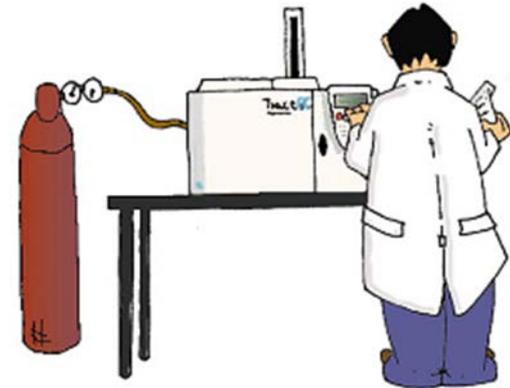


Sci
Spec

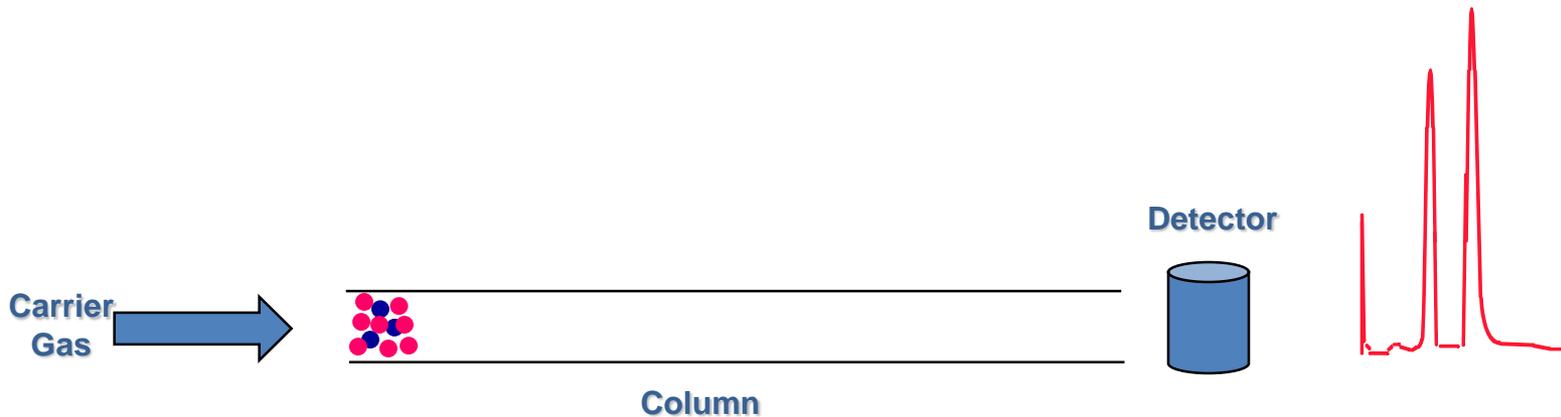


Gas Chromatograph Technology

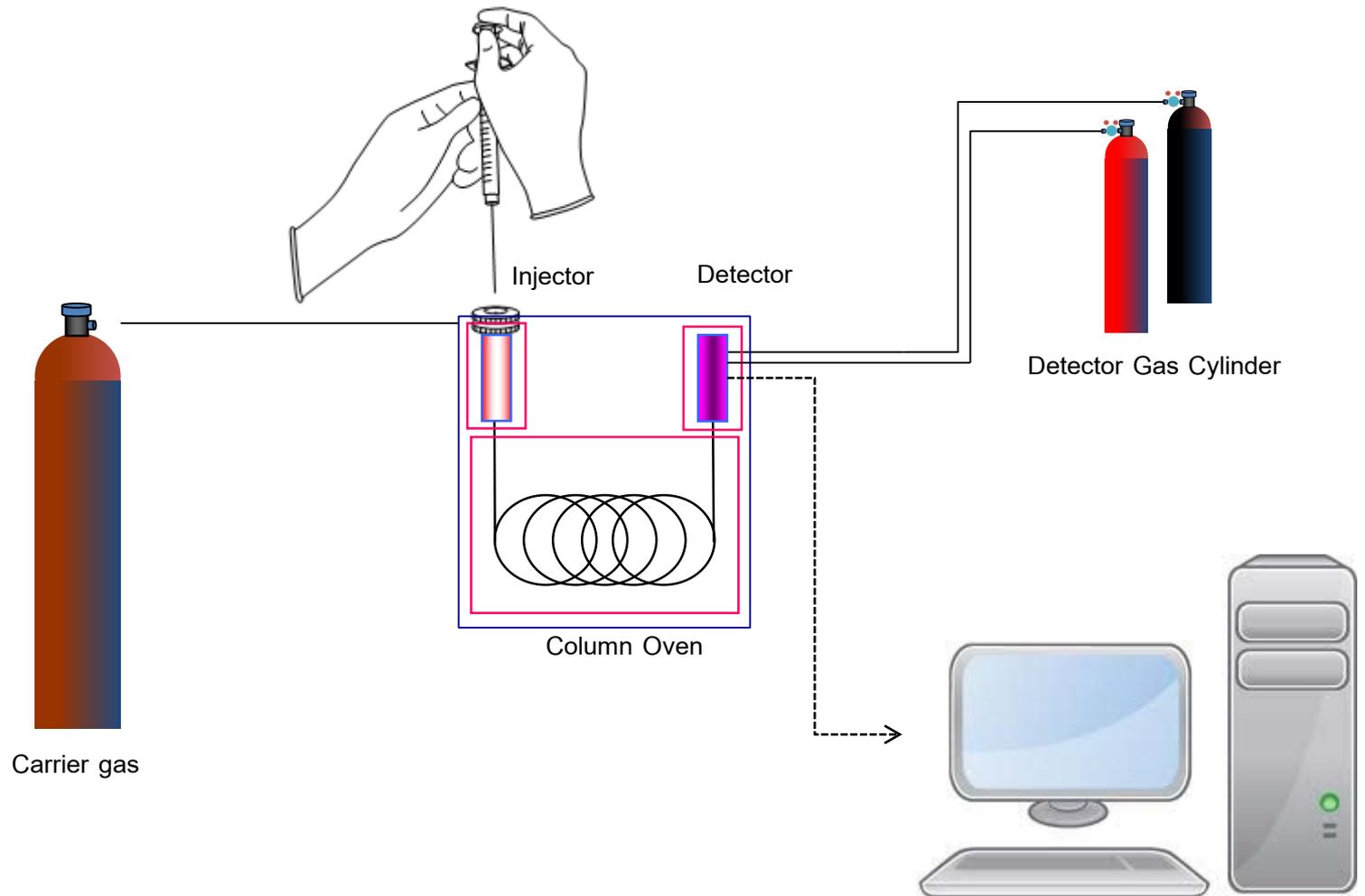
- Chromatography : Analytical technique that depends on **separation of components in sample**
- Sample components are **separated and detected**
- Separation : Between two phases
 - Stationary Phase
 - Mobile phase



- Gas Chromatography (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



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:

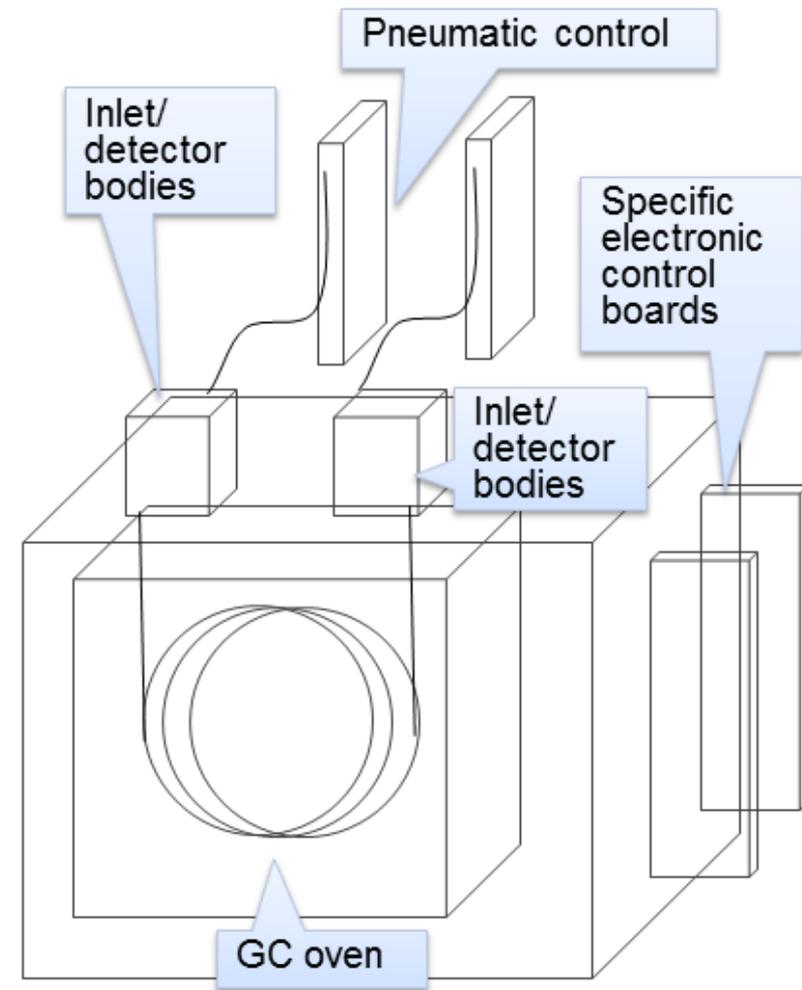
Injectors: SSL - SSL backflush - PTV - PTV backflush - Helium Saver SSL - GSV

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

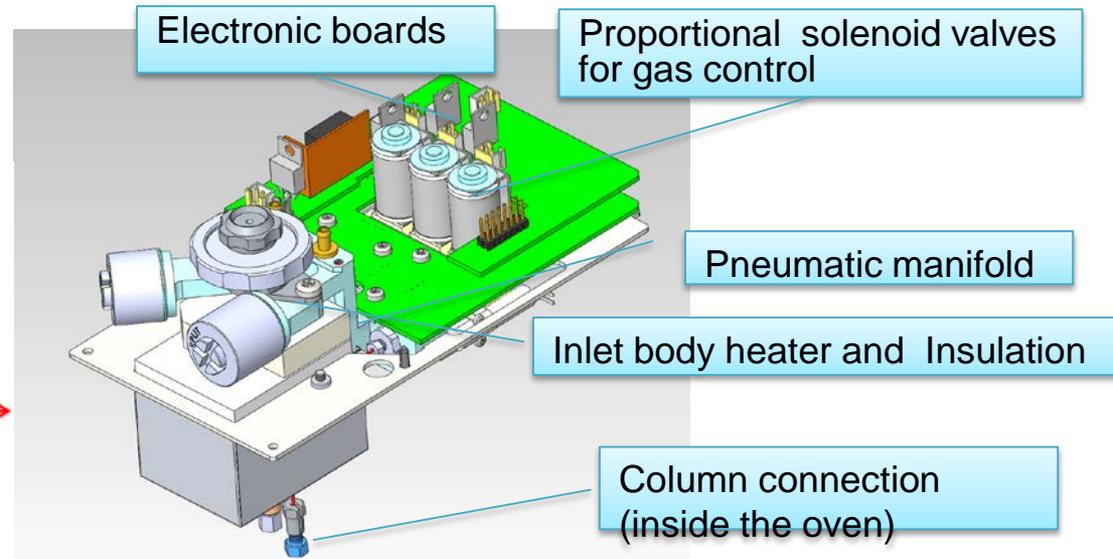
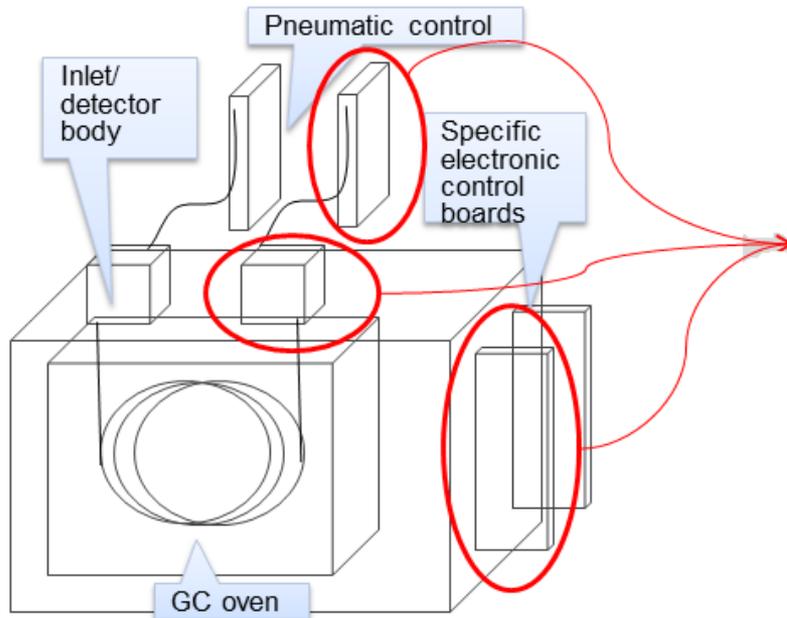
Other Options: Microfluidic devices, Auxiliary Oven, Inj/Oven Cryo, Aux carrier

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

- 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





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: **Sept. 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.

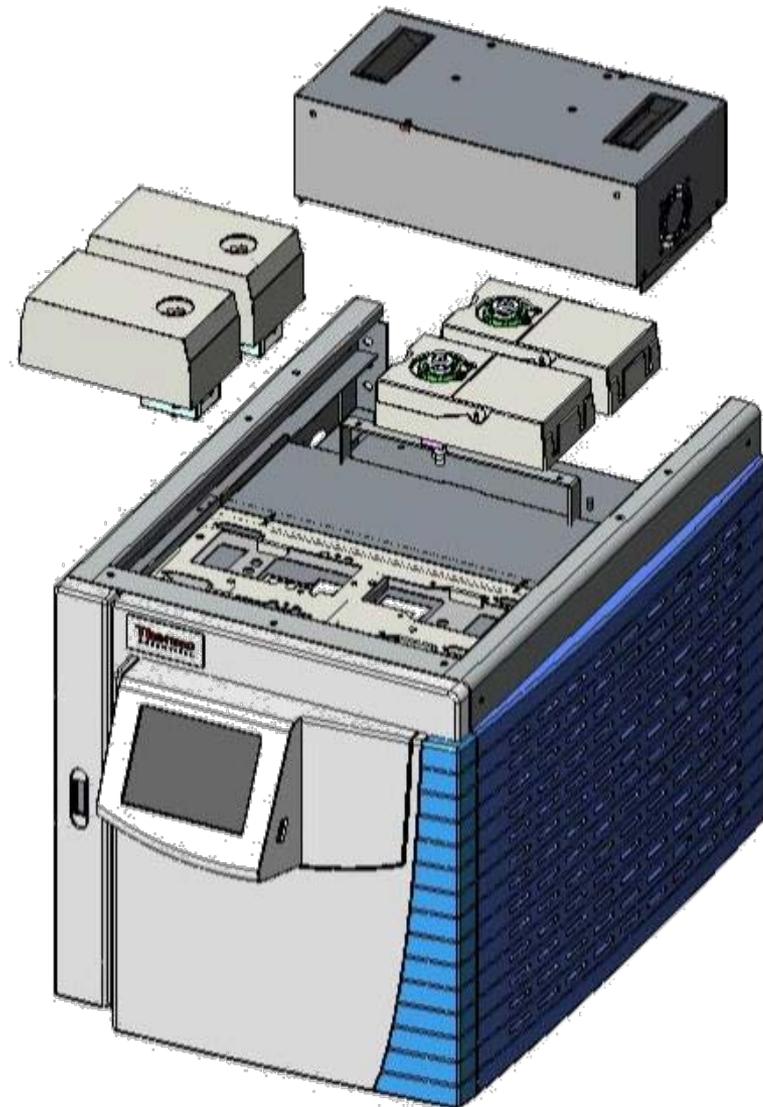
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(Continued)

