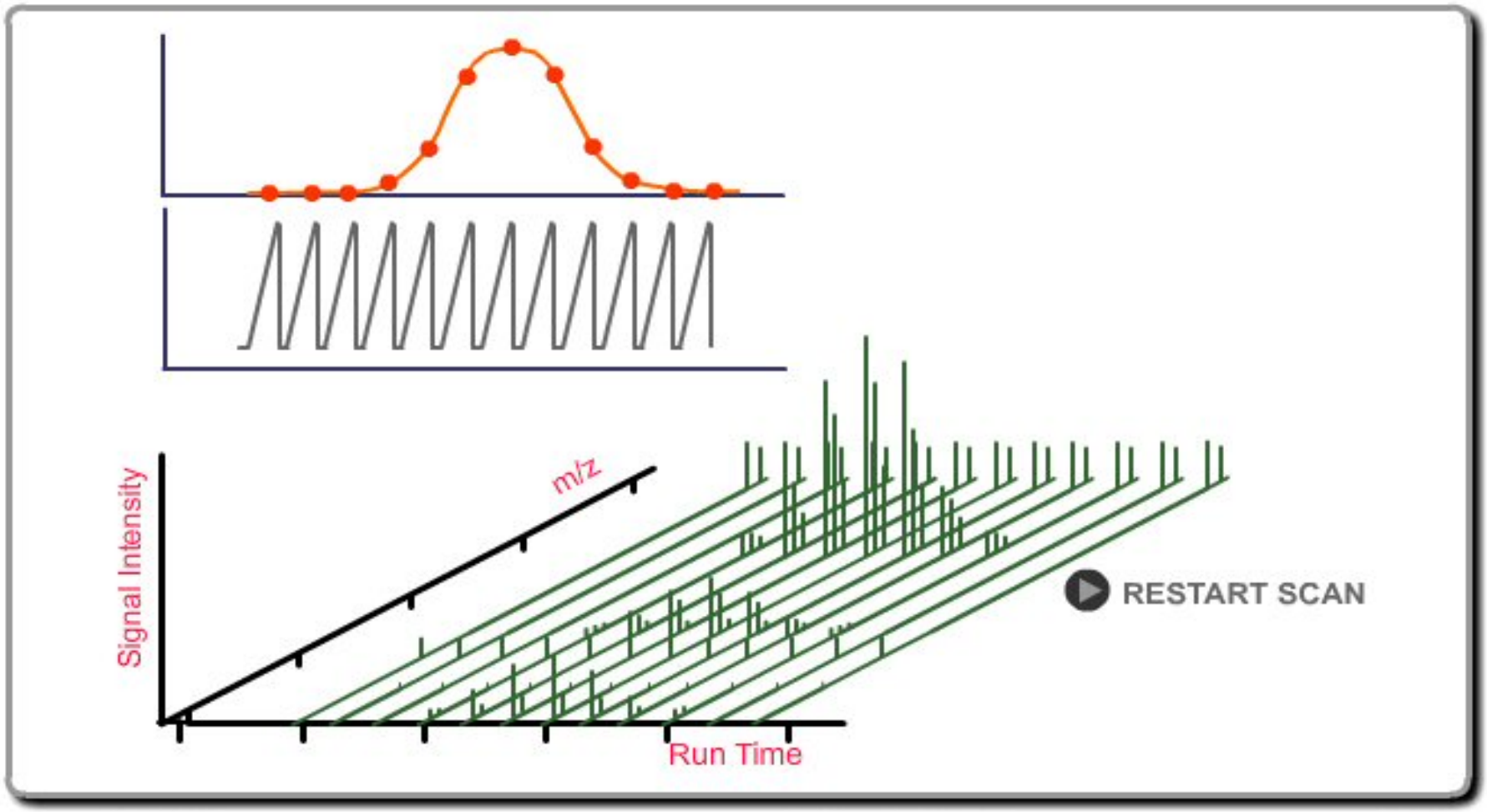


m/z=109

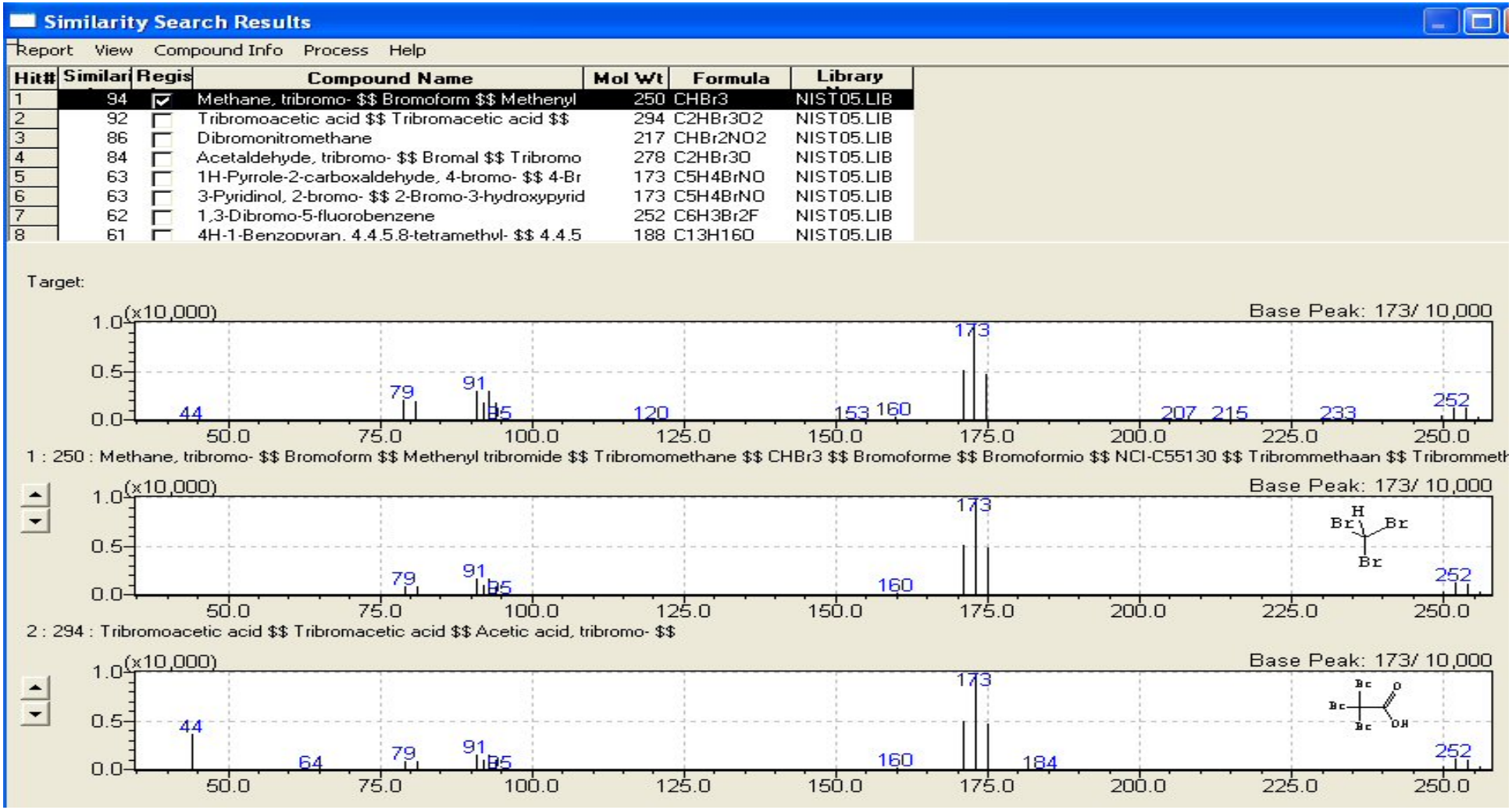


m/z=85

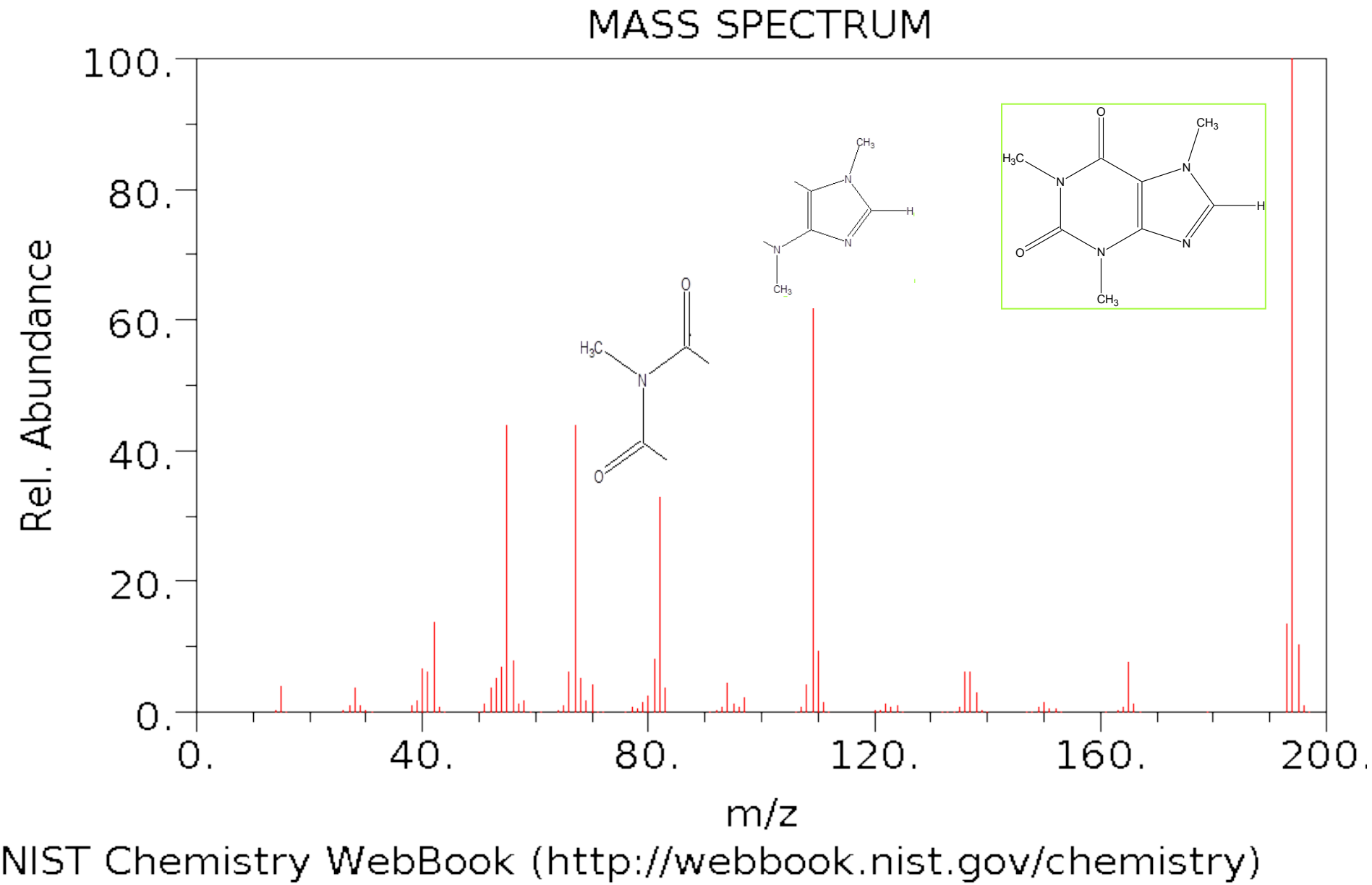
The GCMS integrates by m/z at retention time and provides spectral data



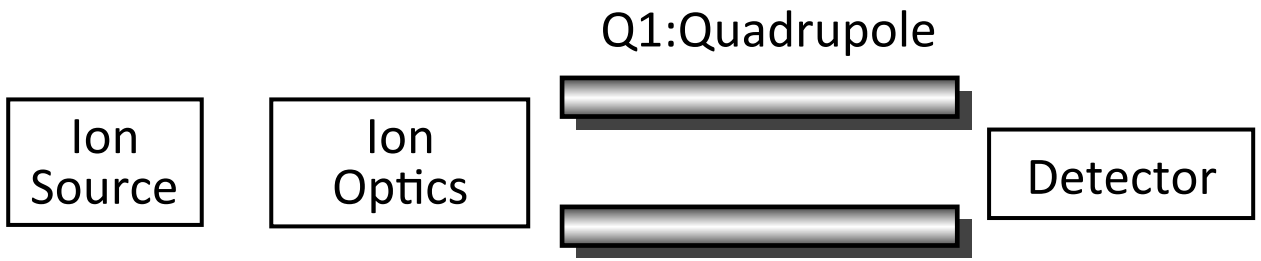
