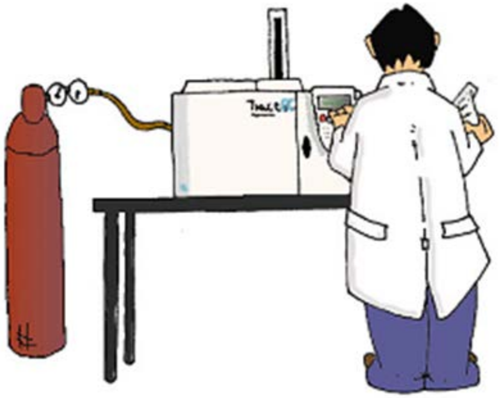
Gas Chromatograph Technology

Chromatography

- Chromatography : Analytical technique that depends on separation of components in sample

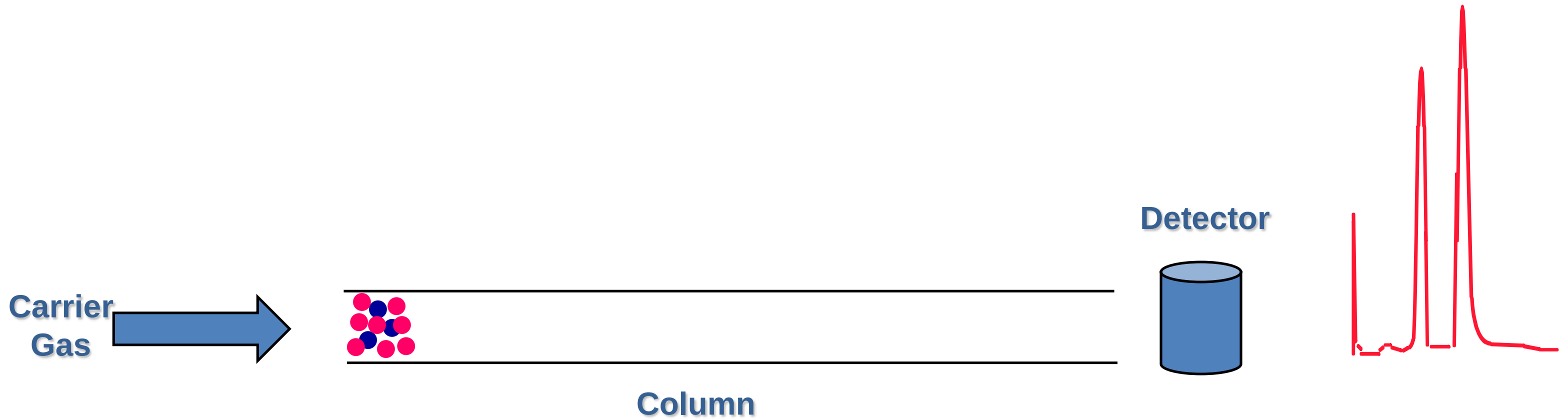
- Sample components are separated and detected

- Separation : Between two phases
  - Stationary Phase
  - Mobile phase

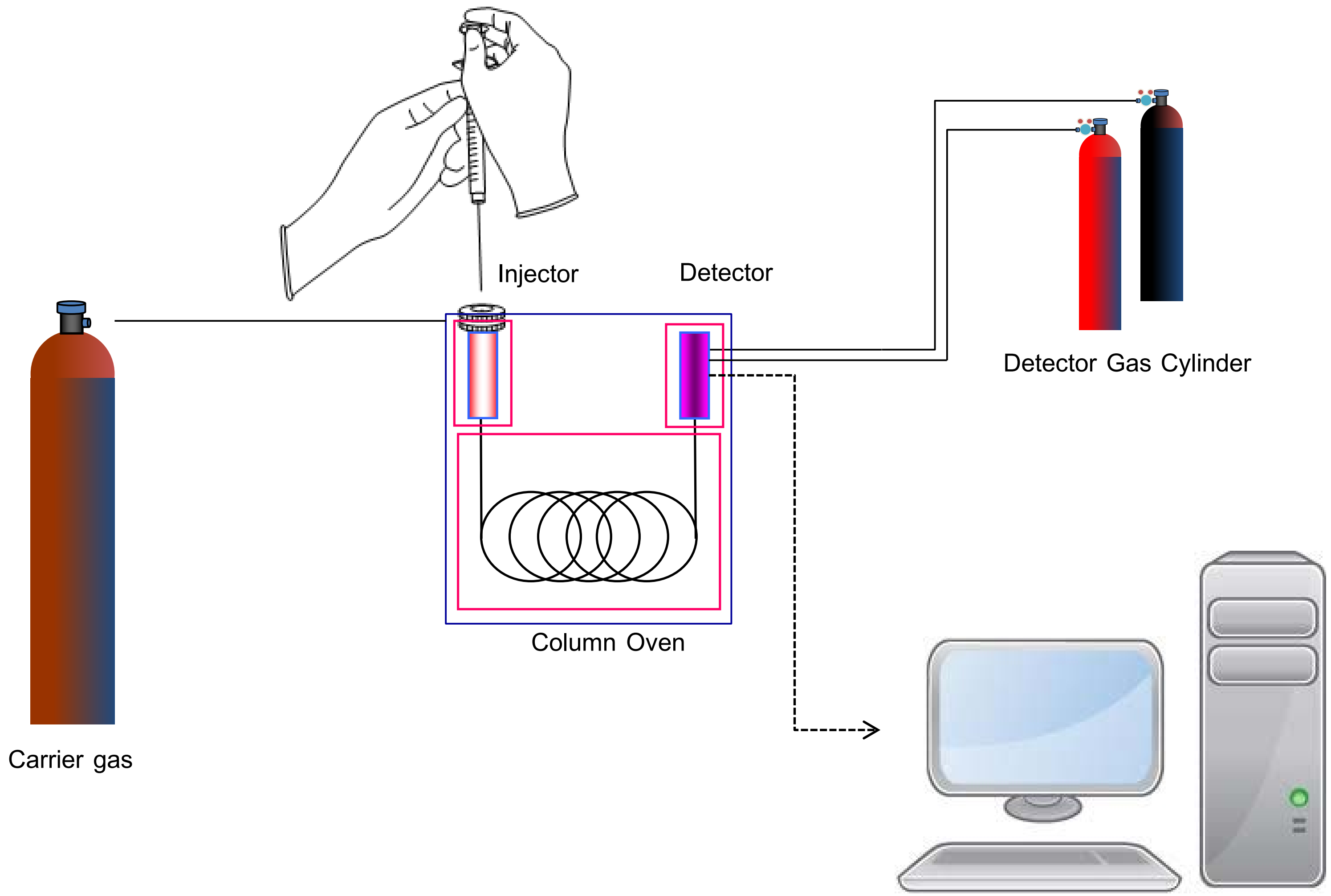


Gas Chromatography

- Gas Chromatography (GC) : Chromatography technique which gas is used as mobile phase
- Sample will be injected into the system, Injection port where all components are vaporized and swept into the column
- Sample components will then be separated according to the interaction with stationary phase and eluted to detector.



GC System Components



Sci Spec

TRACE 1300 Series GC

TRACE 1310 GC: Touch screen interface provides instant access for ease of use and local control

TRACE 1300 GC: Local built-in ultra-simplified user interface – two buttons and four LEDs

Modules available:

Injectors: SSL - SSL backflush - PTV - PTV backflush - Helium Saver SSL - GSV

Detectors: FID - TCD - ECD - NPD – FPD – PDD - MS*

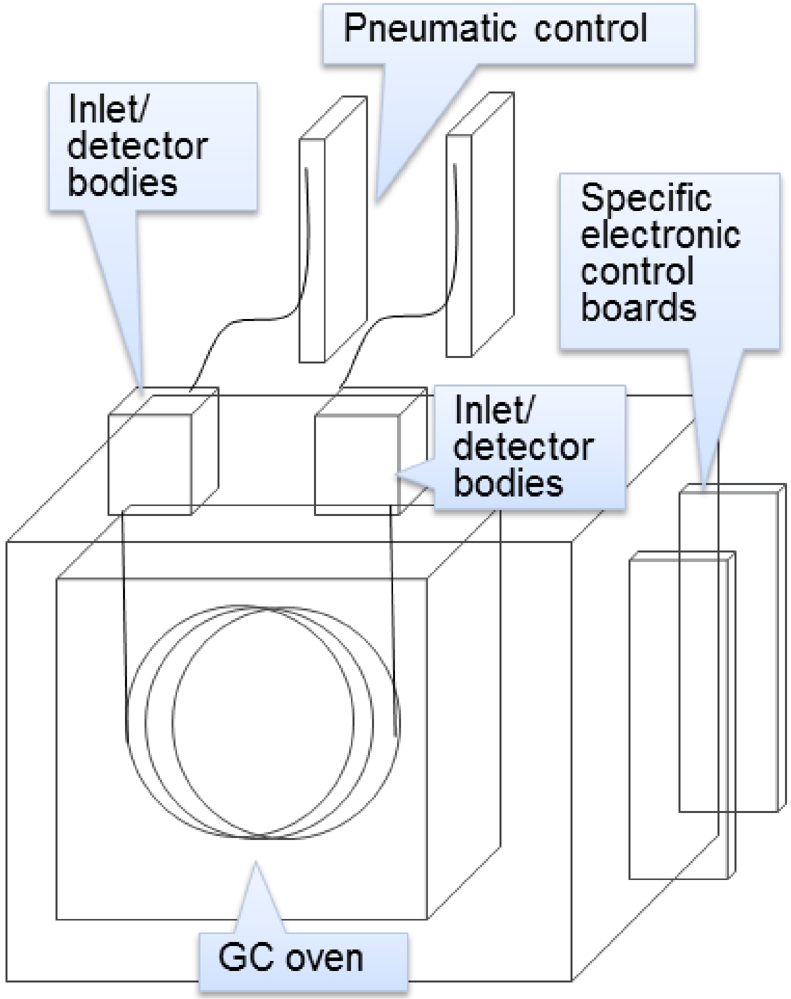
Other Options: Microfluidic devices, Auxiliary Oven, Inj/Oven Cryo, Aux carrier

Software drivers: Chromeleon 7 and 7.2 CDS, Xcalibur, ChromQuest, ChromCard

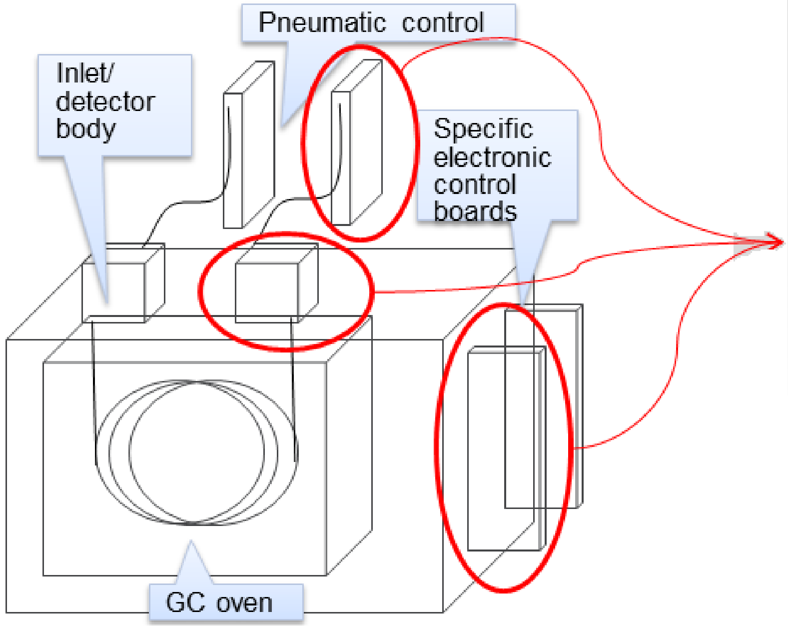
*Supported Thermo Scientific MS: ISQ ™ Series GC-MS; TSQ Series GC-MS/MS; DFS

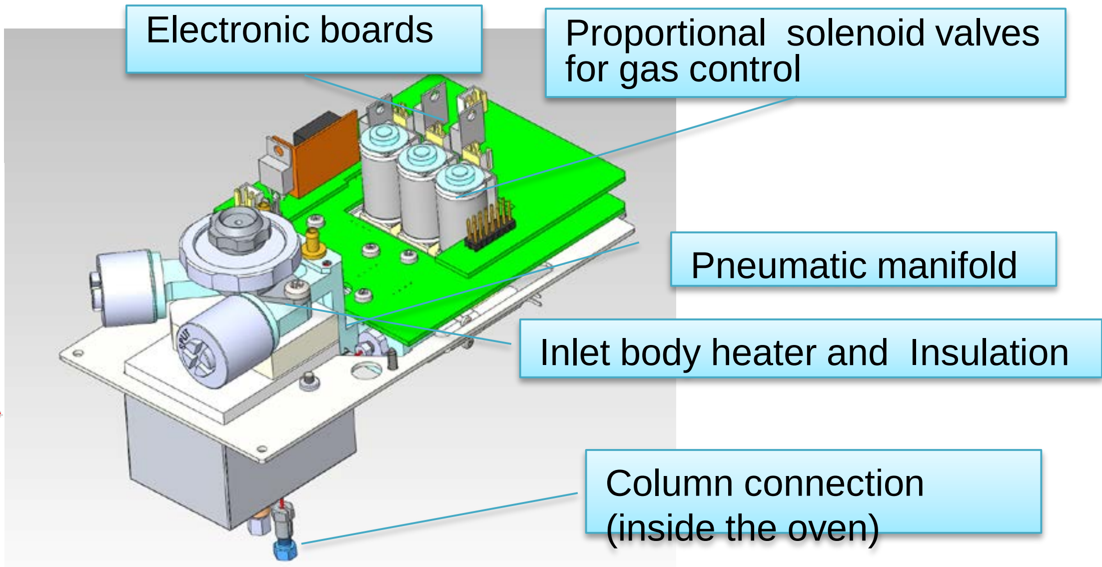
GC Equipment Design since 1955…

- Diverse inlet and detector types are required to run different GC applications
- Inlet and detector bodies are installed on oven top deck and require pneumatic and specific electronics controller
- The large number of options can sum up to thousands of possible combinations and final system configurations
- Typically systems are factory-configured based on orders
- Upgrades or changes in configuration at site is an expensive, difficult and time-consuming operation



A new Modular Approach to GC Instrumentation design





GC with modular design - IP

US008871149B2

(12) **United States Patent**
Zilioli et al.

(10) **Patent No.:** **US 8,871,149 B2**
(45) **Date of Patent:** **Oct. 28, 2014**

(54) **MODULAR GAS CHROMATOGRAPH**

(75) Inventors: **Giacinto Zilioli**, Rodano (IT); **Stefano Pelagatti**, Rodano (IT); **Paolo Magni**, Rodano (IT)

(73) Assignee: **Thermo Fisher Scientific S.p.A.**, Rodano (MI) (IT)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 371 days.

(21) Appl. No.: **13/258,678**

(22) PCT Filed: **Apr. 6, 2009**

(86) PCT No.: **PCT/IT2009/000147**

§ 371 (c)(1), (2), (4) Date: **Sep. 22, 2011**

(58) **Field of Classification Search**
USPC 73/23.41, 23.42, 23.35; 95/87; 96/104, 96/106; 422/89
See application file for complete search history.

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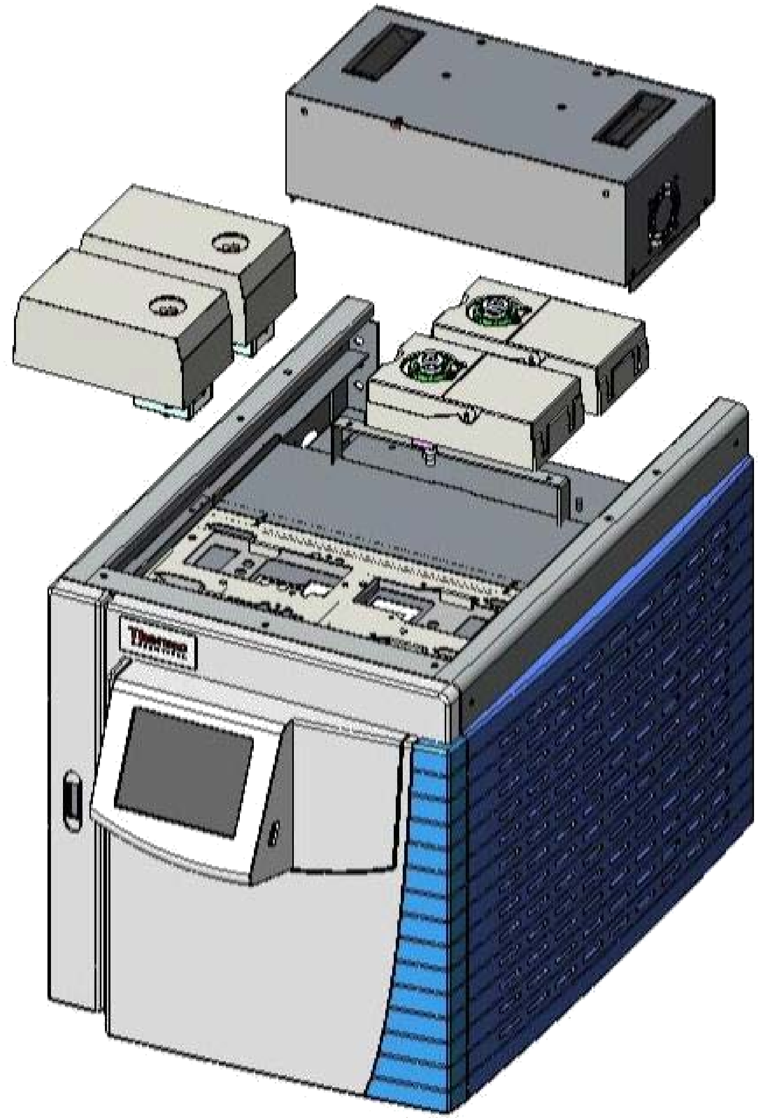
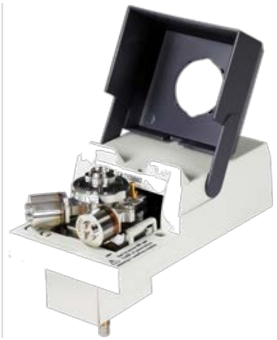
(Continued)

OTHER PUBLICATIONS

- Patent extended in US, EU, JP and CN
  - » Components are analytically tested separately from the assembled final unit.
  - » Components can be kept in stock for fast replacement, upgrading, or change of configuration
  - » Modules would be replaced without requiring a service engineer



TRACE 1300 Series GC “Instant Connect” modules



SSL /SSL bkf

PTV /PTV bkf

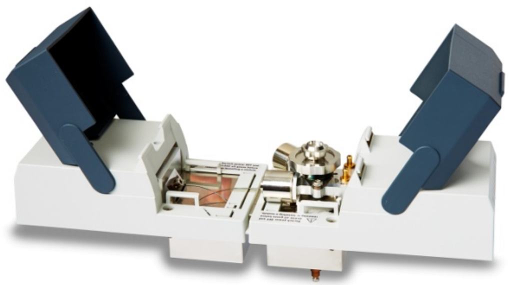
Gas Sampling valve

IEC (Integrated Electronic Control)

Gas Specification

• Up to 18 channels of integrated electronic gas control

• Pressure set points minimum increments: 0.01 kPa-0.001 psi in all ranges



He Saver

Carrier Gas Control Common to all Injectors

• Split ratio: Up to 12500:1

• Pressure range: 0–1000 kPa (0–145 psi)

• Modes: Constant and programmed pressures and flows with gas saver and septum purge

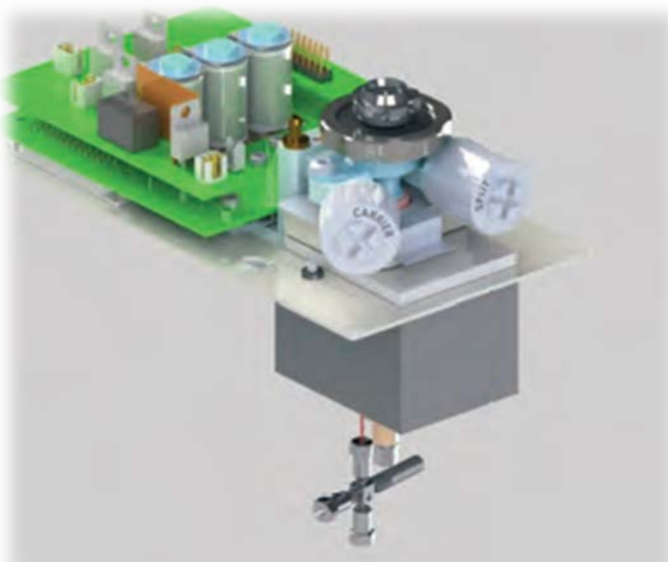
• Total flow setting:

– Control of split flow in 0.1 mL/min increments; split flow OFF or from 5 to 1250 mL/min

– Purge flow: OFF or from 0.5 mL/min

Robust and reliable performance

- Miniaturized IEC (Integrated Electronic gas Control) technology, integral part of each instant connect module
  - Gas manifolds and connections, restrictions and electronic valves built-in
  - 0.001 psi carrier gas control precision throughout the pressure working range, for exceptional retention time stability
  - Modules store all their calibration information allowing minimum variation if replaced on a system

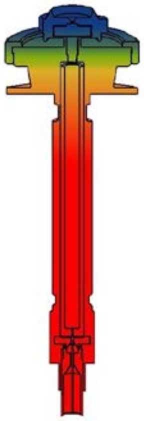


Your Scientific Specialist

TRACE 1300 Series: robust and reliable performance

- **Injector modules**
  - Complete and self-sufficient
    - Include injector body, valves, filters, electronics for temperature and carrier gas control

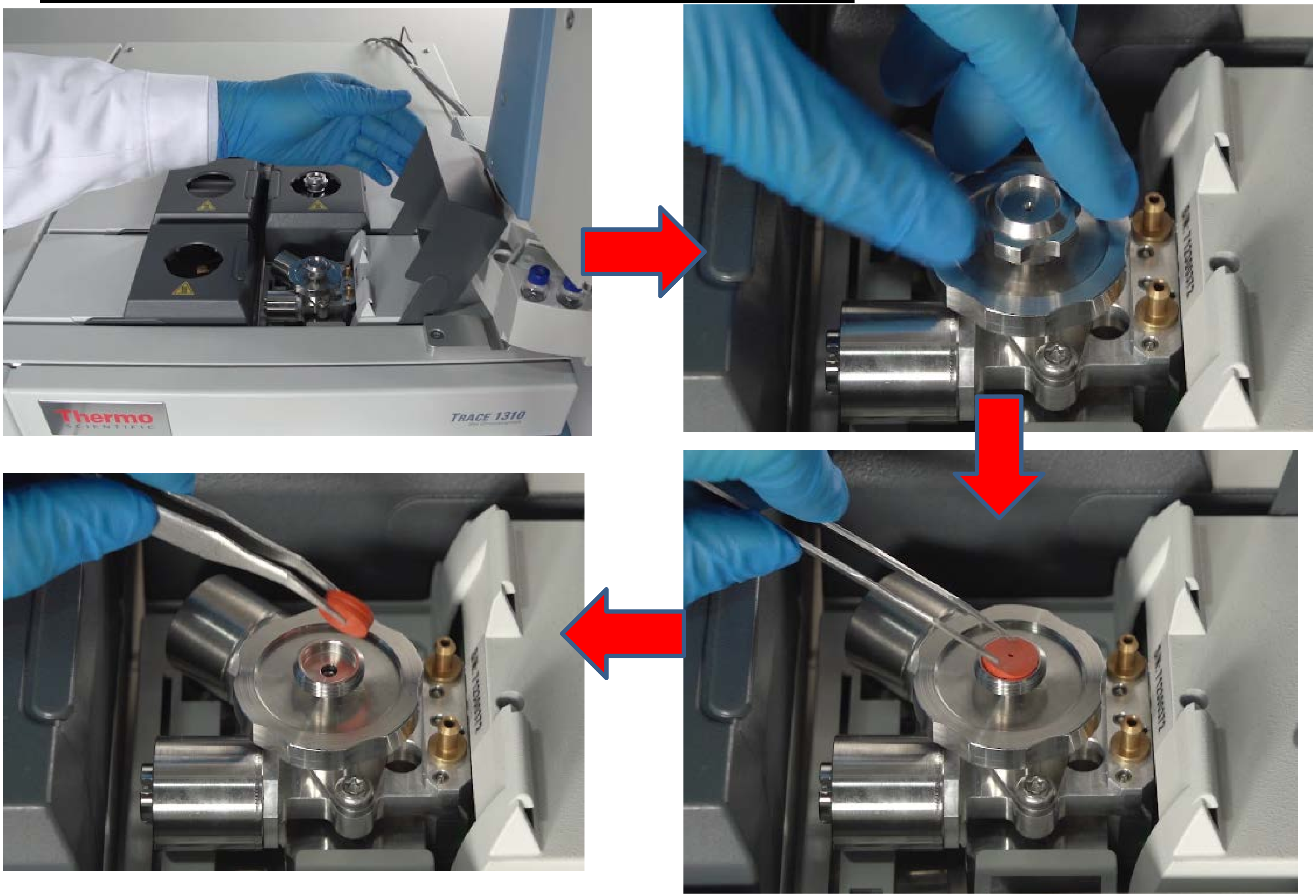
- **SSL specially designed**
  - Cool head and septum
    - Lower septum bleeding
    - Longer septa lifetime for high productivity
    - No septum sticking for quick maintenance
    - Lower air (oxygen) diffusion
    - Column lifetime and MS sensitivity preserved
  - Uniform temperature along liner