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



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



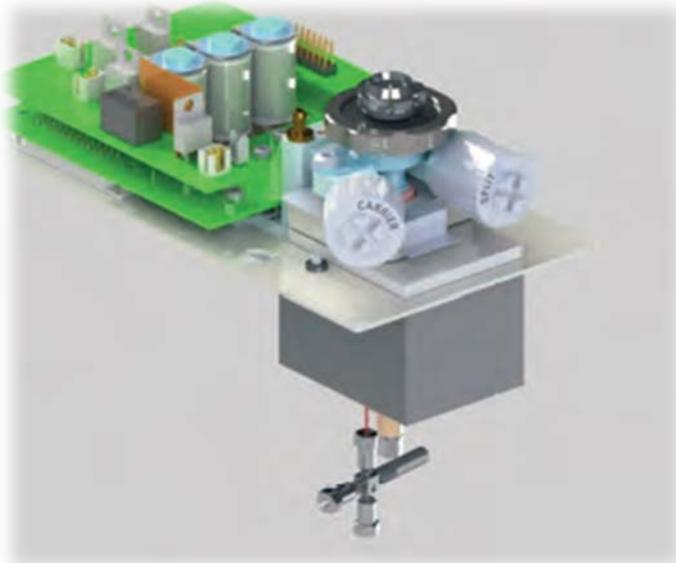
He Saver

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



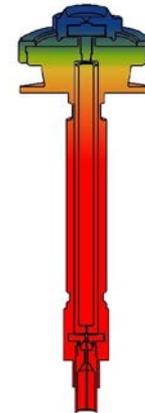
■ Injector modules

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



— SSL specially designed

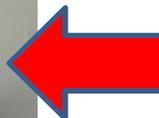
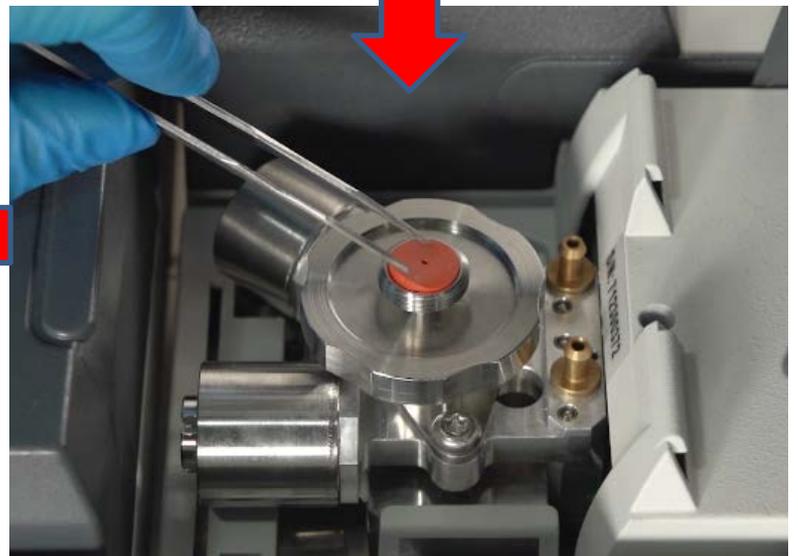
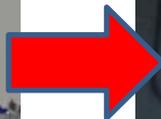
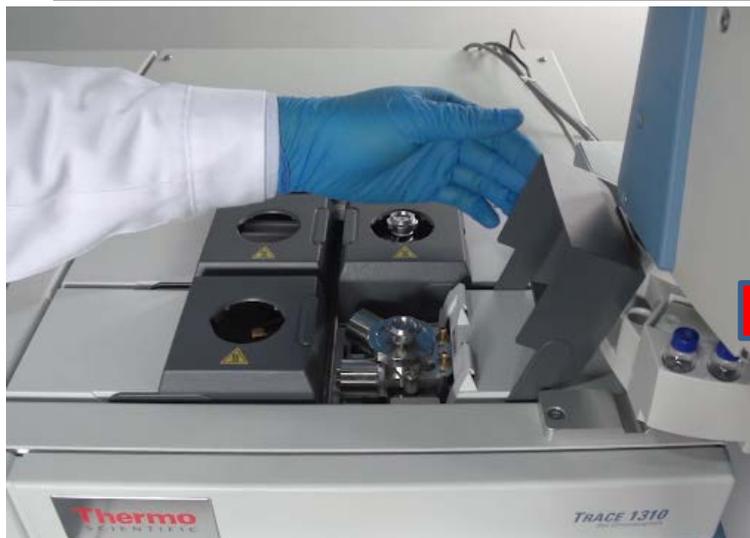
- Cool head and septum
 - Lower septum bleeding
 - Longer septa lifetime for high productivity
 - No septum sticking for quick maintenance
 - Lower air (oxygen) diffusion
 - Column lifetime and MS sensitivity preserved
- Uniform temperature along liner



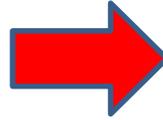


- Proprietary, patented Thermo Scientific “Instant Connect” modules
- Modules are user-installable in less than two minutes
 - Disconnected column from injector.
 - Just remove three screws and put the new module in place
 - No special training, dedicated tools or on-site service engineers required
-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

Injector maintenance



Injector maintenance



Injector maintenance



■ 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



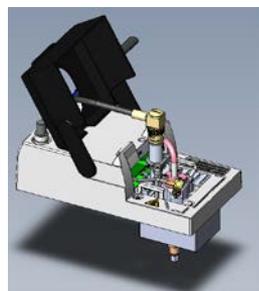
FID



TCD



PDD



NPD



ECD



Trace 1300 Series : Replace Injector Module



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



Sci
Spec

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

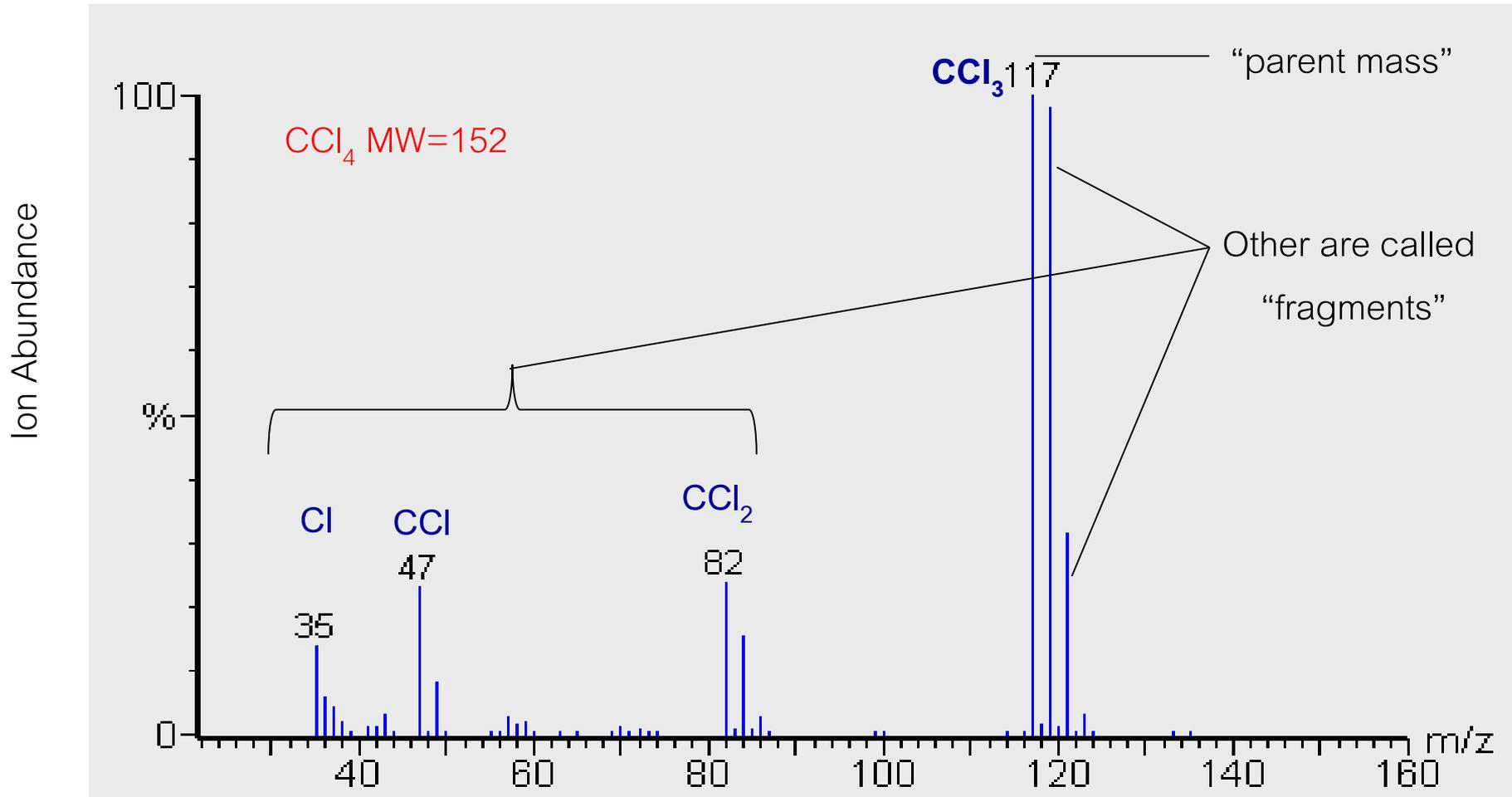


What is Mass Spectrometry?

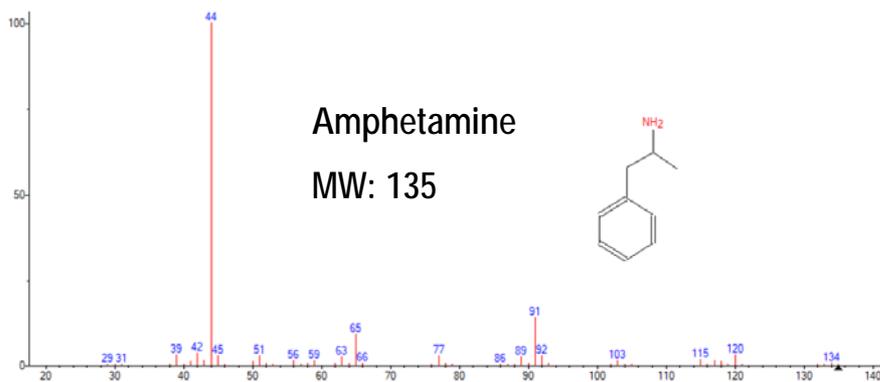
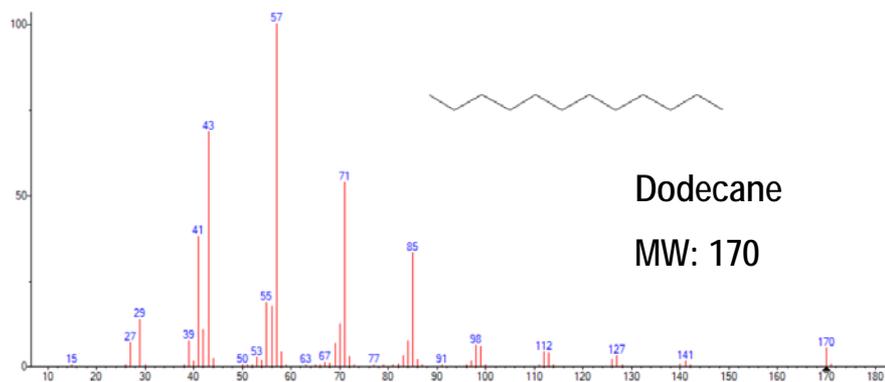
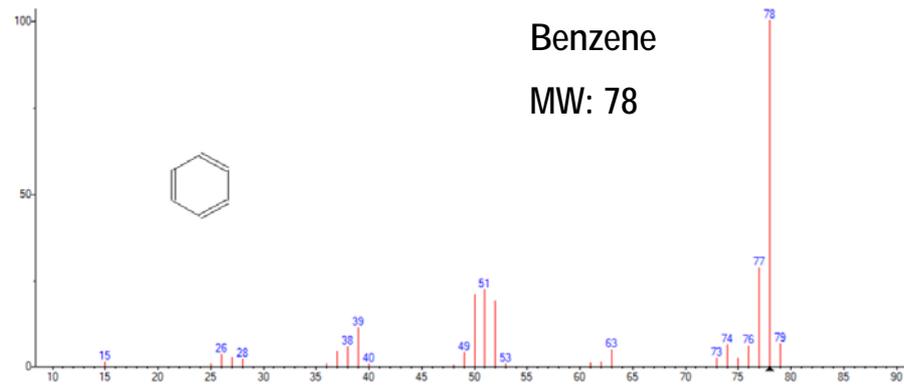
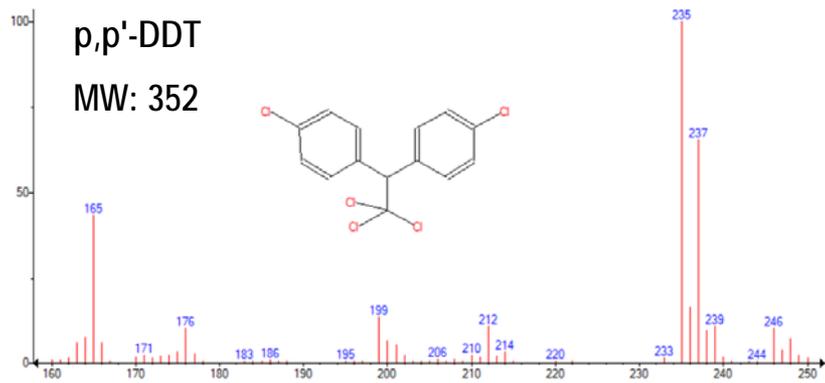
- The production of ions that are subsequently separated or filtered according to their mass-to-charge (m/z) ratio and detected.
- The resulting mass spectrum is a plot of the (relative) abundance of the produced ions as a function of the m/z ratio.”

What is "Mass Spectrum" ?

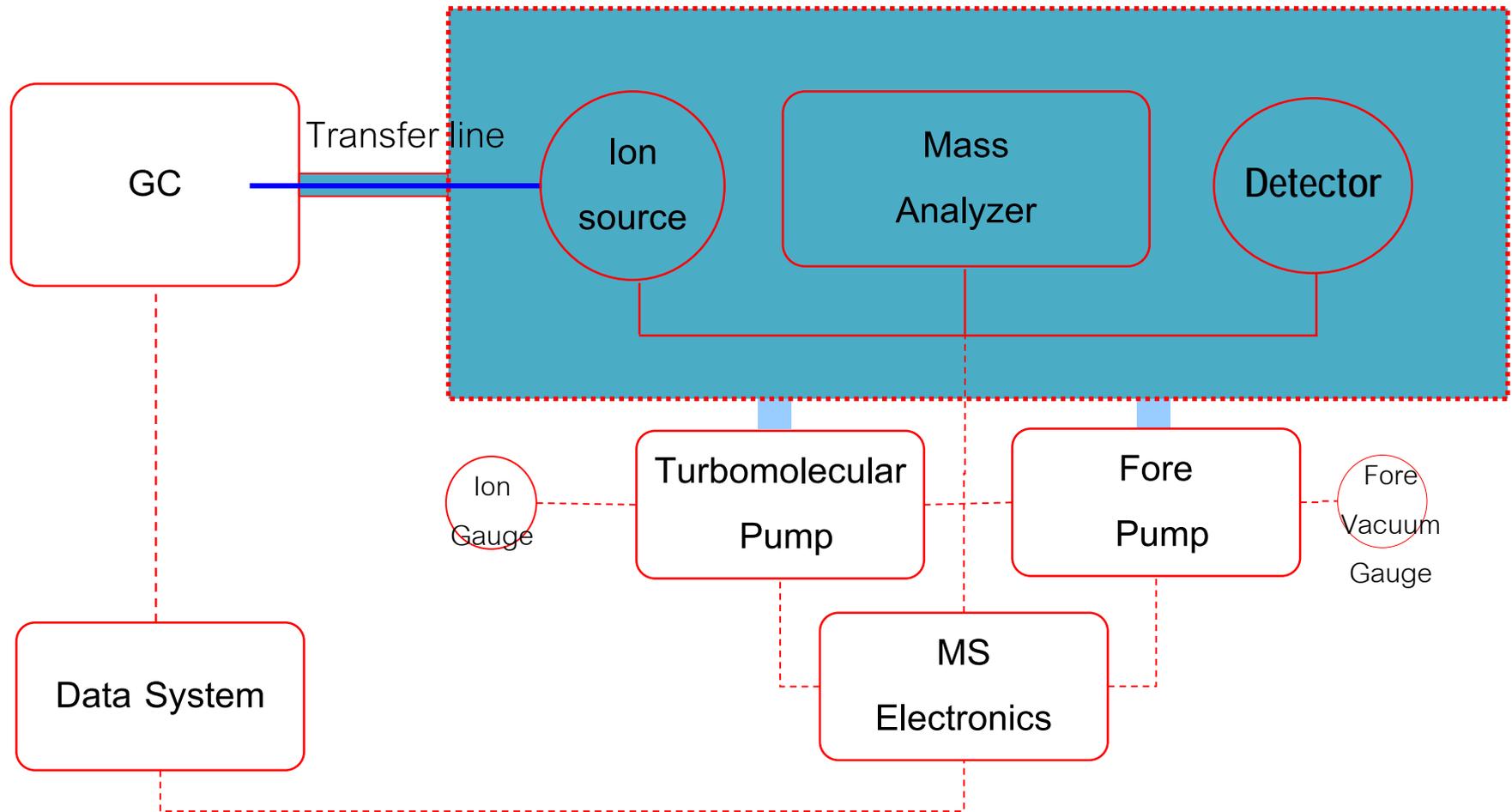
- Graph of Relative Ion Intensity vs. m/z
- Ion Fragments detail structure and molecular weight of compound



Mass Spectrum



Components in GC/MS



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

Affordable first entry
66L/s ExtractaBrite



Accessible high performance
300L/s ExtractaBrite



Ultra high sensitivity and robustness
ISQ 7000 AEI



High-throughput solution
ISQ 7000 NeverVent EI & CI



High-throughput solution
ISQ 7000 NeverVent EI



Perfect for today, ready for tomorrow

- Grows with laboratory requirements
- Base to advanced configurations
- Full field upgrade path