Detected peaks are confirmed for positive identification

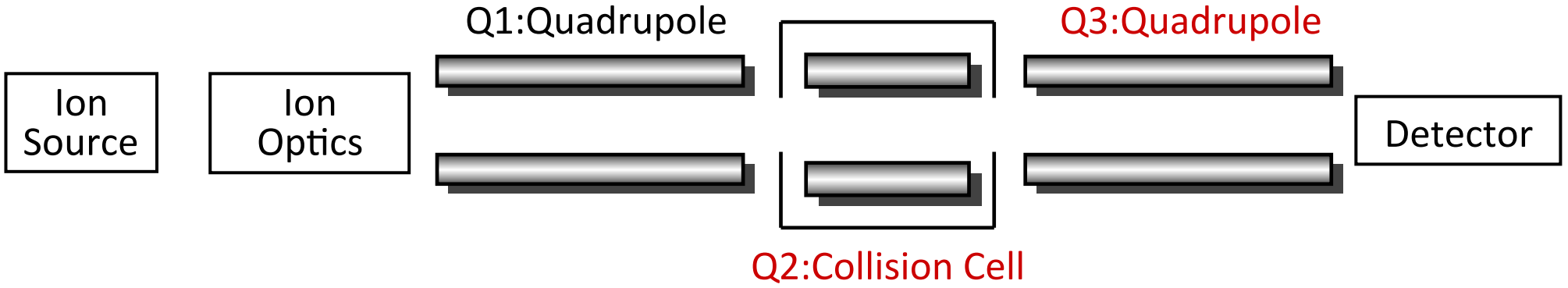


The mass spectra is the fragmentation m/z that elutes at that time



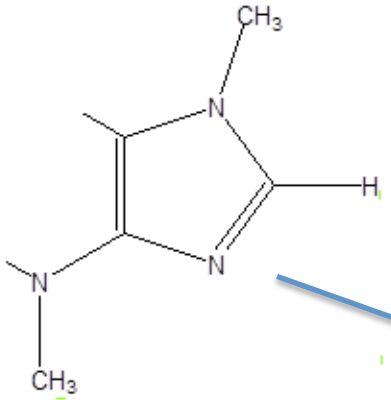
A triple Quadrupole adds a collision cell and another quadrupole