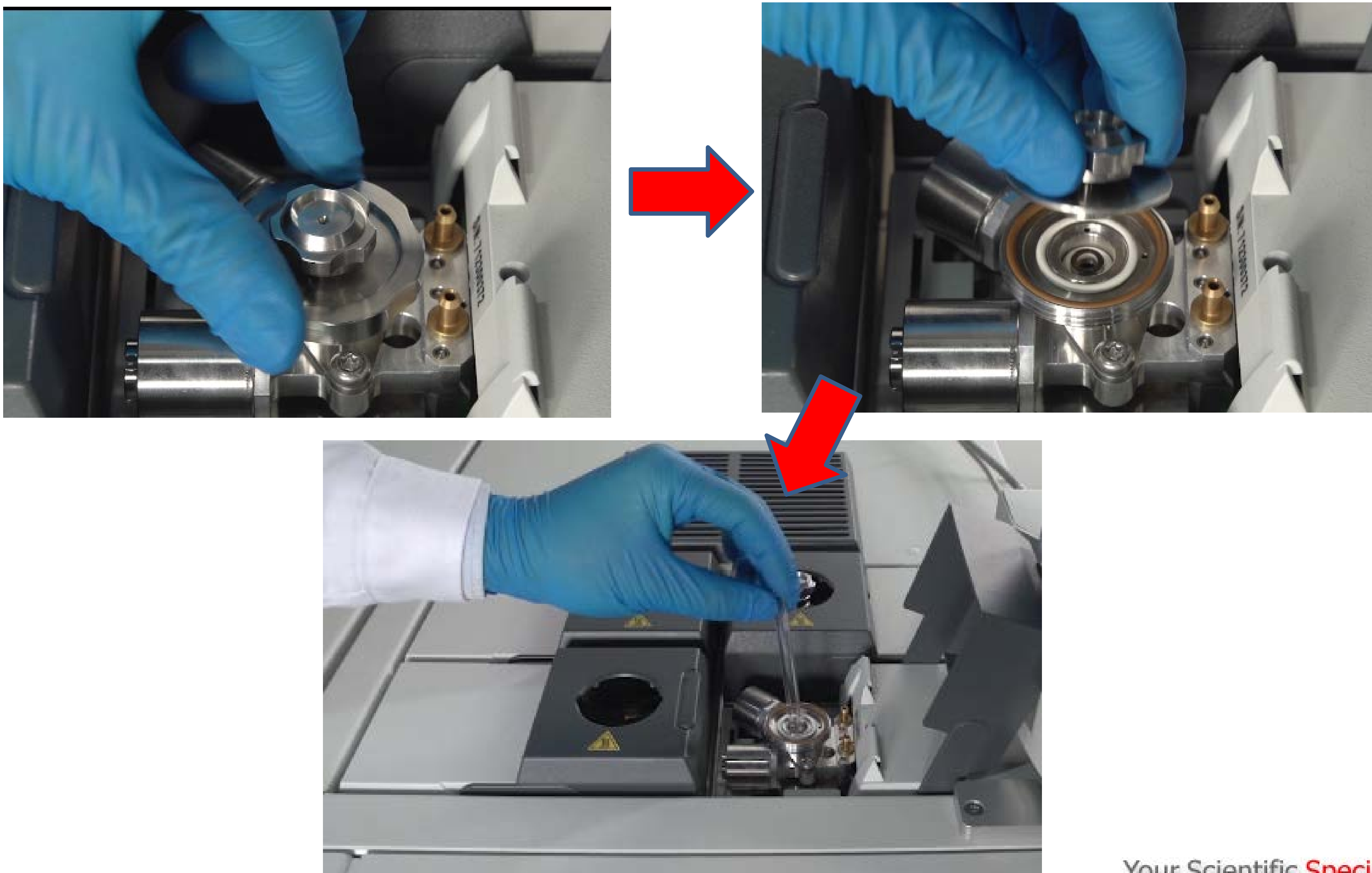
TRACE 1300 Series GC: Tailor Instrument Configuration

- Proprietary, patented Thermo Scientific “Instant Connect” modules
- Modules are user-installable in less than two minutes
  - Disconnected column from injector.
  - Just remove three screws and put the new module in place
  - No special training, dedicated tools or on-site service engineers required
- Every injector and detector is self-sufficient
  - Contains the Integrated Electronic gas Control (IEC)
  - Storing module calibration

Injector maintenance



Injector maintenance



Injector maintenance

Robust and Reliable Performance

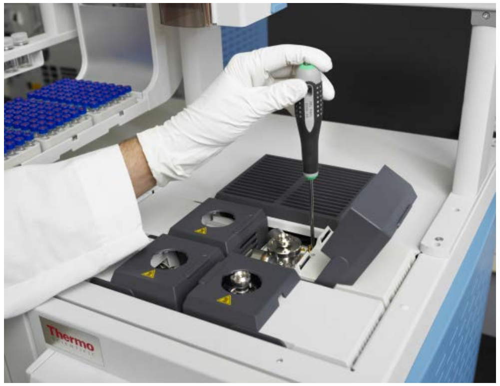
- **Miniaturized instant connect detectors**
  - Available: FID, ECD, TCD, NPD, PDD and FPD (also dual flame)
  - Single bodies including cells, heater and gas feeding
  - Reduced volumes for increased sensitivity
  - Up to four can be mounted and operated at the same time
  - Fast acquisition speed: up to 300 Hz
  - Enhanced Linearity
  - Easy access to removable parts for maintenance

- **Front-end to Mass Spectrometers for increased selectivity and sensitivity**

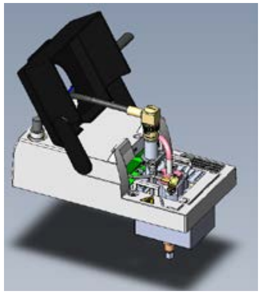
TRACE 1300 Series GC “Detector” modules

FID

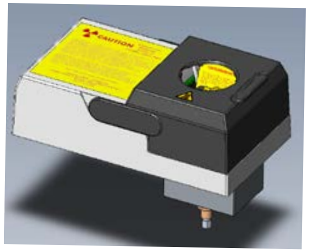
TCD



PDD



NPD



ECD

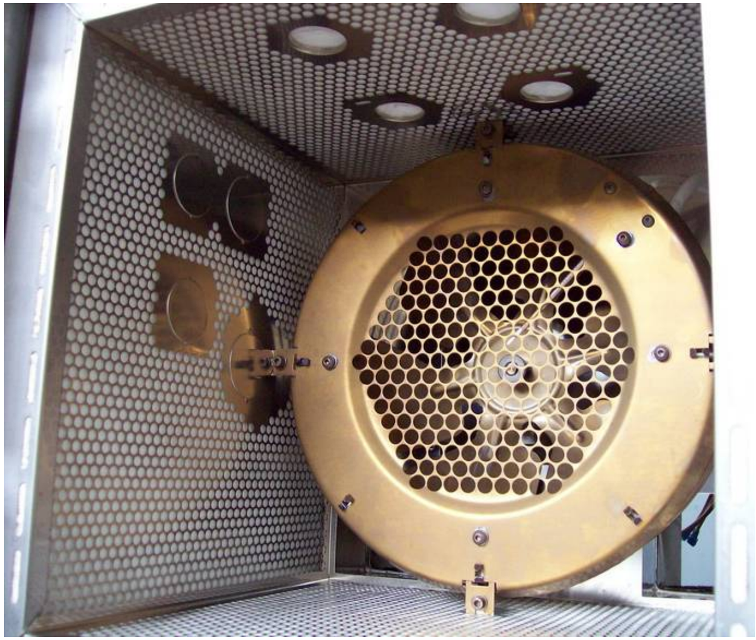
Your Scientific Specialist

Trace 1300 Series : Replace Injector Module

Fast GC Oven

The powerful and robust solution for superior oven performance

- Proprietary oven technology
  - Perforated sheet metal walls and larger exhaust
- Large oven size in a reduced benchspace
  - Up to 2 capillary columns with standard cage
- Fast heating and cooling
  - up to 125 °C/minute
- Both walls accessible
  - Easy MS connections and additional devices



Fundamental of Mass Spectrometer

Why GC/MS?

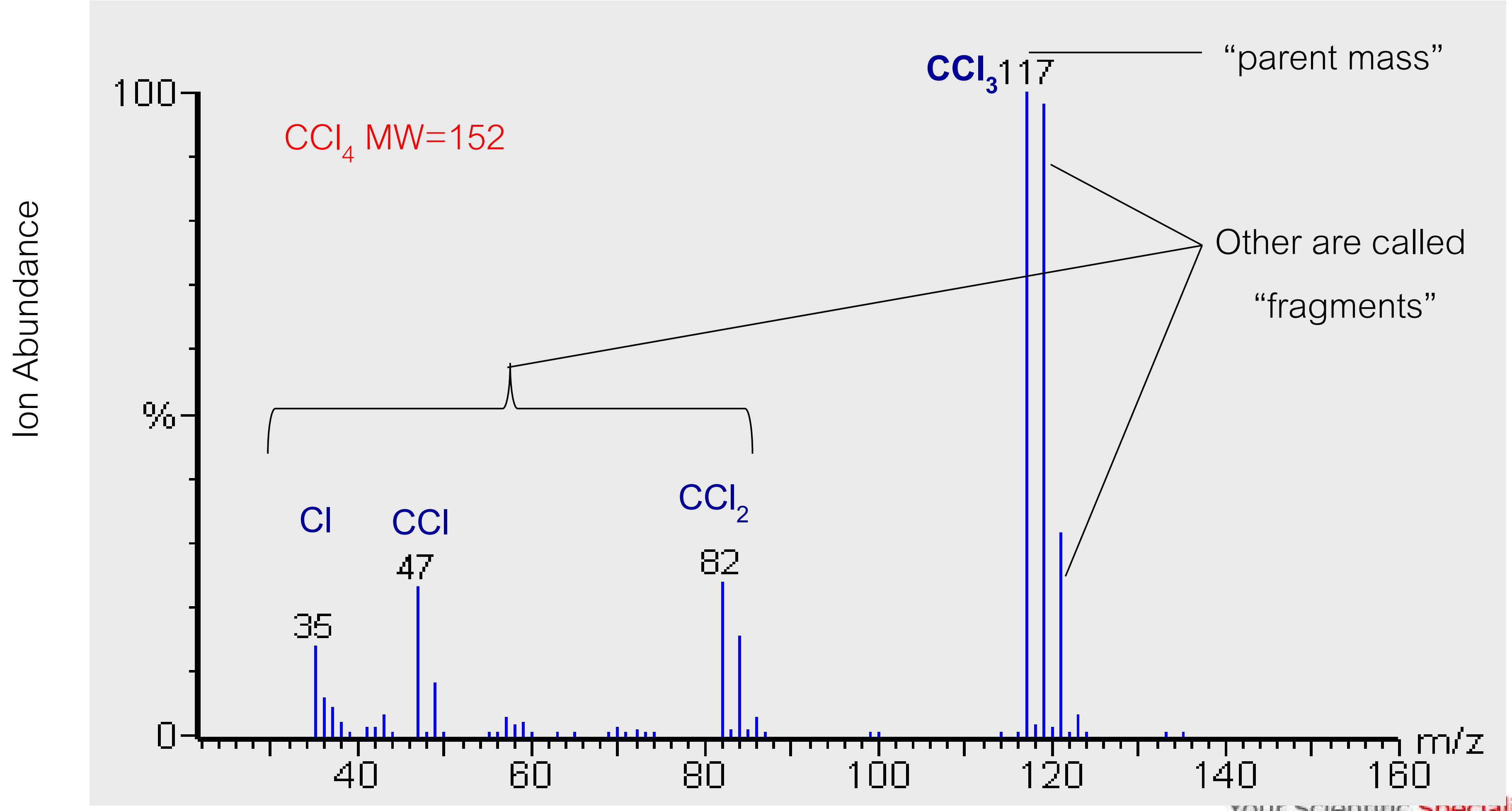
- Universal and specific
  - Full scan for unknown sample
  - SIM, MIM for specific (interested) mass
- High Sensitivity
  - ppt level
- Provides identification with standard or library spectrum
- Interference-free quantitation (SIM or MIM)
- Isotopic information
- Confirmation of other conventional detectors

What is Mass Spectrometry?

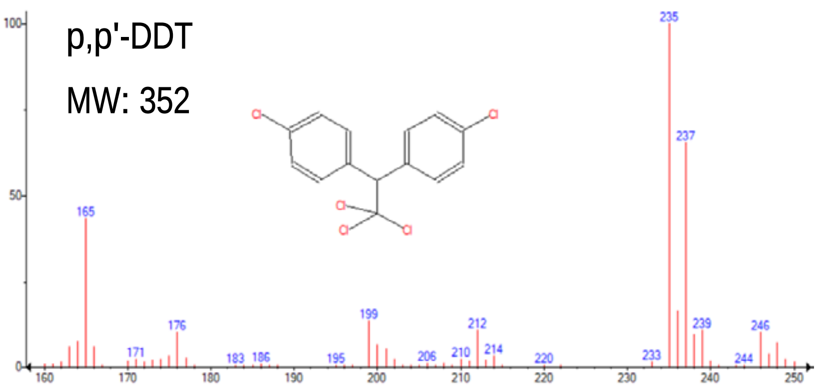
- The production of ions that are subsequently separated or filtered according to their mass-to-charge (m/z) ratio and detected.
- The resulting mass spectrum is a plot of the (relative) abundance of the produced ions as a function of the m/z ratio."

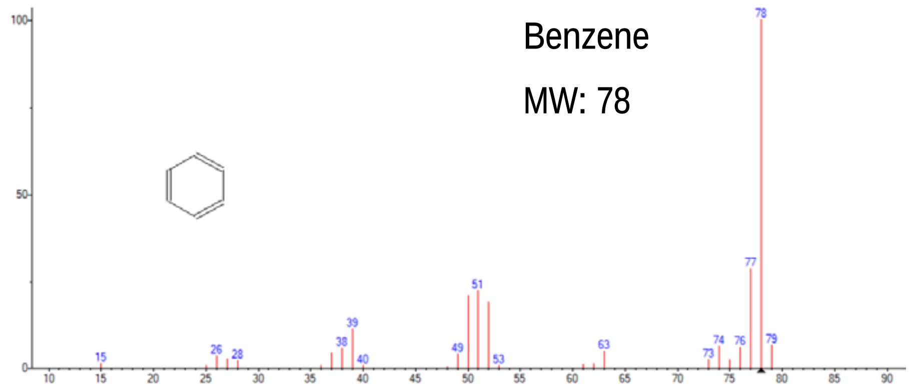
What is “Mass Spectrum” ?

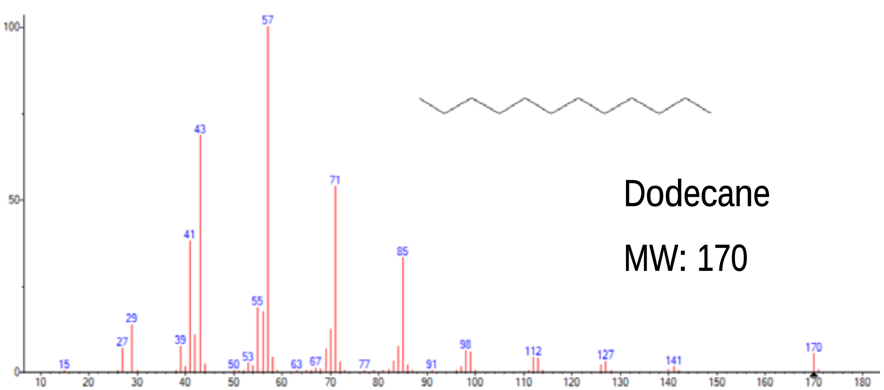
- Graph of Relative Ion Intensity vs. m/z
- Ion Fragments detail structure and molecular weight of compound

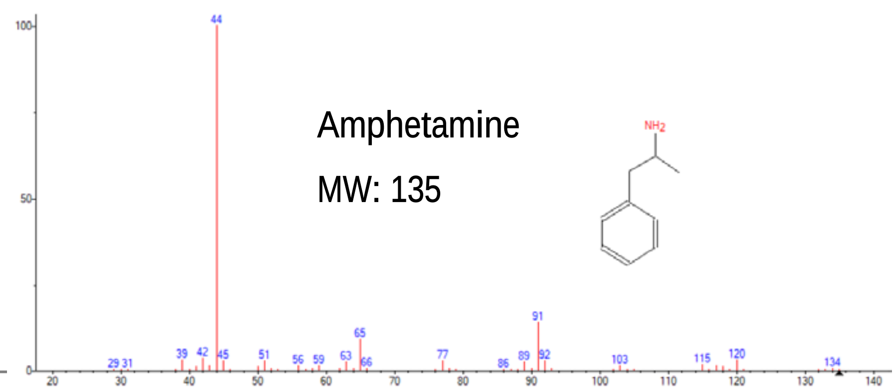


Mass Spectrum









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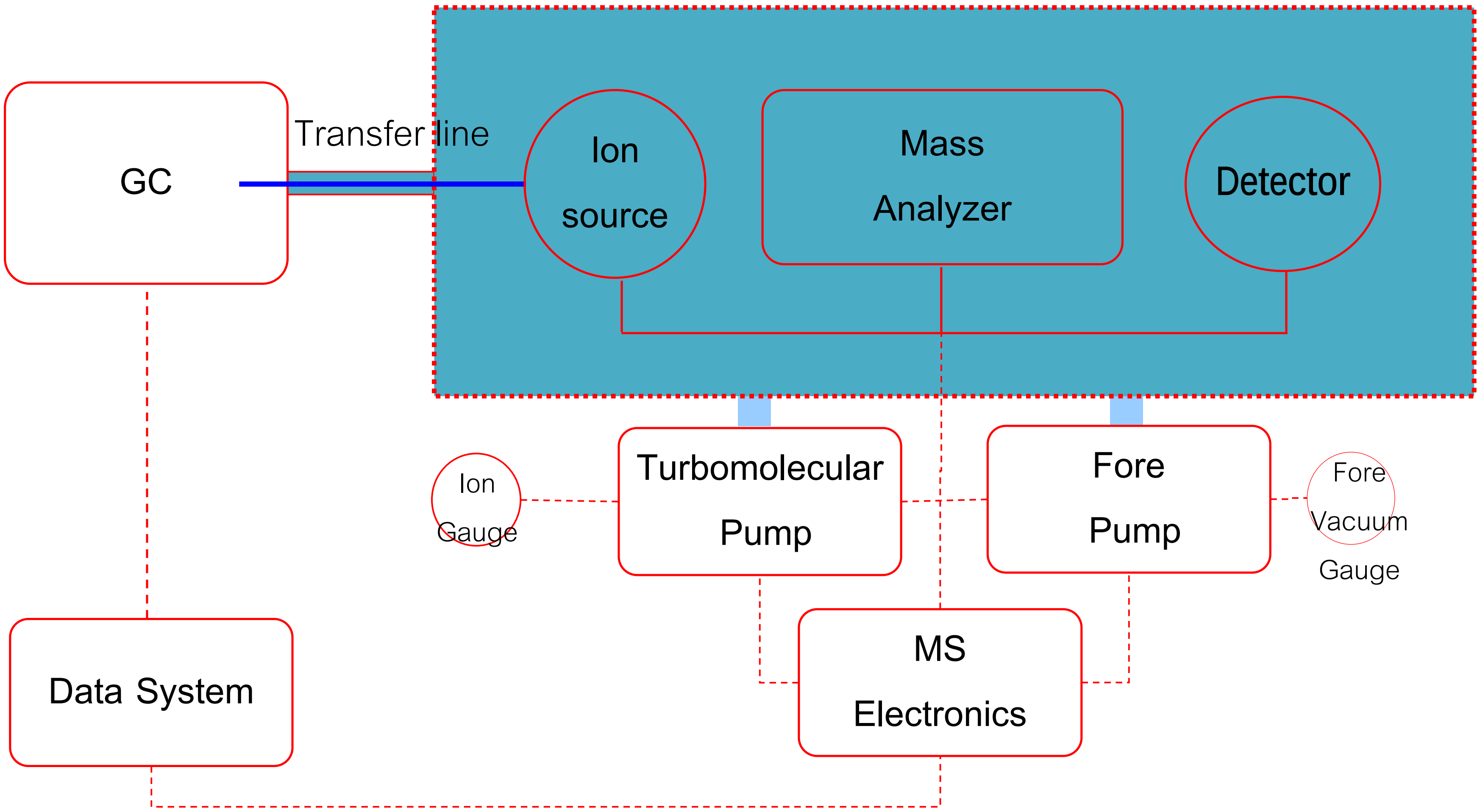
Components in GC/MS



Your Scientific Specialist

ISQ 7000 Series…

Perfect for today, ready for tomorrow

- Fit for purpose GC-MS solution
- Grows with evolving regulatory requirements
- Base to advanced configurations
- Full field upgrade path

Ultra high sensitivity and robustness
ISQ 7000 AEI

High-throughput solution
ISQ 7000 NeverVent EI & CI

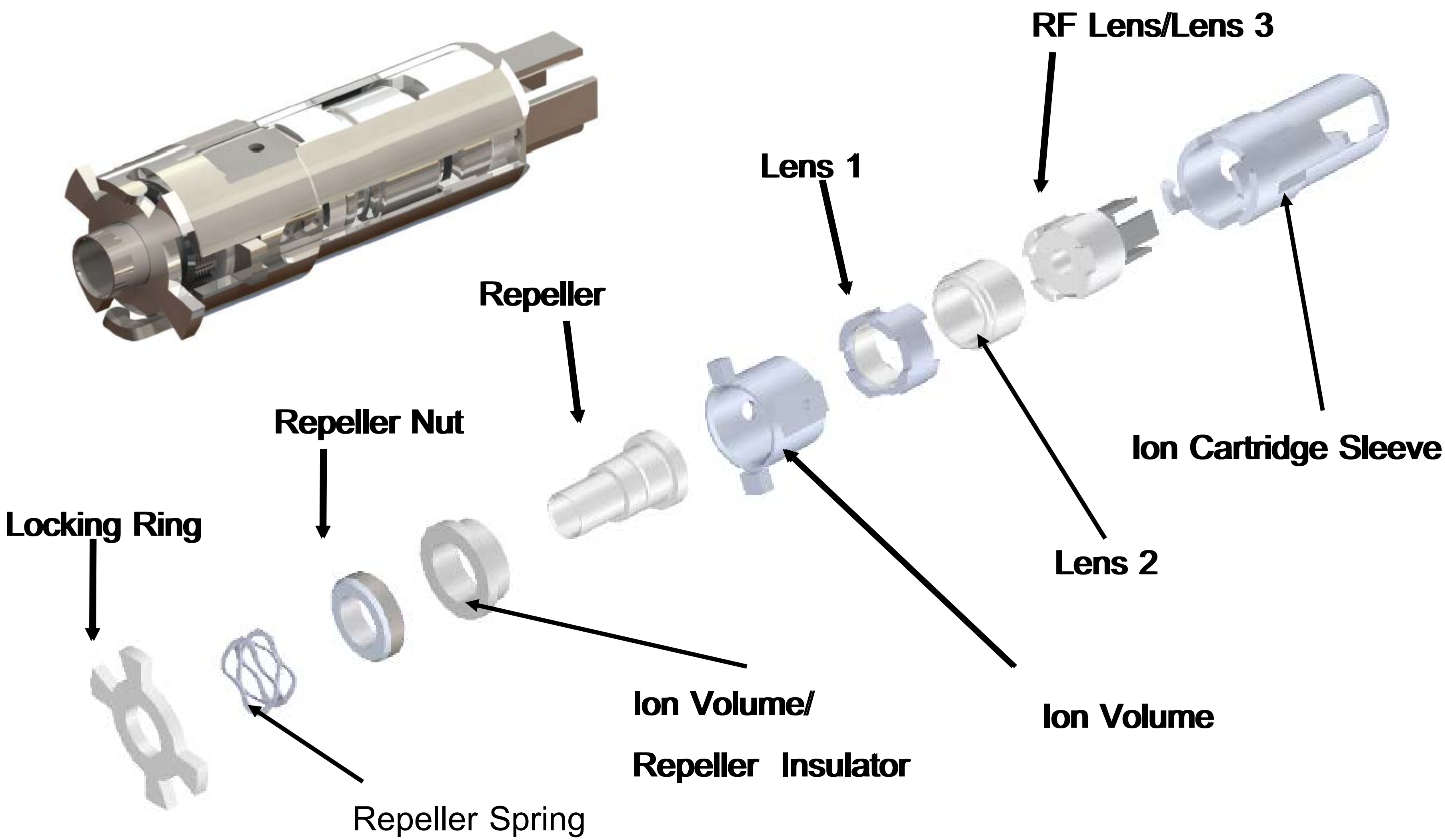
High-throughput solution
ISQ 7000 NeverVent EI

Accessible high performance
300L/s ExtractaBrite

Affordable first entry
66L/s ExtractaBrite

TSQ 9000 Series…

Ion Source Cartridge (iSQ)

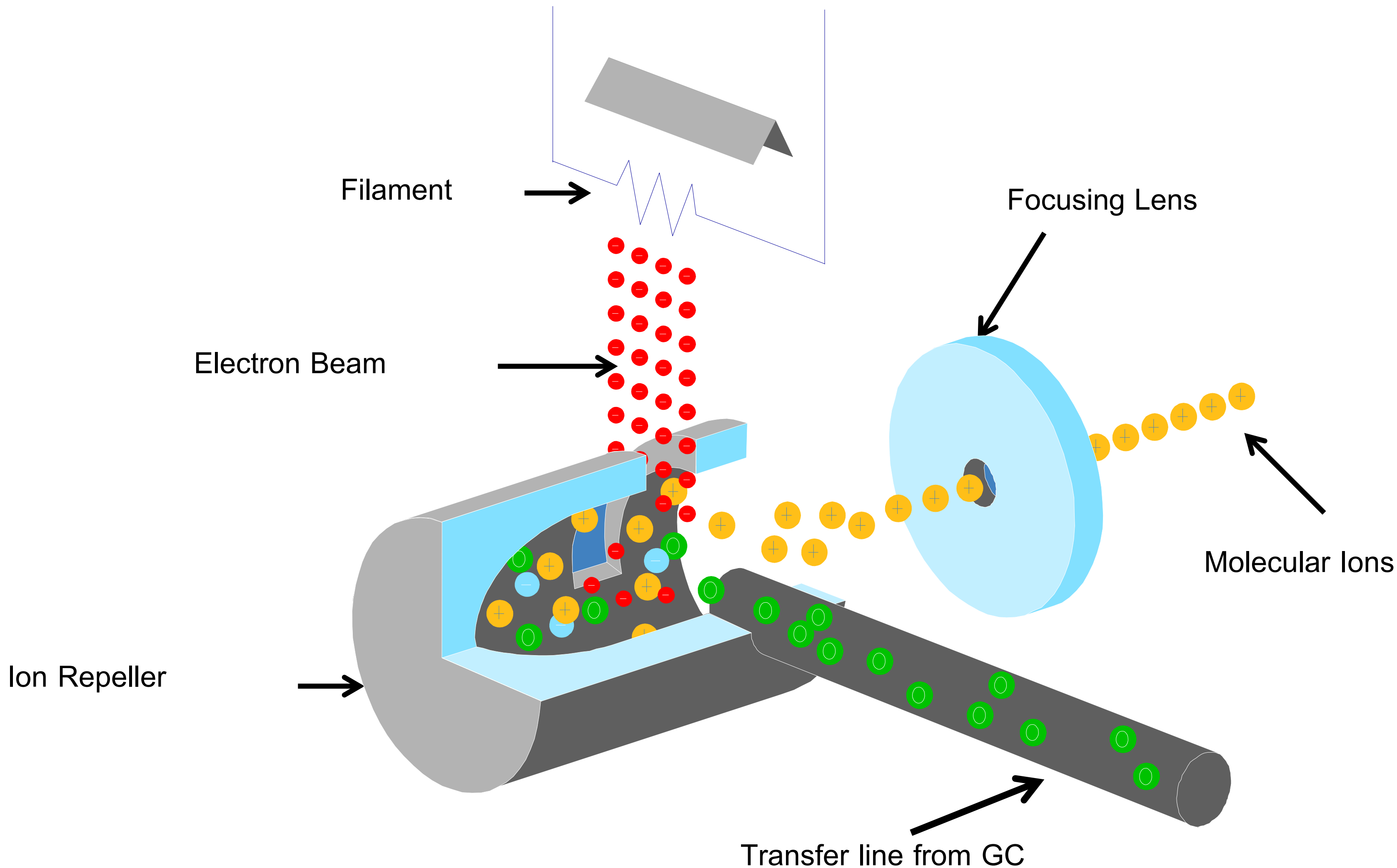


Ionization Methods in GCMS

- Electron Ionization

- Chemical Ionization
  - Positive Ion Chemical Ionization
  - Negative Ion Chemical Ionization