Most accesible entry from SQ>TQ
240L/s ExtractaBrite



Affordable performance
300L/s ExtractaBrite



High-throughput solution
TSQ 9000 NeverVent EI



High-throughput solution
TSQ 9000 NeverVent EI & CI

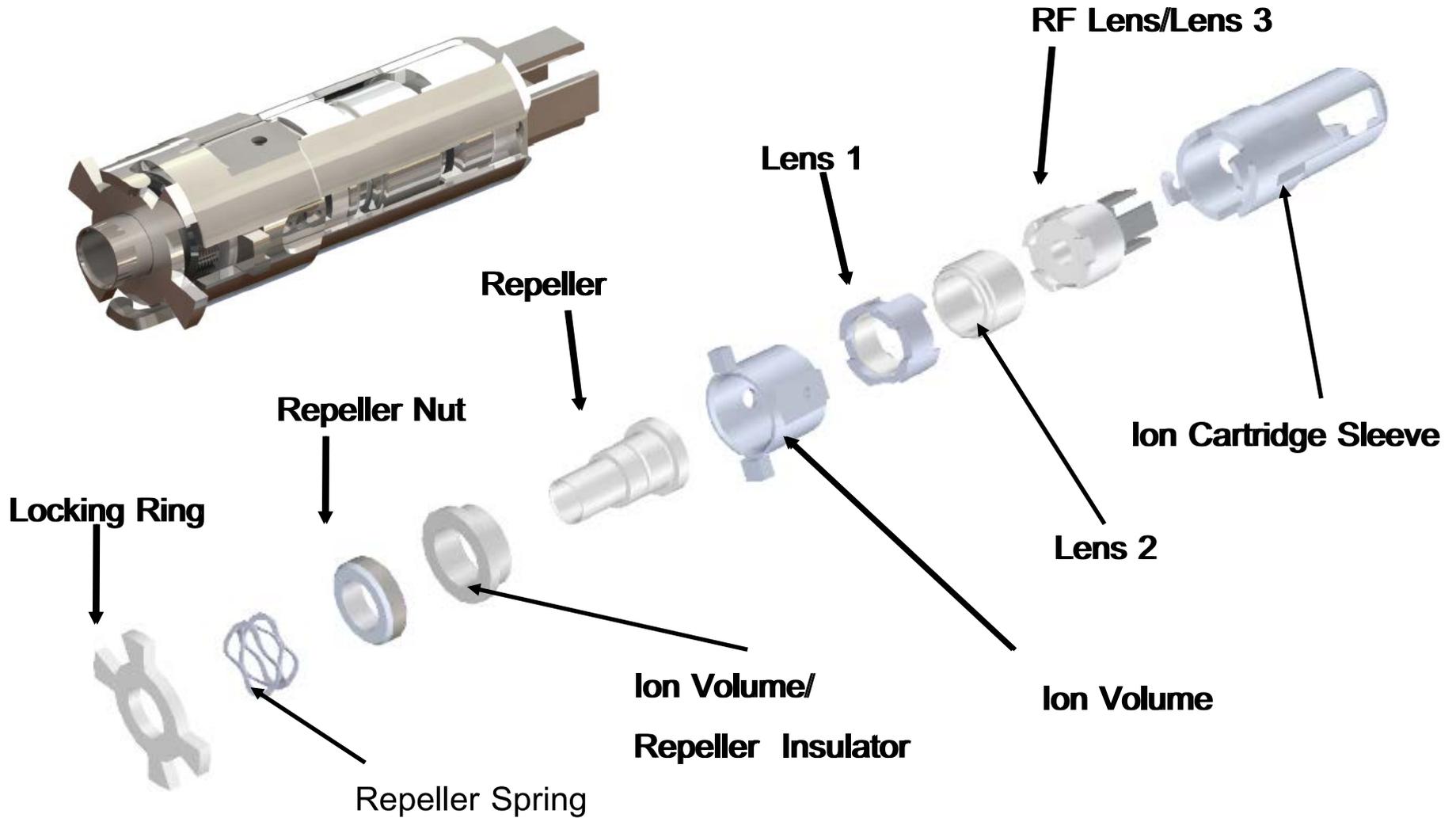


Ultra high performance
and robustness

TSQ 9000 AEI



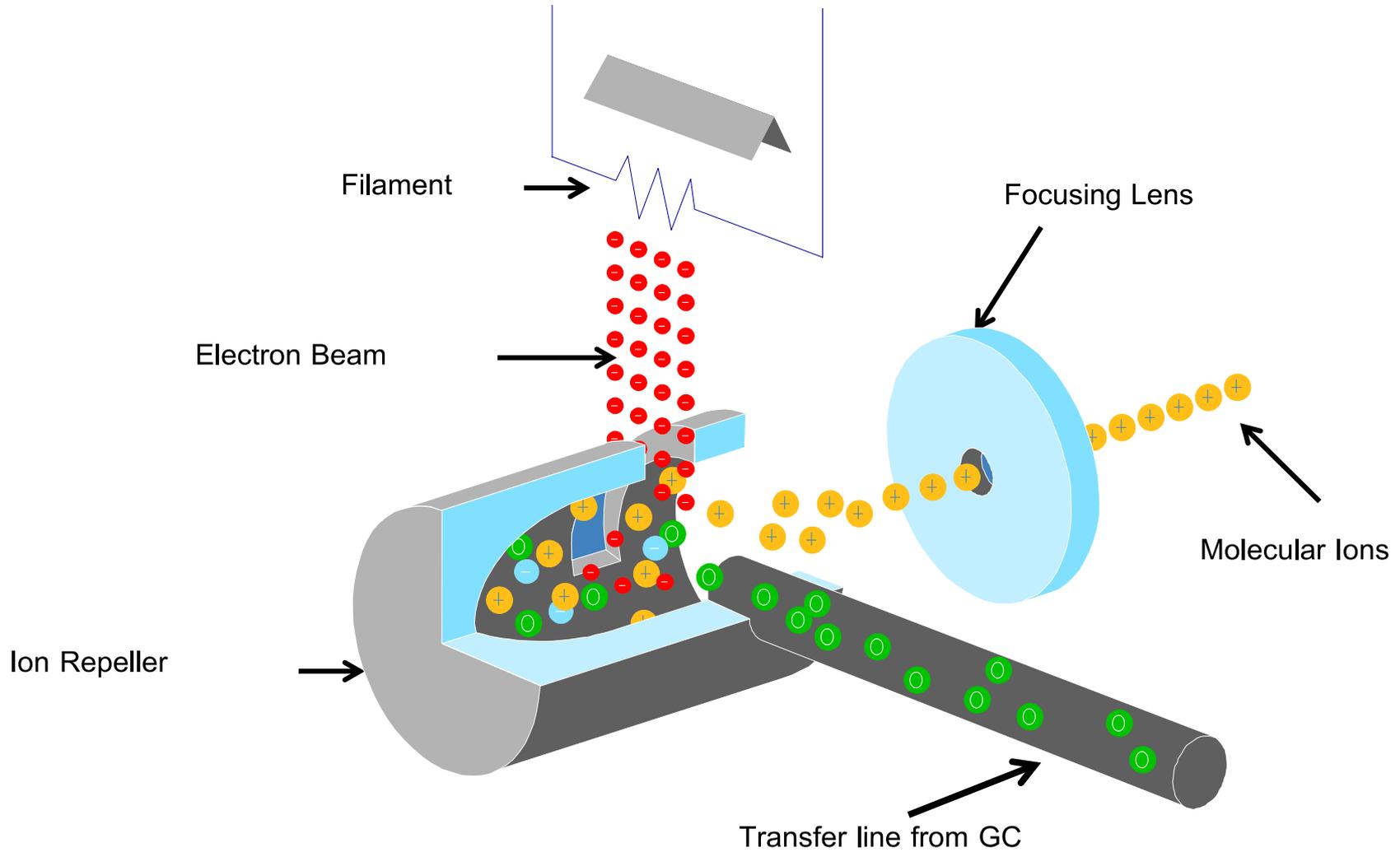
Ion Source Cartridge (iSQ)



- Electron Ionization

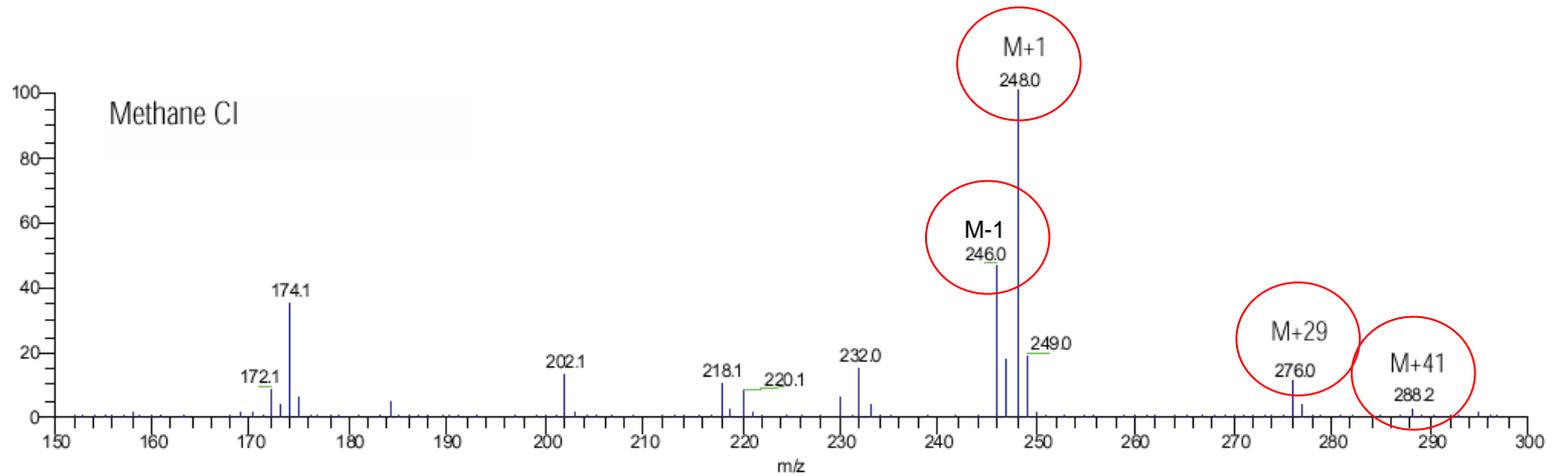
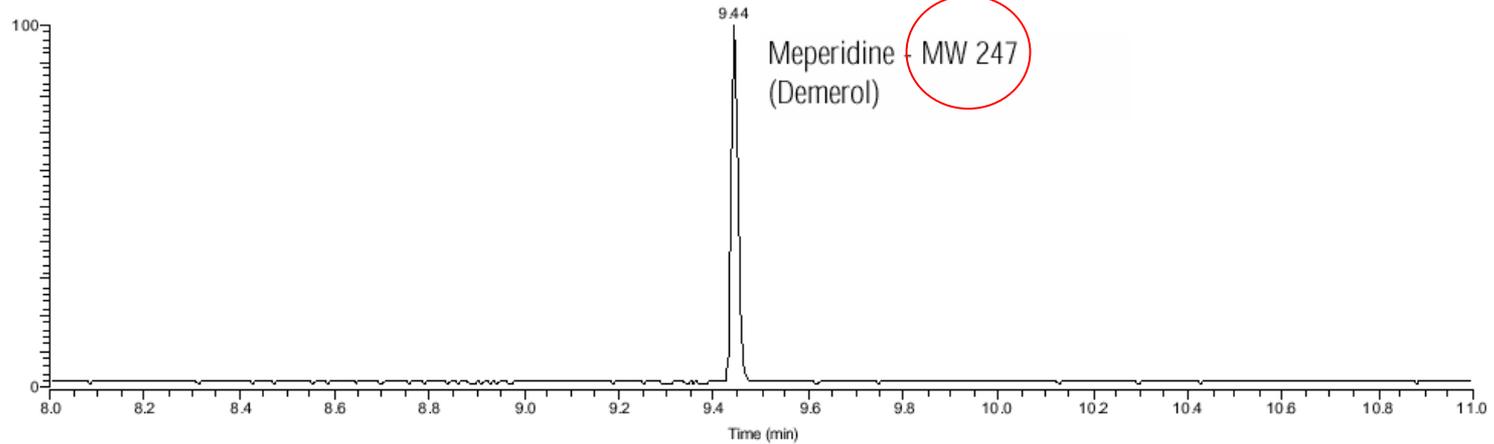
- Chemical Ionization
 - Positive Ion Chemical Ionization
 - Negative Ion Chemical Ionization

Electron Ionization



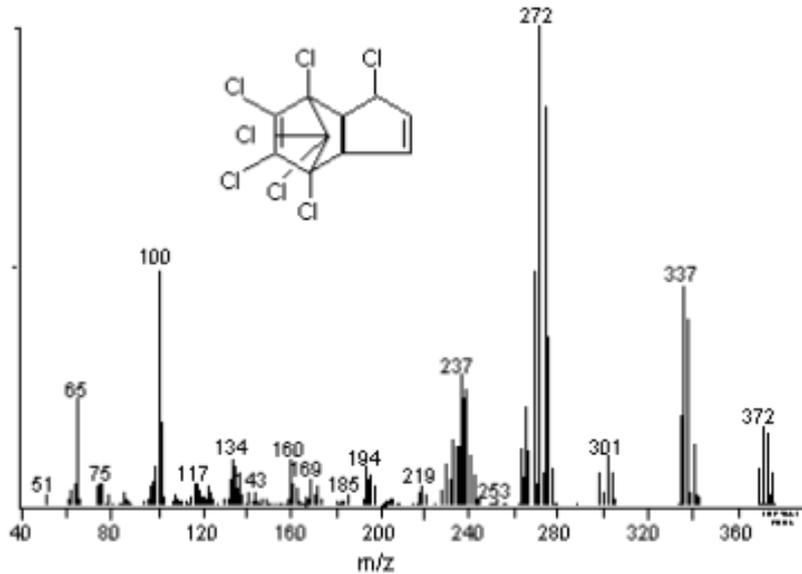
- Reagent gas reacts with electrons to form primary ions
- Primary ions react with CH_4 and form collided ions
- Collided ions react with sample molecules (soft ionization) and form molecular ions
- Molecular ions present in form of $[\text{M}+\text{H}]^+$, $[\text{M}-\text{H}]^+$, $[\text{M}+17]^+$,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

Adduct Formation in PICI



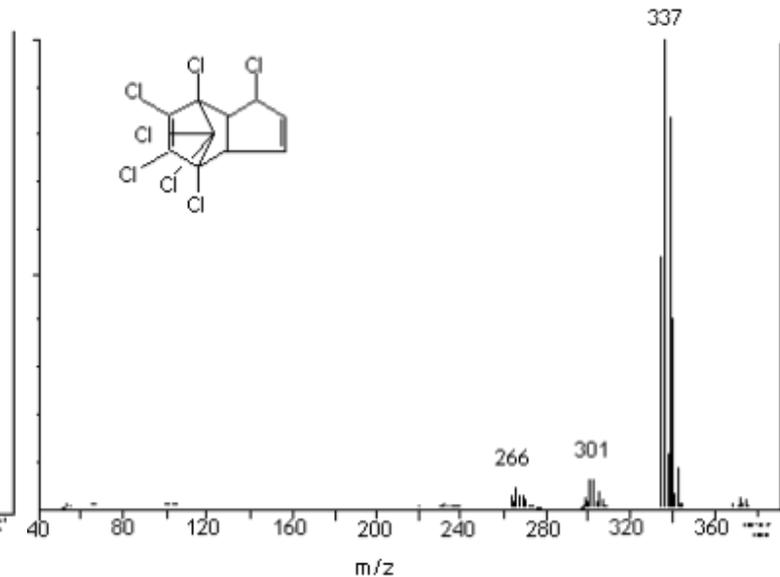
EI versus PCI for Pesticides (heptachlor MW 336)

EI Spectrum of Heptachlor



Intensity is low for any single m/z ion.

PCI Spectrum of Heptachlor



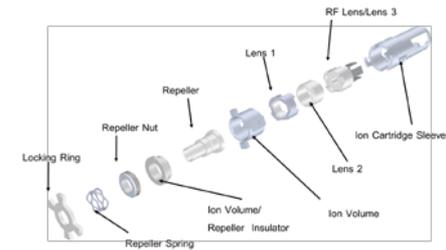
Intensity is concentrated in $[M+H]^+$ ion.

Spectrum is simpler.