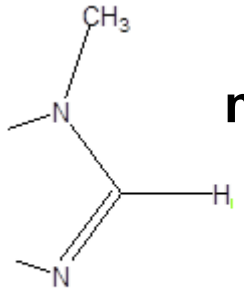


A Collision Cell takes a fragment and busts it further

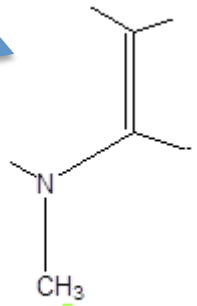
Gas



m/z=109

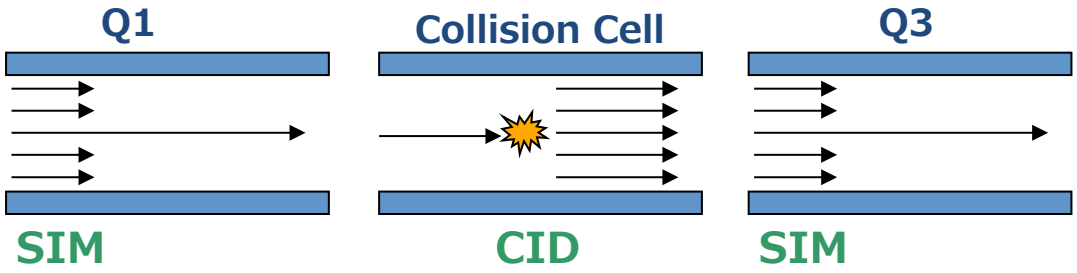


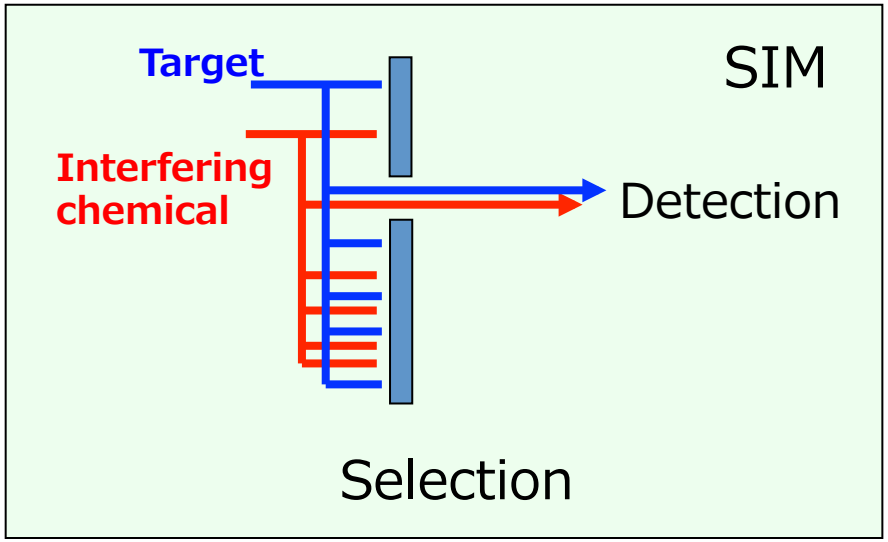
m/z=56



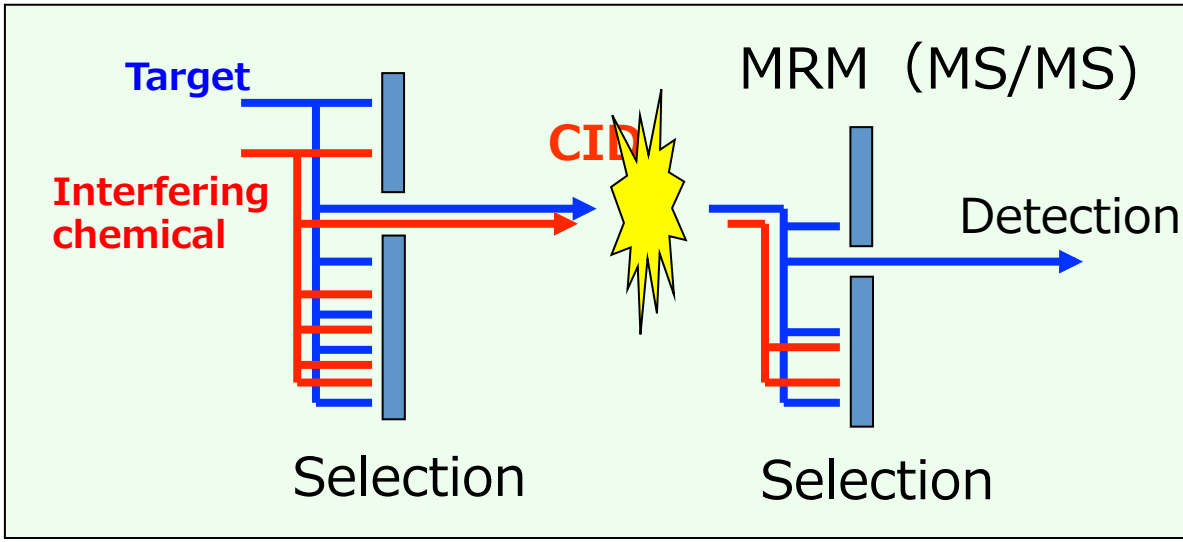
m/z=53

Advantages of Triple Quad (MRM) over Single Quad (SIM)