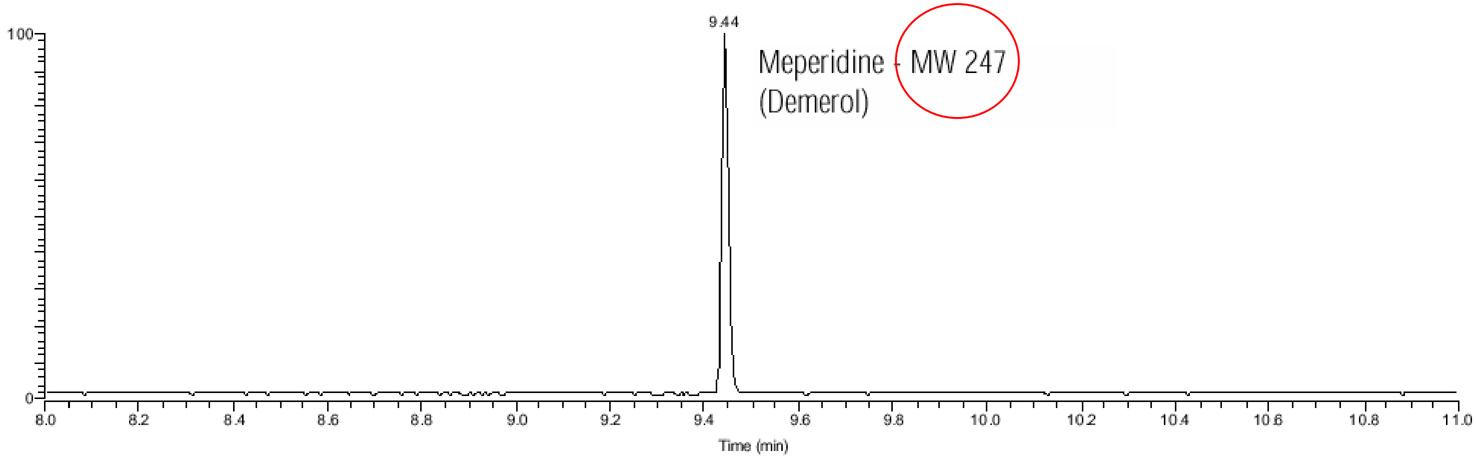
Electron Ionization

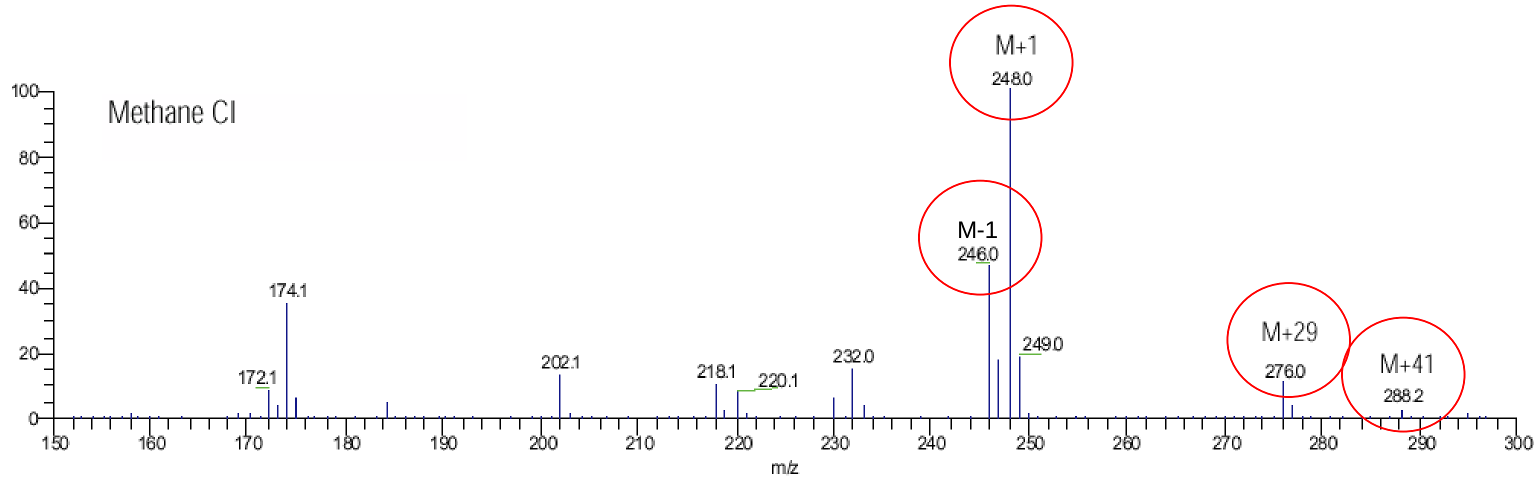


PCI : Positive Ion Chemical Ionization

- Reagent gas reacts with electrons to form primary ions
- Primary ions react with CH_4 and form collided ions
- Collided ions react with sample molecules (soft ionization) and form molecular ions
- Molecular ions present in form of $[M+H]^+$, $[M-H]^+$, $[M+17]^+$,$[M+29]^+$, $[M+41]^+$
- Main use is molecular weight confirmation (clean spectra)
- Example of reagent gas : CH_4, Isobutane

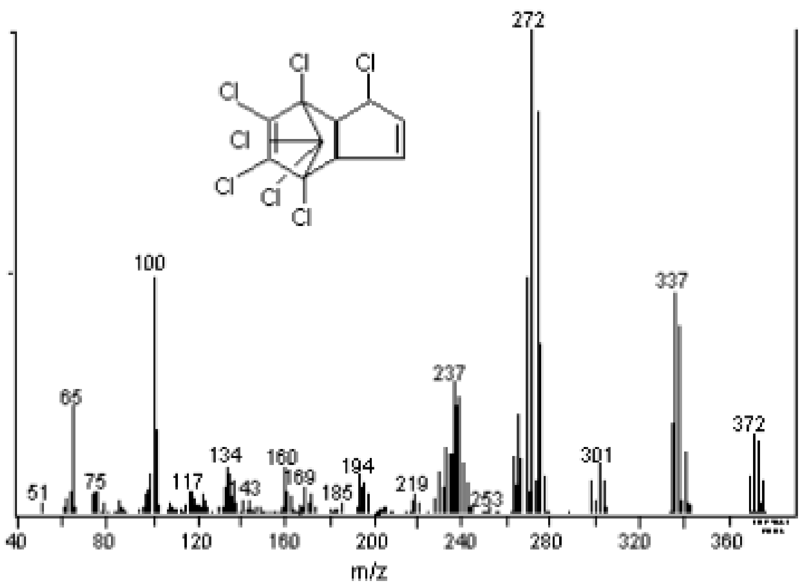
Adduct Formation in PICI





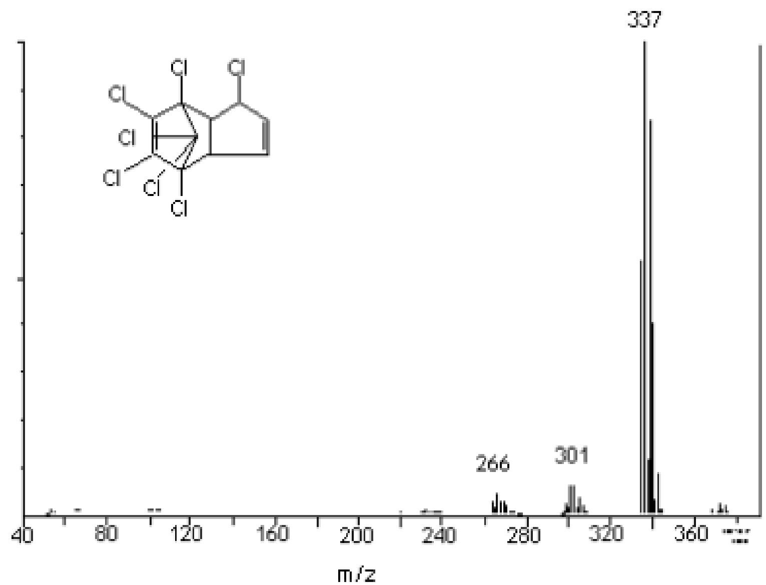
EI versus PCI for Pesticides (heptachlor MW 336)

EI Spectrum of Heptachlor



Intensity is low for any single m/z ion.

PICI Spectrum of Heptachlor



Intensity is concentrated in $[M+H]^+$ ion.

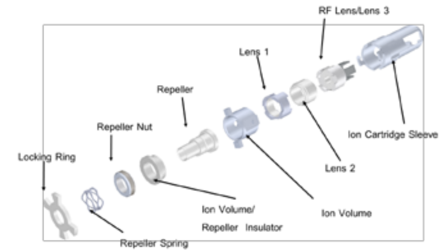
Spectrum is simpler.

In PICI, sample is not fragmented. Therefore, PICI will provide higher ion intensity

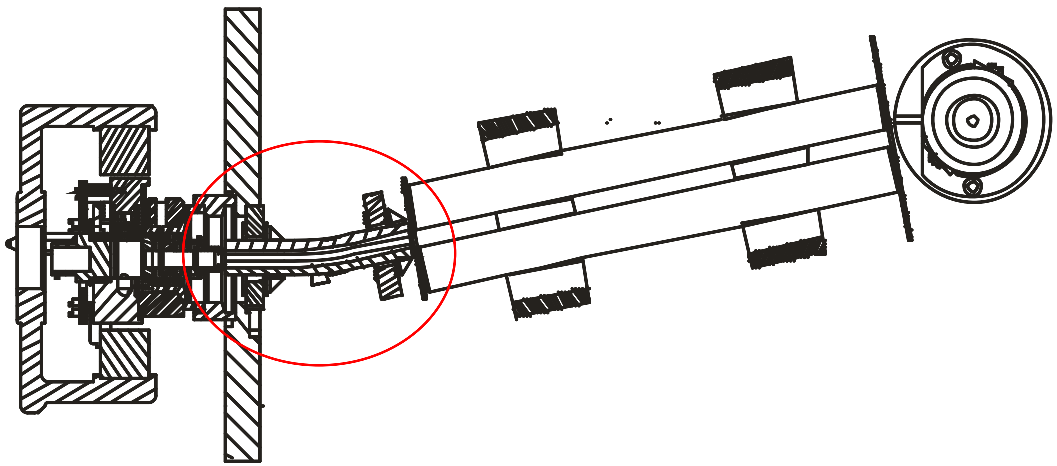
Which means better detection limit when compares with EI

Ion Transmission

- Lens :
  - Applying appropriate voltage to lens can be used to induced molecular ions into certain distance and direction



- Multi-pole rods :
  - quadrupoles , hexapoles, octapoles are widely used to transmit ions for longer distance

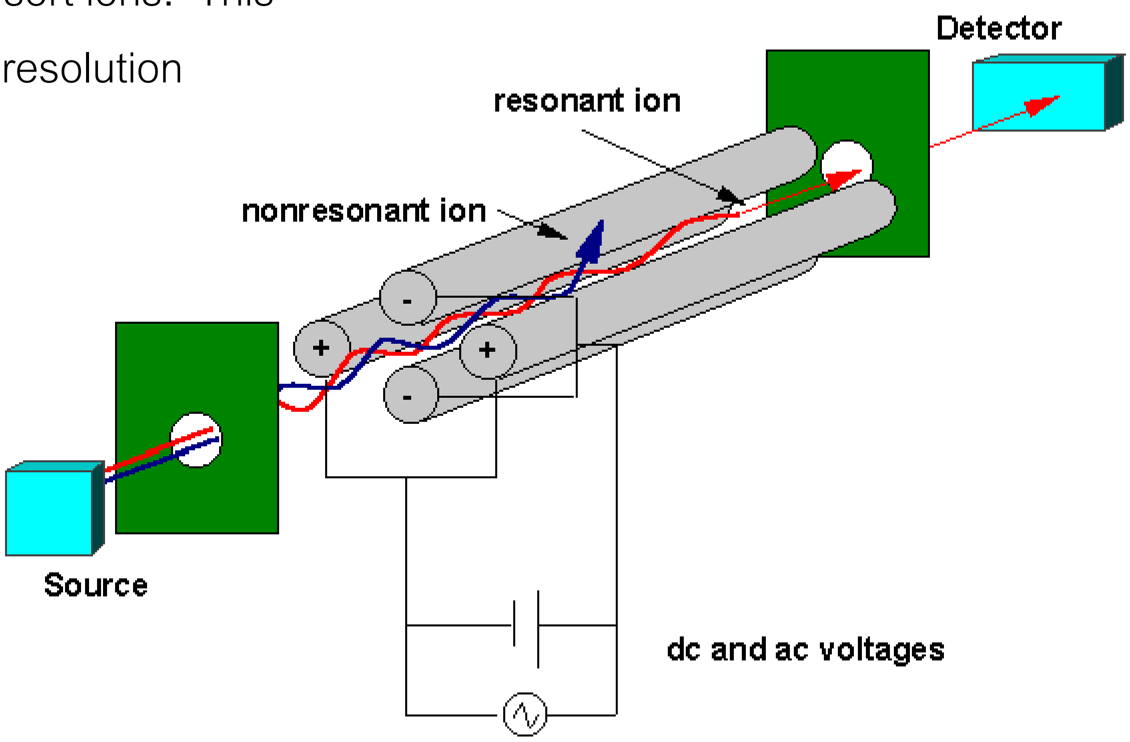


Mass Analyzers

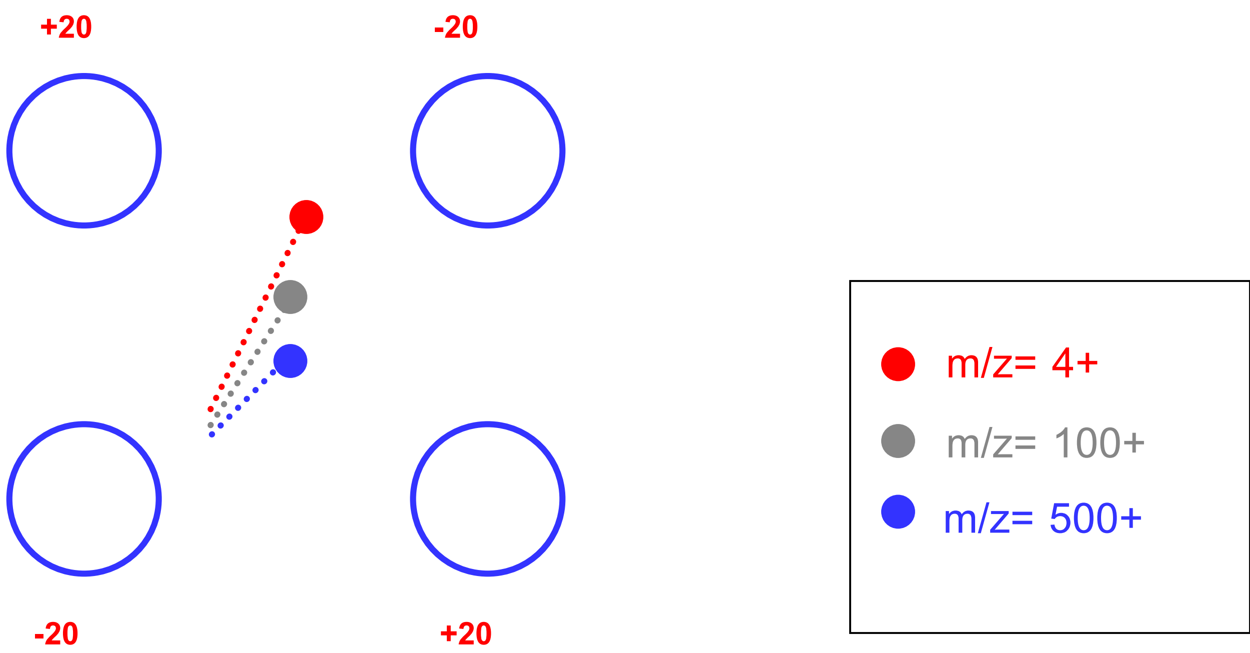
1. Quadrupole *or* Single Quadrupole
2. Triple Quadrupole
3. Time of Flight (TOF)
4. Magnetic Sector
5. Orbitrap

Single Quadrupole Mass Analyzer

Quadrupole - consists of two sets on opposing rods. This mass analyzer uses a combination of RF(AC) and DC modulation to sort ions. This analyzer provides nominal mass resolution