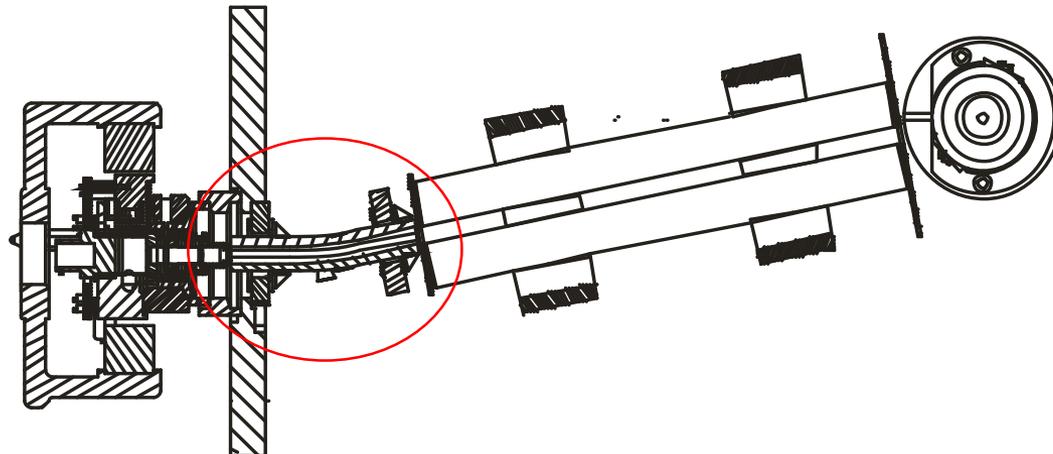
In PCI, sample is not fragmented. Therefore, PCI will provide higher ion intensity

Which means better detection limit when compares with EI

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



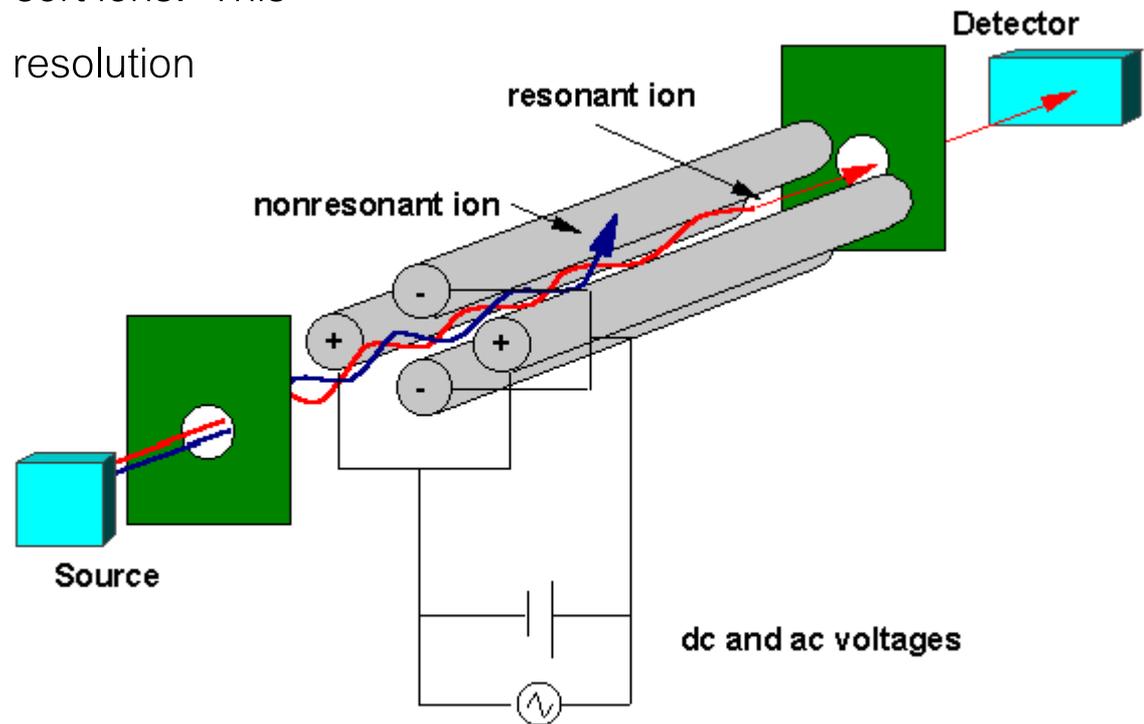
- Multi-pole rods :
 - quadrupoles , hexapoles, octapoles are widely used to transmit ions for longer distance



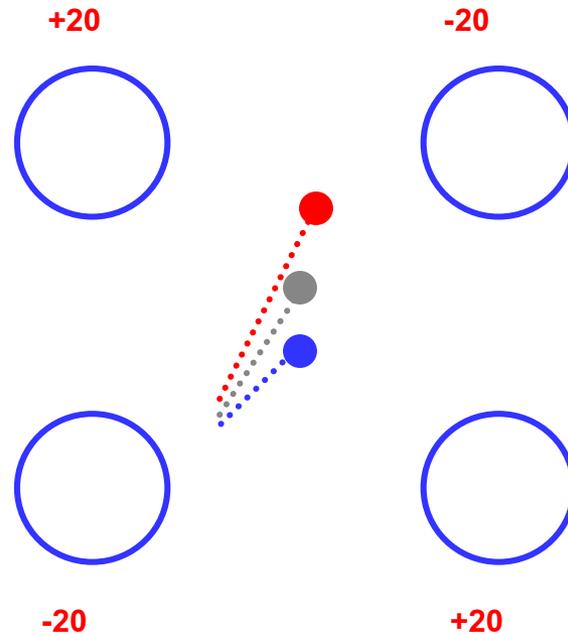
1. Quadrupole *or* Single Quadrupole
2. Triple Quadrupole
3. Time of Flight (TOF)
4. Magnetic Sector
5. Orbitrap

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



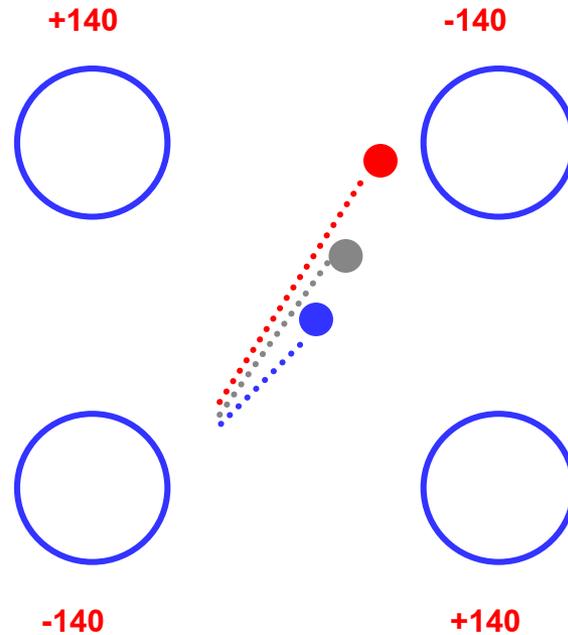
Quadropole Mass Filter Operation



- $m/z = 4+$
- $m/z = 100+$
- $m/z = 500+$

At Time 0

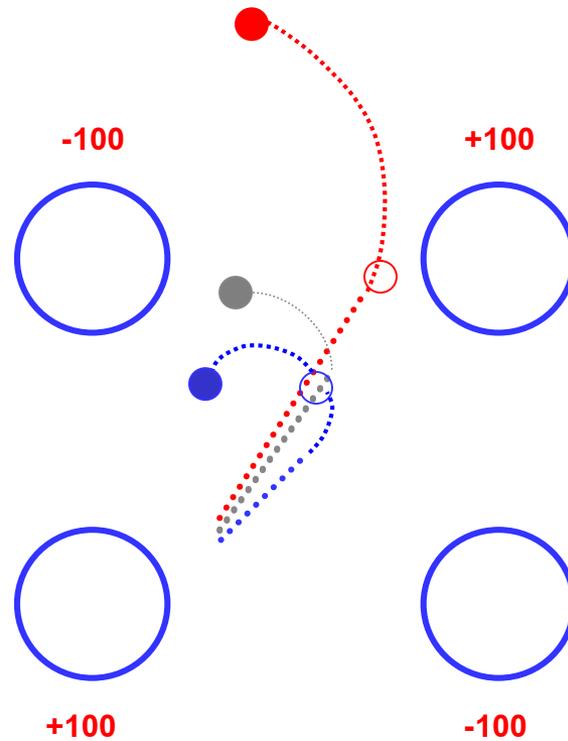
Quadupole Mass Filter Operation



	m/z= 4+
	m/z= 100+
	m/z= 500+

At Time 1

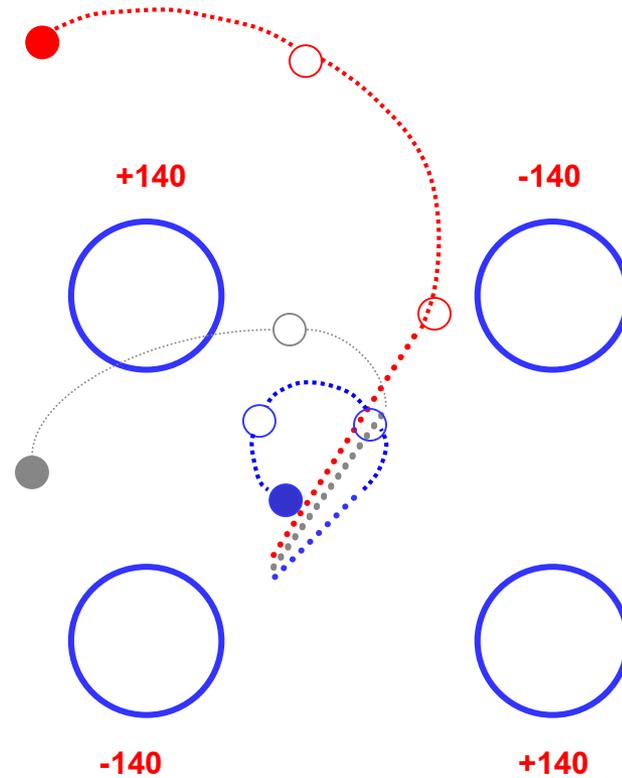
Quadropole Mass Filter Operation



- $m/z = 4+$
- $m/z = 100+$
- $m/z = 500+$

At Time = 2

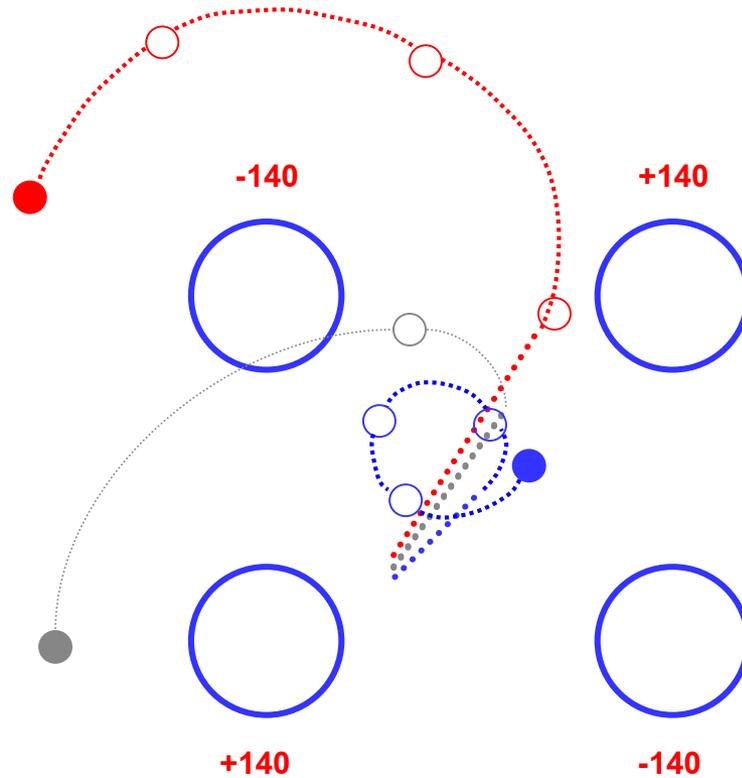
Quadupole Mass Filter Operation



	$m/z = 4+$
	$m/z = 100+$
	$m/z = 500+$

At Time = 3

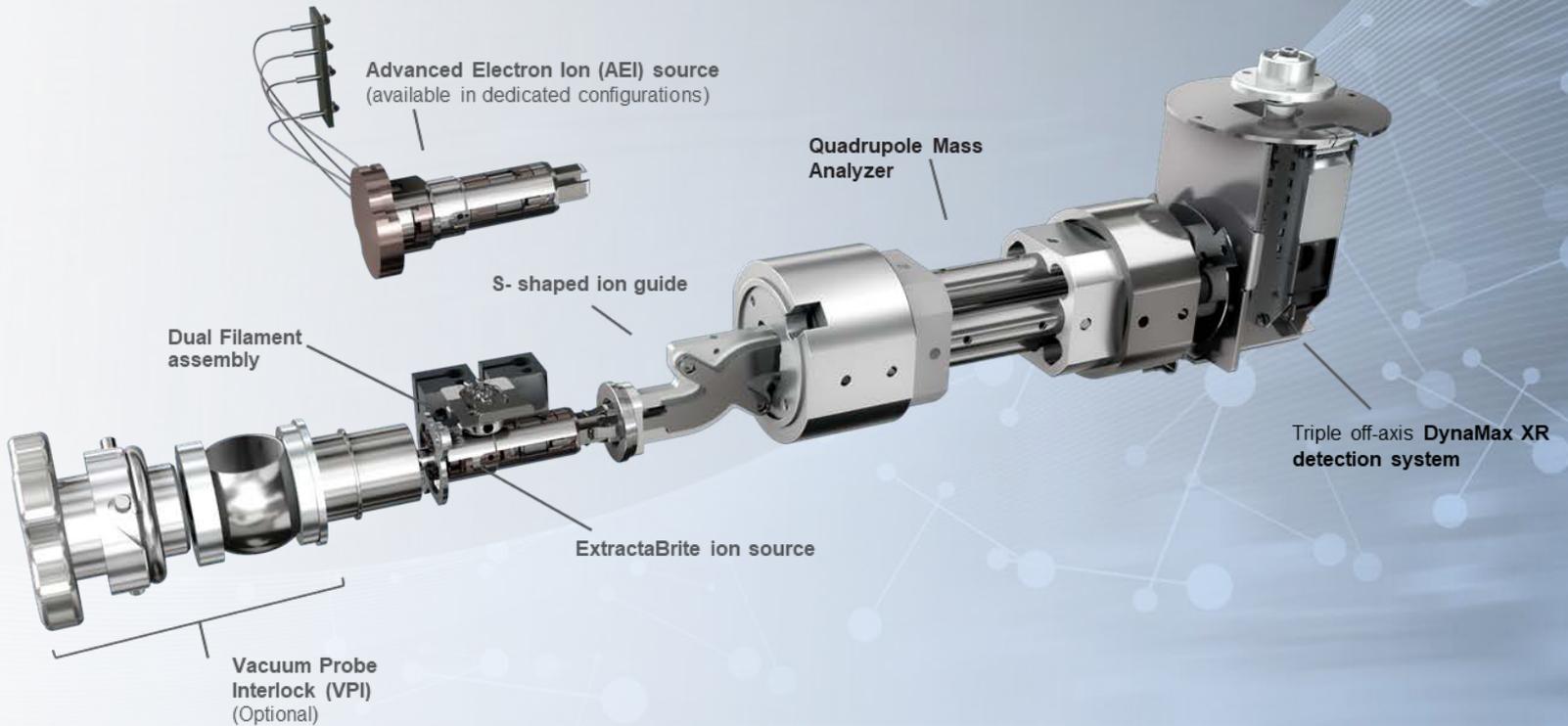
Quadupole Mass Filter Operation



- $m/z = 4+$
- $m/z = 100+$
- $m/z = 500+$

At Time = 4

ISQ 7000 GCMS – Designed with Intention

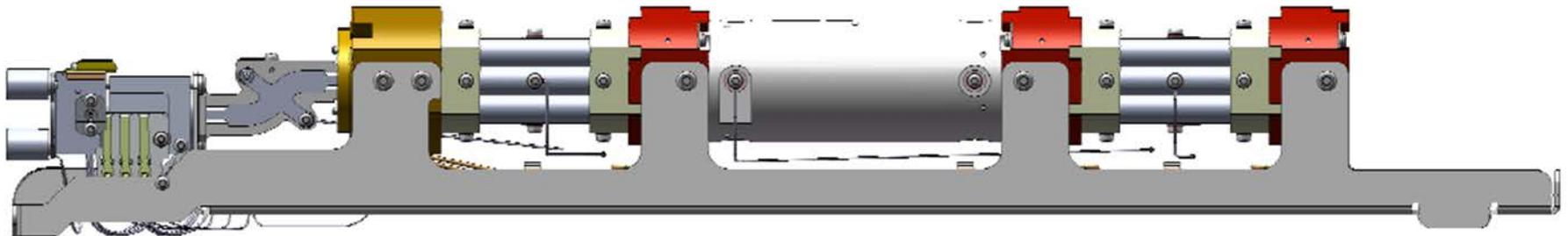


Operation modes in Single Quad MS

- 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

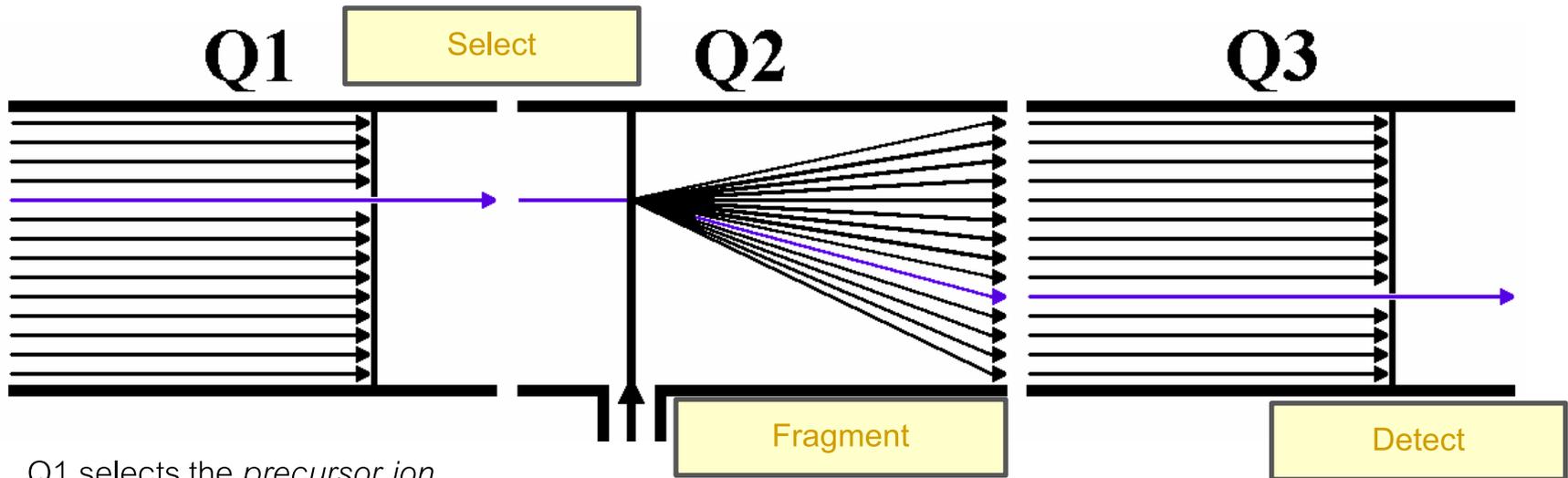
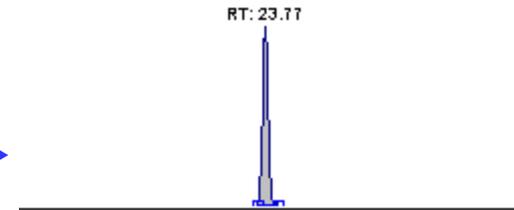
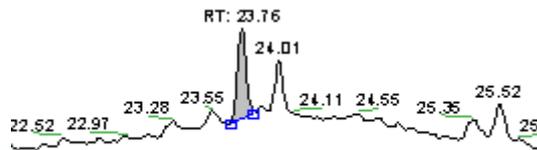
Triple Quadrupole Mass Analyzer