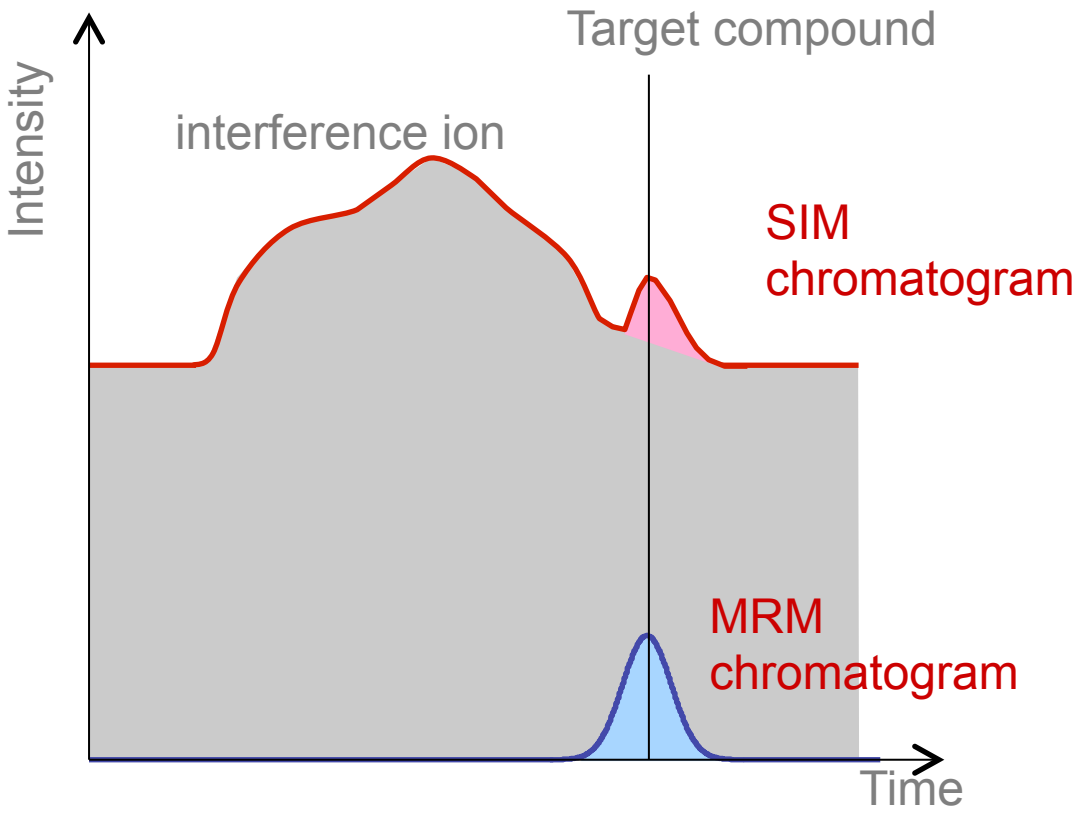


SIM reduces interference, but does not completely eliminate it



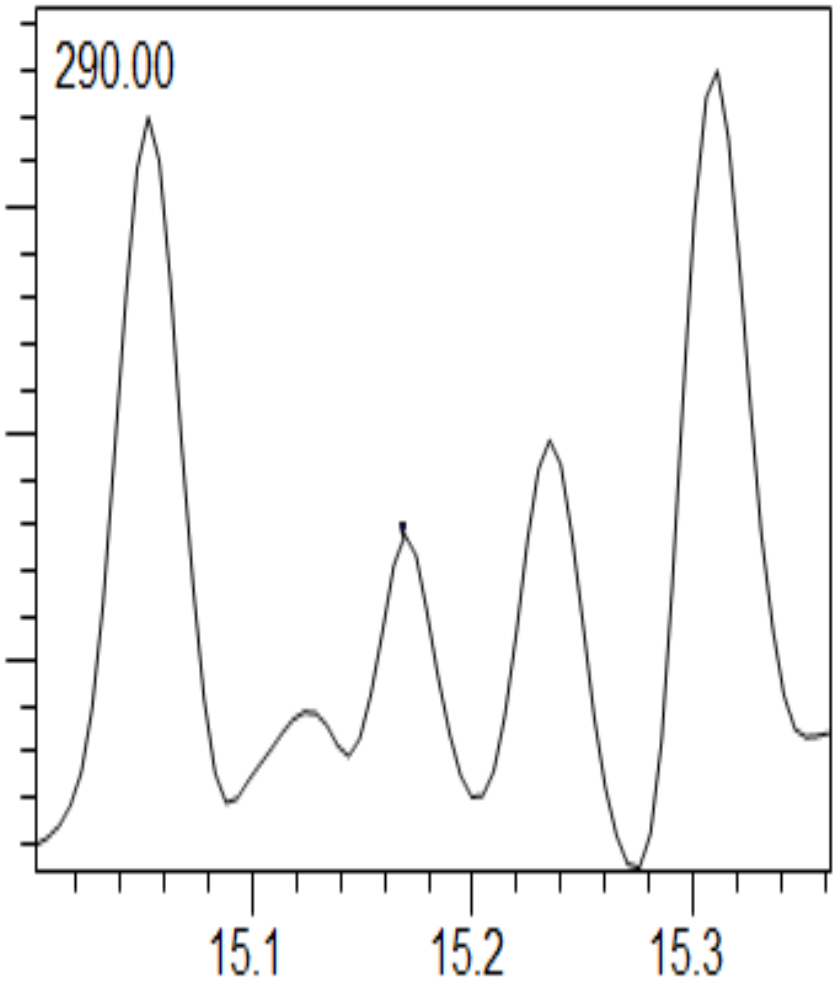
MRM eliminates remaining interference

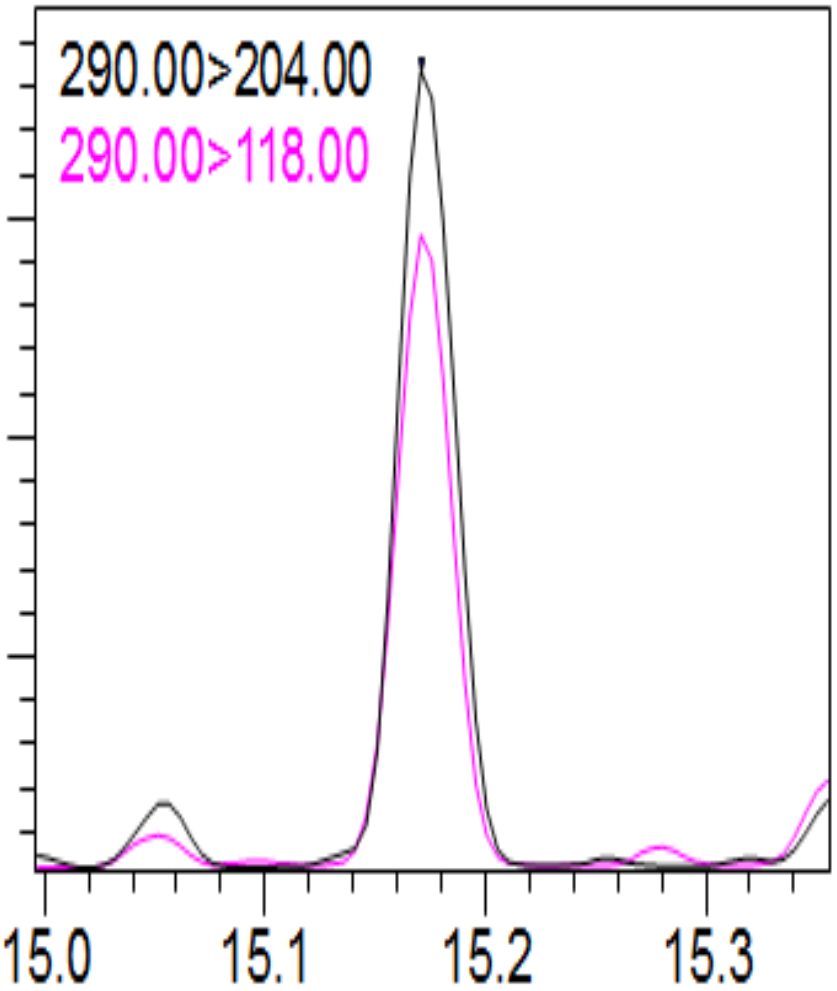
Triple Quad is ideal for GCMS analysis in complex matrices where SIM is problematic



- **S/N ratio is enhanced**
- **Extremely selective for quantitation**
- **10x lower MDL than SIM**
- **Extended linear range**

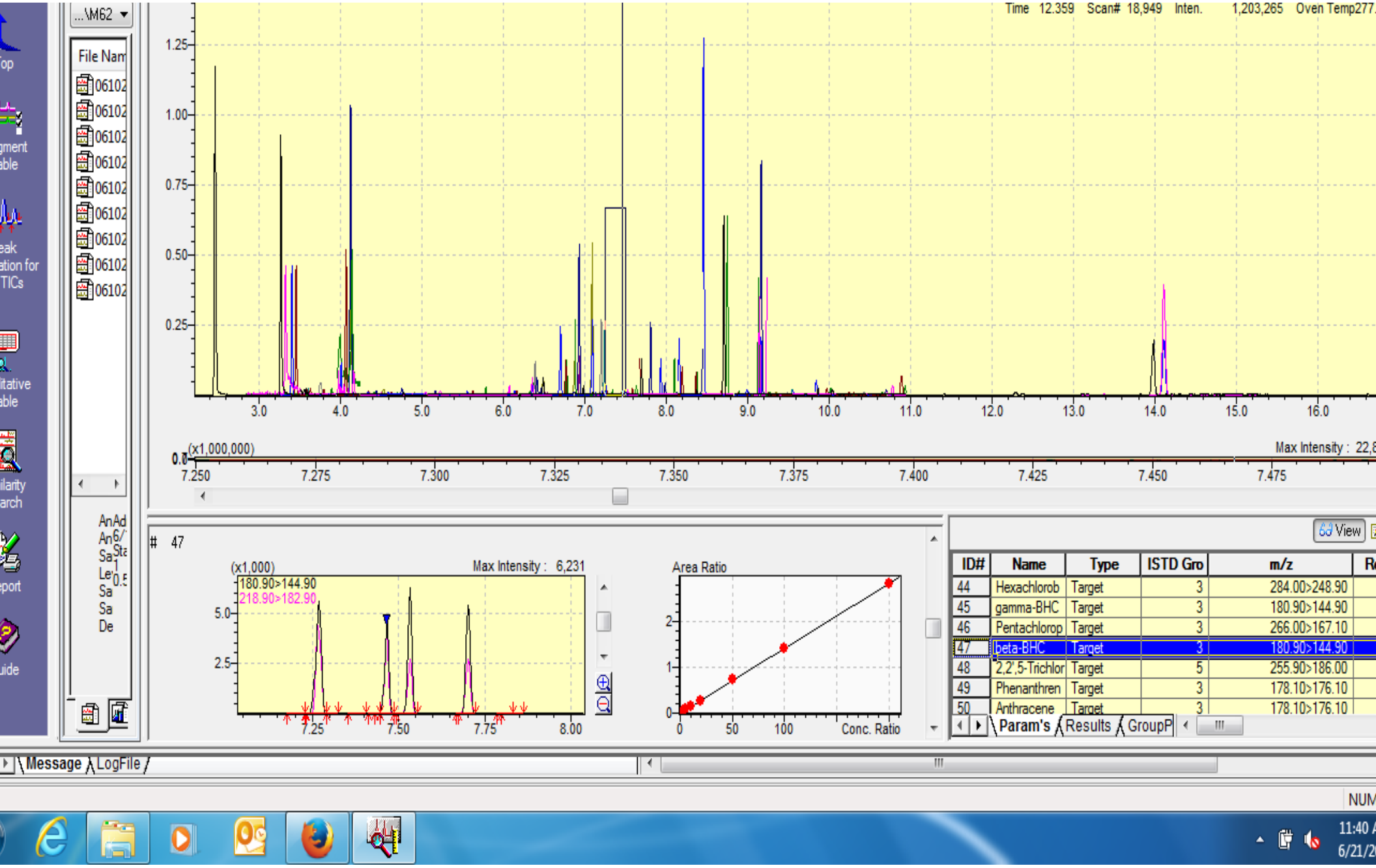
SIM and MRM data showing better detection and selectivity by MRM