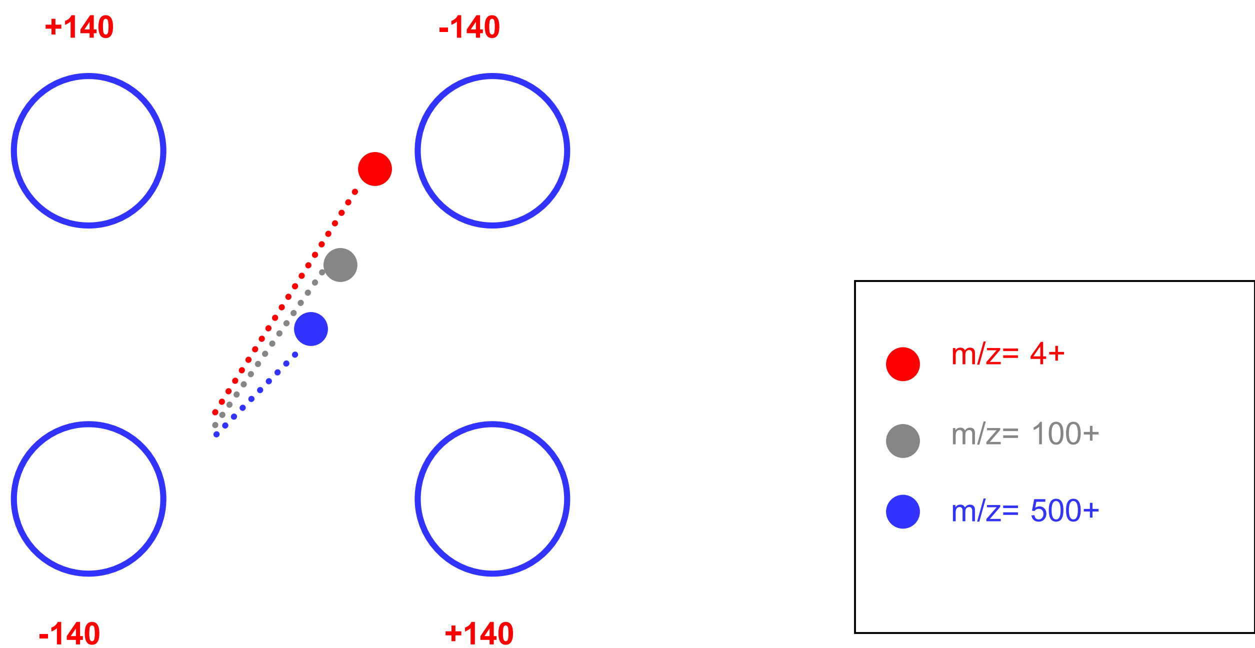


Quadupole Mass Filter Operation



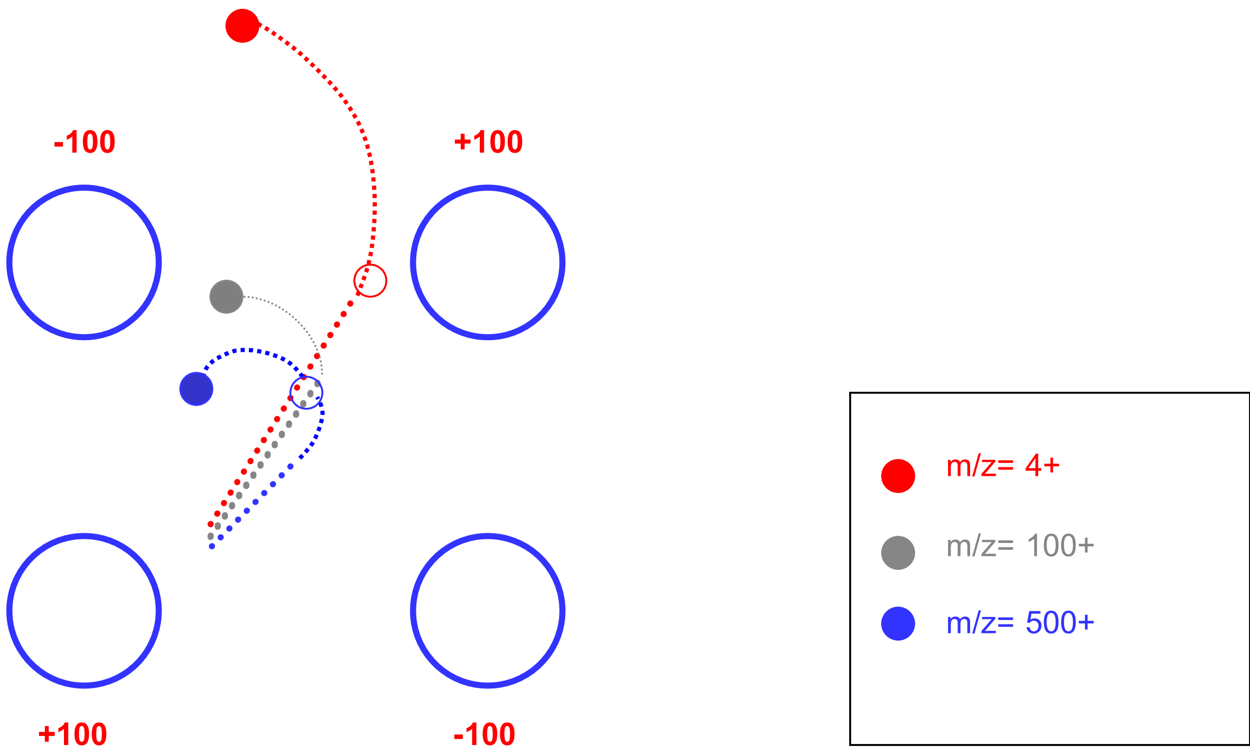
At Time 0

Quadupole Mass Filter Operation



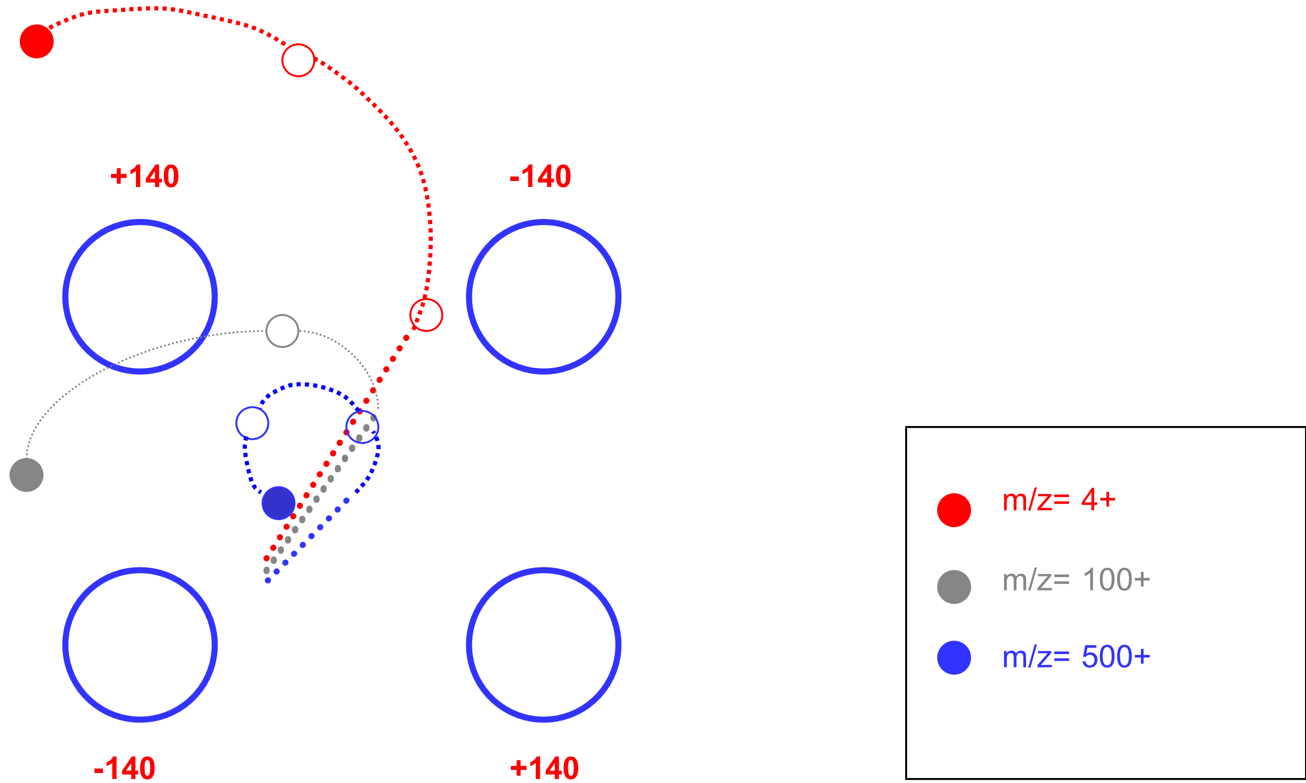
At Time 1

Quadupole Mass Filter Operation



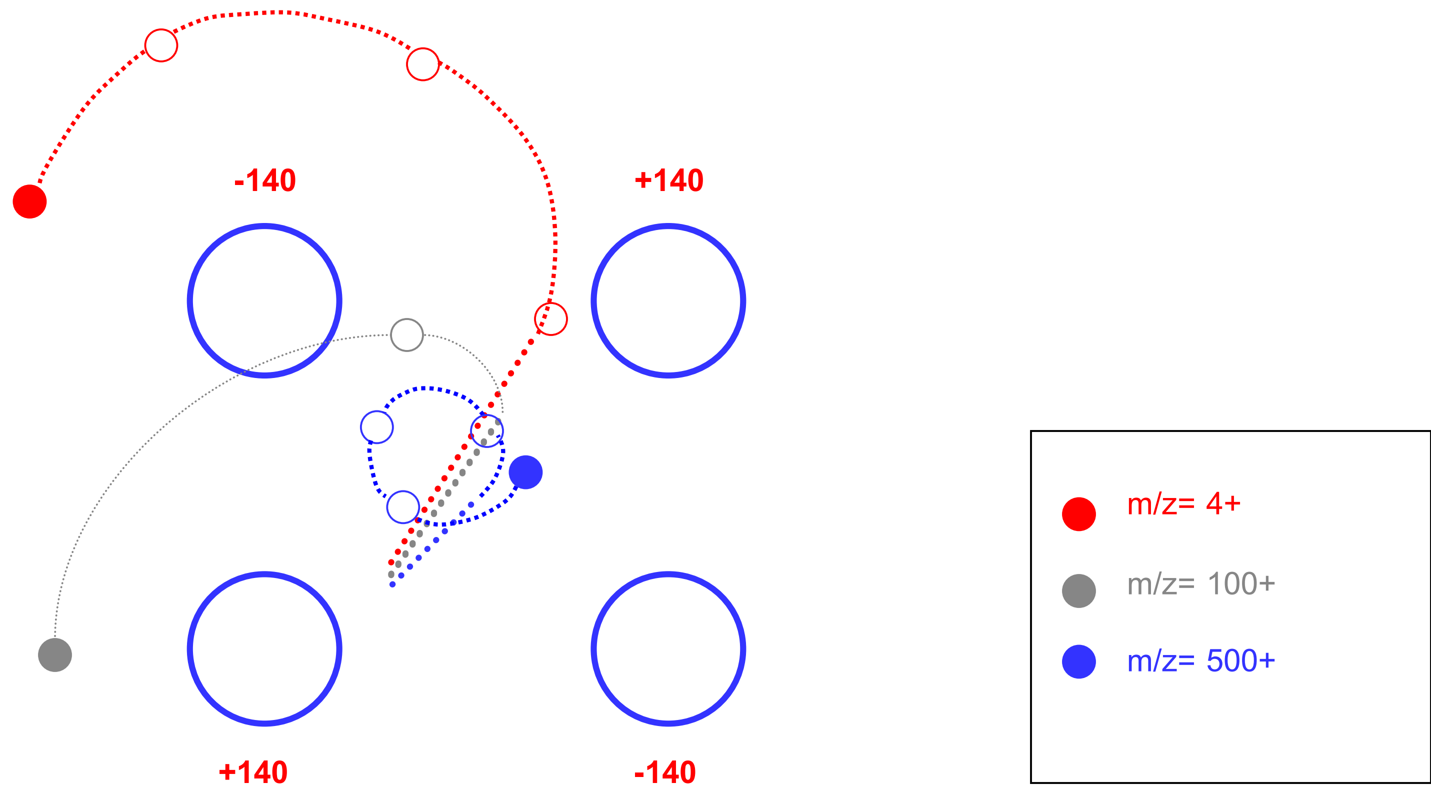
At Time = 2

Quadupole Mass Filter Operation



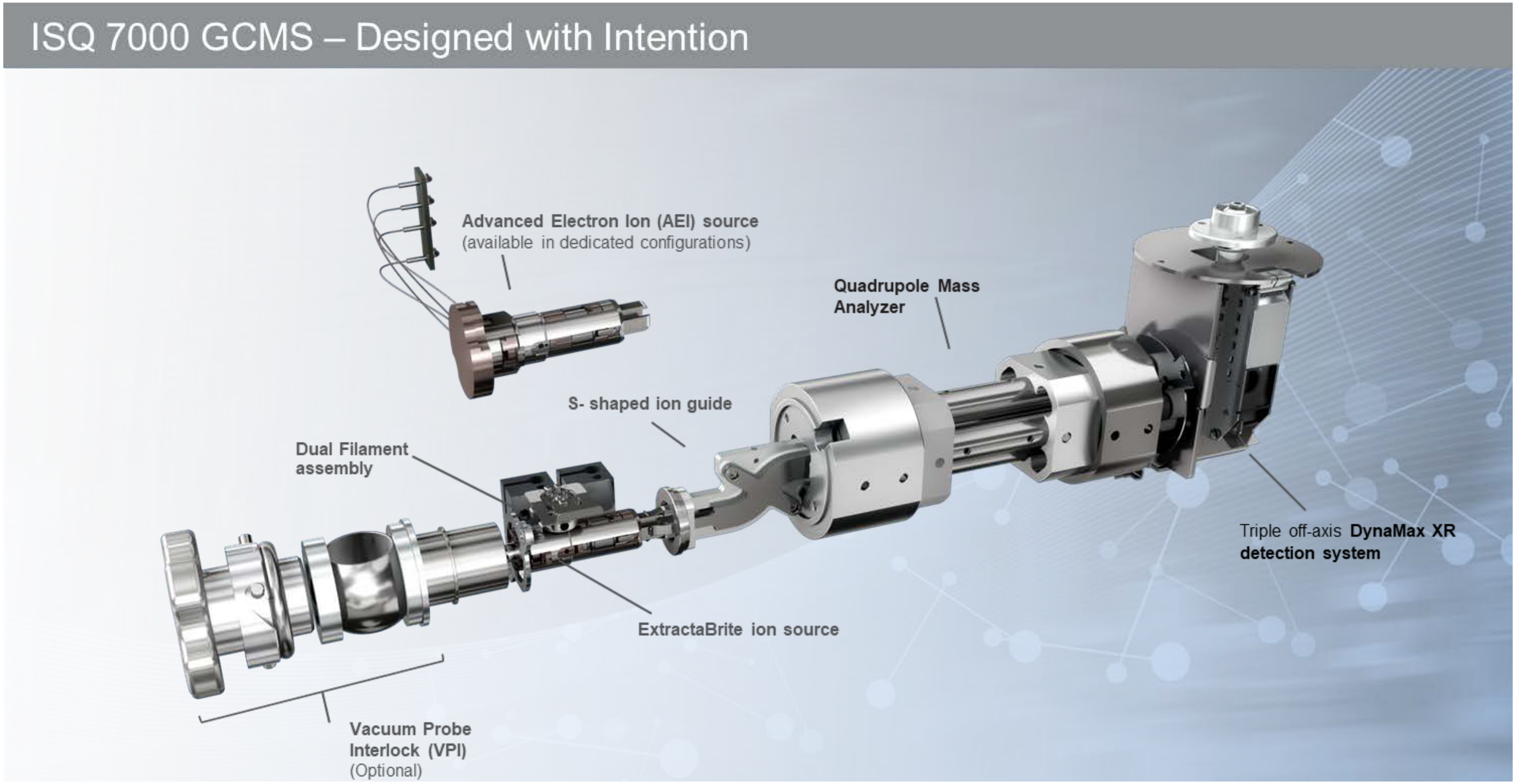
At Time = 3

Quadupole Mass Filter Operation



At Time = 4

ISQ 7000 GCMS – Designed with Intention

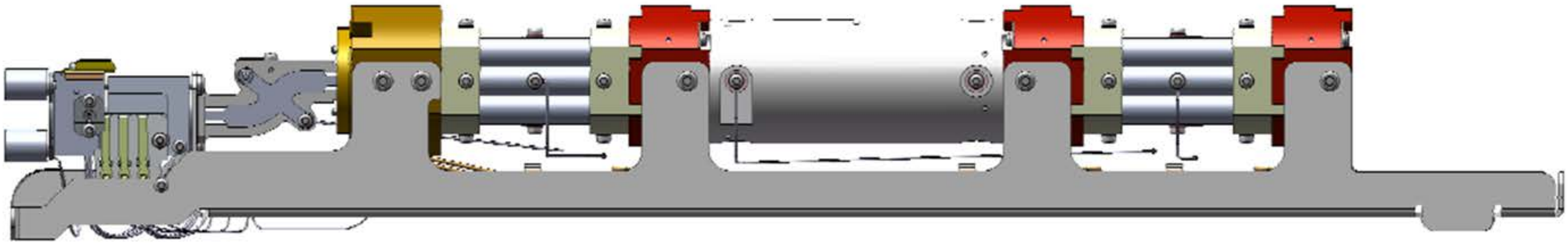


Operation modes in Single Quad MS

- Full Scan
  - Set a mass range to cover sample's molecular ions
  - Get spectrum for identification
  - Good for unknown but Low sensitivity
- Selected Ion Monitoring (SIM)
  - Select one or a few molecular ions those will be monitored
  - Lost spectrum information
  - High sensitivity but may cause false positive error

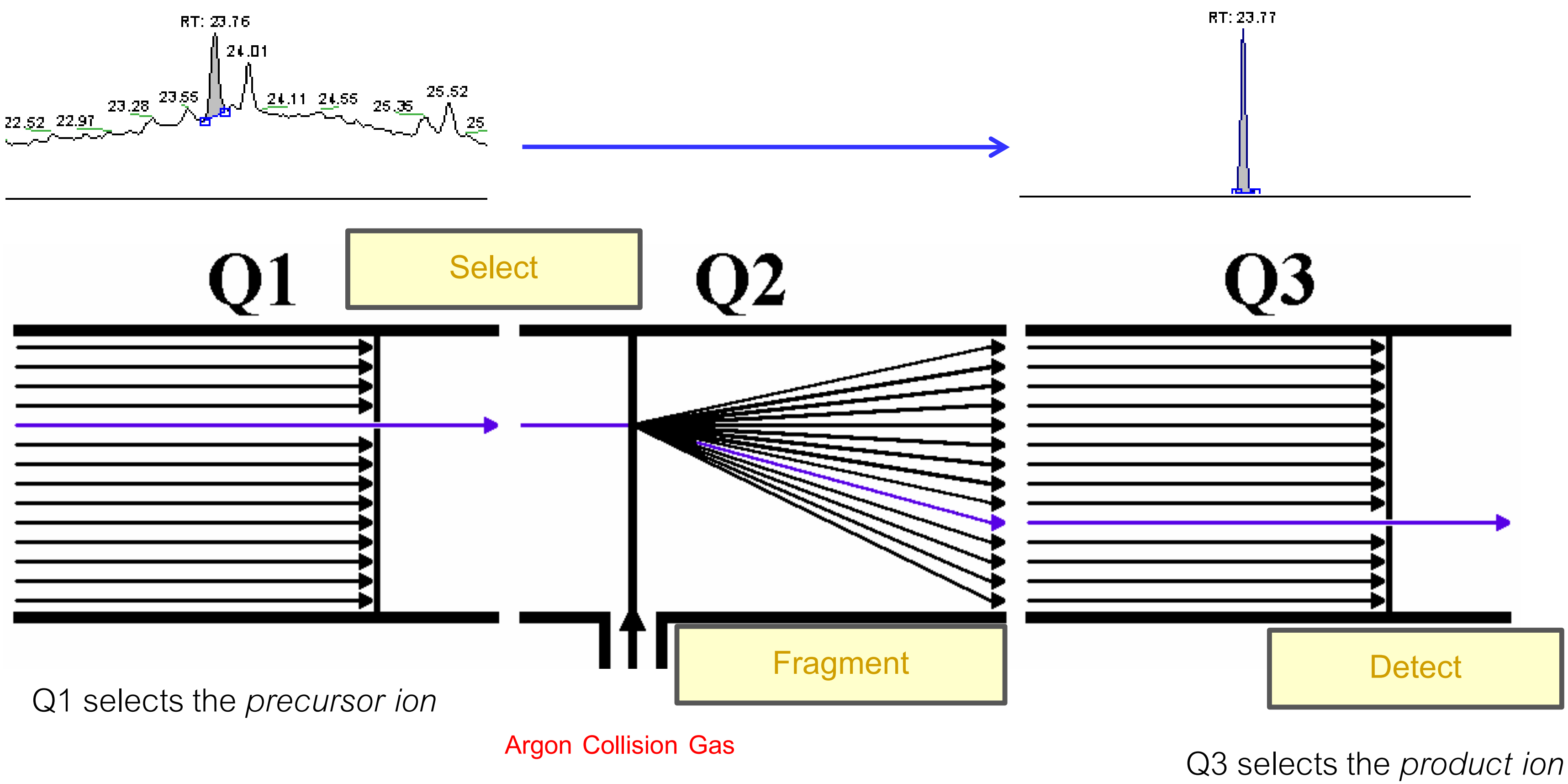
Triple Quadrupole Mass Analyzer

- Triple Quadrupole - consists of two sets of quadrupole with one collision cell in between. This mass analyzer uses a combination of RF and DC modulation to sort ions just like single quadrupole. Q1 and Q3 work like mass filter (using RF and DC) while Q2 works as a Collision cell (RF only and Collided gas). Q1 can selected any precursor (parent mass) and pass it into collision cell (Q2) where precursor are fragmented and pass through Q3 for ion sorting again. This analyzer provides high sensitivity with fast confirmation analysis.

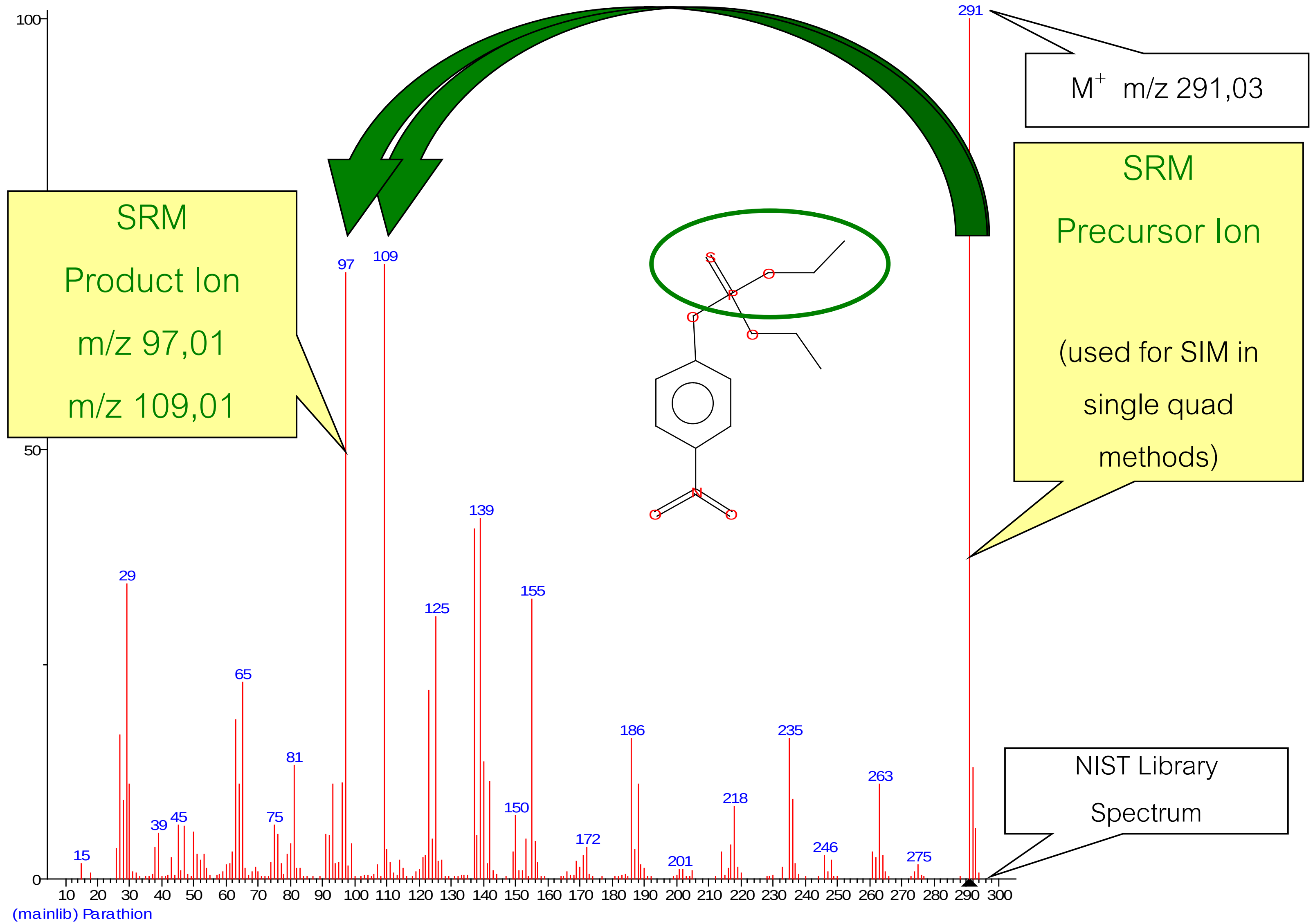


Selected Reaction Monitoring (SRM or MRM)

Quantitation of target compounds in matrix samples



Structure Specific Selectivity by QQQ : Parathion-Ethyl



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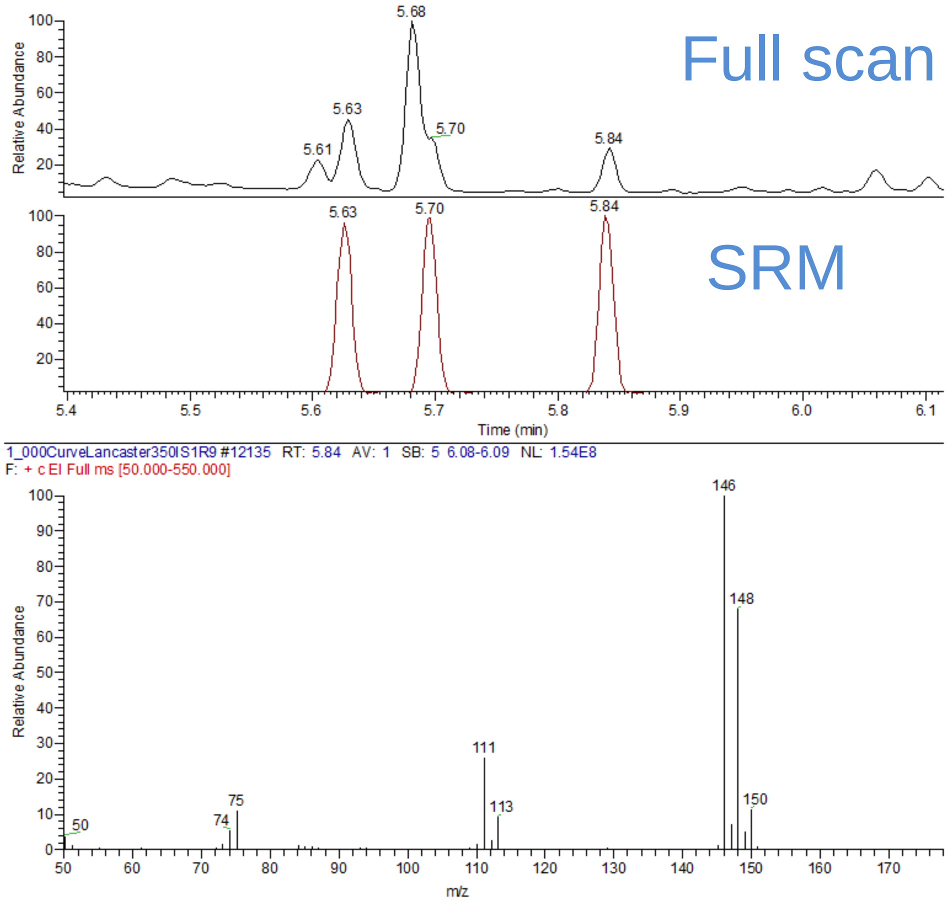
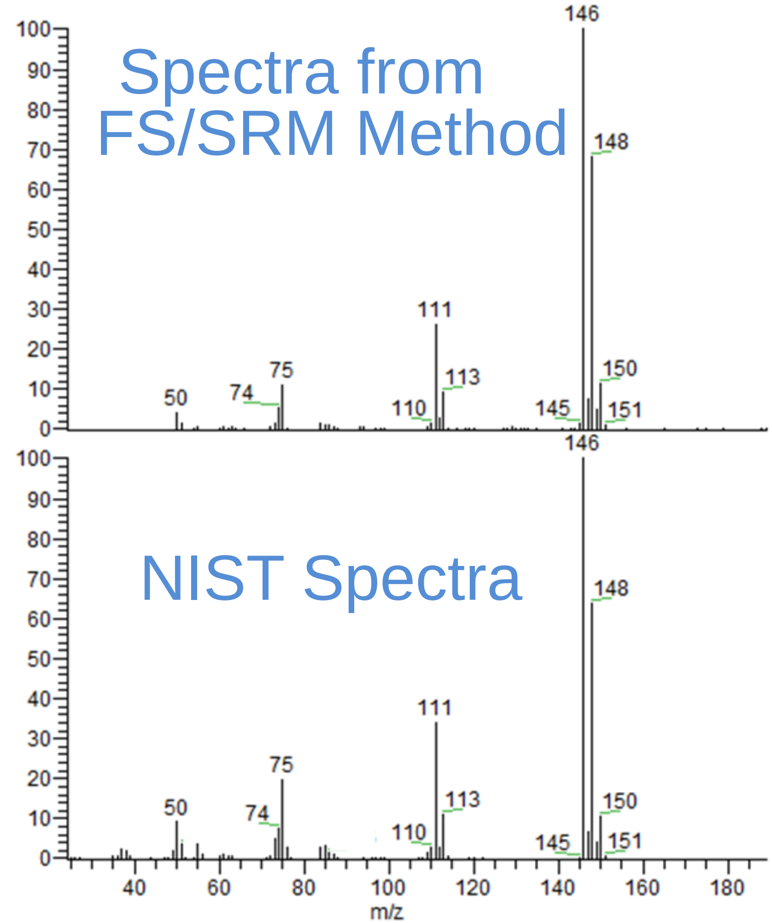
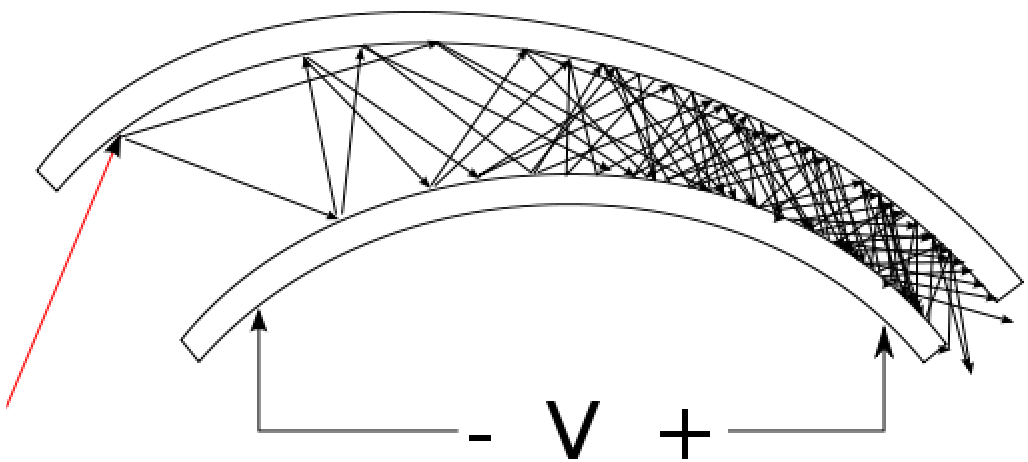
Full scan/SRM Acquisition





Detector : Dynode Electron Multiplier

- Dynode converses Molecular ions into electron
  - Continuous Dynode
  - Discrete Dynode
- Electron are then sent to multiplier for signal enhancing



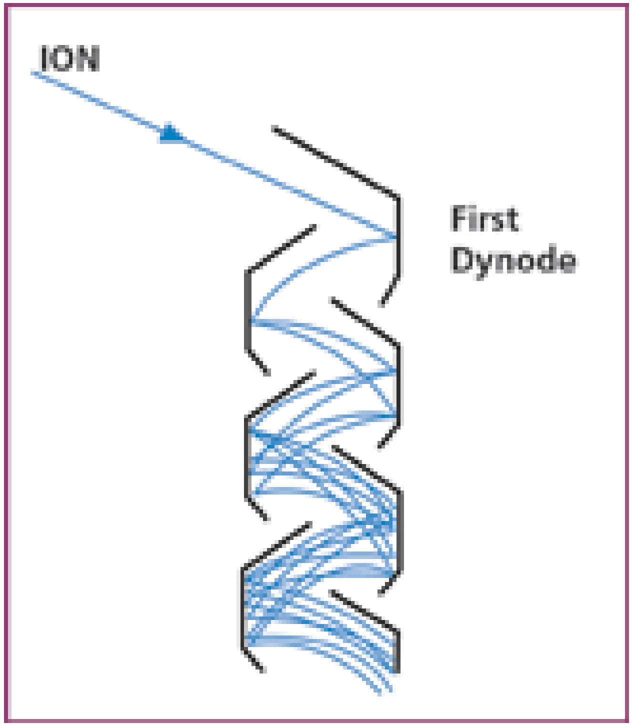
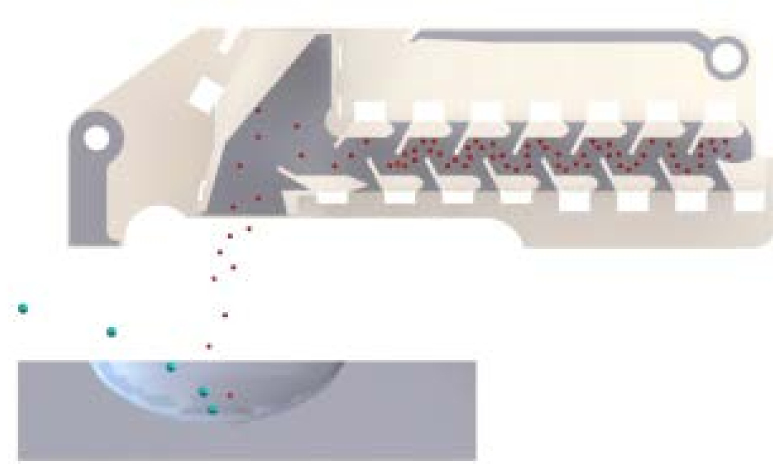


Photo courtesy from SGE & ETP, Wikipedia

Off –axis dynode and EM

- Off axis dynode
  - High voltage is applied (+/-10 KV) for high signal (accelerate ion velocity from mass analyzer to dynode)
  - Induces only molecular ions to hit dynode
- Electrons from dynode hit internal wall of EM.
- Multiplication process amplifies for more signals