- 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

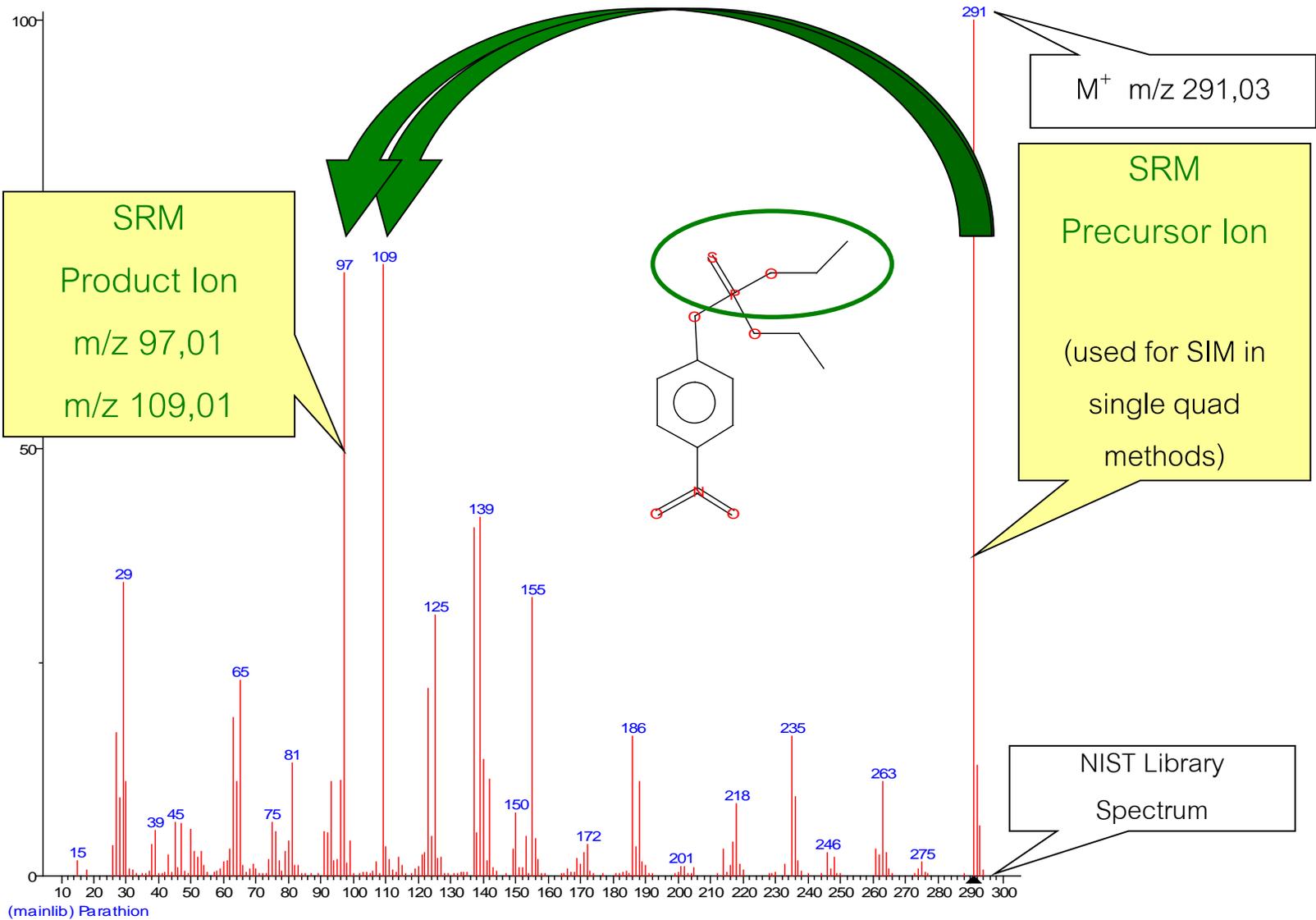


Q1 selects the *precursor ion*

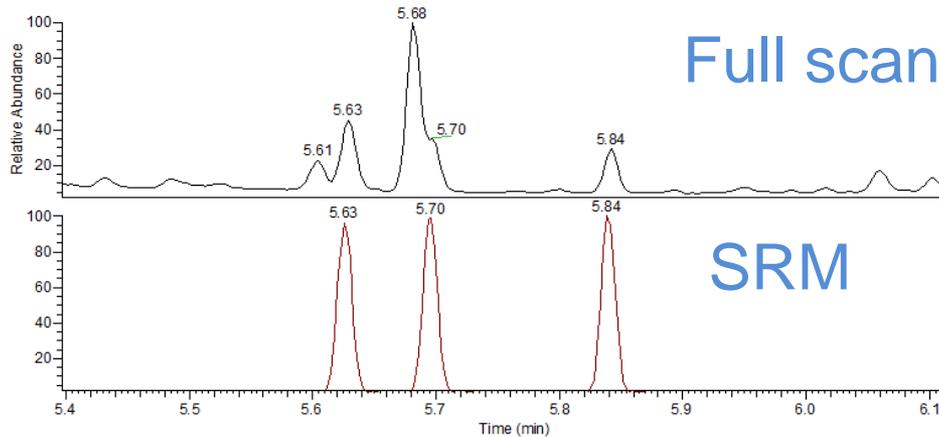
Argon Collision Gas

Q3 selects the *product ion*

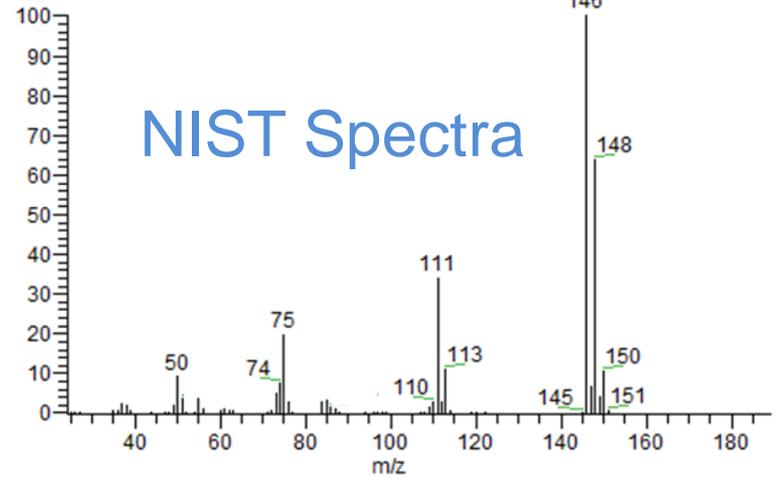
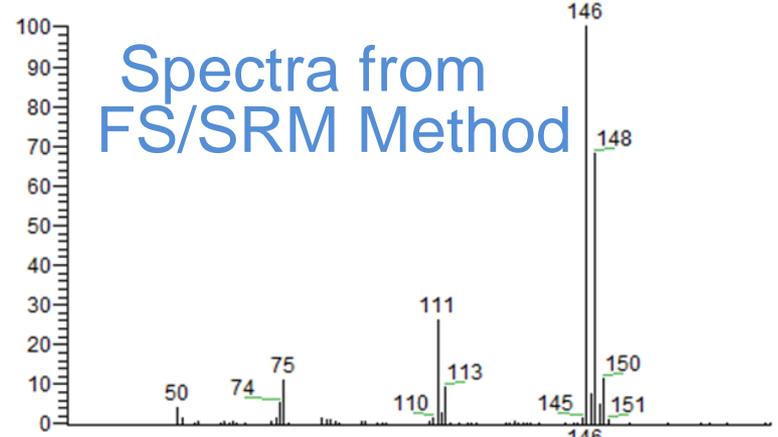
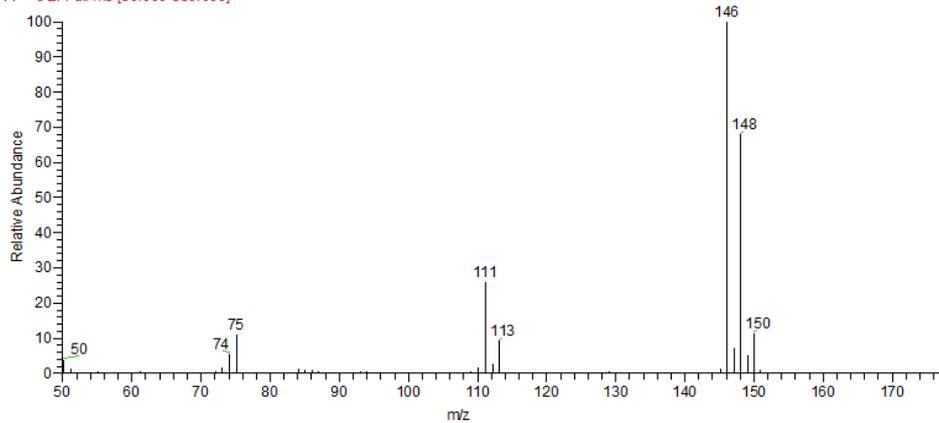
Structure Specific Selectivity by QQQ : Parathion-Ethyl



Full scan/SRM Acquisition



1_000CurveLancaster350IS1R9 #12135 RT: 5.84 AV: 1 SB: 5 6.08-6.09 NL: 1.54E8
F: + c EI Full ms [50.000-550.000]



Detector : Dynode Electron Multiplier

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

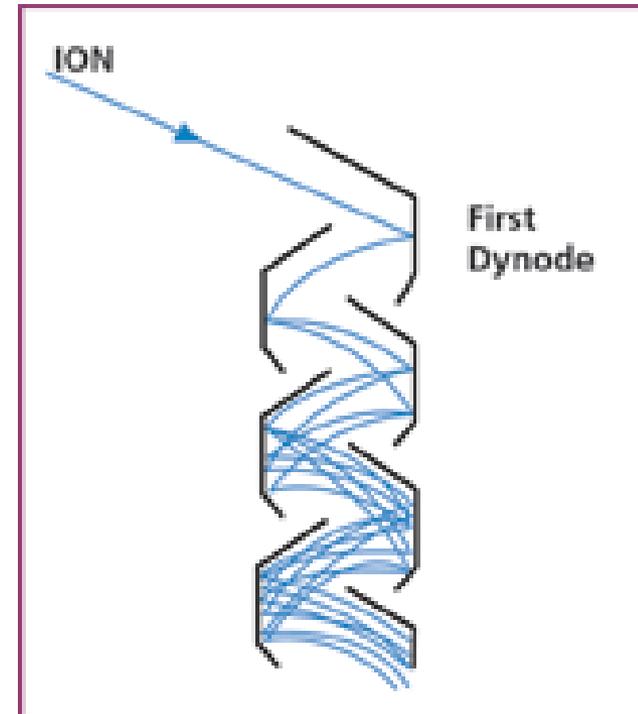
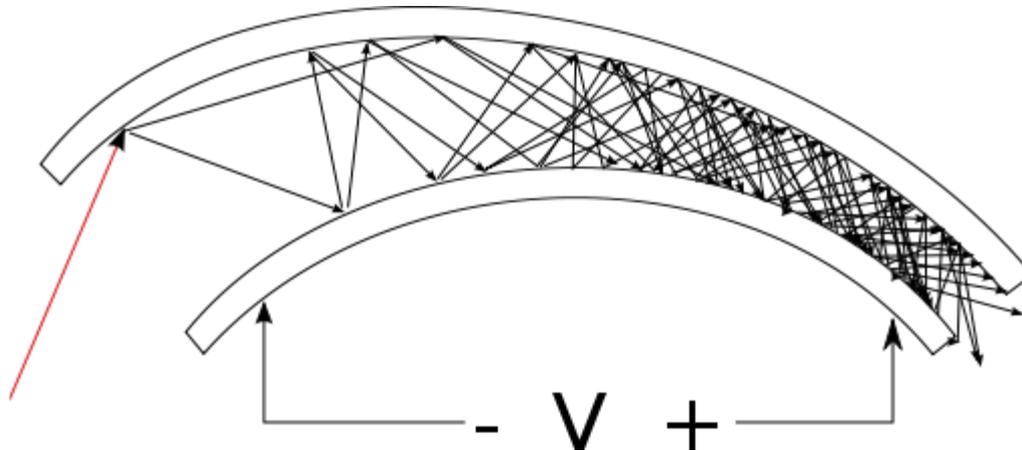
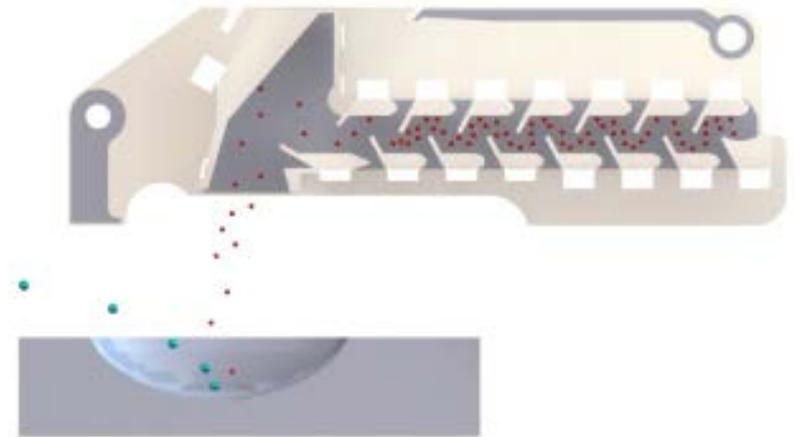


Photo courtesy from SGE & ETP, Wikipedia

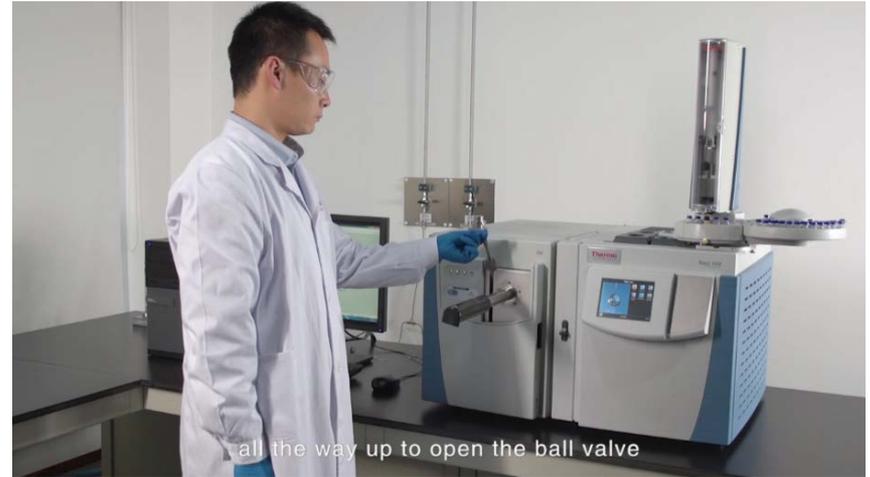
- Off axis dynode
 - High voltage is applied (+/-10 KV) for high signal (accelerate ion velocity from mass analyzer to dynode)
 - Induces only molecular ions to hit dynode
- Electrons from dynode hit internal wall of EM.
- Multiplication process amplifies for more signals