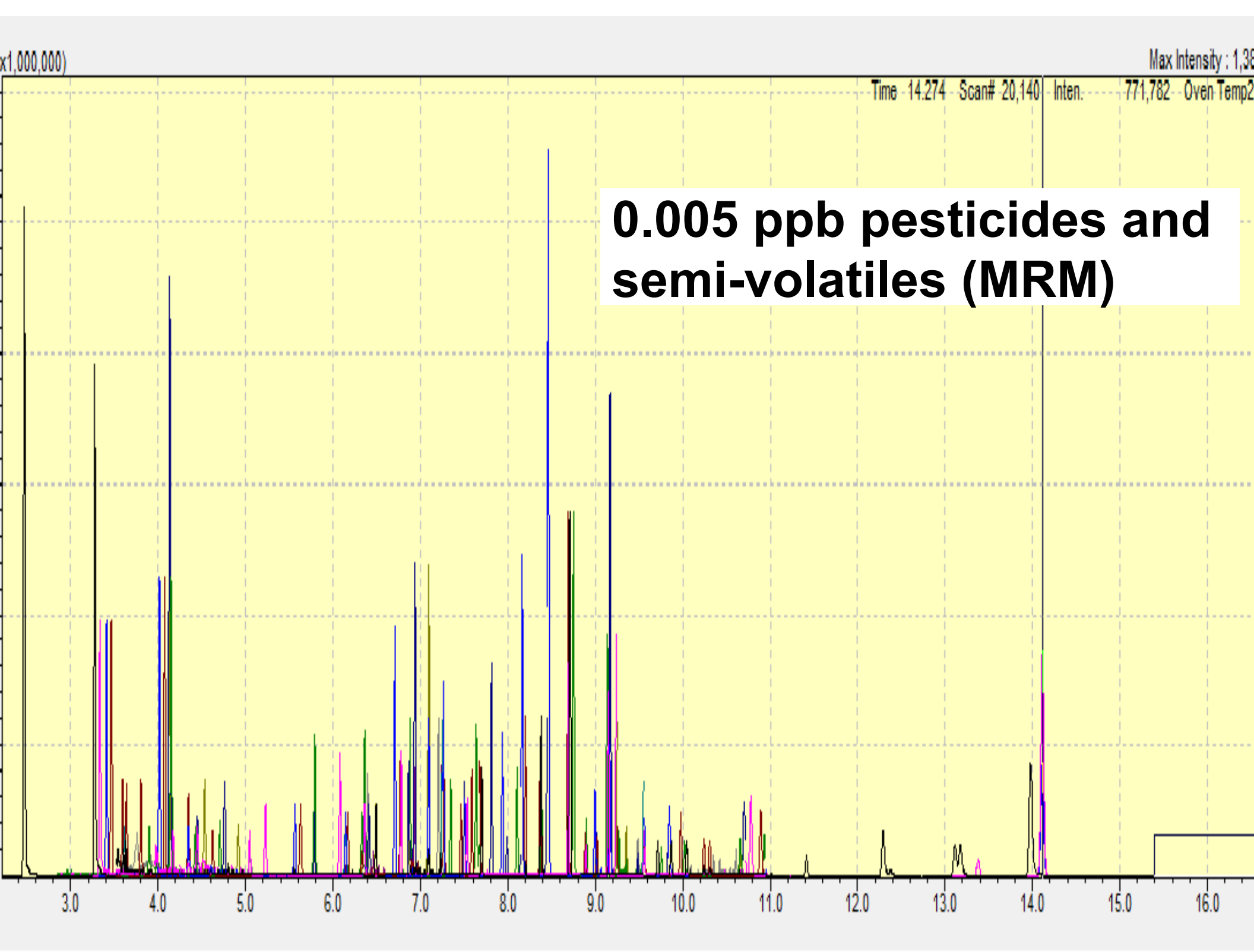




GCMSMS Multiple Reaction Monitoring allows us to see lower concentrations with large dynamic range with less interference

MRM quantitation of 0.0005 ppb – 200 ppb Pesticides and Semi-volatiles




x1,000,000)
Max Intensity : 1,38
Time 14.274 Scan# 20,140 Inten. 771,782 Oven Temp2
0.005 ppb pesticides and semi-volatiles (MRM)
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0

Advantages and Disadvantages of MRM analysis of pesticides and Semi-volatiles

Advantages	Disadvantages
Sensitive enough for pesticides analysis	Too sensitive for semi-volatiles
0.0005 – 200 ppb	0.0005 – 200 ppb
Combine Pesticides with Semi-volatile extract?	Do all pesticides extract?

One possibility for overcoming sensitivity of MRM for Semi-volatiles is extract less sample

1000 ml → 0.0005 – 200 ppb

100 ml → 0.005 – 2000 ppb

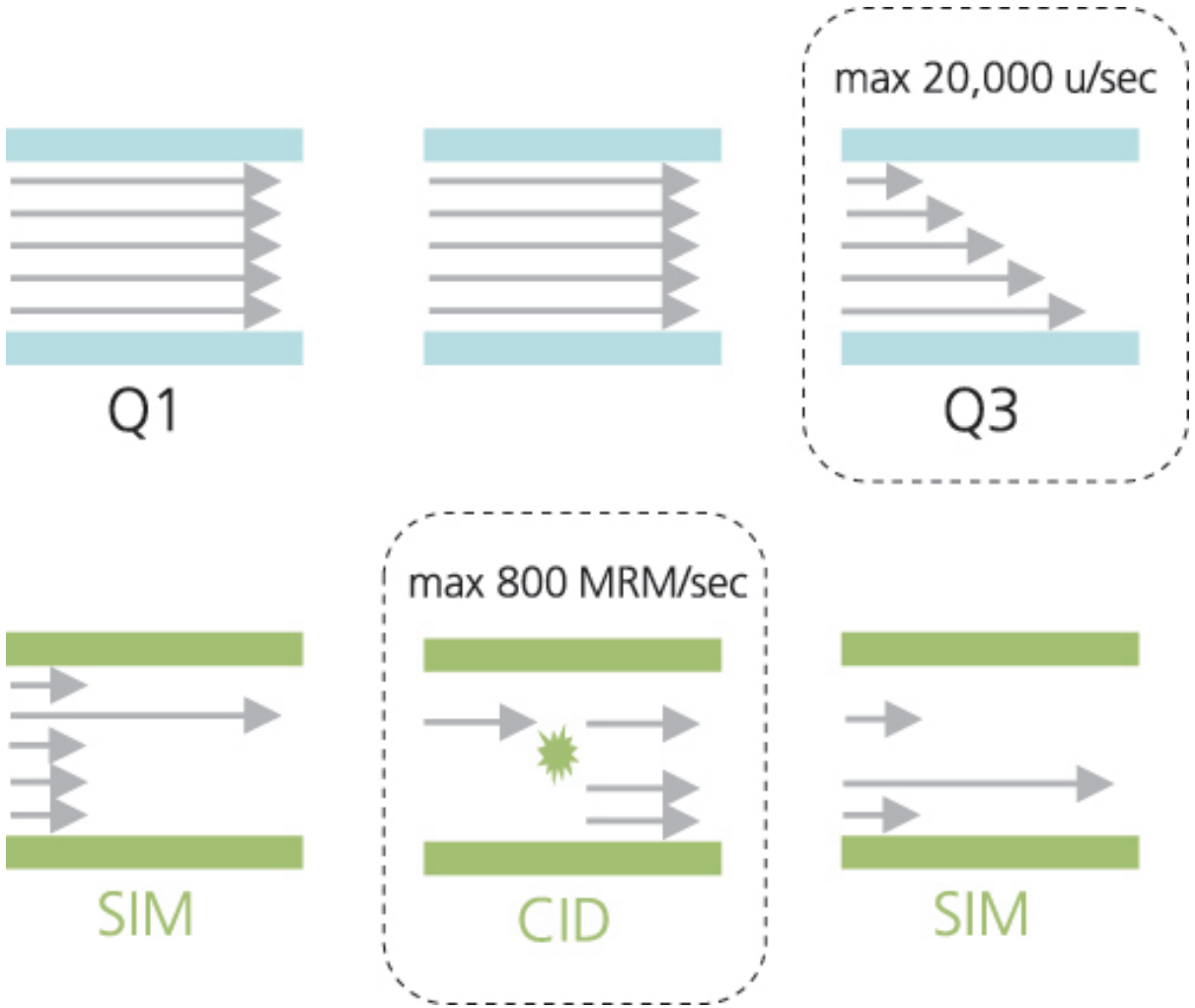
10 ml → 0.05 – 20,000 ppb (20 ppm)

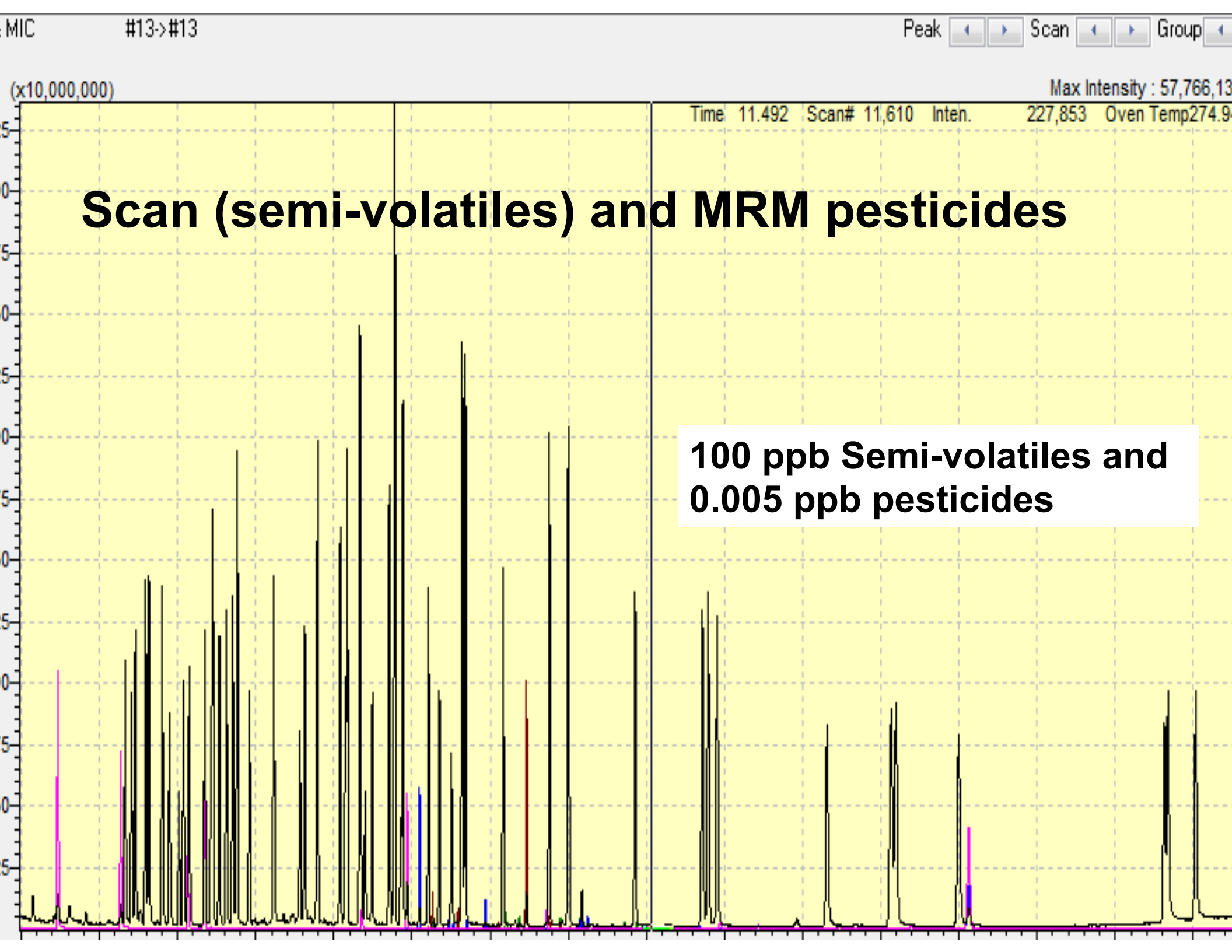
Another possibility for overcoming sensitivity of MRM is to combine extracts