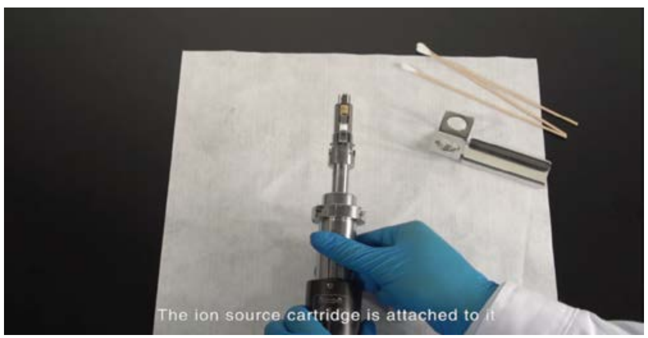
Electron Multiplier



Dynode

Sci Spec

User maintenance :Vaccum probe inter lock

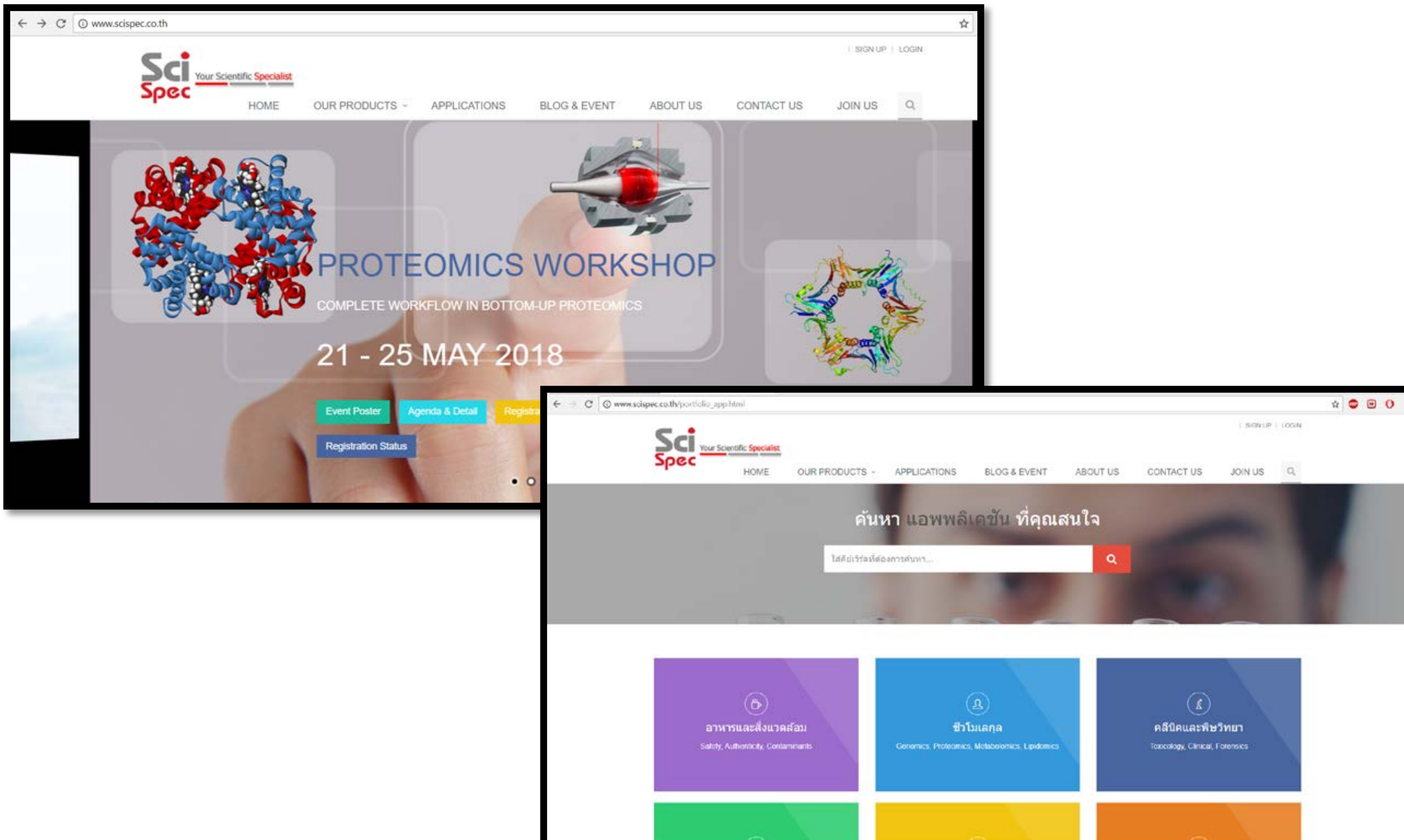


Vacuum probe inter lock

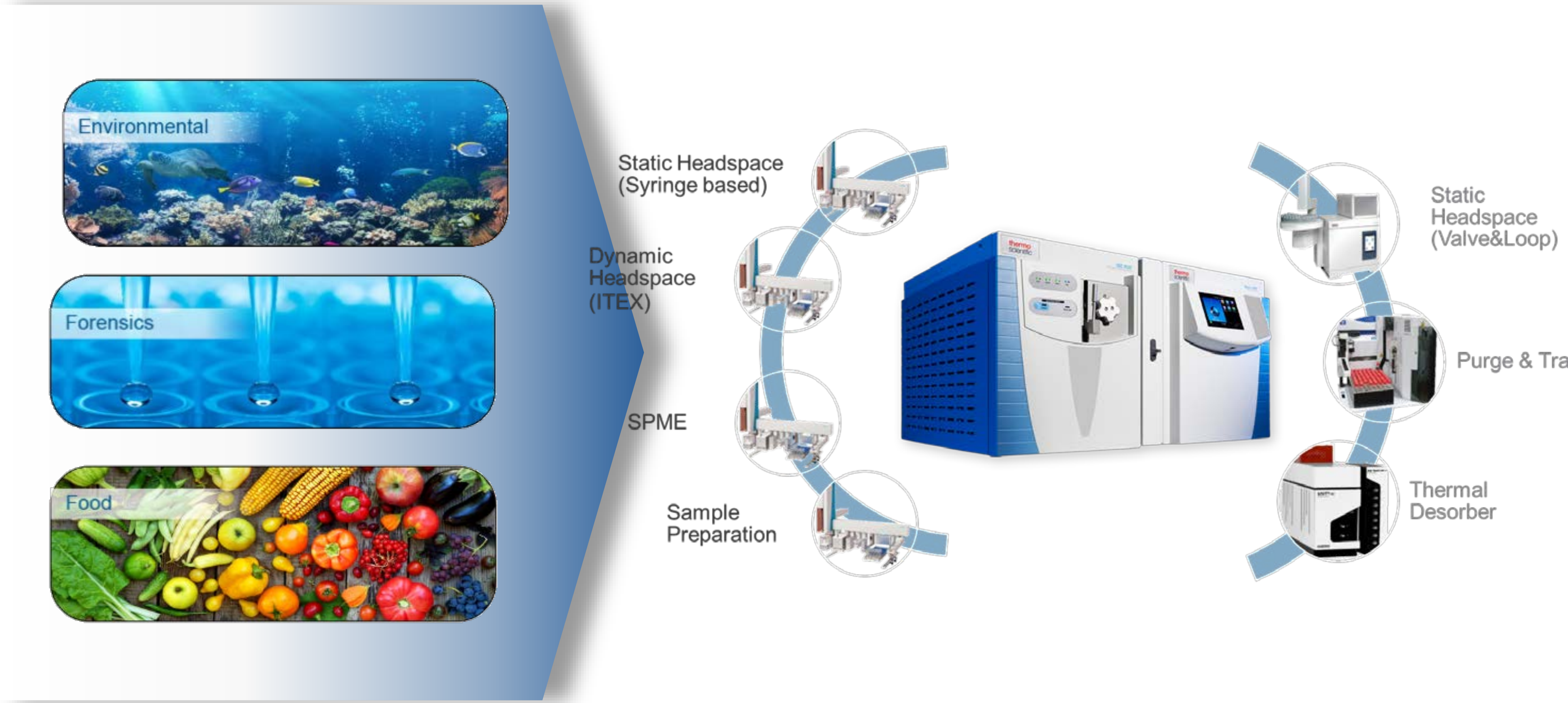
Application……

Scispec website : Application……

www.scispec.co.th



GC and GCMS application support.



Multi-Residue Pesticide Analysis in Herbal Products Using Accelerated Solvent Extraction with a Triple Quadrupole GC-MS/MS System

ASE™ 350

Multi-Residue Pesticide Analysis in Herbal Products Using Accelerated Solvent Extraction with a Triple Quadrupole GC-MS/MS System

Sample Preparation

Dried leaves , fruits or seeds and other herbal products

Weight 10 g of sample.

Mixed with DE and load into the extraction cells.

Concentrated Sample and injection with GC

ASE™ 350

Sample weight	10 g
Extraction solvent	Ethylacetate/cyclo-Hexane 1:1, same as GPC solvent
Temperature	120 °C
Pressure	100 bar
Extraction time	5 min, 1 cycle
Flushing with solvent	60% of cell volume
Flushing with nitrogen	100 s

Multi-Residue Pesticide Analysis in Herbal Products Using Accelerated Solvent Extraction with a Triple Quadrupole GC-MS/MS System

GC : Condition

Injector PTV	Splitless mode
Base temperature	50 °C
Transfer	10 °C/s to 250 °C, until end of run
Flow	Constant flow, 1.2 mL/min, helium
Analytical column	40 m, ID 0.18 mm, 0.18 µm film, 5%-phenyl phase (5MS type)
Pre-column	5 m, ID 0.18 mm, empty deactivated, no backflush
Column oven	Temperature programmed
Start	70 °C, for 1.50 min
Ramp 1	15 °C/min to 190 °C
Ramp 2	7 °C/min to 290 °C, 12 min
Transfer line	250 °C

MS/MS : Condition

Ion source temperature	220 °C
MRM Detection	Timed SRM mode (see Appendix)

Sci Spec

SRM : More than 80 compound

Pesticide Name	RT (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (V)
Difluorobenzamid Degradation (Isocyanat)	6.93	152.93	90.01	20
Difluorobenzamid Degradation (Isocyanat)	6.93	152.93	125.01	20
Carbofuran 1	8.80	149.06	121.05	10
Carbofuran 1	8.80	164.08	149.07	10
Difluorobenzamid Degradation	8.62	141.00	63.11	25
Difluorobenzamid Degradation	8.62	141.00	113.09	15
Biphenyl-d10_ISTD	9.24	160.00	160.16	10
Biphenyl	9.28	154.08	153.08	15
Biphenyl	9.28	153.08	152.08	15
Carbofuran-3-hydroxy 1	10.43	137.05	81.01	18
Carbofuran-3-hydroxy 1	10.43	180.05	137.01	15
Tetrahydrophthalimid	10.84	151.04	79.01	25
Tetrahydrophthalimid	10.84	151.04	122.09	10
O-Phenylphenol	11.00	170.07	141.06	20
O-Phenylphenol	11.00	170.07	115.05	20
Molinate	11.10	187.10	126.07	10
Molinate	11.10	126.07	98.05	5
Chlorfenprop methyl	11.59	196.00	165.00	10
Chlorfenprop methyl	11.59	165.00	137.00	10
Fenobucarb	11.20	121.07	77.05	15
Fenobucarb	11.20	150.09	121.07	10
Propachlor	11.76	176.06	120.04	10
Propachlor	11.76	120.04	92.03	10
Propachlor	11.76	169.06	120.04	10
Propachlor	11.76	196.07	120.04	10
Cycloate	11.98	154.10	83.05	10
Cycloate	11.98	215.13	154.10	5
Diphenylamin	11.49	169.01	168.09	20
Diphenylamin	11.49	169.01	167.09	20
Chloropropham	12.26	213.06	127.03	15
Chloropropham	12.26	213.06	171.04	10
Phosmet-oxon	12.09	160.00	132.96	15
Phosmet-oxon	12.09	104.00	75.88	10
Phosmet-oxon	12.09	160.00	76.96	20
Prometon	13.10	225.16	183.13	10
Prometon	13.10	225.16	210.15	10
Carbofuran 2	13.13	149.06	121.05	10
Carbofuran 2	13.13	164.08	149.07	10
Profluralin	13.22	318.10	199.06	15
Profluralin	13.22	330.23	252.45	25
Swep	13.46	187.05	123.95	18
Swep	13.46	219.11	174.02	15
Trietazine	13.48	229.14	200.14	15
Trietazine	13.48	214.14	186.10	15
Dimethipin	13.53	117.98	57.97	10

Pesticide Name	RT (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (V)
Dimethipin	13.53	210.10	76.02	10
Terbutylazin	12.97	214.10	132.06	10
Terbutylazin	12.97	214.10	104.05	10
Propyzamid	13.04	173.01	145.01	15
Propyzamid	13.04	173.01	109.01	18
Propyzamid	13.04	175.02	147.01	15
Propyzamid	13.04	254.02	226.02	15
Isocarbamide	13.67	142.03	70.01	15
Isocarbamide	13.67	142.03	113.01	10
Dinoseb	13.92	211.13	116.99	15
Dinoseb	13.92	211.13	163.11	10
Terbazil	13.42	161.05	88.03	15
Terbazil	13.42	160.05	76.02	15
Bromocylen	14.37	358.79	242.85	15
Bromocylen	14.37	356.93	241.24	15
Dimethenamid	14.60	230.06	154.04	10
Dimethenamid	14.60	232.06	154.04	10
Dimethachlor	14.61	197.08	148.06	10
Dimethachlor	14.61	199.08	148.06	10
Acetochlor	14.65	174.11	146.15	15
Acetochlor	14.65	223.19	147.17	10
Desmetryn	14.68	213.11	171.08	10
Desmetryn	14.68	213.11	198.10	10
Flurprimidol	14.77	269.12	106.98	20
Alachlor	14.26	188.10	160.07	10
Alachlor	14.26	188.10	130.12	25
Alachlor	14.26	237.14	160.15	10
Metribuzin	14.14	198.08	82.03	20
Metribuzin	14.14	198.08	89.04	16
Propanil	15.00	217.01	161.00	10
Propanil	15.00	219.01	163.00	10
Fipronildesulfinyl	14.15	333.00	231.20	20
Fipronildesulfinyl	14.15	333.00	281.30	20
Carbofuran-3-hydroxy 2	15.02	137.05	81.01	18
Carbofuran-3-hydroxy 2	15.02	180.05	137.01	15
Prometryn	14.49	241.14	184.10	15
Prometryn	14.49	226.13	184.10	12
Tridiphan	15.18	186.94	158.94	15
Tridiphan	15.18	219.09	184.09	20
Ethofumesat	14.80	206.82	160.86	10
Ethofumesat	14.80	285.75	206.82	12
Pentanochlor	15.73	141.05	106.05	15
Pentanochlor	15.73	239.05	141.05	15
Chlorpyrifos	15.78	257.97	165.98	20
Chlorpyrifos	15.78	314.05	258.18	15
Bromacil	15.03	205.01	188.01	15
Bromacil	15.03	207.01	190.01	15

Pesticide Name	RT (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (V)
Anthrachinon	15.44	207.97	151.99	20
Anthrachinon	15.44	180.04	152.05	15
Anthrachinon	15.44	207.97	180.10	10
Nithrothal isopropyl	16.09	236.08	194.07	10
Nithrothal isopropyl	16.09	236.08	148.05	20
Triadimefon	15.41	208.07	181.06	10
Triadimefon	15.41	210.07	183.06	10
Tiocarbazil	16.15	156.08	100.05	8
Tiocarbazil	16.15	279.10	156.07	6
Tetraconazol	15.39	336.02	218.01	20
Tetraconazol	15.39	338.02	220.01	20
Butralin	15.54	266.14	220.11	15
Butralin	15.54	266.14	190.10	15
Dicapthon	15.44	262.00	262.00	9
Dicapthon	15.44	262.00	216.00	13
Crufomat	16.30	256.20	226.15	25
Crufomat	16.30	276.20	182.09	10
Allethrin	16.17	123.07	80.98	10
Allethrin	16.17	136.04	92.98	10
Dinobuton	16.89	163.06	116.04	15
Dinobuton	16.89	211.07	117.04	18
Penconazol	16.89	248.06	157.04	25
Penconazol	16.89	248.06	192.04	15
Pyrifenox 1	16.17	262.03	192.02	20
Pyrifenox 1	16.17	262.03	200.02	20
Pyrifenox 2	16.81	262.03	192.02	20
Pyrifenox 2	16.81	262.03	200.02	20
Famophos (Famphur)	20.16	218.07	108.94	15
Famophos (Famphur)	20.16	218.07	126.95	20
Iprodion Degradation	18.63	186.87	123.99	20
Iprodion Degradation	18.63	186.87	159.02	15
Iprodion Degradation	18.63	243.94	187.02	10
Iprodion	20.57	314.06	245.25	15
Iprodion	20.57	186.99	123.87	20
Iprodion	20.57	316.00	247.35	15
Iprodion	20.57	316.00	273.11	10
Propiconazol 1	19.38	259.02	173.02	20
Propiconazol 1	19.38	172.94	144.91	15
Propiconazol 2	19.54	259.02	173.02	20
Propiconazol 2	19.54	172.94	144.91	15
Pyraflufen-ethyl	20.30	412.02	349.02	15
Pyraflufen-ethyl	20.30	349.02	307.02	15
Clodinafop-propargyl	20.36	349.05	266.04	15
Clodinafop-propargyl	20.36	349.05	238.04	15
Lenacil	20.70	153.05	136.06	15

Pesticide Name	RT (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (V)
Paclobutrazole	17.75	238.11	127.06	15
Chinomethionat	17.78	206.06	147.98	15
Chinomethionat	17.78	234.08	206.06	10
Napropamid	18.07	271.16	128.07	5
Napropamid	18.07	128.07	72.04	10
Flutriafol	18.11	219.07	123.04	15
Flutriafol	18.11	123.04	75.03	15
Flurodifen	18.14	190.02	126.01	10
Flurodifen	18.14	190.02	146.01	5
Bisphenol A	18.17	213.14	119.06	15
Bisphenol A	18.17	213.14	164.99	20
Bisphenol A	18.17	228.15	213.07	10
Chlorfenson_ISTD	18.20	302.00	110.90	20
Hexaconazol	18.22	214.08	159.07	20
Hexaconazol	18.22	214.08	151.98	25
Imazalil	18.24	172.96	144.96	15
Imazalil	18.24	172.96	108.95	25
Isoprothiolan	18.24	203.99	117.95	7
Isoprothiolan	18.24	203.99	84.90	25
Isoprothiolan	18.24	290.06	118.03	15
Flamprop-methyl	18.39	230.05	170.04	10
Flamprop-methyl	18.39	276.06	105.02	10
Kresoximmethyl	18.48	206.10	131.09	15
Kresoximmethyl	18.48	206.10	116.01	10
Buprofezin	18.51	175.08	116.96	20
Buprofezin	18.51	175.08	131.99	15
Buprofezin	18.51	249.16	105.93	20

Pesticide Name	RT (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (V)
Azinphosmethyl	22.95	160.00	132.00	10
Azinphosmethyl	22.95	160.00	104.64	10
Pyriproxyfen	23.06	136.00	77.92	20
Fenamirol	23.55	251.02	139.01	15
Fenamirol	23.55	330.03	139.01	10
Pyridaben	24.50	364.14	309.12	5
Pyridaben	24.50	309.12	147.06	15
Fluquinconazol	24.59	340.01	298.01	22
Fluquinconazol	24.59	342.01	300.01	22
Etofenprox	26.05	163.09	107.06	16
Etofenprox	26.05	163.09	135.07	10
Etofenprox	26.05	376.14	135.02	30
Etofenprox	26.05	376.14	163.09	10
Silafluofen	26.25	179.00	151.00	7
Silafluofen	26.25	286.13	258.12	15
Difenconazol 1	26.91	323.05	265.04	15
Difenconazol 1	26.91	325.05	267.04	20
Difenconazol 2	27.05	323.05	265.04	15
Difenconazol 2	27.05	325.05	267.04	20
Indoxacarb	28.55	264.02	176.14	10
Indoxacarb	28.55	264.02	148.03	20
Indoxacarb	28.55	321.05	289.34	10

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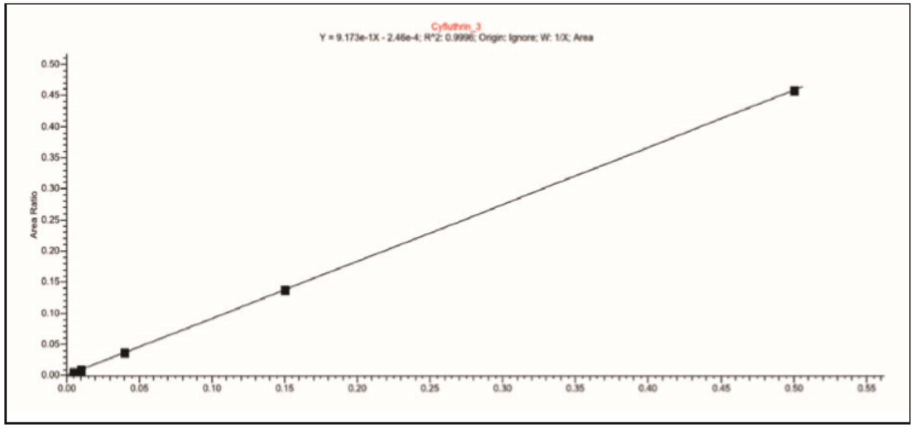
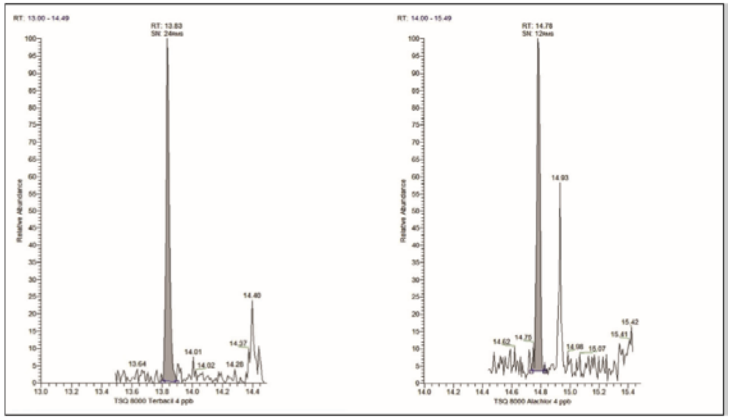
Calibration and Detection limit.

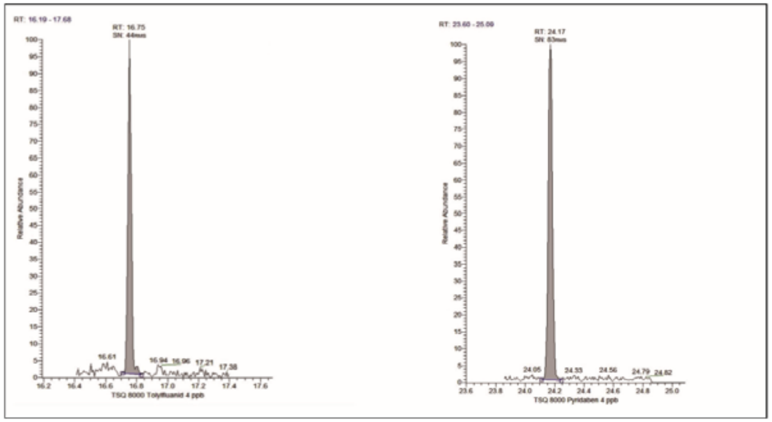
Calibration level : 0.004 µg/mL to 1.0 µg/mL(This range represents an analyte concentration of 0.01 to 2.5 mg/kg in the samples)



Pesticide	RT [min]	S/N @ 4 ppb
Terbacil	13:83	24
Alachlor	14:78	12
Tolylfluanid	16:75	44
Pyridaben	24:17	83

Sensitivity (LOD)





Terbacill Alachor Tolyfluanid Pyridaben

Sample Result…..

Sample Matrix	Pesticide Residues Found	Concentration (mg/kg)
Dried Herbs	o-Phenylphenol	0.017
Dried Herbs	Tebuconazol	0.023
Dried Fruit	Diflubenzuron	0.049
Dried Fruit	Myclobutanil	0.023
Dried Fruit	Propargit	0.479
Dried Fruit	Tebuconazol	0.081
Dried Fruit	Difenconazol	0.013
Dried Herbs	Picoxystrobin	0.228
Dried Herbs	Picoxystrobin	0.233
Dried Herbs	o-Phenylphenol	0.011
Herbal Tea	o-Phenylphenol	0.014
Herbal Tea	o-Phenylphenol	0.011
Herbal Tea	Terbutylazin	0.016


Multi-Residue Pesticide Analysis in Herbal Products Using Accelerated Solvent Extraction with a Triple Quadrupole GC-MS/MS System

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Nicole Rueckert, Johann Kirchner, Elmar Häfner, Phytolab GmbH & Co KG, Vestenbergsgreuth, Germany

Application Note 52291

Key Words
Pesticides, Tea, Herbal products, ASE, SRM, MRM, Multi-residue analysis, TSQ 8000 GC-MS/MS

Introduction
The residue analysis of pesticides has developed in recent years into a comprehensive methodology for the detection of many hundreds of potential contaminating compounds. A multi-residue method for herbal products and teas is faced with additional challenges from the worldwide

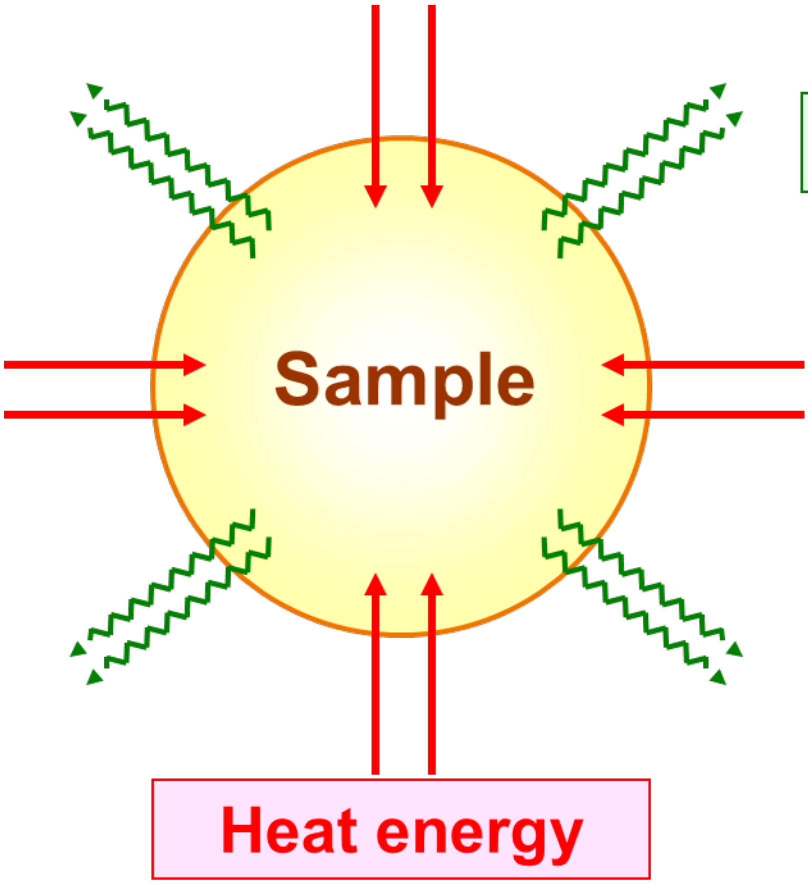
Thermo SCIENTIFIC

Application note 52291

- PY-GCMS

Pyrolyzer

Information from polymeric Materials by Heating



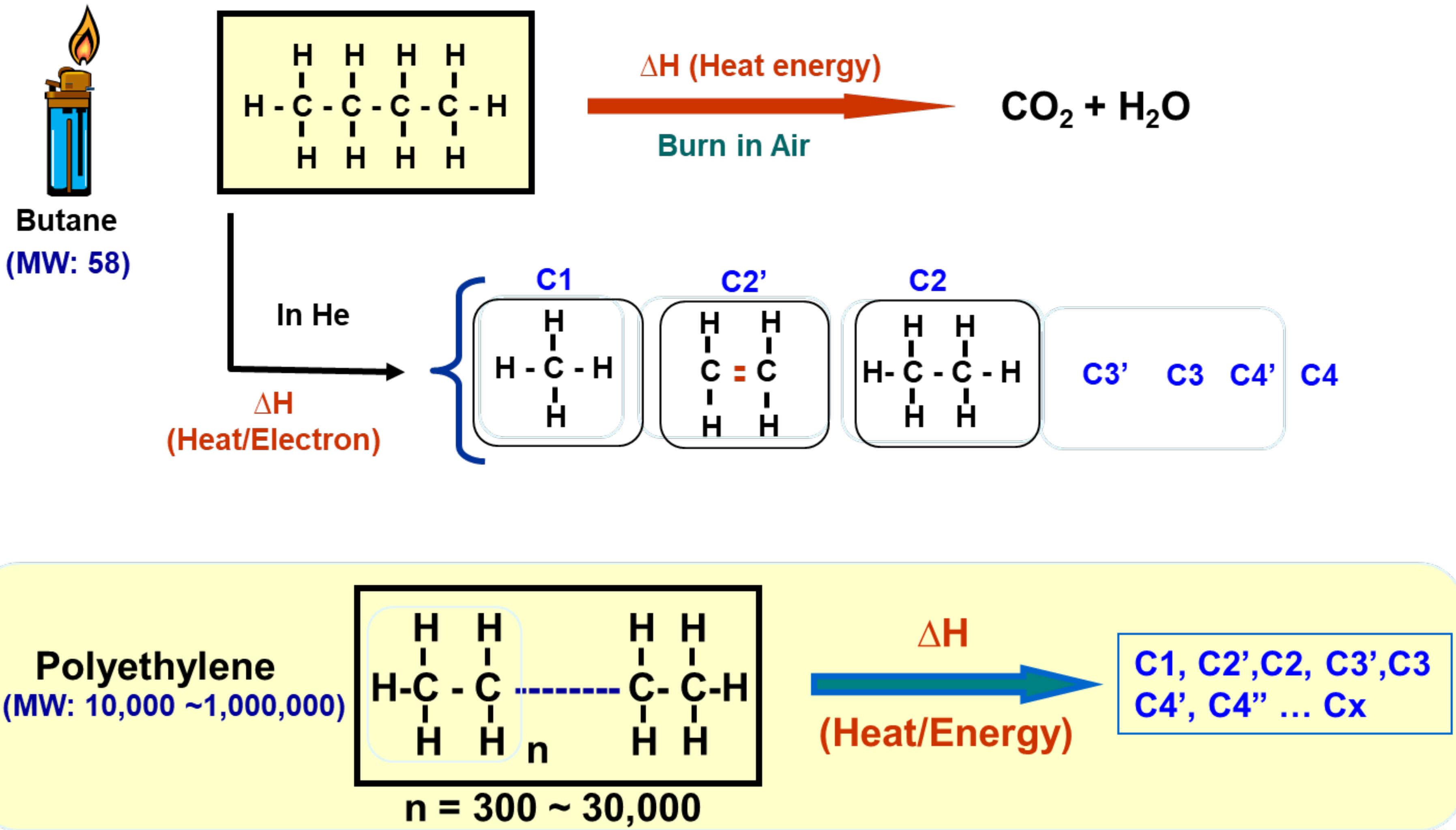
Information

- Weight loss: **TGA**
- Enthalpy change: **DTA, DSC**
- Mechanical change: **TMA, Dilatometry**
- Evolved gas
  - volume: **EGA (volume of gas)**
  - qualification & quantification:

Py-GC/MS
TD-GC/MS
UV/Py-GC/MS
EGA/MS
Py/MS

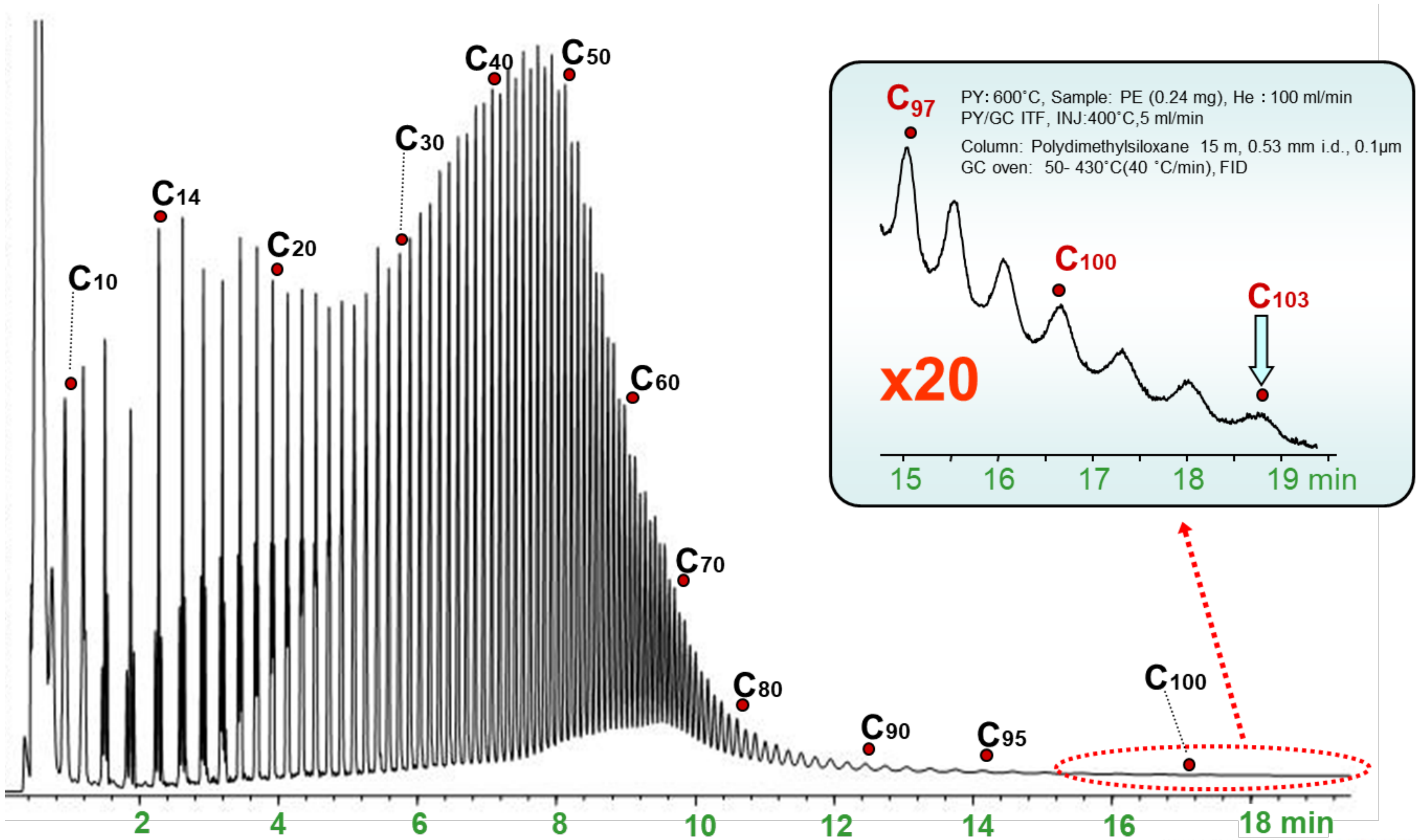
Pyrolyzer

Pyrolysis of Polymeric materials and pyrolyzates



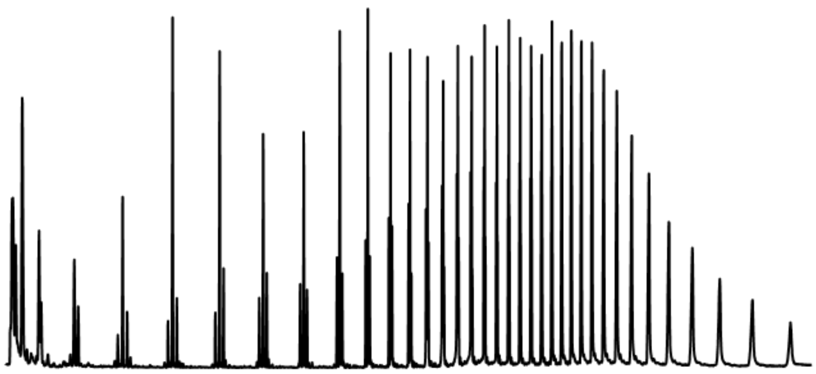
Pyrolyzer

Typical pyrogram of polyethylene at 600ºC

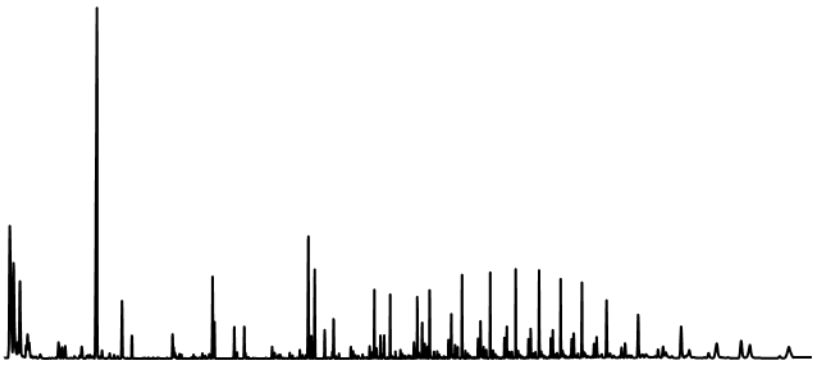


Typical pyrograms

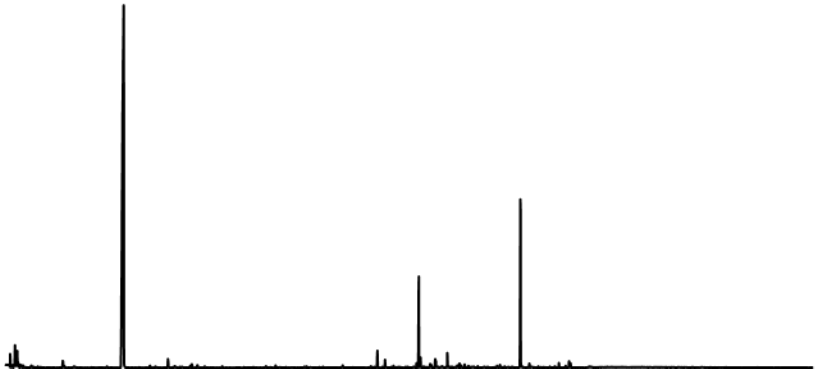
Polyethylene



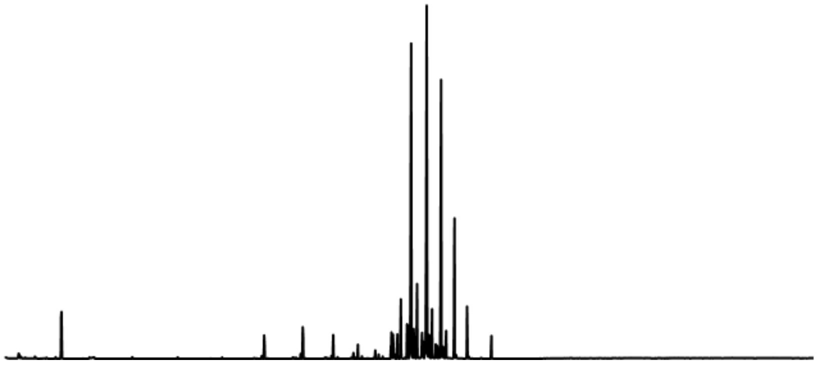
Polypropylene



Polystyrene



Higher methacrylate copolymer

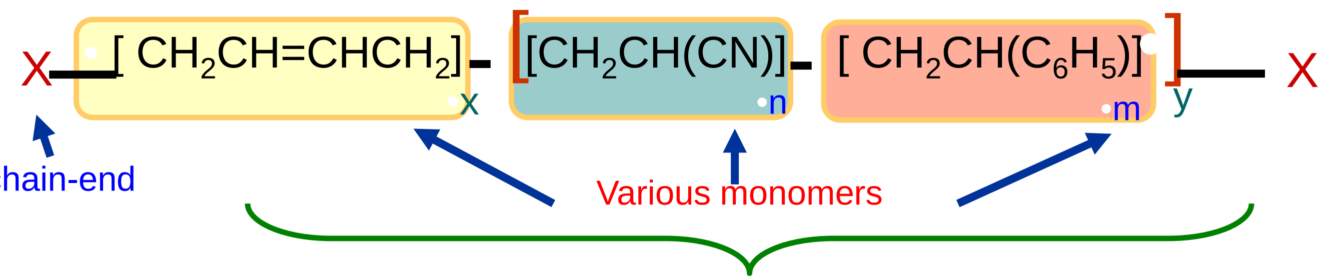


Characterization of Polymers by PY-GC/MS

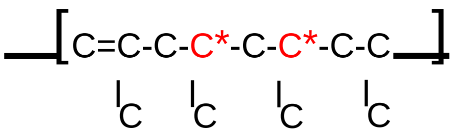
A: Identification of polymeric materials

Unknown materials (PP/ PVC/ SBR?)

B: Structural characterization of polymers



MW / Sequence distributions (x-n-m-n..)
Blend or copolymer (X+Y or X&Y)



stereo regularity

C: Mechanisms and kinetics of polymer degradation

D: Qualitative and quantitative analysis of additives

ตัวอย่างการวิเคราะห์ด้วย PY-GCMS

สภาวะเครื่อง GCMS

- Injector
  - Temperature 300 °C
  - Split 200:1
  - Carrier gas flow 1.0 ml/min
- Oven
  - Initial 70 °C hold 1min ramp 1 ; 10 °C/min to 320 °C hold 8 min.
- MS
  - Temperature 250 °C
  - Scan 35-550 amu.

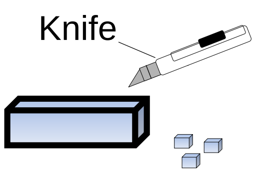
สภาวะเครื่อง Pyrolyzer

- Single-Shot Analysis
- Furnace Temperature 600 °C
- Interface Temperature 300 °C

Sample cup

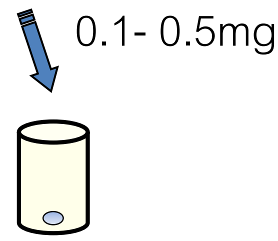
ขั้นตอนการเตรียมตัวอย่าง

Step 1



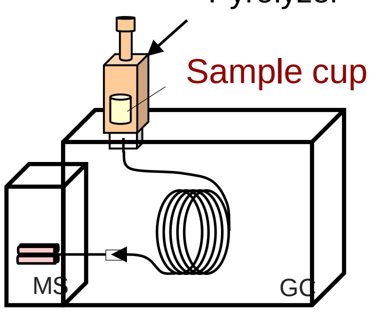
Step 2

Place a sample in the sample cup



No solvent extraction

Step 3



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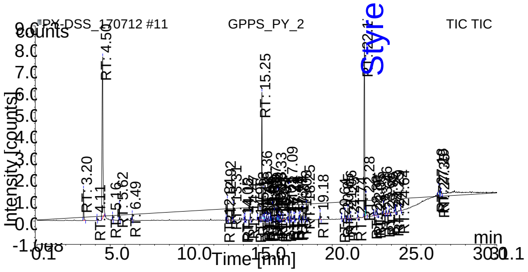
ผลการวิเคราะห์ตัวอย่างที่ 1



Styrene

EMDP

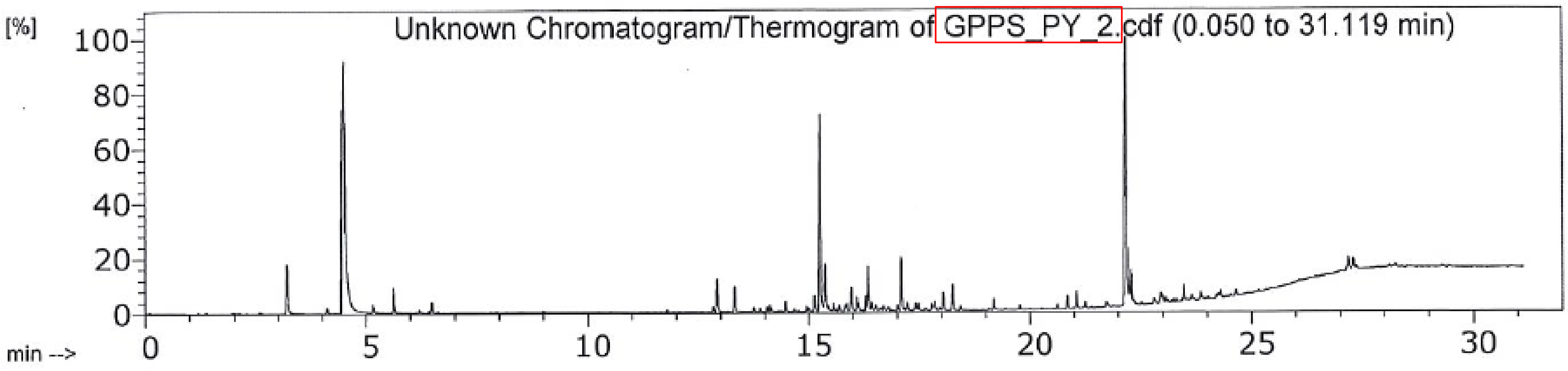
(2,3-diphenylcyclopropyl) methyl phenyl sulfoxide ,*trans*

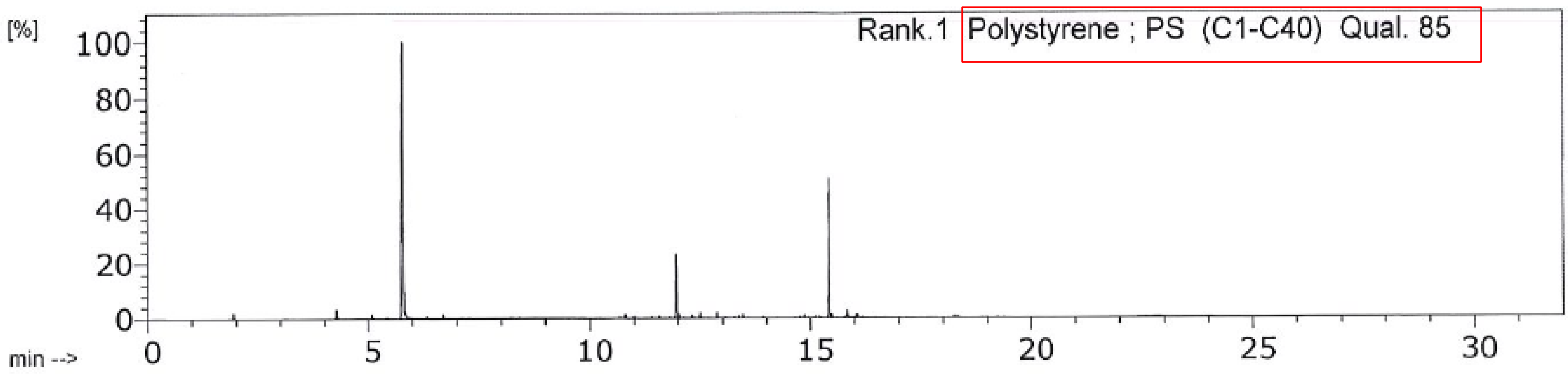
Toluene

Ethyl benzene

Methyl styrene

ผลการวิเคราะห์เมื่อเทียบกับฐานข้อมูลด้านพอลิเมอร์ผ่านซอฟแวร์ F-Search

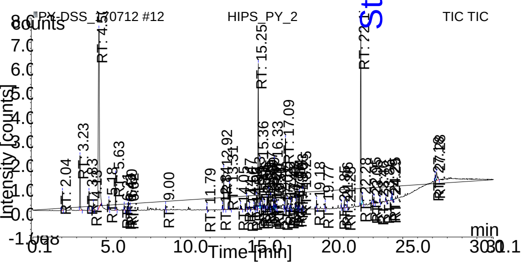




Rank.2 : Styrene-butadiene copolymer ABA block, 85% styrene (C1-C40) Qual. 85

Rank.3 : Acrylonitrile-Butadiene-Styrene copolymer ; ABS (C1-C40) Qual.84

ผลการวิเคราะห์ตัวอย่างที่ 2



Styrene

EMDP

(2,3-diphenylcyclopropyl) methyl phenyl sulfoxide, *trans*

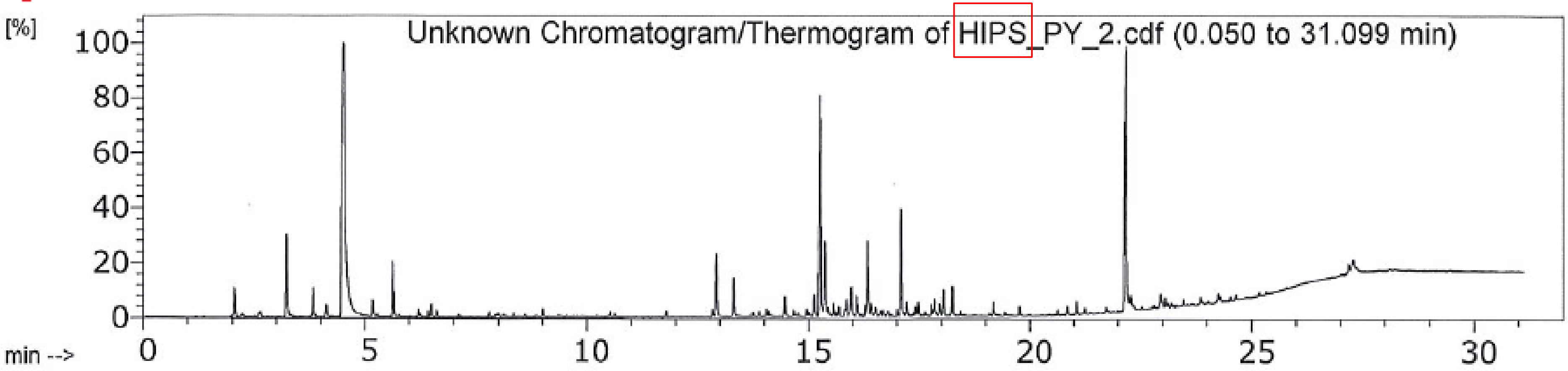
1,3 - butadiene

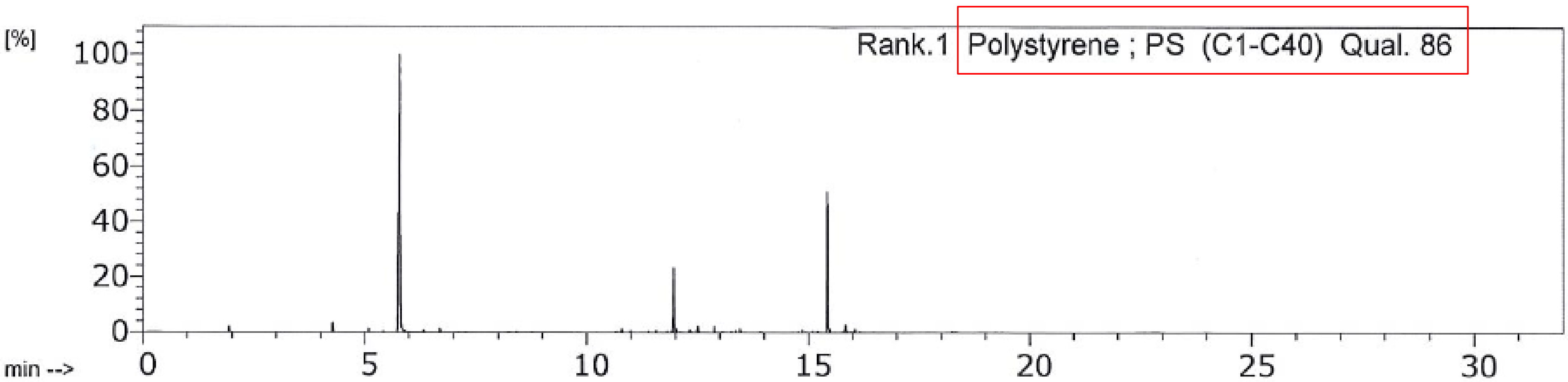
Toluene

Ethyl benzene

Methyl styrene

ผลการวิเคราะห์เมื่อเทียบกับฐานข้อมูลด้านพอลิเมอร์ ผ่านซอฟแวร์ F-Search

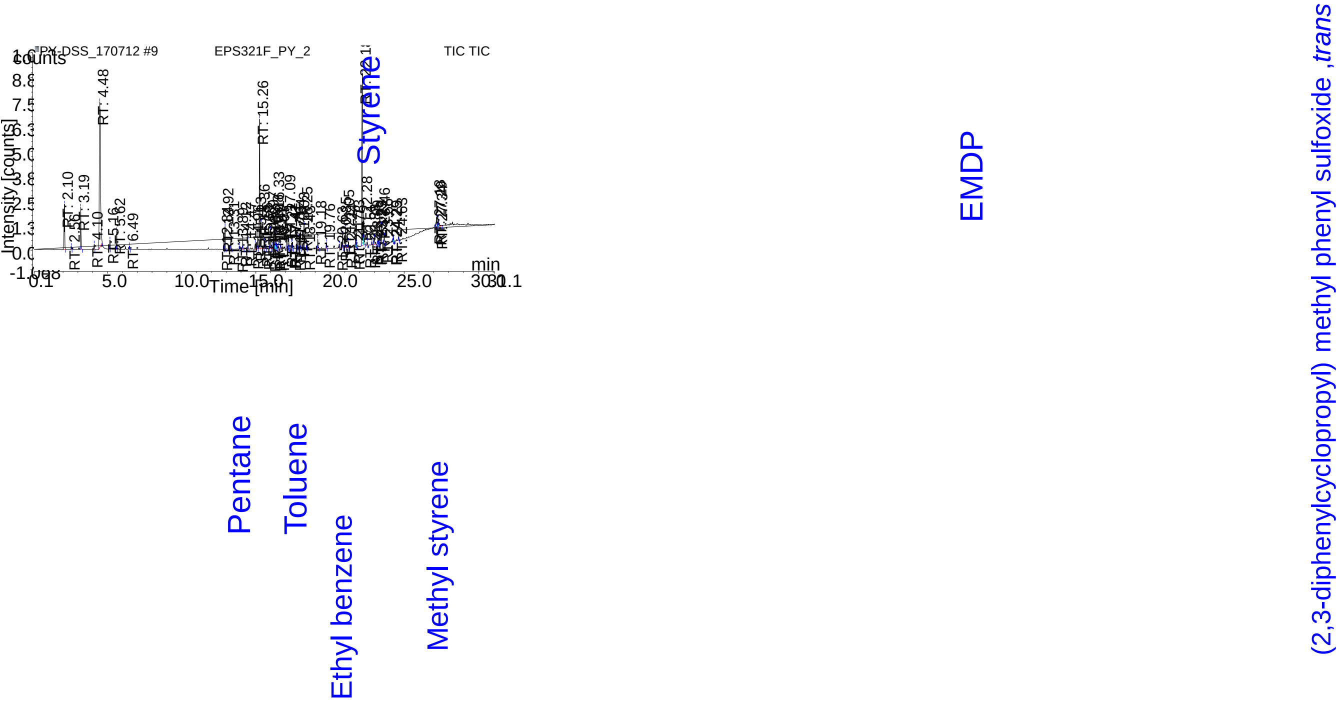




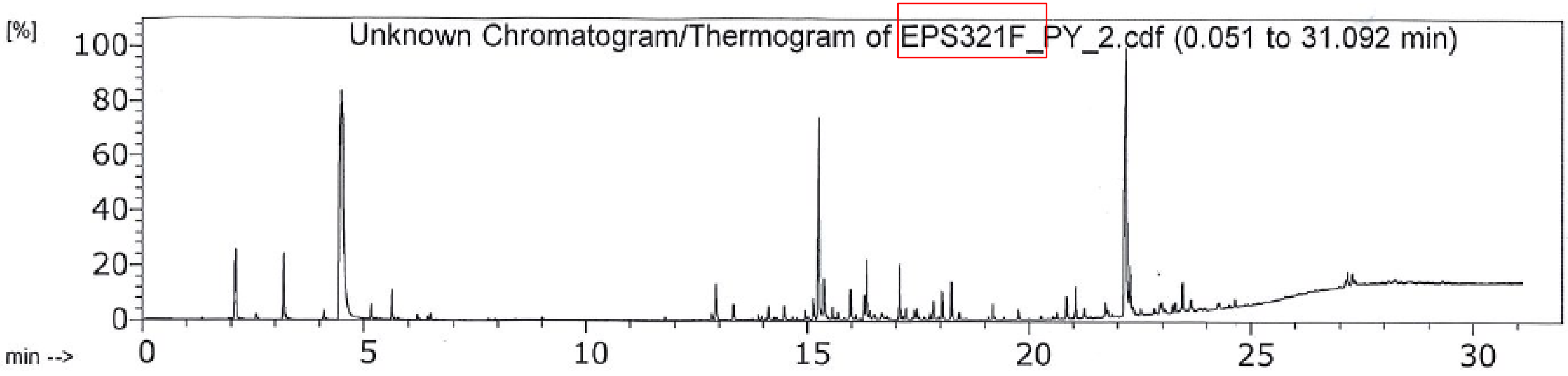
Rank.2 : Acrylonitrile-Butadiene-Styrene copolymer ; ABS (C1-C40) Qual.86