Electron Multiplier



Dynode

User maintenance :Vaccum probe inter lock



all the way up to open the ball valve

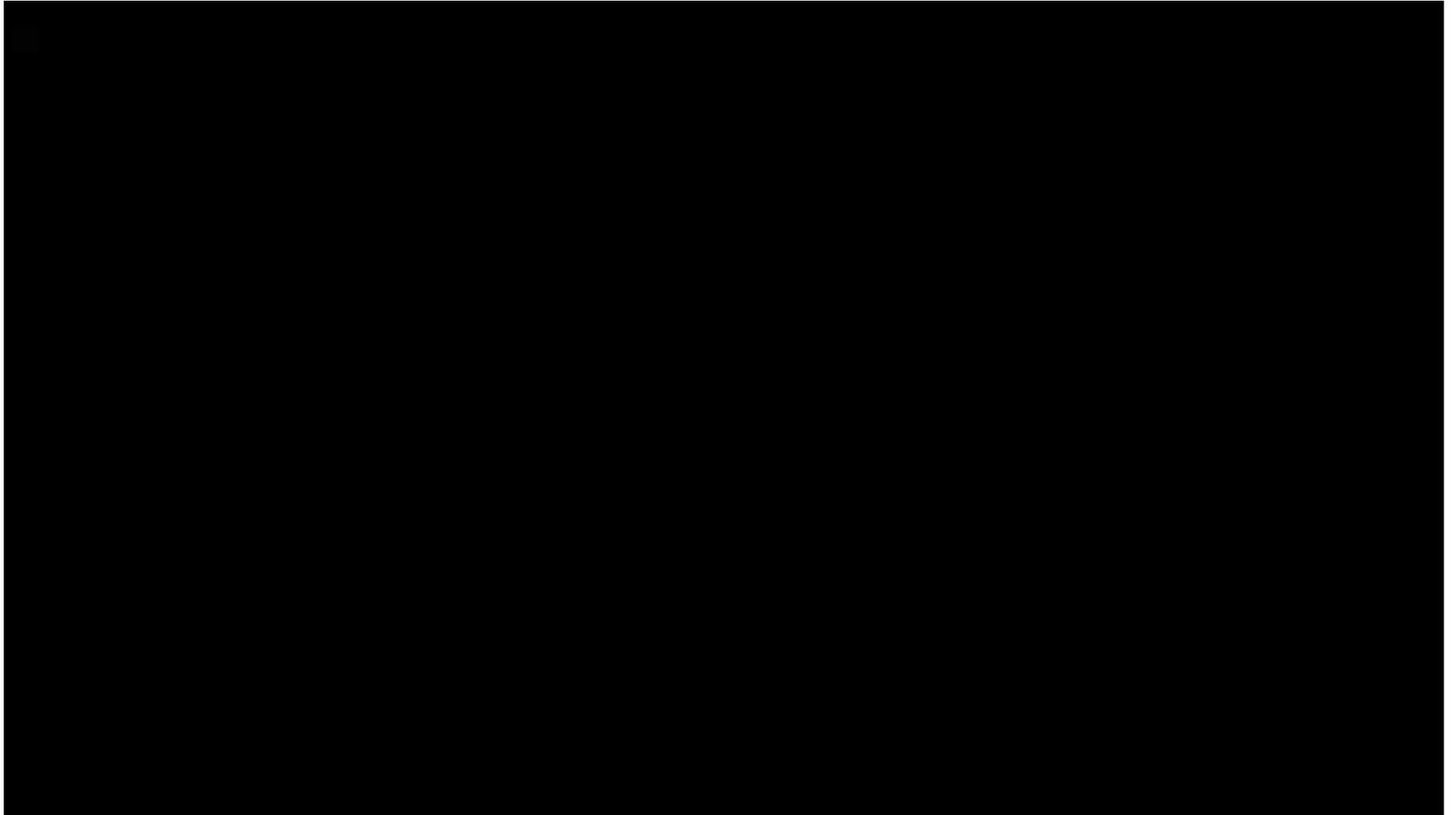


The ion source cartridge is attached to it



from the vacuum manifold into the exchange tool

Vacuum probe inter lock



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

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Application Note: 10212

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 years into a comprehensive methodology for the analysis of many hundreds of potential contaminating compounds. A multi-residue method for herbal products is faced with additional challenges from the world origin of the products and the complex matrix of dried materials. In the due quality control of raw materials, the unknown or undeclared local plant protection treatments must be taken into account a wide variety of potential pesticide contamination. Dried leaves, fruits or seeds and other herbal products for medical use deliver highly complex extracts from sample preparation due to the rich content of active ingredients, essential oils and the typical high boiling natural polymer compounds from broken cells, leaf and fruit skins. A thorough clean up of the extracted sample can lead to losses of critical analytes of interest. A complete characterization of pesticide, and other residues is done by both LC and GC-MS/MS to cover the complete range of functional groups.

This application report describes the methodology used for the multi-residue analysis of herbal products using accelerated solvent extraction (ASE) and gel permeation chromatography (GPC) for sample preparation, detection and quantitation by Thermo Scientific TSQ 8000 GC-MS/MS system.



Application Note: 10212

Determination of Total FAME and Linolenic Acid Methyl Ester in Pure Biodiesel (B100) by GC in Compliance with EN 14103

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Application Note: 30112

Key Words

- TRACE GC Ultra
- Biodiesel (B100)
- EN 14103
- Linolenic acid methyl ester
- Total FAME

Introduction

In order for biodiesel to be commercialized as pure biofuel or blending stock for heating and diesel fuels, it must meet a set of requirements defined in ASTM D6751 and EN 14214 standard specifications.^{1,2} These specifications indicate the maximum allowable concentrations of contaminants in pure biodiesel (B100) finished product, along with other chemical-physical properties necessary for a safe and satisfactory engine operation.

Gas chromatography (GC) is commonly adopted to characterize pure biodiesel (B100) according to the following standard methods:

- EN 14103: Determination of Total FAMES (fatty acid methyl esters) and Linolenic Methyl Ester (C18:3)
- EN 14105/ASTM D6584: Determination of Free and Total Glycerine^{4,5,6,7}
- EN 14110: Determination of residual Methanol^{8,9}

Comprehensive Thermo Scientific GC solutions have been developed in compliance with each of these methods, based on the Thermo Scientific TRACE GC Ultra™ and the versatile TriPlus™ autosampler (Figure 1). This application note relates to the determination of total FAME and linolenic acid methyl ester in biodiesel according to EN 14103.



Figure 1: Thermo Scientific TRACE GC Ultra with TriPlus autosampler

Introduction

The cetane number distribution of biodiesel fuels is a reliable characteristic parameter for calculating standard methods. The cetane number is defined as the ratio of the cetane acid methyl ester (C16) to a reference fuel consisting of a mixture of cetane and heptadecane. This GC analysis is in accordance with EN 14214:2003 of FAME composition. FAME is achieved by a method is suitable between C14 and C22.

Key Words

- DFS
- Dioxin
- Furans-like PCBs
- Furans
- HRGC/HRMS

Methods

Instrumentation
A Thermo Scientific PTV inlet with heated detector (FID), a Chrom-Carb detector, and a Thermo Scientific 0.25 mm ID, 0.3 µm film thickness column.

Sample Preparation
Accurately weigh 10 mL vial, then internal standard.

Operation of PTV
When FAMES are analyzed, sample volume is increased to a few nanoliters to accumulate inside the PTV. This increases the resolution and reduces the column bleed.

Confirmation of Low Level Dioxins and Furans in Dirty Matrix Samples using High Resolution GC/MS

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Application Note: 52242

Key Words

- ISQ Single Quadrupole GC-MS
- HRGC/HRMS

Introduction

Over the past 30 years, dioxin TEQ levels and body burden levels in the general population have been on the decline and continue to decrease.^{1,2} More than 90% of human exposure to dioxins and dioxin-like substances is through food.³ With increasingly lower dioxin levels in food, feed, and tissues, more demanding limits of detection, selectivity, sensitivity and QC checks are required to confirm their presence at these ever decreasing levels.



Figure 1: Thermo Scientific DFS High Resolution GC/MS with two TRACE GC Ultra™ and TriPlus™ Autosampler.

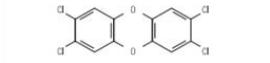


Figure 2: 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

Because HRGC/HRMS possesses all of the above criteria, it has become the most efficient analytical technique for this application, and is now required for dioxin analysis in food and feed by European directives, as well as by the US EPA for Method 1631 Re-B¹⁰. Also, because of its specificity, HRGC/HRMS is required by these directives for the positive confirmation of the existence of the analyte in the sample.

The new directives demonstrate the continuing need for even more sensitive analytical instrumentation. As an example, the new methods for confirmation require limits of quantitation (LOQ) to be 80% lower than the lowest reported level in the method. This requires the instrumentation to reach even lower levels of detection, and reduce the necessary sample volumes needed for analysis.



Identification and Quantification of Impurities in Wines by GC/MS

Benedicte Gauriat-Dorval, Eric Phillips, Stacy Crain, Trisa Robarge, Thermo Fisher Scientific, Austin, TX, USA (With special thanks to members of Oenologie Center of Grezillac)

Introduction

While wine makers have historically used gas chromatography and mass spectrometry (GC/MS) to detect pesticides, they now more commonly use the technique to supplement quality control checks of wine taste. Without GC/MS,



Figure 1: ISQ Single Quadrupole GC-MS system

that determine wine purity on site rather than having to send samples for expensive, external analysis. In this report, we present the design and results of this study, including the experimental method used to detect impurities and the concentration ranges that compare GC/MS with human detection.

Methods

For this experiment, several targeted molecule types that affect wine quality were analyzed using an ISQ™ Single Quadrupole GC-MS system (Figure 1). Table 1 contains a brief description of the effects on wine quality of the four target molecule types, and examples of how GC/MS analysis can provide value in quality control.

Isotopologues	Benefit of GC/MS Analysis
produced in various steps of wine metabolism. The two isotopologues are the wine an "animal" or "yeast" quality.	GC/MS can detect 4-ethylphenol and 4-ethylguaiacol in lower concentration than human tasters. GC/MS can also detect the presence of 4-vinylphenol and 4-vinylguaiacol, intermediaries in Shertansuoye yeast metabolism and allow wine makers to discard contaminated batches.
and derived from mold in a wine's taste.	Detecting gossypol in wine alerts makers to the presence of mold in their grapes and allows them to locate and treat a contaminated plot of land.
wine from halophenols, prevent wood degradation wine a moldy odor.	Assays provide information of an organoplastic defect in wine production and help identify contamination sources.
maturation markers, and a wine's taste (PMP) note.	Determining the levels of IBMP and IPMP in wine affects harvesting decisions.

Isotopologues on Wine
produced in various steps of wine metabolism. The two isotopologues are the wine an "animal" or "yeast" quality.

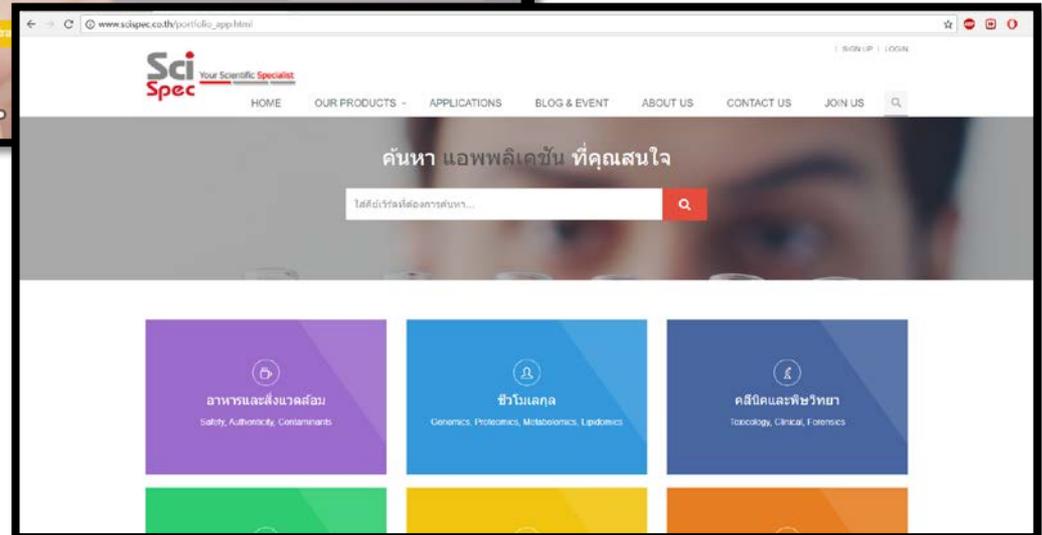
The injection was performed using the hot needle technique. The empty needle was heated up in the injector for 2-3 seconds before injecting the sample, thus eliminating any discrimination of higher boiling congeners.

The DFS mass spectrometer was set up in the multiple ion detection mode (MID) at a resolution of 10,000 (10% valley definition). FC43 was used as a reference compound to provide the inherent lock and call masses. These reference masses are monitored scan-to-scan to insure the highest mass precision, stability and ruggedness necessary for routine target compound analysis on a high resolution mass spectrometer. For all native dioxin/furan congeners, as well as for their specific ¹³C labeled internal standards, one quantification mass and one ratio mass were implemented in the MID set up, as shown in Table 2. The effective resolution is constantly monitored on the reference masses and documented in the data files for each MID window.

Modifications of the MID descriptor used in this application might be necessary for different applications. As an example, the EPA method 1613 standards typically do not contain the octa-furan ¹³C labeled internal standard, so the masses in brackets in Table 2 can be deleted for a pure EPA 1613 MID set up. To set the boundaries of the MID retention time windows for each individual congener group, a window defining standard (such as a fly ash) must be used to properly set the MID time windows.

Scispec website : Application.....

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Static Headspace
(Syringe based)

Dynamic
Headspace
(ITEX)

SPME

Sample
Preparation

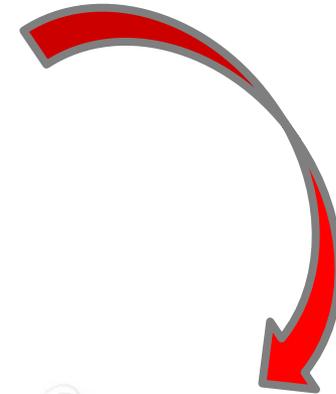


Static
Headspace
(Valve&Loop)

Purge & Tra

Thermal
Desorber

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



ASE™ 350

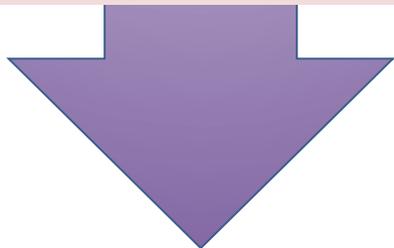
Sample Preparation

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)

SRM : More than 80 compound

Pesticide Name	RT (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (V)
Diffuorobenzamid Degradation (Isocyanat)	6.93	152.93	90.01	20
Diffuorobenzamid 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
Diffuorobenzamid Degradation	8.62	141.00	63.11	25
Diffuorobenzamid 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
Chloroprotham	12.26	213.06	127.03	15
Chloroprotham	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
Profuralin	13.22	318.10	199.06	15
Profuralin	13.22	330.23	252.45	25
Sweep	13.46	187.05	123.95	18
Sweep	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
Bromoclyen	14.37	358.79	242.85	15
Bromoclyen	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	267.97	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

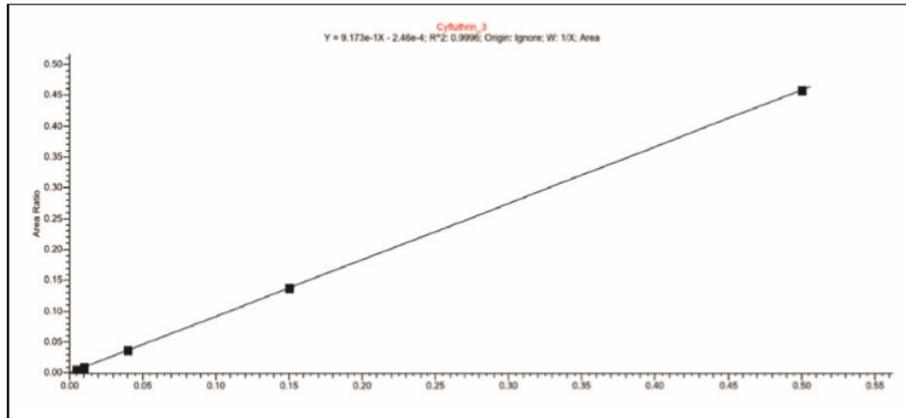
Pesticide Name	RT (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (V)
Anthrachinon	15.44	207.97	151.99	20
Anthrachinon	15.44	180.04	152.05	15
Anthrachinon	15.44	207.97	180.10	10
Nitrothal isopropyl	16.09	236.08	194.07	10
Nitrothal isopropyl	16.09	236.08	148.05	20
Triadimefon	15.41	208.07	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)
Paclobotrazole	17.75	238.11	127.06	15
Chinomethionat	17.78	206.06	147.98	10
Chinomethionat	17.78	234.08	206.06	15
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
Famprop-methyl	18.39	230.05	170.04	10
Famprop-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
Fenamisol	23.55	251.02	139.01	15
Fenamisol	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
Silaflluofen	26.25	179.00	151.00	7
Silaflluofen	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

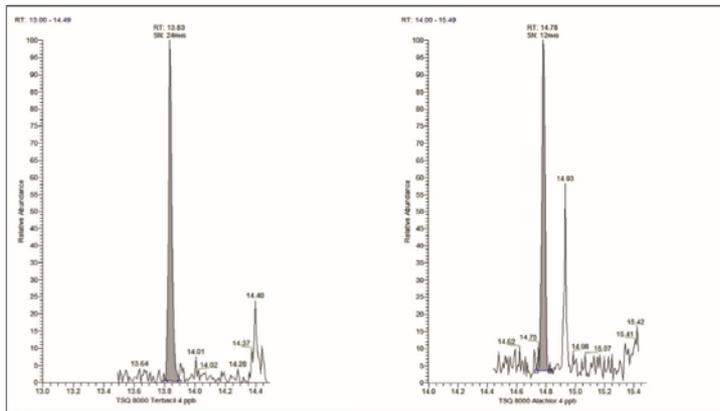
Calibration and Detection limit.