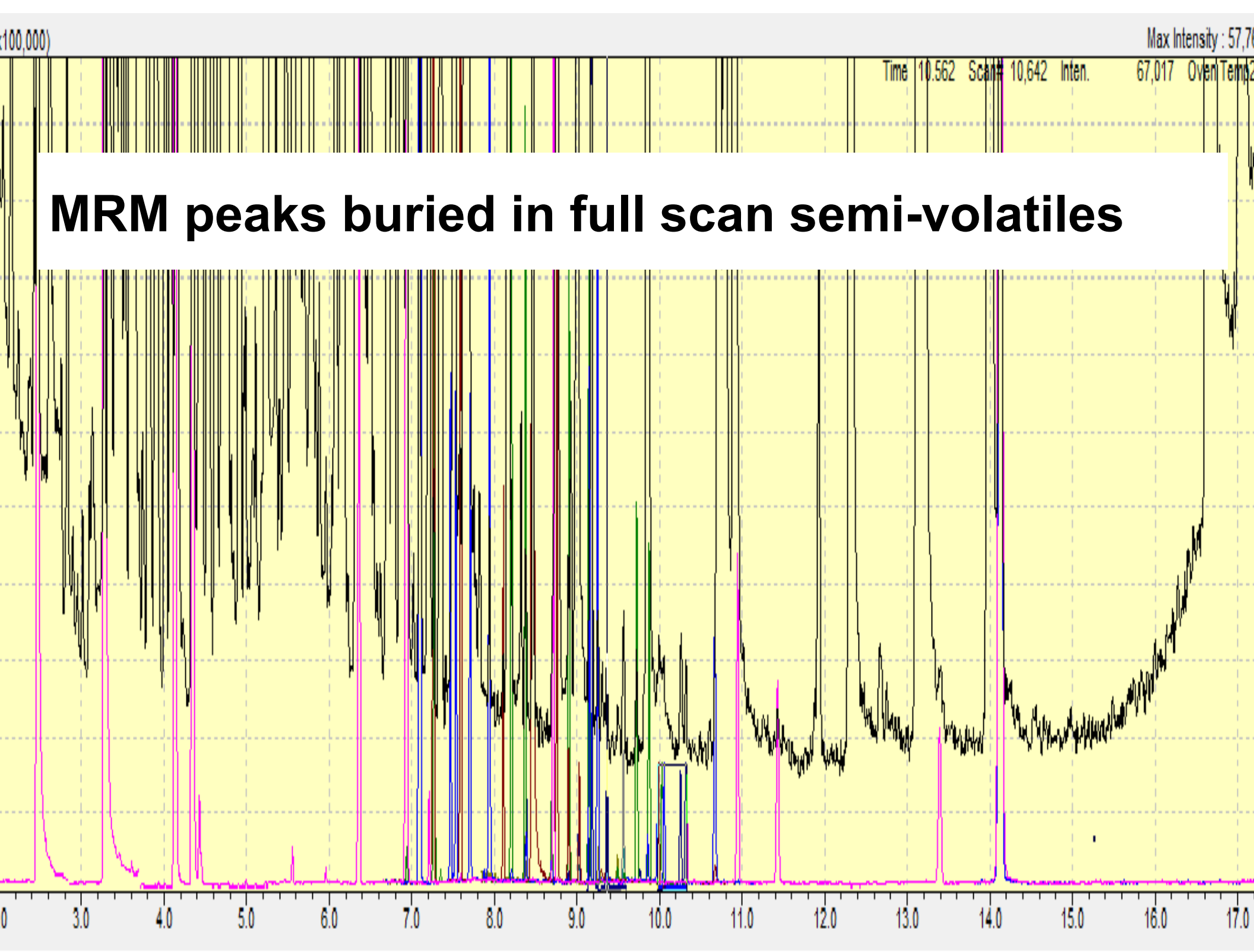
Semi-volatile (100 µl)

Pesticide (900 µl)

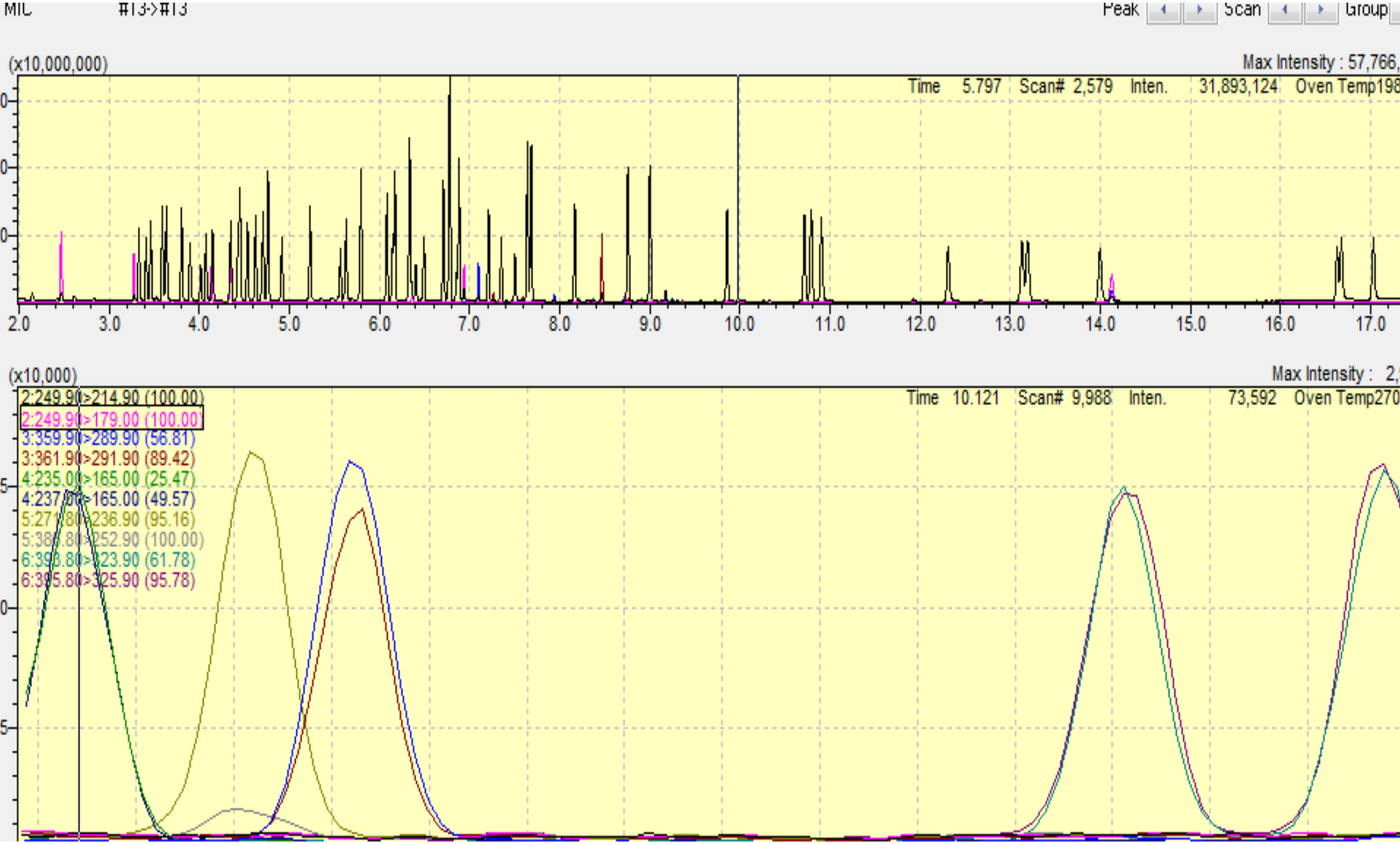
But, the triple quad can operate in single quad mode and/or Scan/MRM