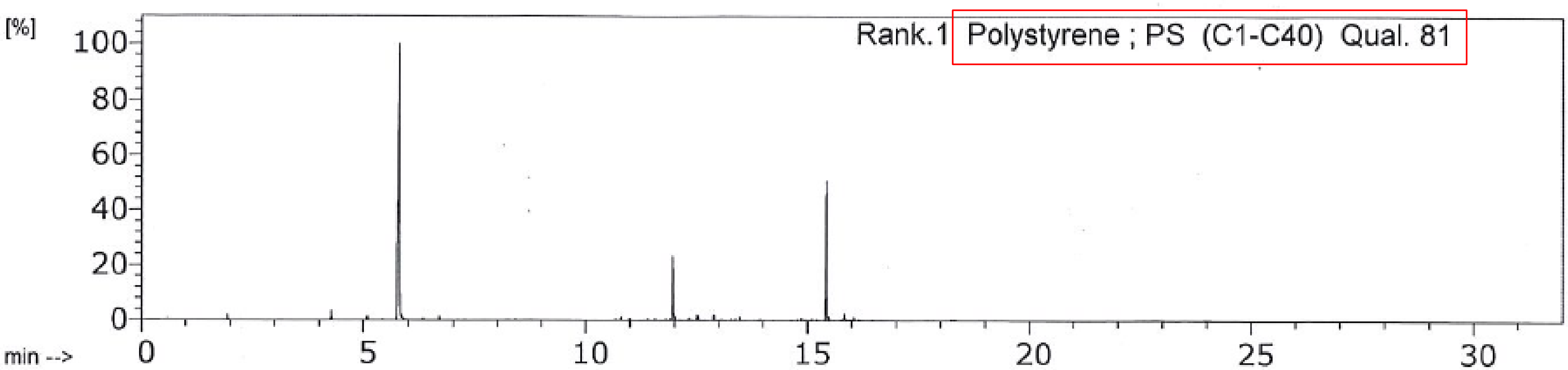
Rank.3 : Styrene-butadiene copolymer ABA block, 85% styrene (C1-C40) Qual. 86

ผลการวิเคราะห์ตัวอย่างที่ 3



ผลการวิเคราะห์เมื่อเทียบกับฐานข้อมูลด้านพอลิเมอร์ผ่านซอฟแวร์ F-Search

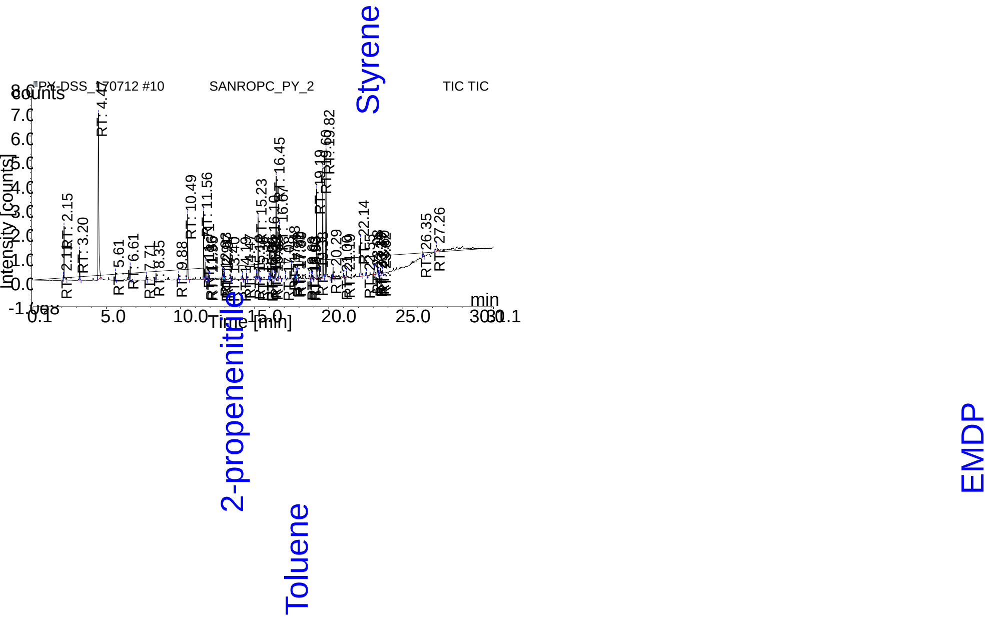




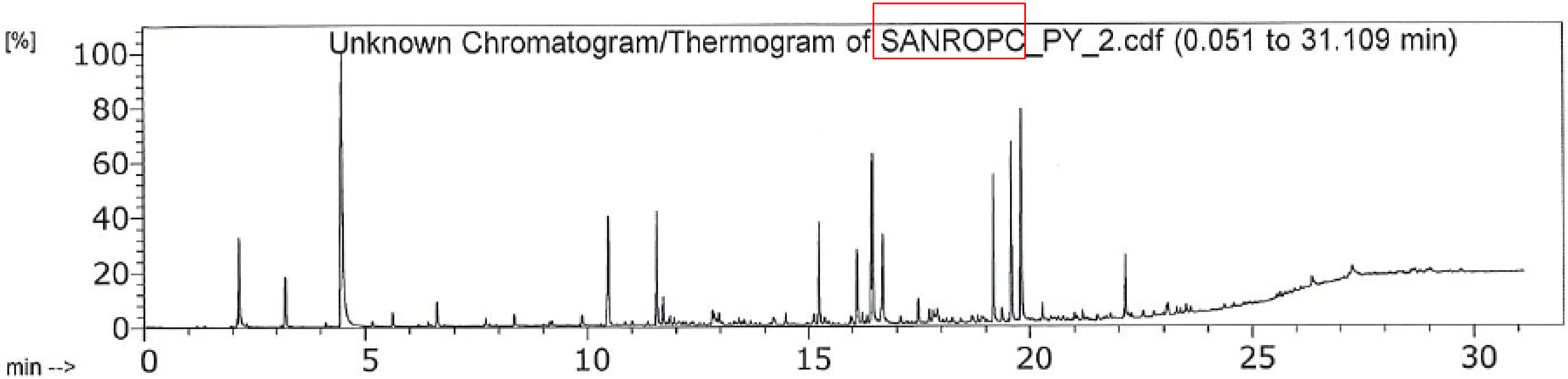
Rank.2 : Acrylonitrile-Butadiene-Styrene copolymer ; ABS (C1-C40) Qual.81

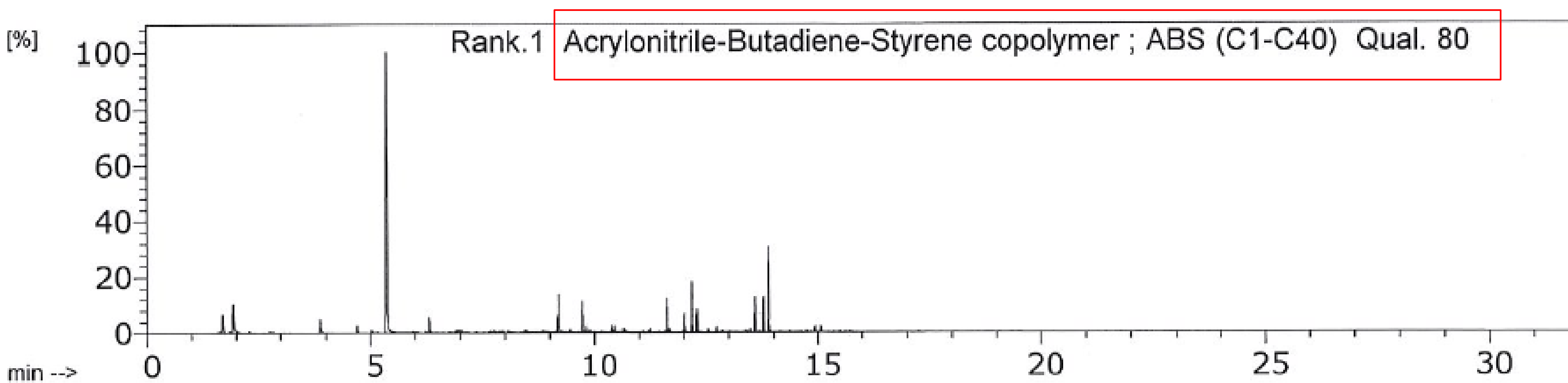
Rank.3 : Styrene-butadiene copolymer ABA block, 85% styrene (C1-C40) Qual. 81

ผลการวิเคราะห์ตัวอย่างที่ 4



ผลการวิเคราะห์เมื่อเทียบกับฐานข้อมูลด้านพอลิเมอร์ ผ่านซอฟแวร์ F-Search



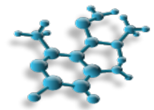


Rank.2 : Acrylonitrile-Butadiene-Styrene copolymer ; ABS (C1-C40) Qual.79

Rank.3 : Acrylonitrile styrene copolymer ; AS (C1-C40) Qual.76

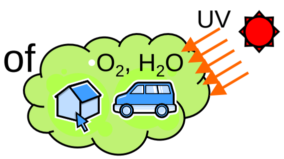
การประยุกต์ใช้ PY-GCMS

1: Characterization of polymers



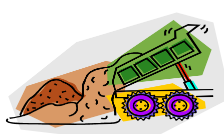
2: Quality control

3: Degradation/life evaluation of polymeric materials

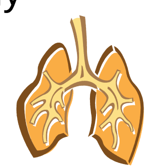


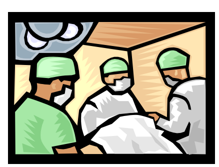
4: Recycling of polymeric materials, biomass utilization

5: Organic geochemistry and soil chemistry



6: Clinical science, pathology





7: Biochemistry, microbiology

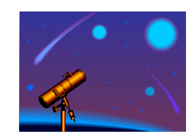
8: Coal liquefaction, energy conservation

9: Forensic science

10: Wood science, pulp industry

11: Tobacco smoke, toxicology

12: Extraterrestrial science



13: Environmental science

Analysis PAHs in extender oils

Topics to be discussed

- Introduction PAHs
- Sample Preparation
- GCMSMS method
- Analysis PAHs
- LOD&LOQ
- Example of sample result
- Comment

Introduction

- Polycyclic aromatic hydrocarbons (PAHs) in extender oils and tyres are produced using extender oils that may contain PAHs not added intentionally.
- PAHs are considered as toxic substances classified according to Directive 67/548/EEC as carcinogenic, mutagenic and toxic for reproduction.

Scope for analysis.

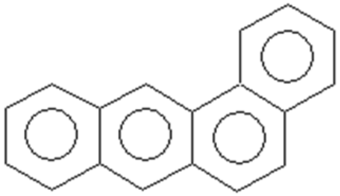
- EU standard specifies a procedure for determination of benzo(a)pyrene and sum of the eight individual polyaromatic hydrocarbons in extender oils. ***listed in Table1***
- Sample Preparation Method : BS EN 16143:2013

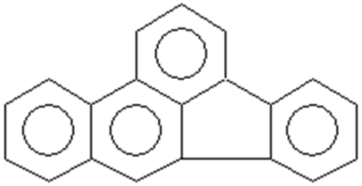
Name of PAH	Abbreviation	CAS Registry number
Benzo(a)pyrene	BaP	50-32-8
Benzo(e)pyrene	BeP	192-97-2
Benzo(a)anthracene	BaA	56-55-3
Chrysene	CHR	218-01-9
Benzo(b)fluoranthene	BbFA	205-99-2
Benzo(j)fluoranthene	BjFA	205-82-3
Benzo(k)fluoranthene	BkFA	207-08-9
Dibenzo(a,h)anthracene	DBahA	53-70-3

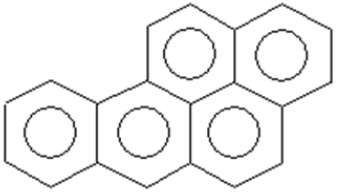
Table 1- List of individual PAHs in extender oils

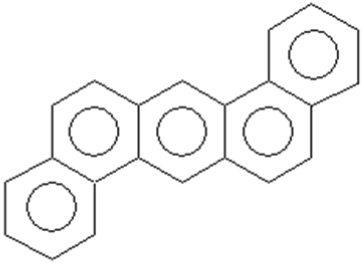
PAHs...

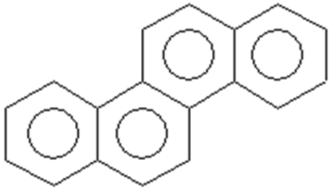
Consists of 8 natives of PAHs
MW range 228-278 amu (16PAHs could be up to 300+)

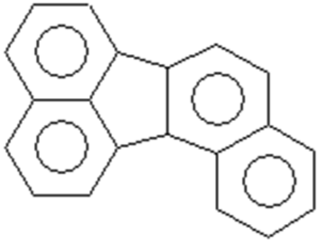

Benzo(a)anthracene

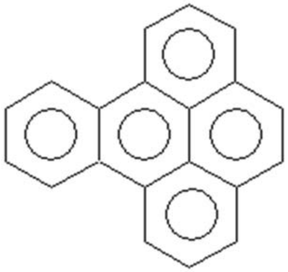

Benzo(b)fluoranthene

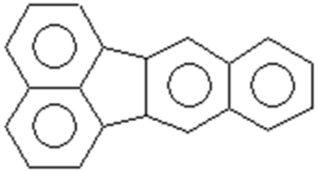

Benzo(a)pyrene


Dibenzo(a,h)anthracene


Chrysene


Benzo(j)fluoranthene


Benzo(e)pyrene


Benzo(k)fluoranthene

$C_{18}H_{12}$
MW. 228 g/mol

$C_{20}H_{12}$
MW. 252 g/mol

$C_{20}H_{12}$
MW. 252 g/mol

$C_{22}H_{14}$
MW. 278 g/mol

Sample Preparation Process

(1) Prepares sample solution

Weight Sample 70 ± 0.1 mg into Vol. flask 5 ml

Dissolve with 2 ml of n-Pentane and Spike internal Std. (deuterated IS)

(2) Deactivates silica

Deactivate Silica gel by stirring with 7% (m/m) of water for 24 h.

(3) 1st sample extraction (8 Hours)

3.1 Mix deactivated silica (in 2) 5 g with n-Pentane

*3.2 Load silica gel into chromatographic column (16 cm. L X 1 cm. ID)**

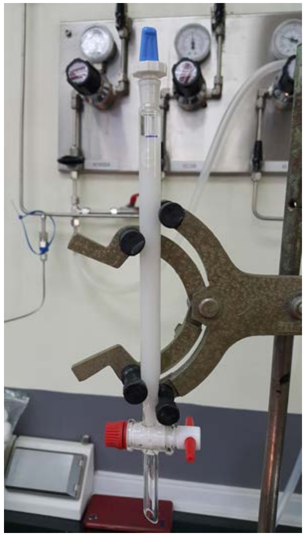
3.3 Flush silica gel with 10 ml n-Pentane through the column (discard)

3.4 Load sample (1) into column (before n-Pentane vanish form silica gel surface).

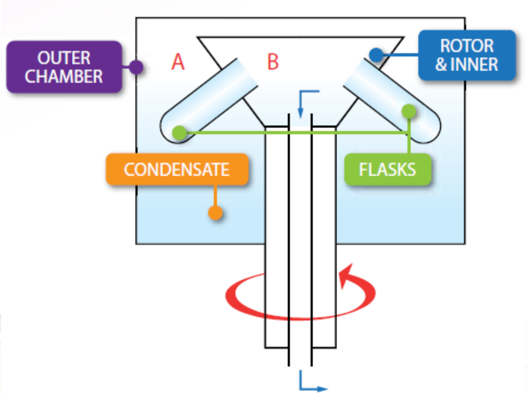
3.5 Rinse sample container with 2 ml n-Pentane.(not critical) and pour into column.

*3.6 Elute sample by Cyclohexane 75 ml (several portion) and collect the eluents.***

3.7 Evaporate eluent (3.6) under 35 C till final volume 1ml.


Pack column


Extracting



extended lenth of column to 25 cm. convenient for sample loading

*** pressurized with N2 (1 bar est.) for faster elution*

Sample Preparation Process

(4) Sample clean up (Sephadex LH20) (6 hours)

4.1 Mix 5 g. of Sephadex with IPA .. leave for overnight.

4.2 Load Sephadex into chromatographic column (12 cm L X 2.3 cm ID)

4.3 Add 1 ml IPA into (3.7) and load into column.

4.4 Rinse sample vessel with IPA (1 ml) and load into column.

4.5 Elute with IPA at 1 ml/min, Discard the first 24 ml eluent.

4.6 Collect eluent portion (@24-70 ml) in drying vessel

4.7 Evaporate eluent (4.6) under 35 C till nearly dry.

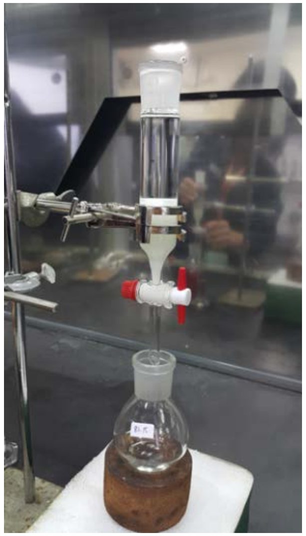
4.8 Add 2 ml Acetone and evaporate till dry.

4.9 Dissolve with CycloC6 and transfer into 1 ml Vol.Flask

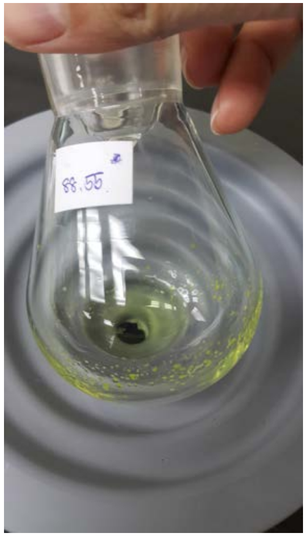
4.10 Add injection standard (DE) 0.2 ml and make up volume to 1 ml with CycloC6*

4.11 Make up volume to 1 ml wth Cyclohexane.

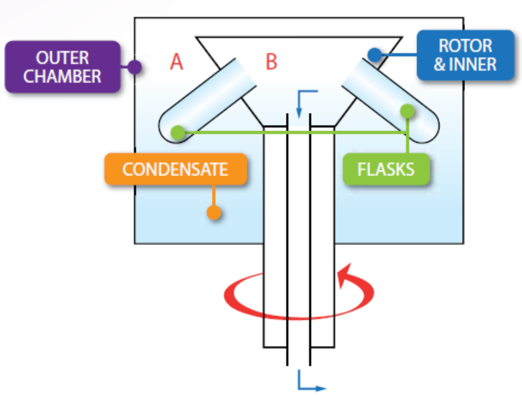
4.12 Analyze with GCMSMS.



Fraction collecting



Dissolved Solution



*DE = Decafluorodiphenyl

Instrument Method

GC parameters

Parameter	Value
GC-column	60 m x 0.25 mm ID x 0.25 µm
Stationary phase	17% phenyl-methylpolysiloxane
Temperature program	Initial 90 °C hold 1min 20°C /min to 250 °C 4°C /min to 330 °C hold 10 min
Injection	PTV, Splitless
Injection temperature	275 °C
Injection Volume	1 µL
Carrier gas	He UHP grade 1.2 ml/min

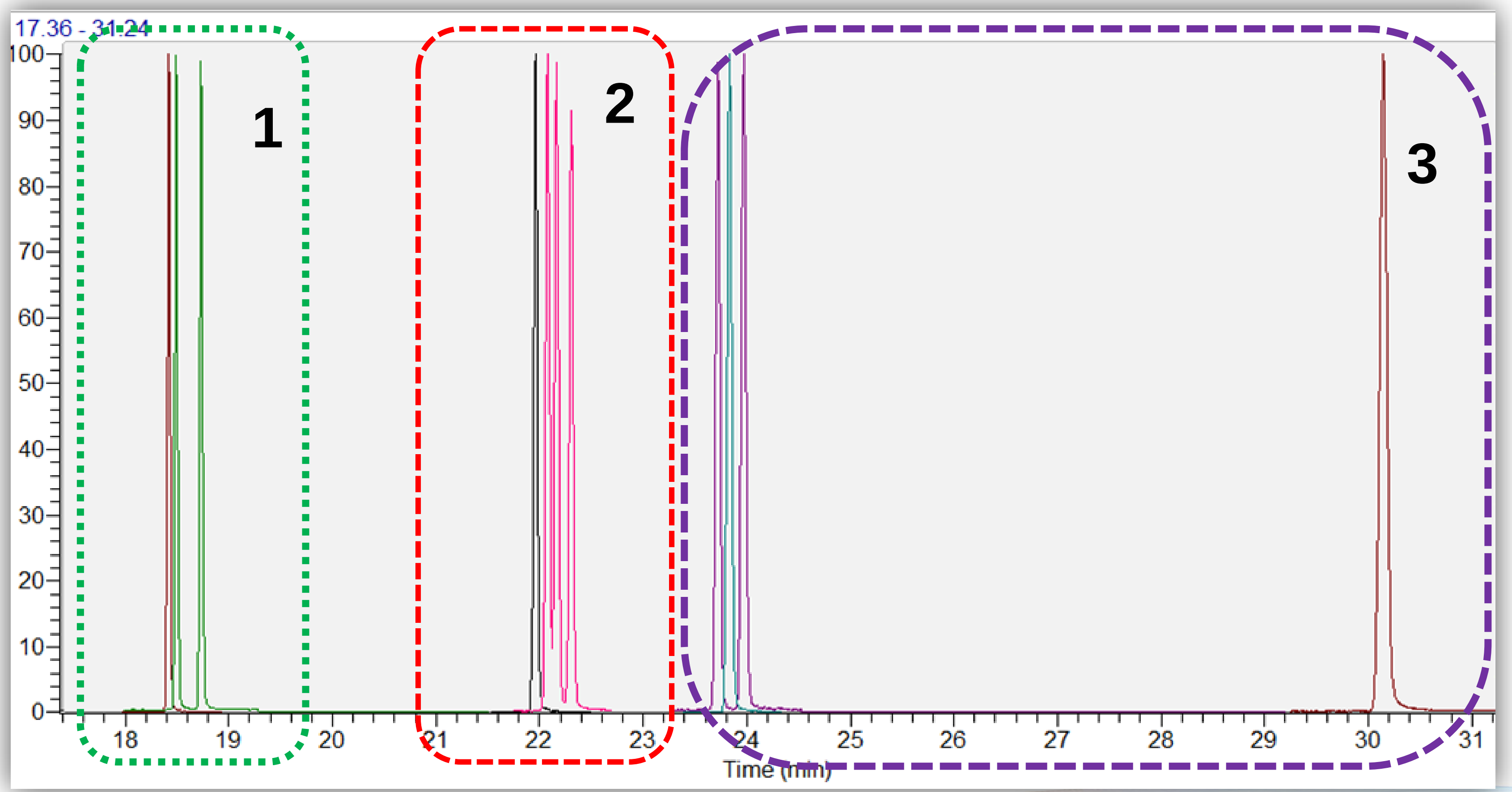
Instrument Method

- **Mass Spectrometer : EI – Temp 250 C/ TL Temp 330/**
- **MSMS –** SRM Q1 resolution 0.7 FWHM, Q3 Resolution 0.7 FWHM

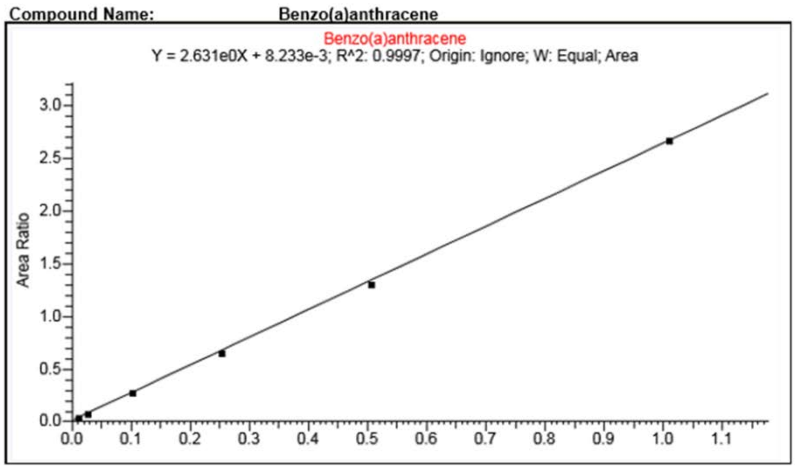
Component	RT	mass	product mass	Collision energy
Decfluorodiphynly	5.84	333.9	233.9	35
		333.9	264.9	25
Benzo(a)antracene-D12	18.46	240.1	212.1	25
		240.1	236	30
Benzo(a)antracene	18.53	228.1	202	25
		228.1	226	30
Chrysene	18.77	228.1	202	25
		228.1	226	30
Benzo(b)Fluoranthene-D12	22.02	264.1	236	30
		264.1	260	35
Benzo(b)fluoranthene	22.13	252.1	226	25
		252.1	250	30
Benzo(k)fluoranthene	22.22	252.1	226.1	25
		252.1	250	35
Benzo(j)fluoranthene	22.36	252.1	226	25
		252.1	250	30
Benzo(e)pyrene	23.78	252.1	226.1	30
		251.1	250	30
Benzo(a)pyrene-D12	23.89	264.2	236.1	30
		264.2	260	35
Benzo(a)pyrene	24.03	252.1	226.1	35
		251.1	250	30
Dibenzo(a,h)anthracene	30.23	278.1	276	35
		278.1	276.2	50