Calibration level : 0.004 $\mu\text{g/mL}$ to 1.0 $\mu\text{g/mL}$ (This range represents an analyte concentration of 0.01 to 2.5 mg/kg in the samples)

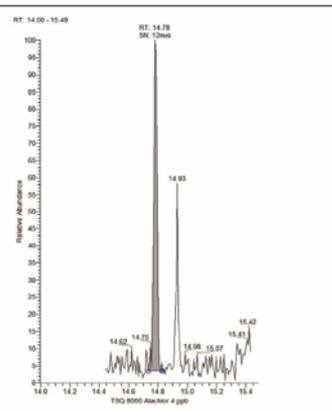


Pesticide	RT [min]	S/N @ 4 ppb
Terbacil	13:83	24
Alachlor	14:78	12
Tolyfluanid	16:75	44
Pyridaben	24:17	83

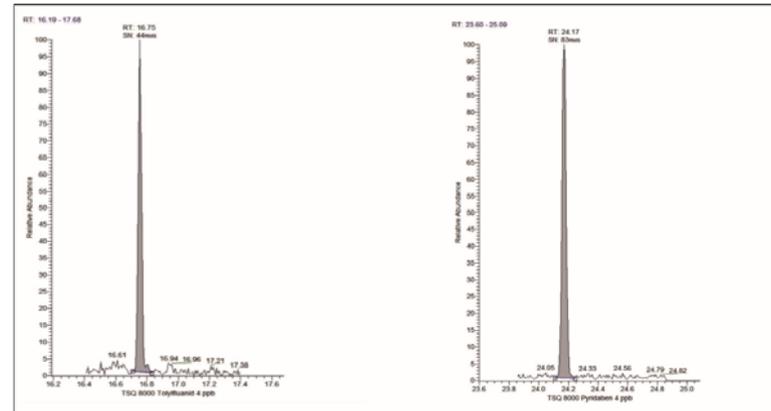
Sensitivity (LOD)



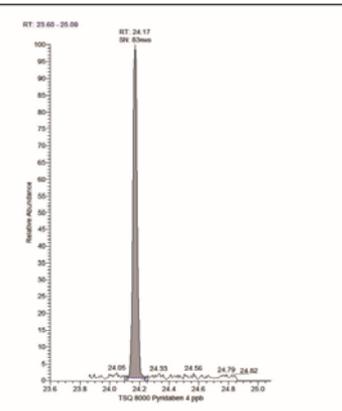
Terbacil



Alachlor



Tolyfluanid



Pyridaben

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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Key Words
 Pesticides, Tea, Herbal products, ASE, SFM, 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 origin of the products and the complex matrix of the dried ingredients. In the strict quality control of raw materials, the unknown or unlabeled local plant protection treatments must be taken into account with a wide variety of potential pesticide contaminations. Dried leaves, fruits or seeds and other herbal products of medical use deliver highly complex extracts from the sample preparation due to the rich content of active ingredients, essential oils and the typical high boiling natural polymer compounds from broken cells, leaves or fruit skins. A thorough clean up of the extracted sample can lead to losses of critical analytes of interest. A complete characterization of pesticide and other residues, contamination is done by both LC and GC-MS/MS to cover the complete range of functional groups.

This application report describes the methodology used for the multi-residue pesticide analysis of herbal products using accelerated solvent extraction (ASE) and pH partition chromatography (GPC) sample preparation with detection and quantitation by the Thermo Scientific TSQ 8000 GC-MS/MS system.



A routine screening method for more than 200 pesticide compounds was applied to a wide variety of different sample types, ranging from regular black tea or sage leaves, to exotic like lemongrass and herbs of medicinal and fragrance use like thyme and chamomile. The data processing and reporting was achieved by using the Thermo Scientific TraceFinder quantification software suite.

The sensitivity requirement for this analysis was determined by the regulatory background. The analysis of pesticide residues in tea and herbal products follows the regulations of the European Directorate General for Health and Consumer Affairs (SANCO) for Method Validation and Quality Control Procedures for Pesticide Residue Analysis in Food and Feed (1). The sensitivity requirements for these products as referenced in the Codex Alimentarius (2) result in maximum residue levels of 0.01 mg/kg for most of the pesticide compounds.



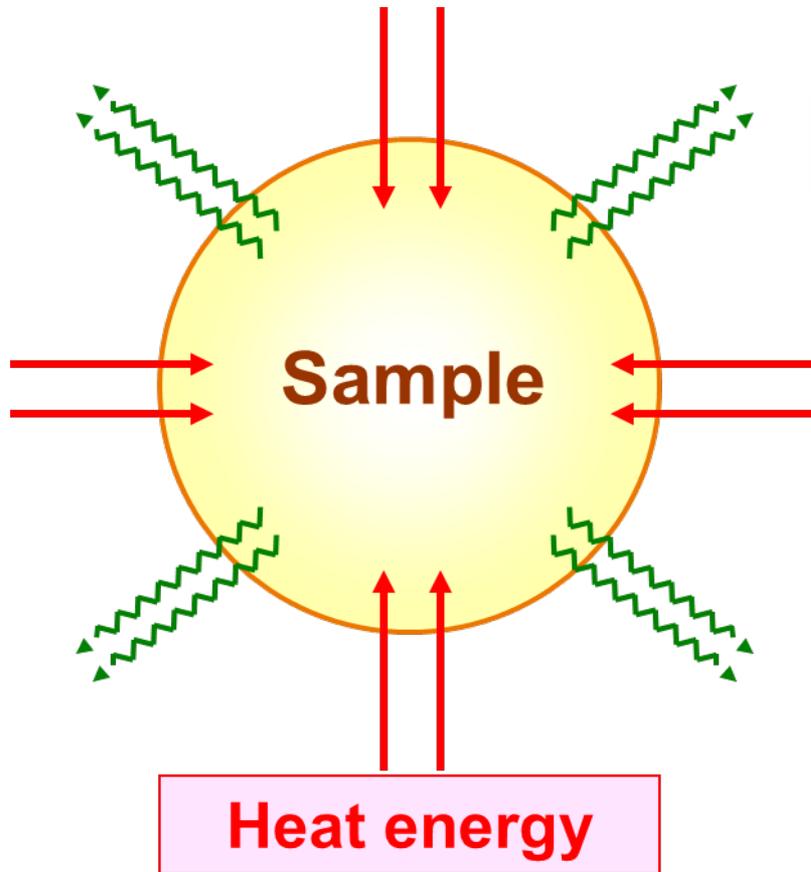
Thermo SCIENTIFIC

Application note 52291

● PY-GCMS



Information from polymeric Materials by Heating

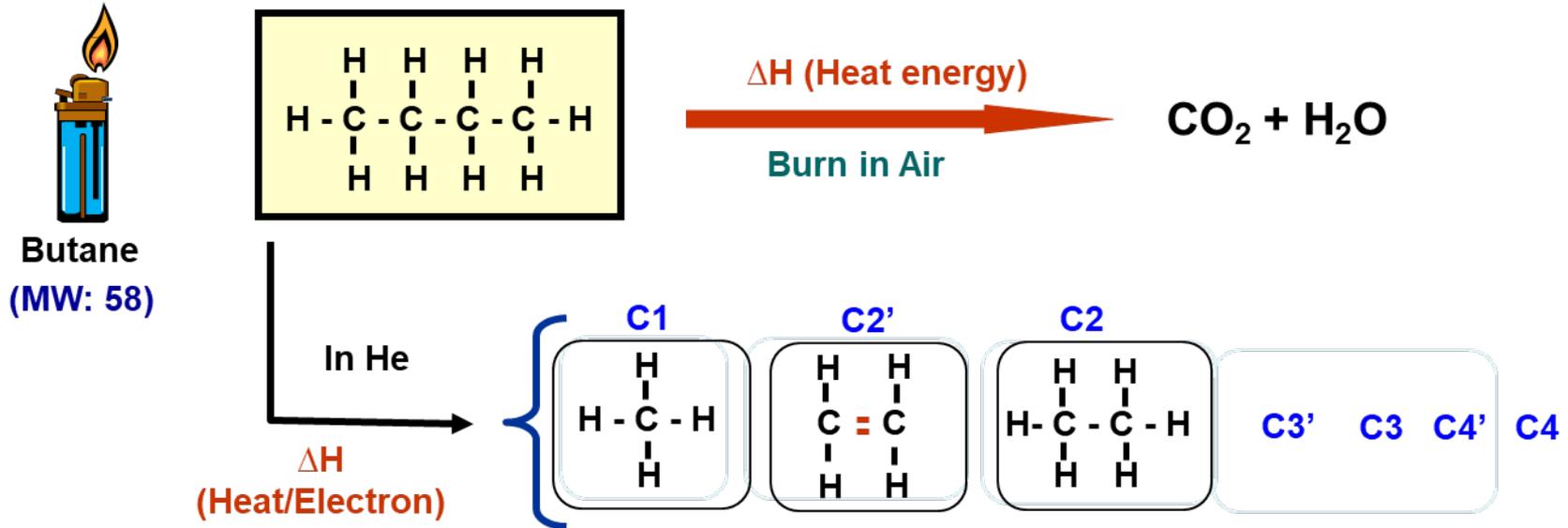


Information

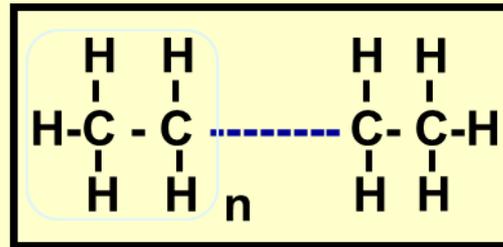
- Weight loss: **TGA**
- Enthalpy change: **DTA, DSC**
- Mechanical change: **TMA, Dilatometry**
- Evolved gas
 - volume: **EGA (volume of gas)**
 - qualification & quantification:

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

Pyrolysis of Polymeric materials and pyrolyzates



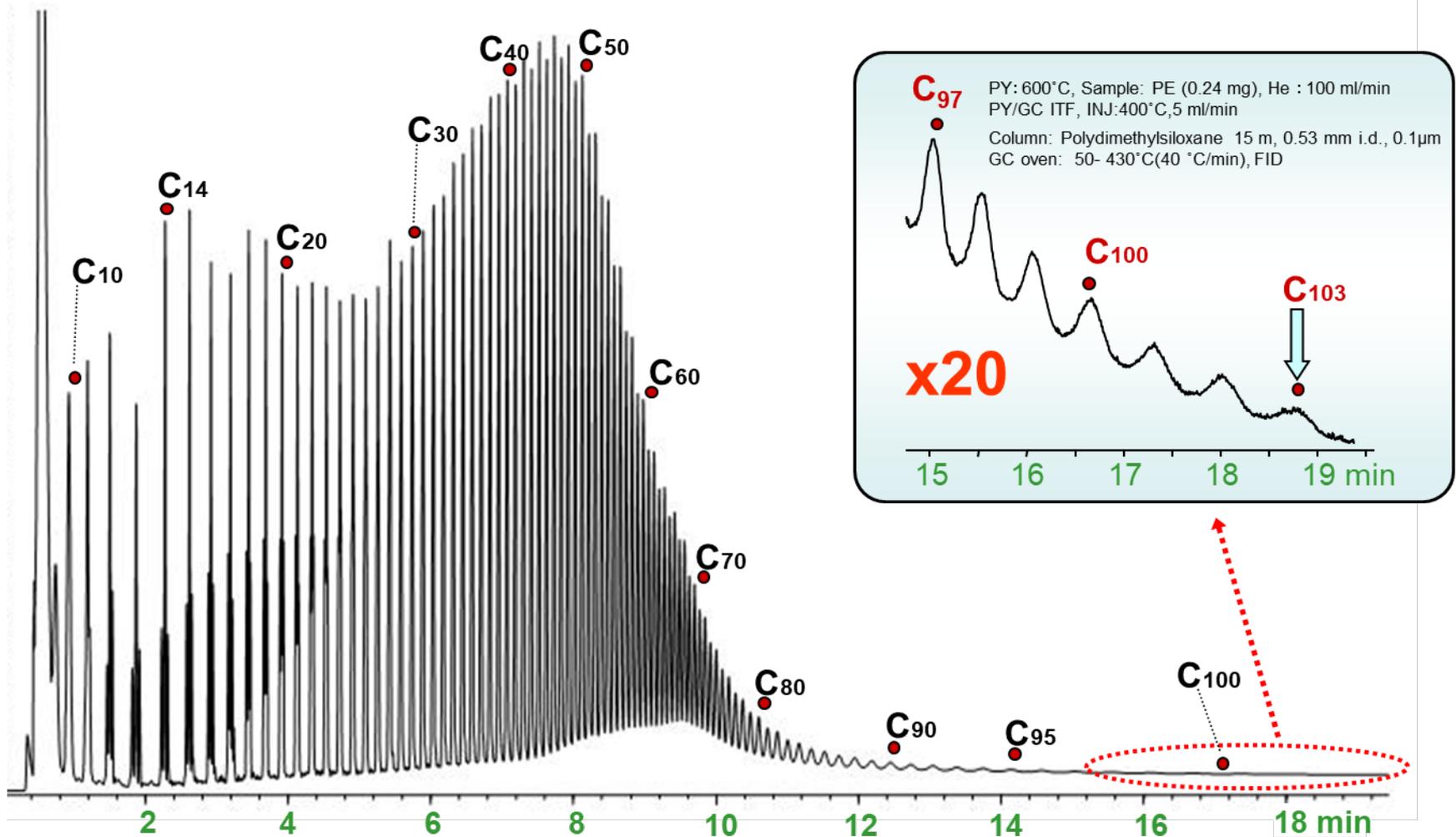
Polyethylene
(MW: 10,000 ~ 1,000,000)



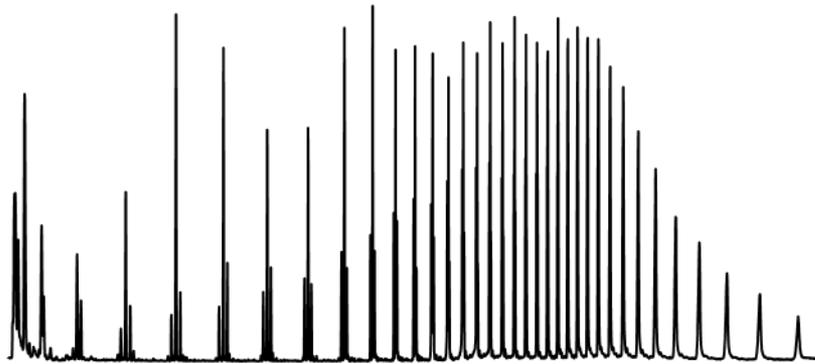
ΔH
(Heat/Energy)

C1, C2', C2, C3', C3
C4', C4'' ... Cx

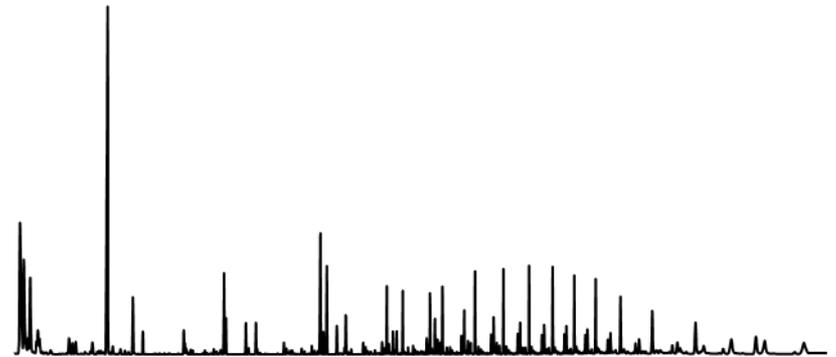
Typical pyrogram of polyethylene at 600°C



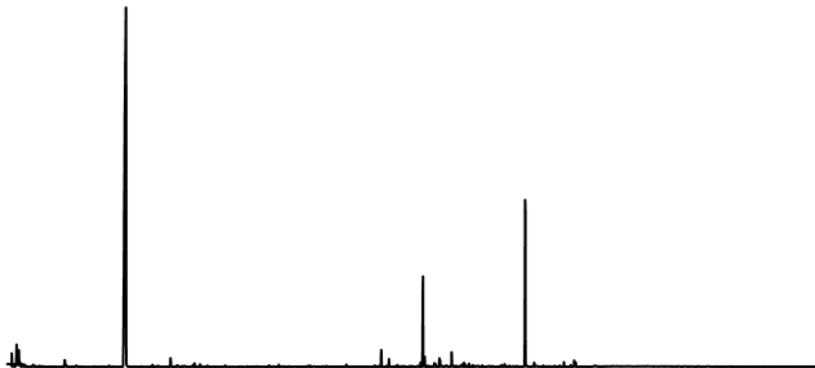
Polyethylene



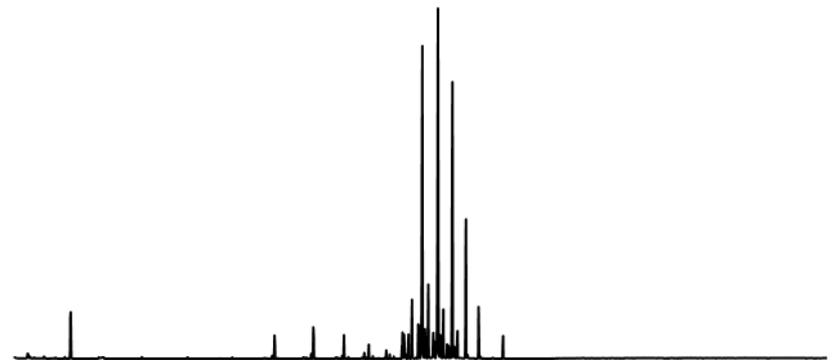
Polypropylene



Polystyrene



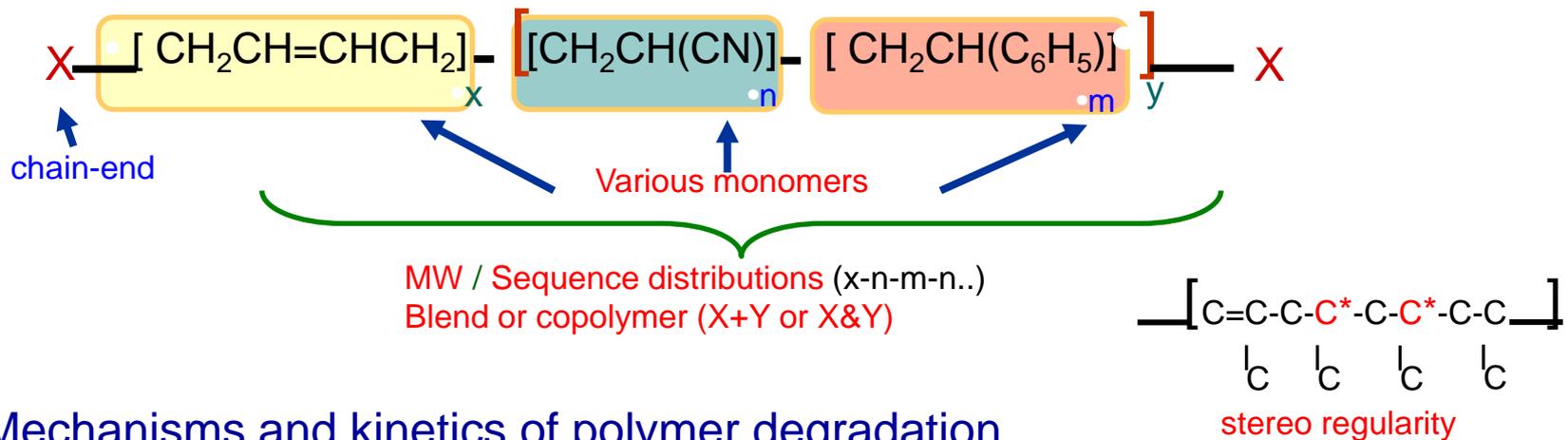
Higher methacrylate copolymer



A: Identification of polymeric materials

Unknown materials (PP/ PVC/ SBR?)