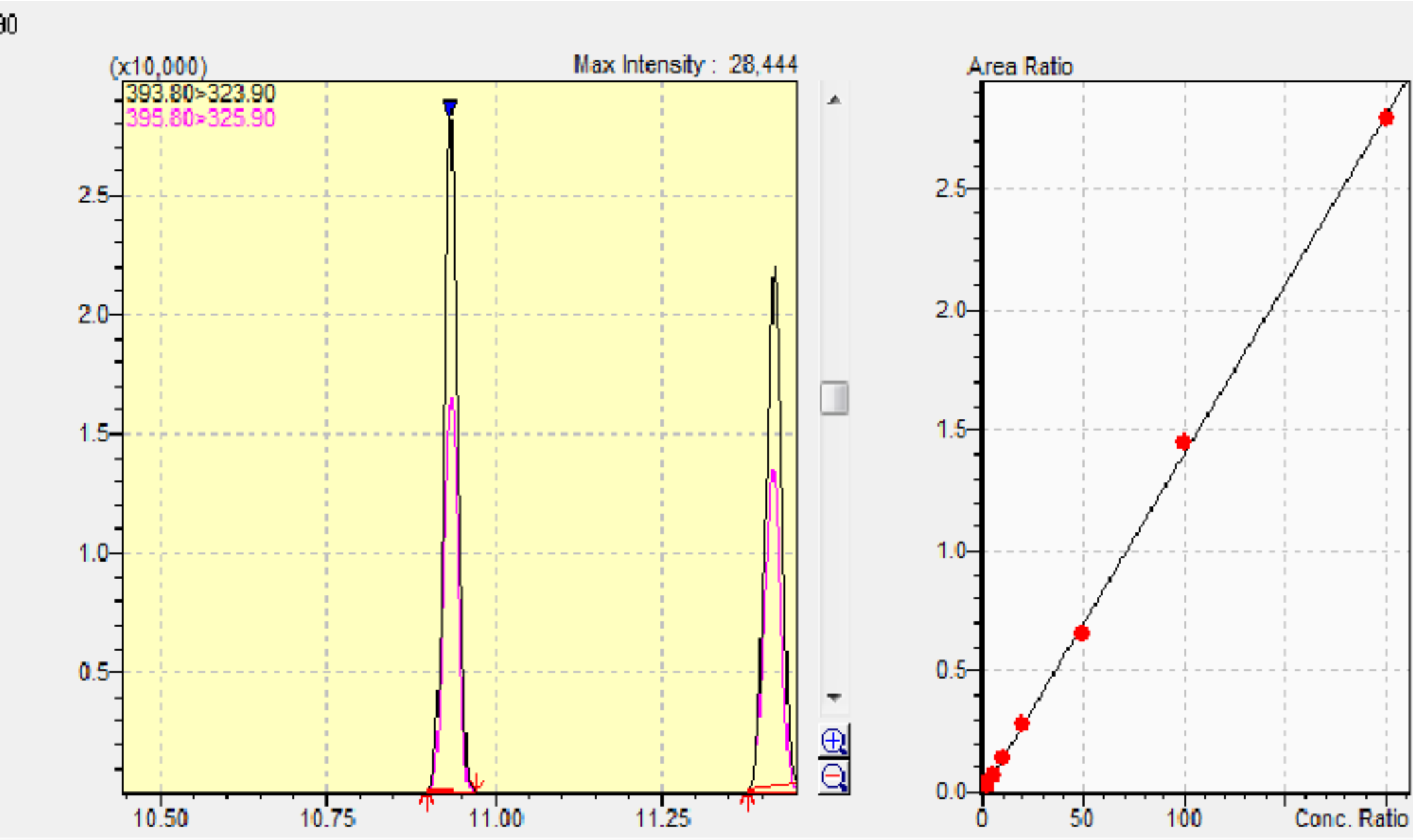

MIC
#13->#13
Peak
Scan
Group
(x10,000,000)
Max Intensity : 57,766,13
Time 11.492 Scan# 11,610 Inten. 227,853 Oven Temp274.9
Scan (semi-volatiles) and MRM pesticides
100 ppb Semi-volatiles and
0.005 ppb pesticides


Max Intensity : 57,7
Time 10.562 Scan# 10,642 Inten. 67,017 Oven Temp
MRM peaks buried in full scan semi-volatiles
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0

Chromatogram showing MRM Quantitation of 0.005 ppb DDT



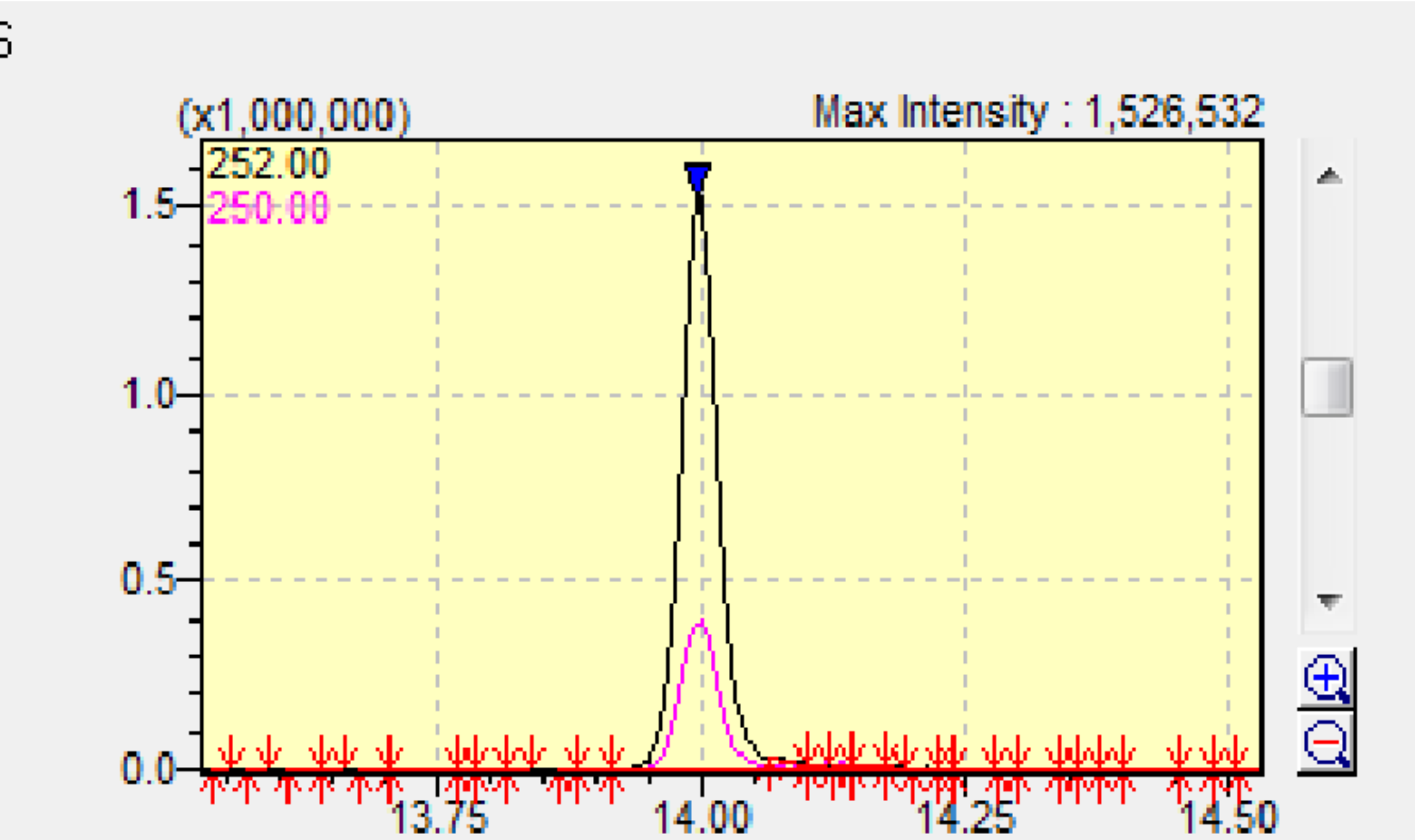
Chromatogram showing 0.005 ppb PCB congener and MRM Quantitation with curve