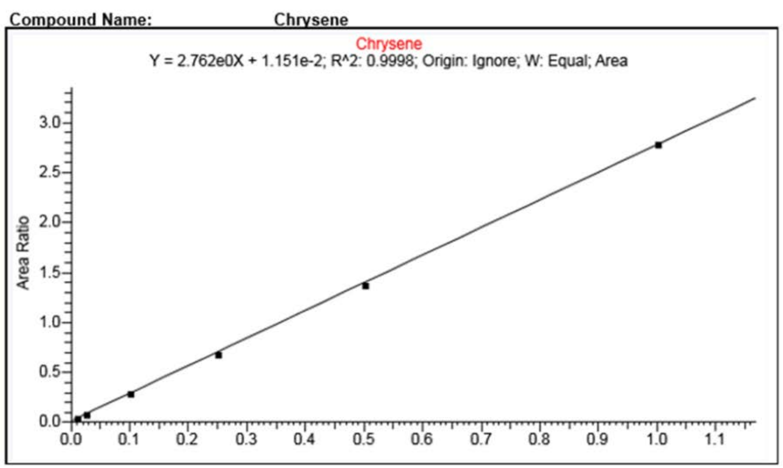
8 PAHs Standard

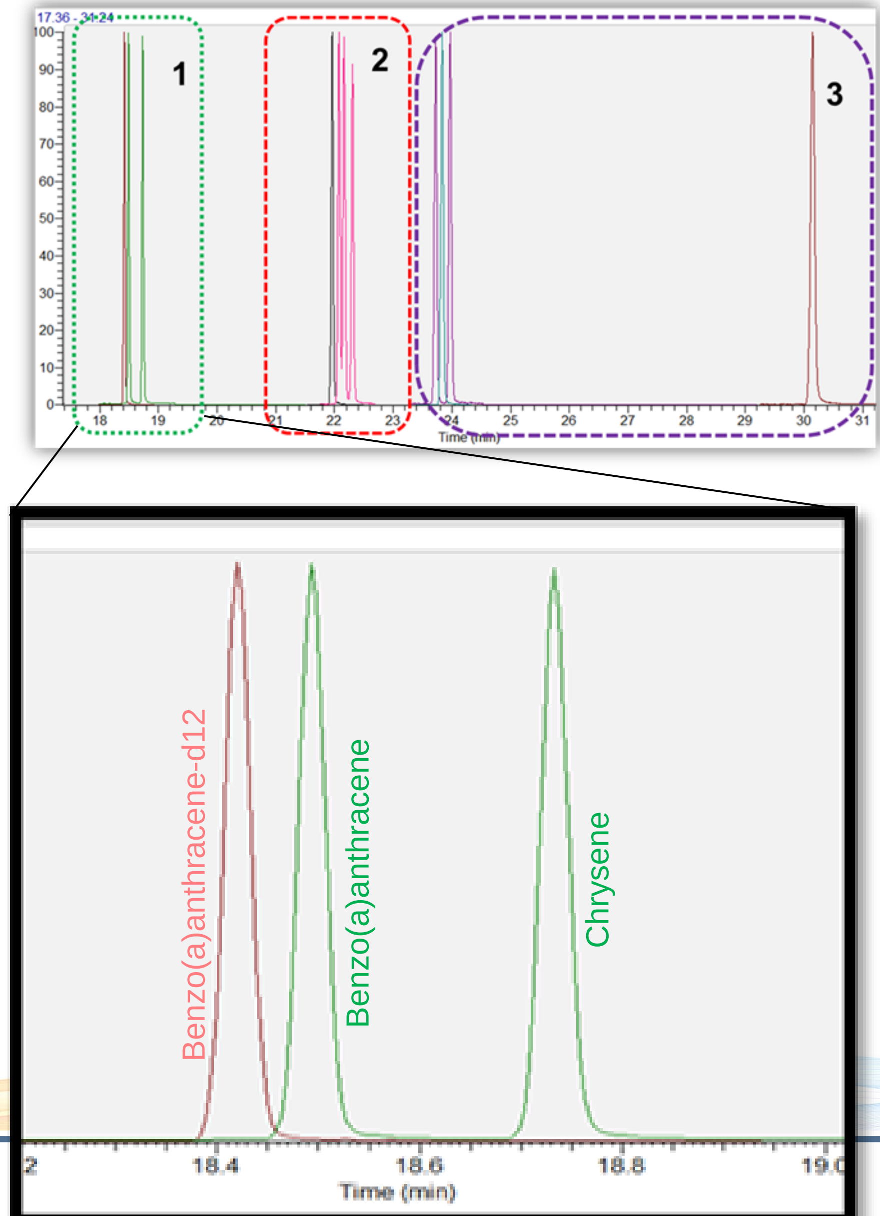
TIC



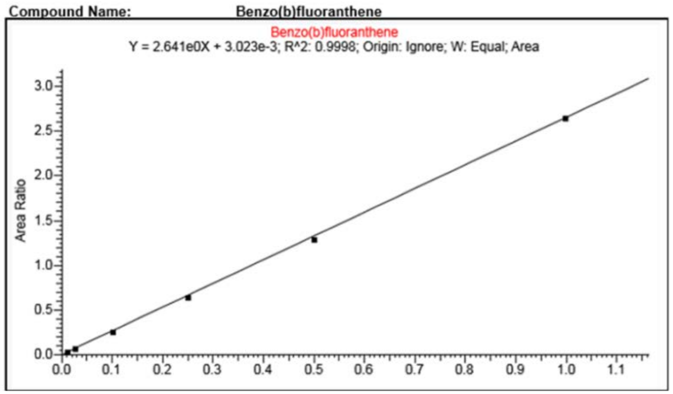
Chromatogram (1) –Standard 8 PAHs with 3 IS(d12)

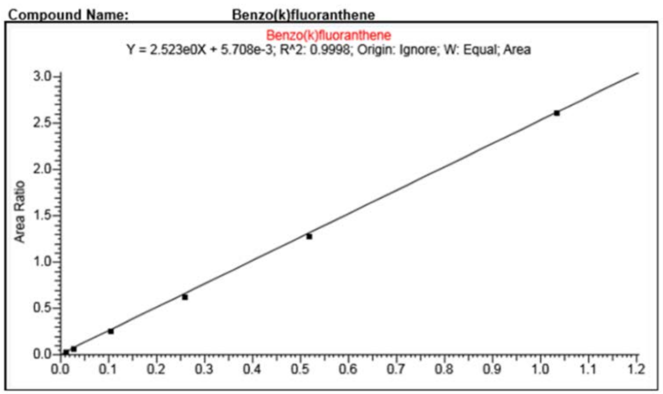


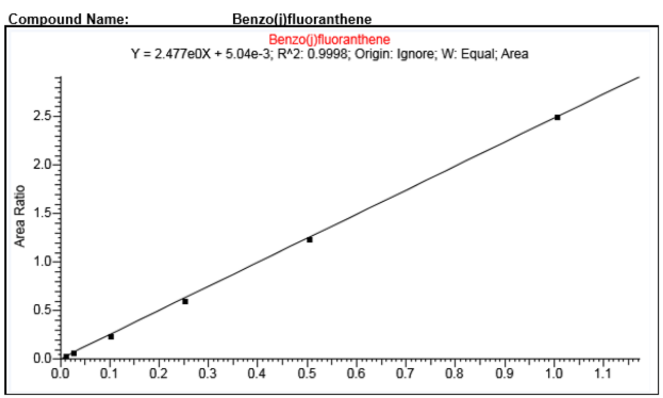


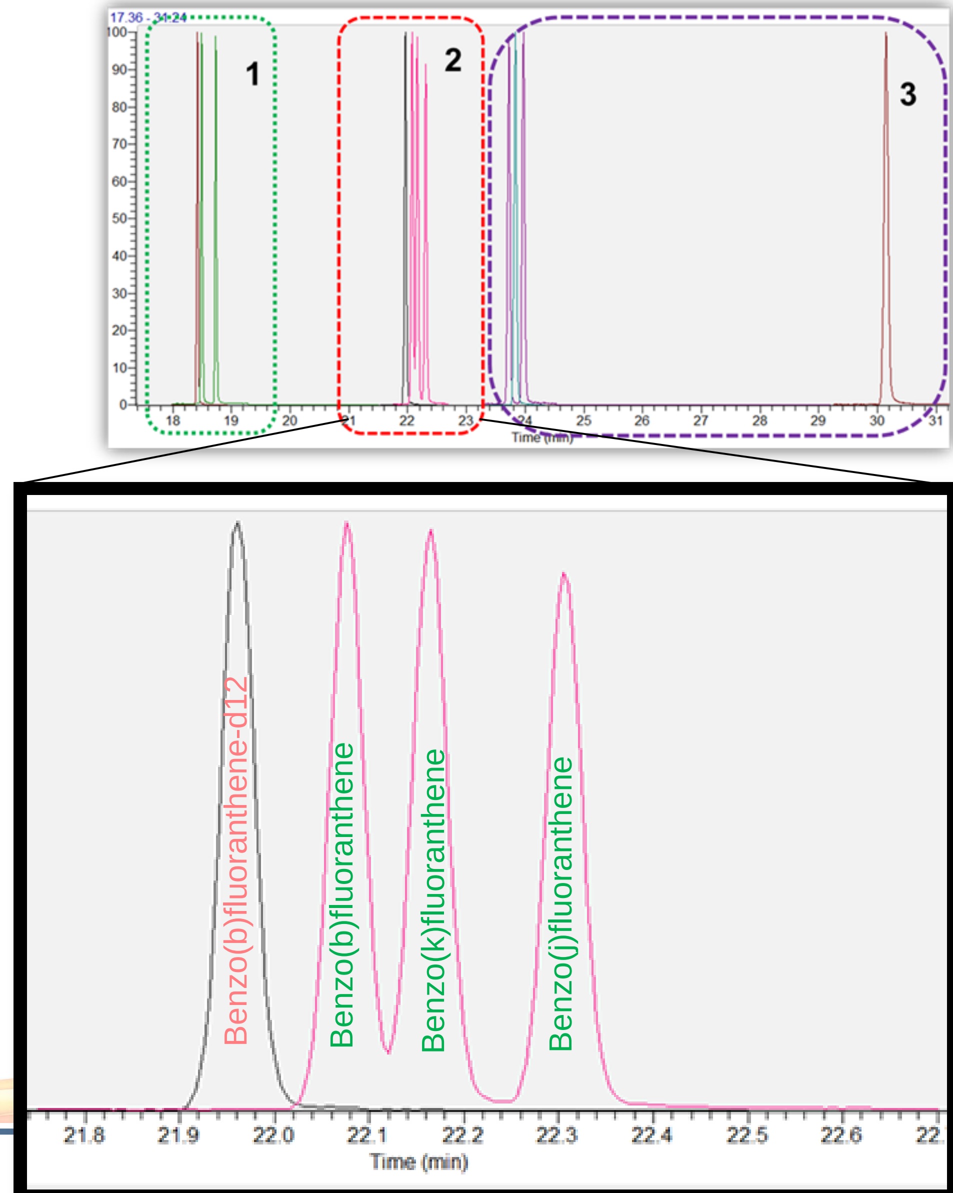


Chromatogram (2) –Standard 8 PAHs with 3 IS(d12)

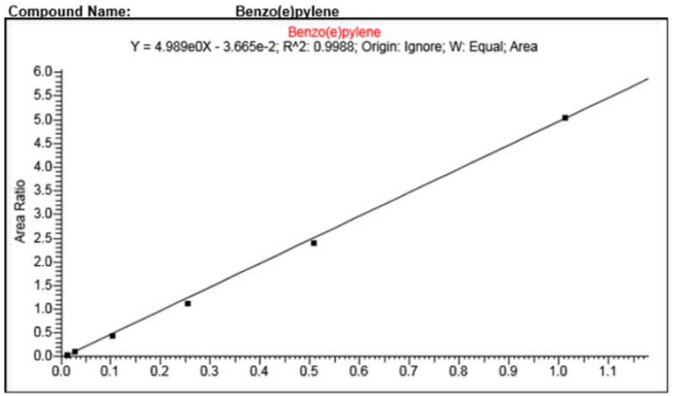


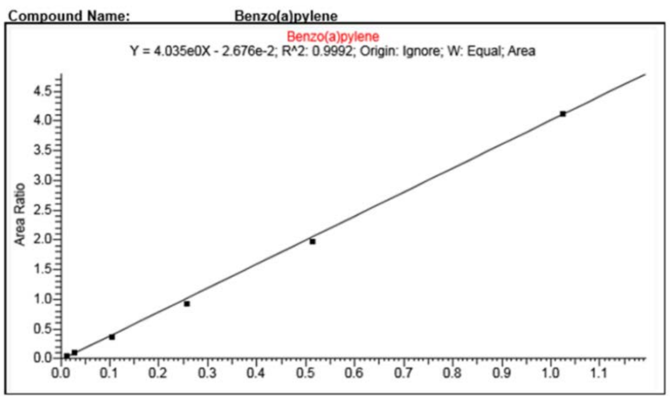


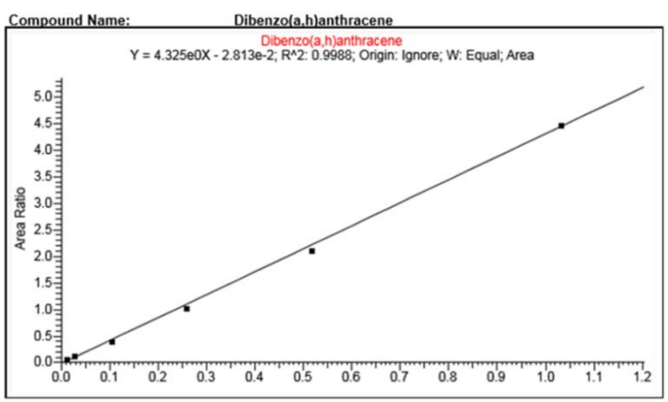


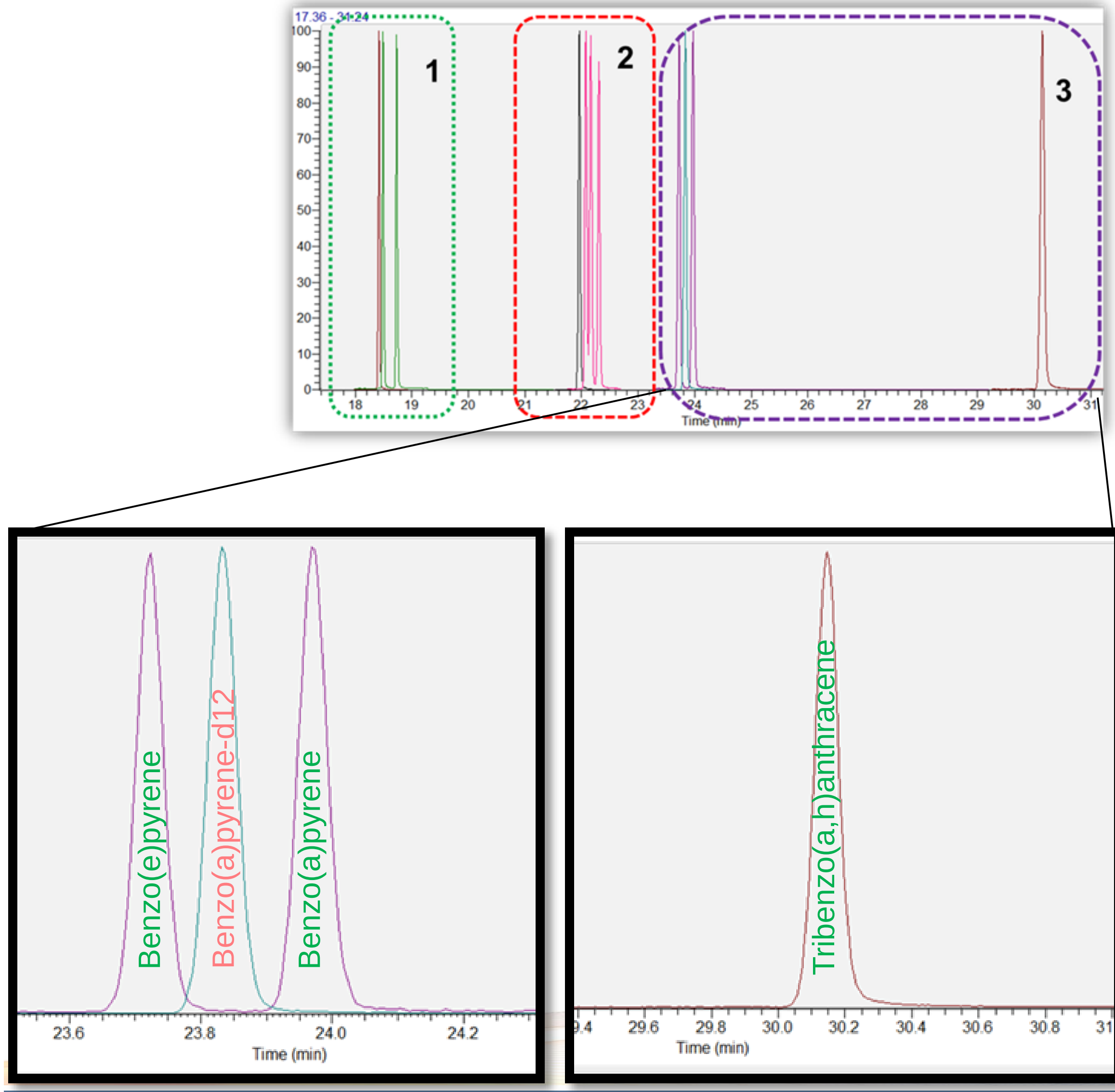


Chromatogram (3) –Standard 8 PAHs with 3 IS(d12)









LOD/LOQ

- Calculated from 10 replicate runs of TDAE sample (Treated Distillate Aromatic Extracted)

No.	PAHs (mg/kg)							
	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(j)fluoranthene	Benzo(e)pylene	Benzo(a)pylene	Dibenzo(a,h)anthracene
1	0.226	0.370	0.198	0.186	0.103	-0.507	0.144	0.125
2	0.220	0.367	0.177	0.165	0.117	-0.510	0.130	0.148
3	0.222	0.361	0.184	0.182	0.127	-0.507	0.137	0.124
4	0.236	0.375	0.194	0.178	0.136	-0.511	0.147	0.149
5	0.221	0.372	0.204	0.168	0.118	-0.518	0.129	0.150
6	0.224	0.366	0.189	0.180	0.117	-0.510	0.129	0.142
7	0.236	0.363	0.192	0.194	0.123	-0.535	0.122	0.139
8	0.221	0.368	0.204	0.178	0.133	-0.509	0.126	0.135
9	0.247	0.369	0.181	0.166	0.118	-0.509	0.125	0.144
10	0.231	0.362	0.202	0.169	0.130	-0.507	0.115	0.147
SD	**0.0089**	**0.0045**	**0.0097**	**0.0095**	**0.0097**	**0.0086**	**0.0098**	**0.0095**
LOD	**0.0267**	**0.0134**	**0.0291**	**0.0285**	**0.0291**	**0.0258**	**0.0294**	**0.0286**
LOQ	**0.0891**	**0.0447**	**0.0969**	**0.0951**	**0.0972**	**0.0860**	**0.0980**	**0.0955**

8 compounds of PAHs have LOQ less than 0.1 mg/kg

Peak Confirmation

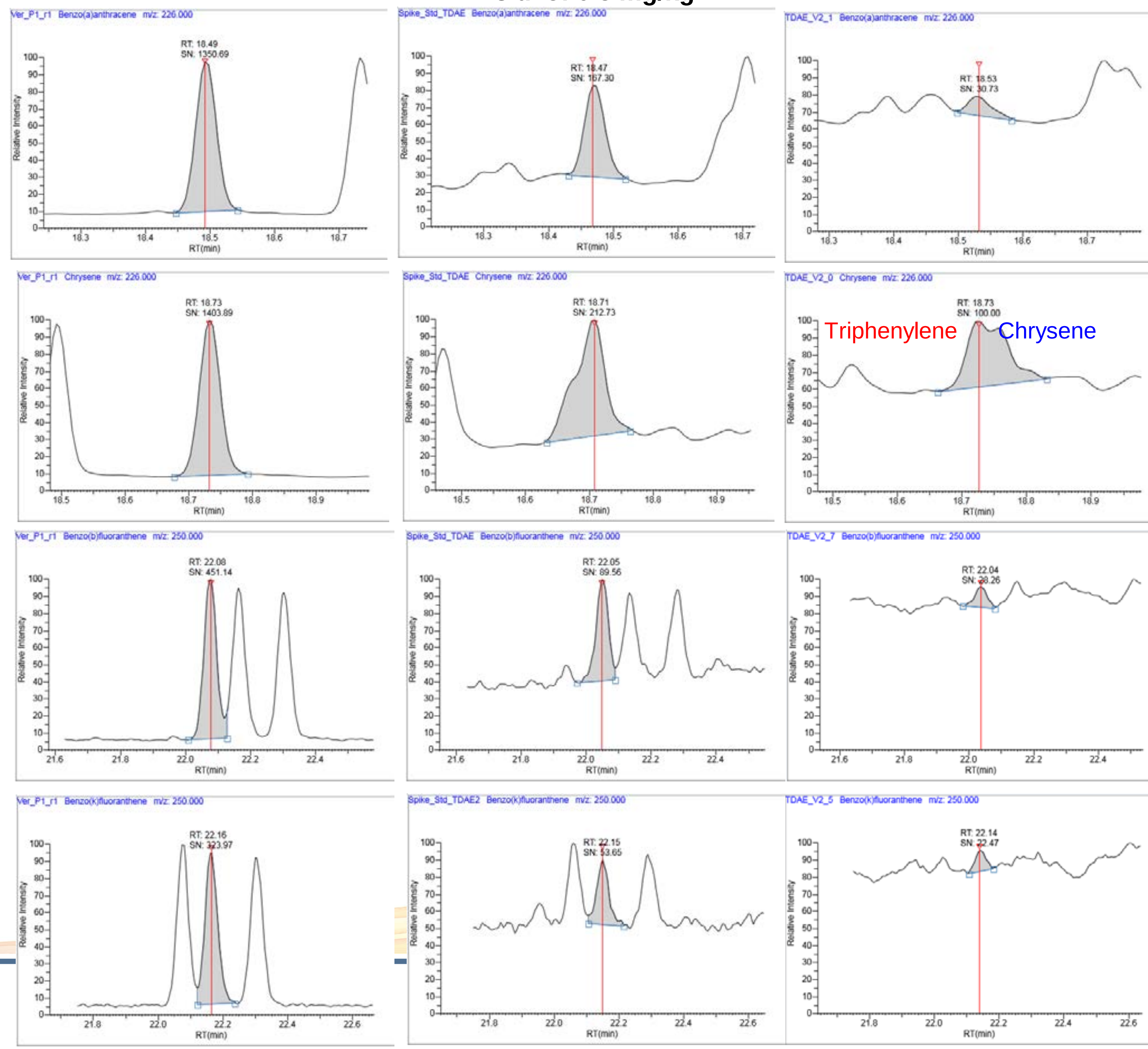
	QC Check	Sample spiked 3 ul of 0.5 mg/kg	Sample(TDAE)

Benzo(a)anthracene

Chrysene

Benzo(b)fluoranthene

Benzo(k)fluoranthene



Peak Confirmation

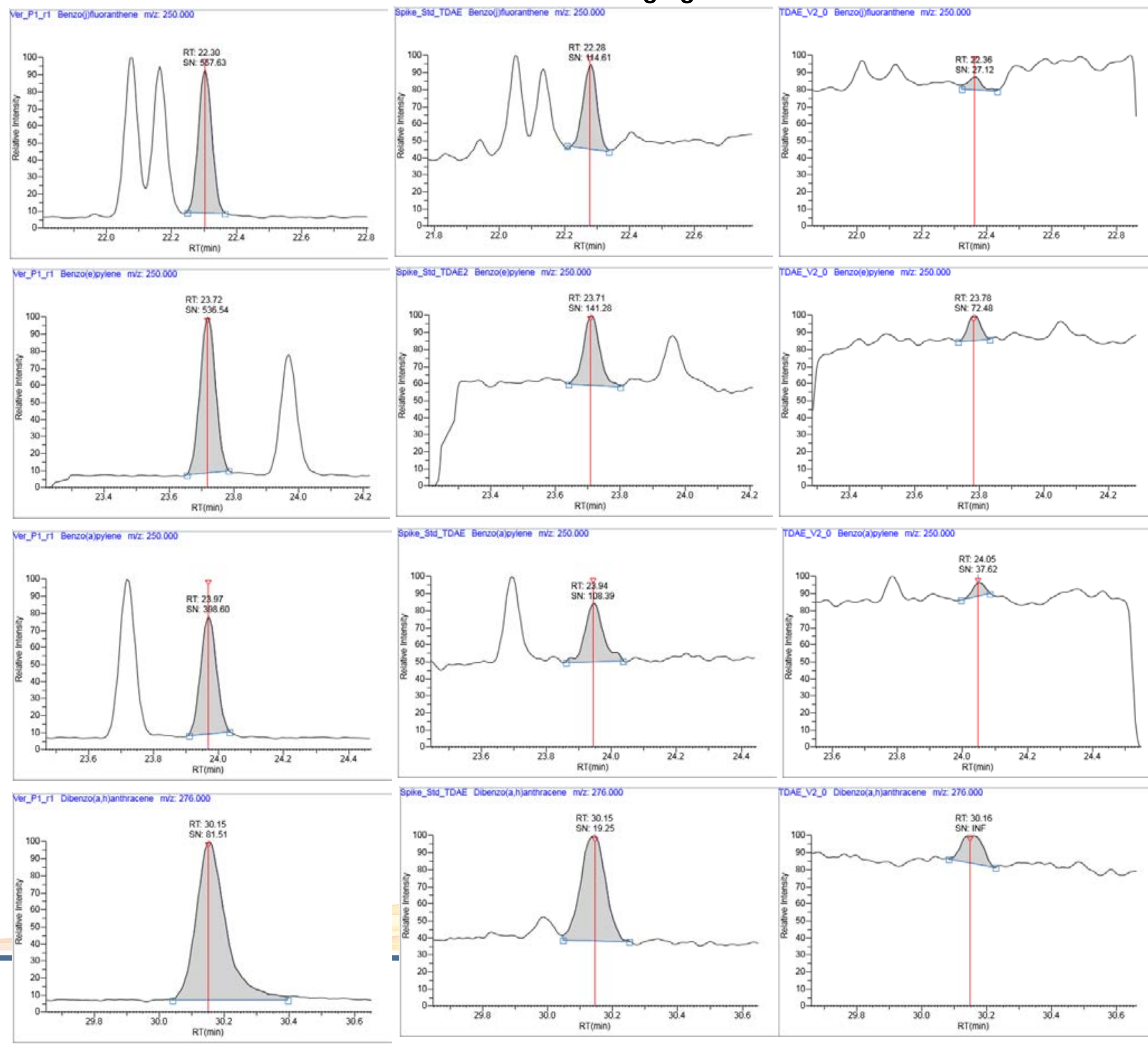
QC Check | **Sample spiked 3 ul of 0.5 mg/kg** | **Sample-TDAE**

Benzo(j)fluoranthene

Benzo(e)pyrene

Benzo(a)pyrene

Dibenzo(a,h)anthracene



Result.. Recovery

- Two batches of analysis (2 replicates for each batch) from same sample (RPO)
- Recovery of PAHs : Deuterated IS vs. Injection Standard (Decafluorodiphenyl)
- BIU acceptable recovery is between 50% and 150%

Internal standard	Standard amount (mg)	Sample		Calculated amount (mg)	%Recovery	Acceptable Criteria of %Recovery	Verified
		RPO_V1_Re01	RPO_V1_Re02				
Benzo(a)anthracene-d12	4008	4663.572	4719.434	4691.503	117.05	(50-150)	Pass
Benzo(b)fluoranthene-d12	4216	5684.548	5493.625	5589.087	132.57	(50-150)	Pass
Benzo(a)pyrene-d12	4060	5389.764	5301.968	5345.866	131.67	(50-150)	Pass
		RPO_V2_Re01	RPO_V2_Re02				
Benzo(a)anthracene-d12	4008	3532.543	3532.543	3532.543	88.14	(50-150)	Pass
Benzo(b)fluoranthene-d12	4216	3249.254	3249.254	3249.254	77.07	(50-150)	Pass
Benzo(a)pyrene-d12	4060	3319.878	3319.878	3319.878	81.77	(50-150)	Pass

Comments

- Complicated & time consuming sample preparation – requires skills and prone to error
- Improvement in separation (triphenylene vs. chrysene) can be done upon availability of standard (triphenylene).
- Comparison study of purification between the two steps i.e. Silica Gel vs. Silica Gel & Sephadex are not so much different.
- New development on sample prep in order to reduce work loads and improve analysis result.

Q&A