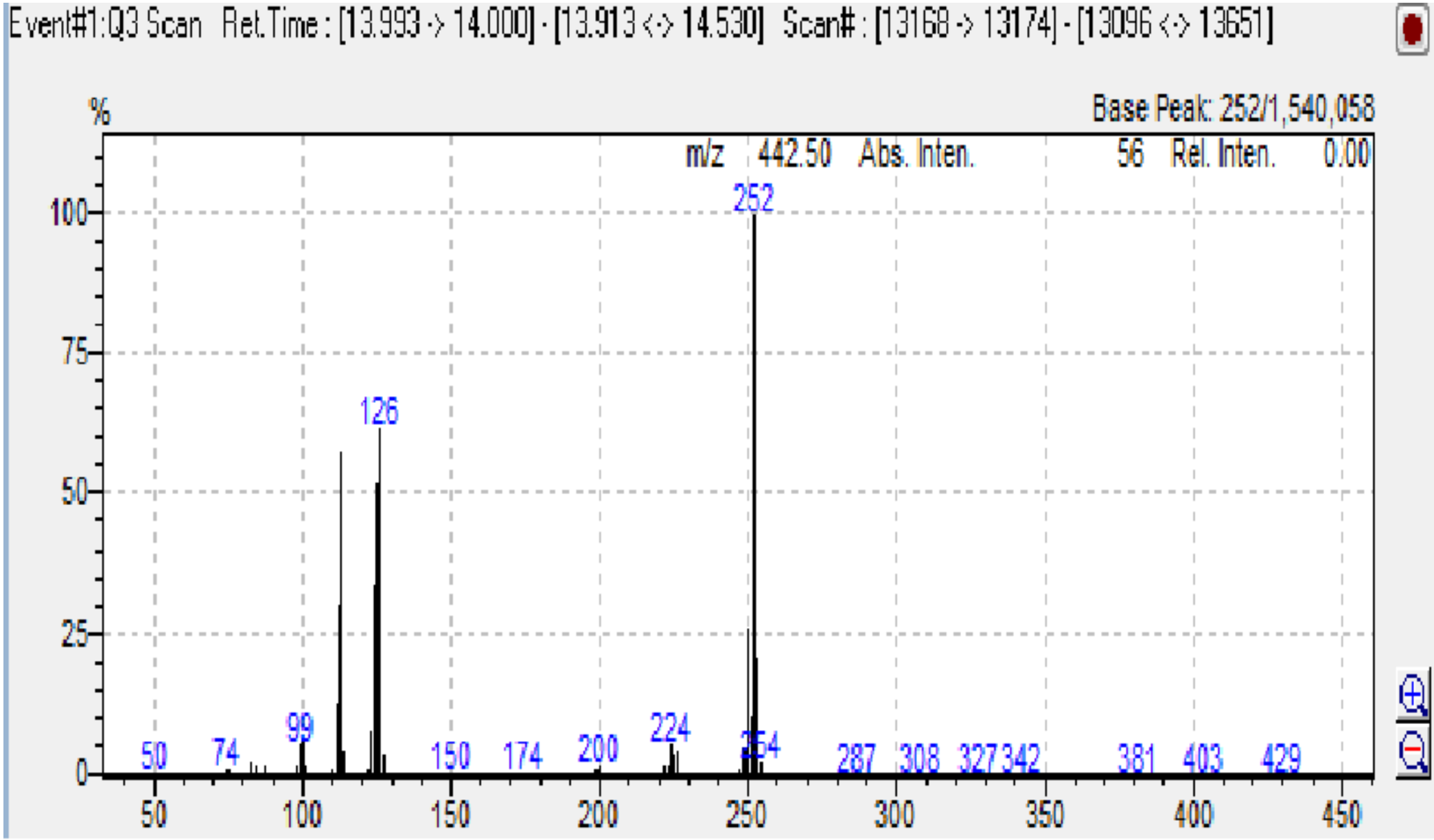
Method Table showing Full Scan for Semi-volatiles and MRM for Pesticides

3	Benzo(b)fluor	Target	4	252.00	13.155	0	ppm	250.00	1	1:Q
4	Benzo(k)fluor	Target	4	252.00	13.224	0	ppm	250.00	1	1:Q
5	2,2',3,3',4,4',	Target	5	461.70>391.80	13.467	0	ppm	463.70>393.80	1	2:M
6	Benzo(a)pyre	Target	4	252.00	14.027	0	ppm	250.00	1	1:Q
7	Decachlorobi	ISTD	5	497.70>427.80	14.130	0	ppm	499.70>429.80	1	2:M
8	Decafluorobi	ISTD	4	214.00>179.10	14.150	0	ppm	178.00>160.60	1	3:M
9	Indeno(1,2,3-	Target	4	276.00	16.649	0	ppm	274.00	1	1:Q
00	Benzo(g,h,i)p	Target	4	276.00	16.695	0	ppm	274.00	1	1:Q

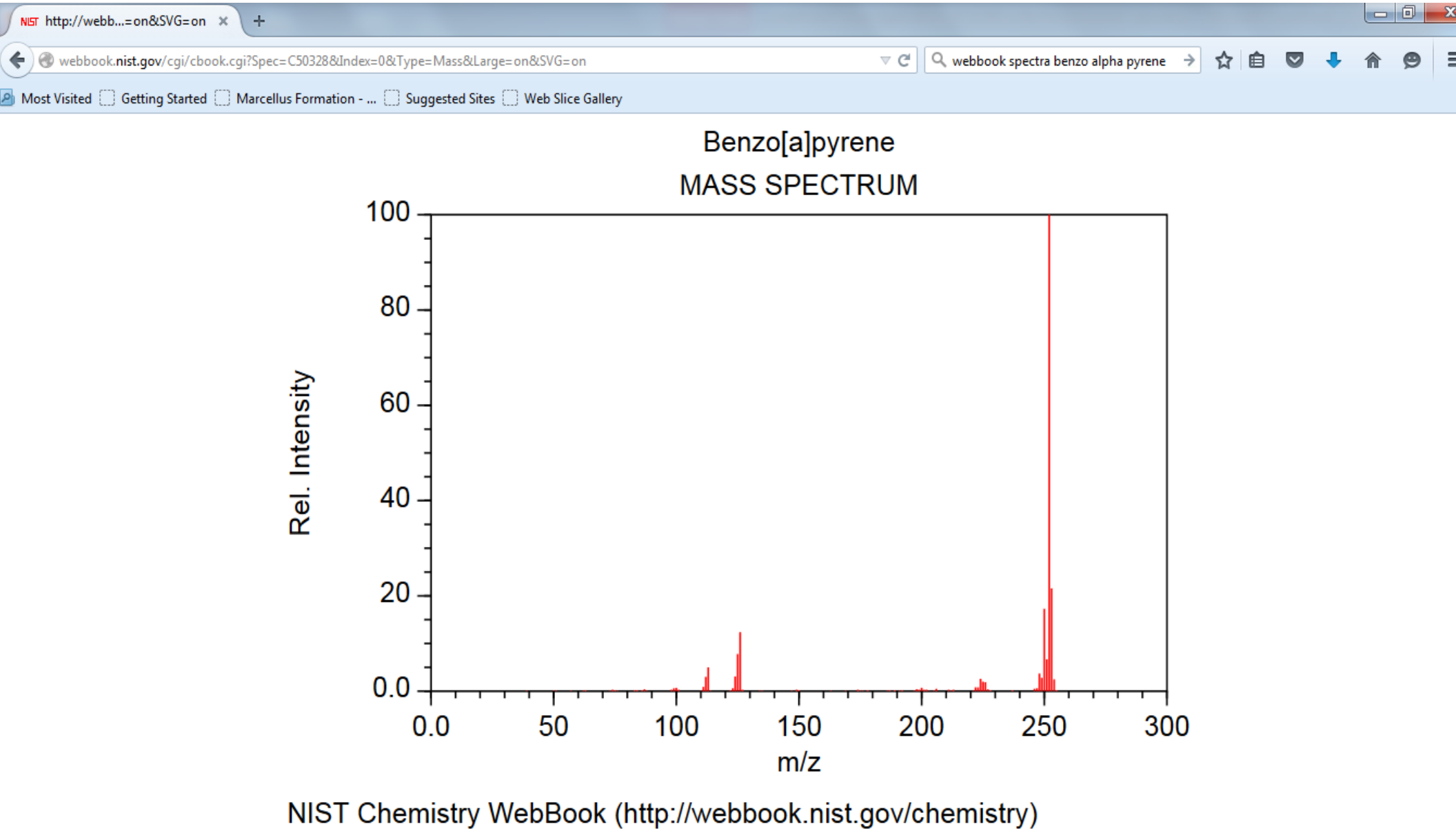
Full Scan for quantitation of Benzo (a) pyrene



Full scan spectra of 10 ppb Benzo (a) pyrene (Scan/MRM mode)



NIST spectra of Benzo (a) pyrene



Advantages of Scan/MRM quantitation of Semi-volatiles and Pesticides

- Capable of pesticides/PCB and Semi-volatiles in one injection/extraction
  - 0.0005 – 200 ppb pesticides
  - 0.01 – 2000 ppb Semi-Volatiles

Thank You, for more information contact me

- wclipps@shimadzu.com