B: Structural characterization of polymers



C: Mechanisms and kinetics of polymer degradation

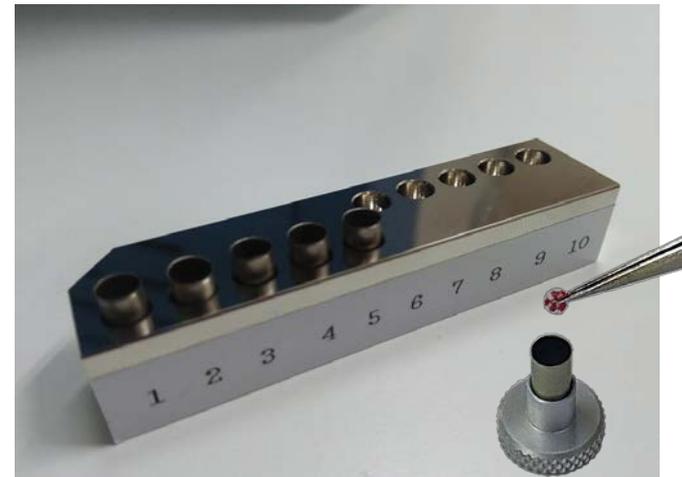
D: Qualitative and quantitative analysis of additives

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.

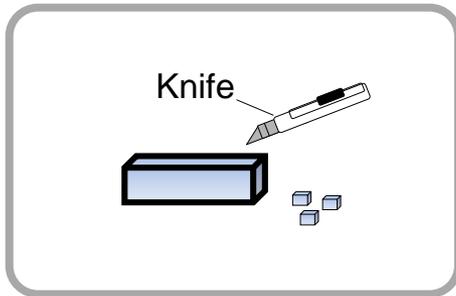
สภาวะเครื่อง Pyrolyzer

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



Sample cup

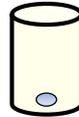
• Step 1



• Step 2

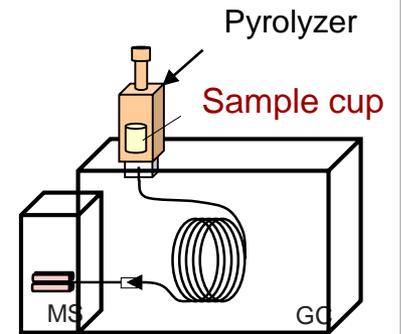
Place a sample
in the sample cup

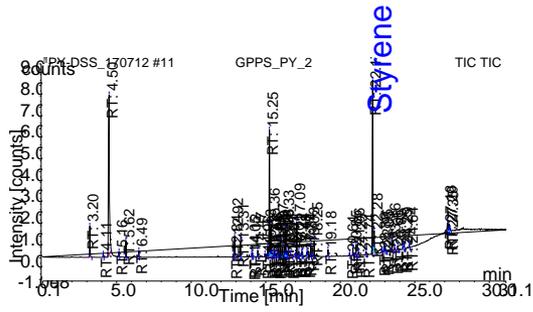
0.1- 0.5mg



No solvent extraction

• Step 3

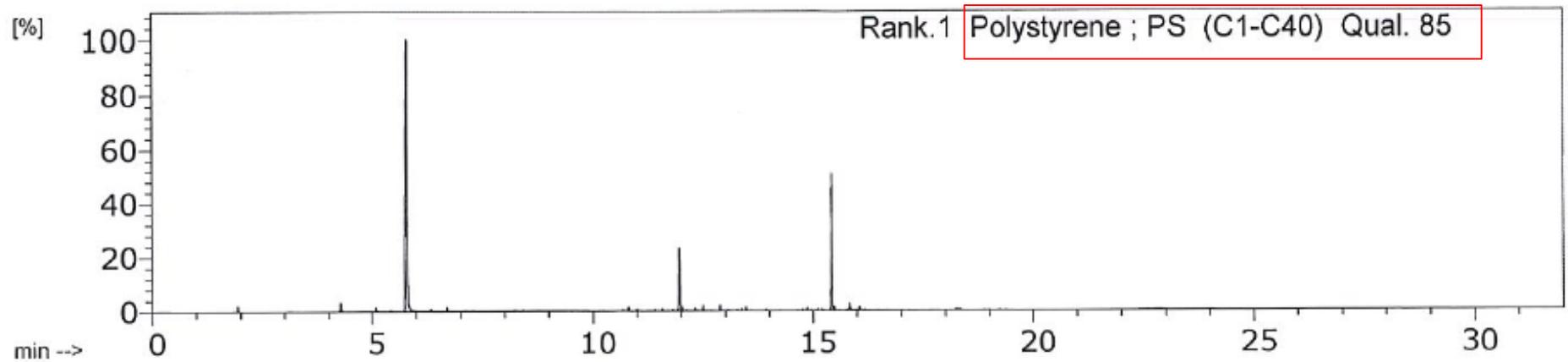
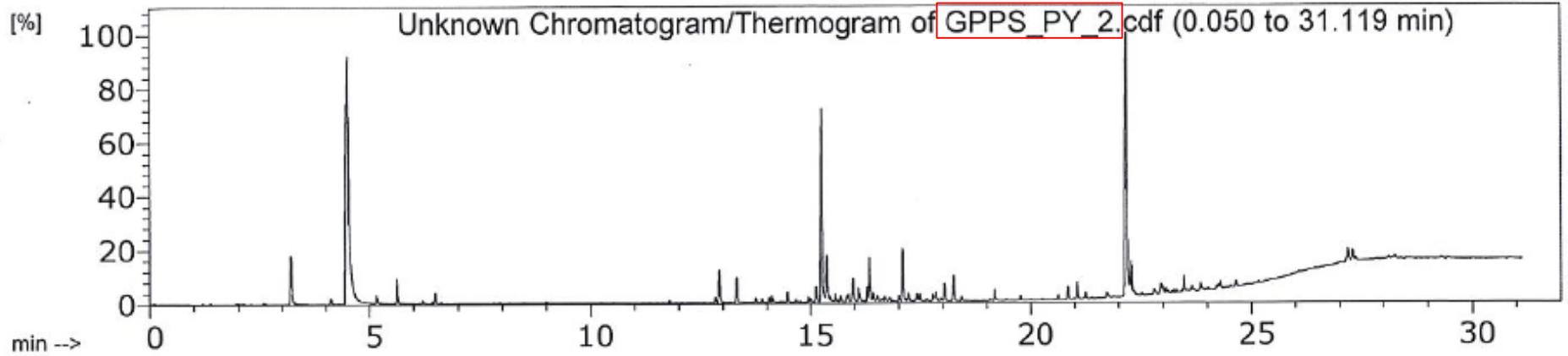




EMDP

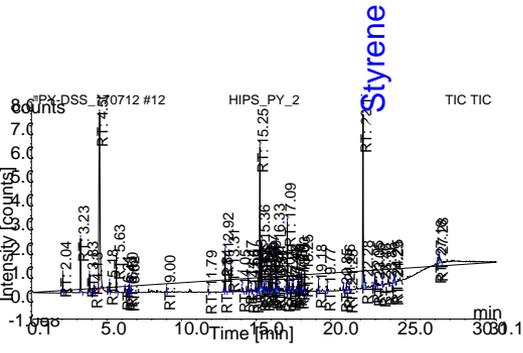
(2,3-diphenylcyclopropyl) methyl phenyl sulfoxide ,trans

ผ่านซอฟต์แวร์ 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



1,3 - butadiene

Toluene

Ethyl benzene

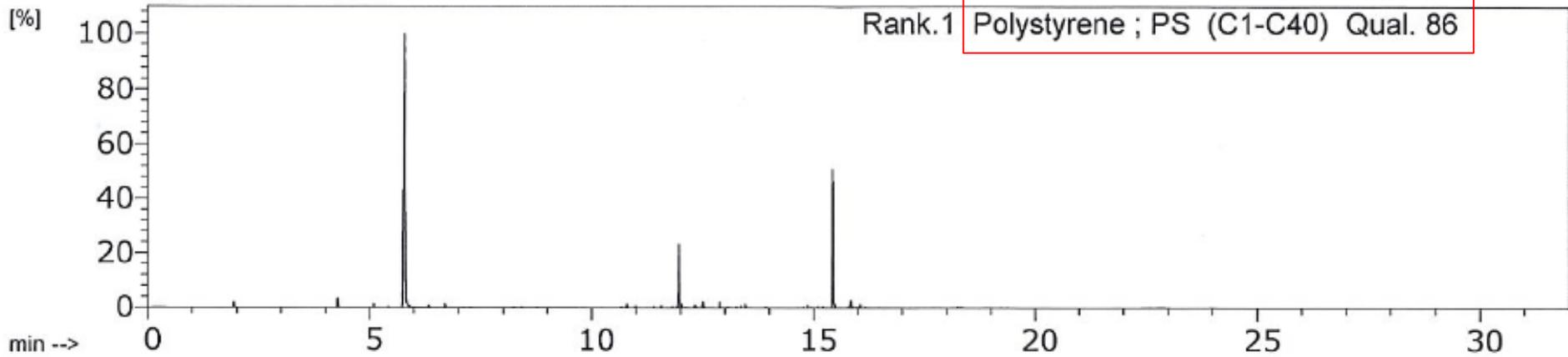
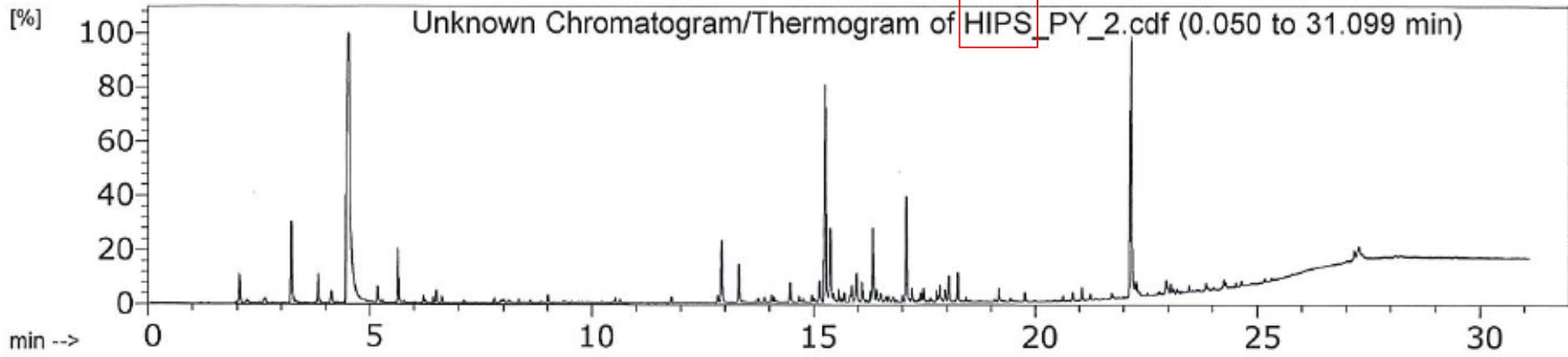
Methyl styrene

Styrene

EMDP

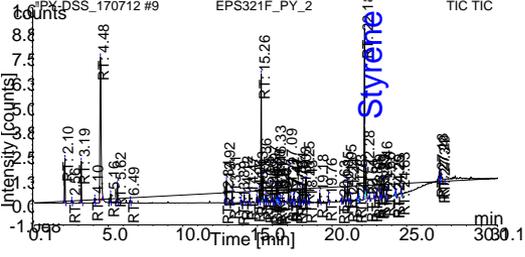
(2,3-diphenylcyclopropyl) methyl phenyl sulfoxide, trans

ผ่านซอฟต์แวร์ 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



Pentane

Toluene

Ethyl benzene

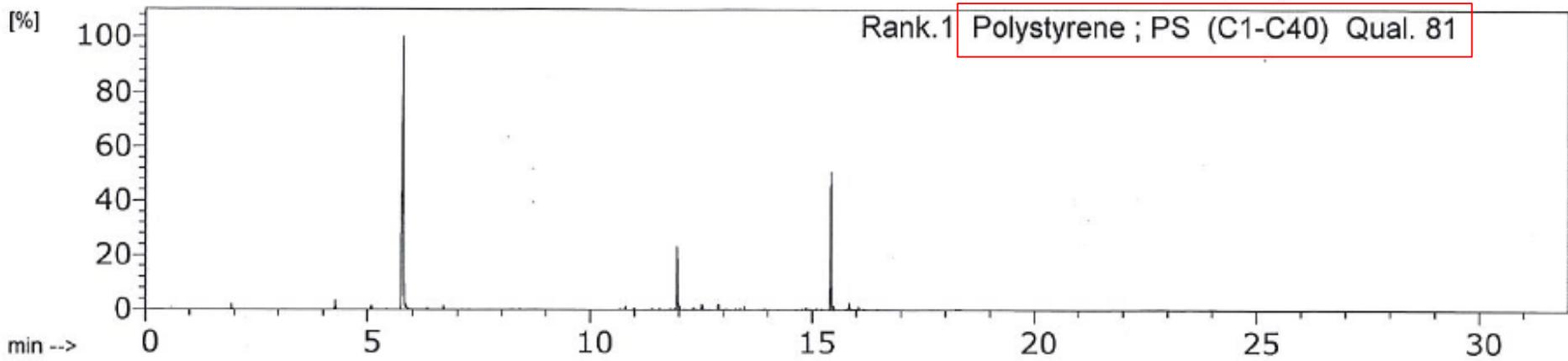
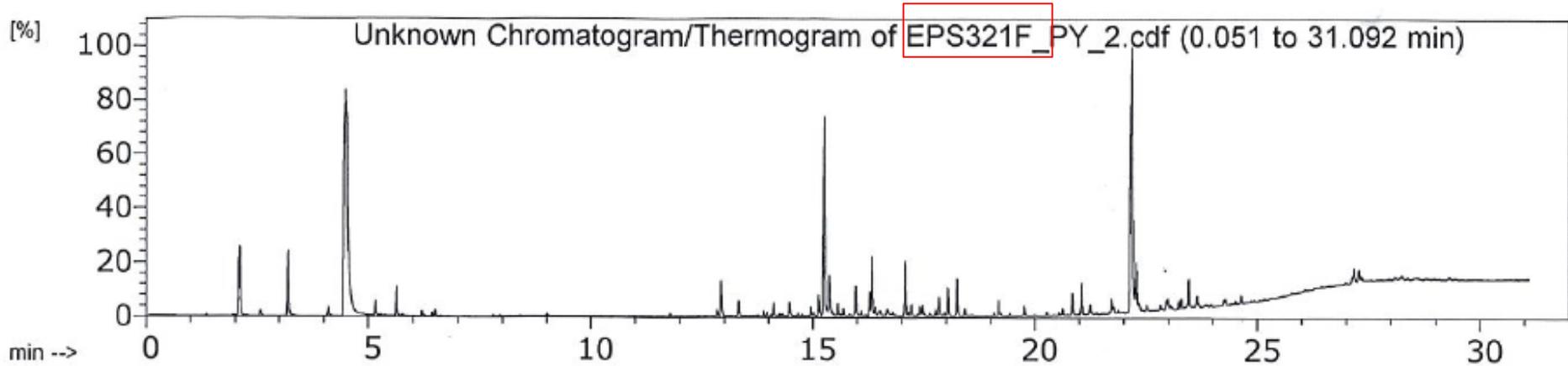
Methyl styrene

Styrene

EMDP

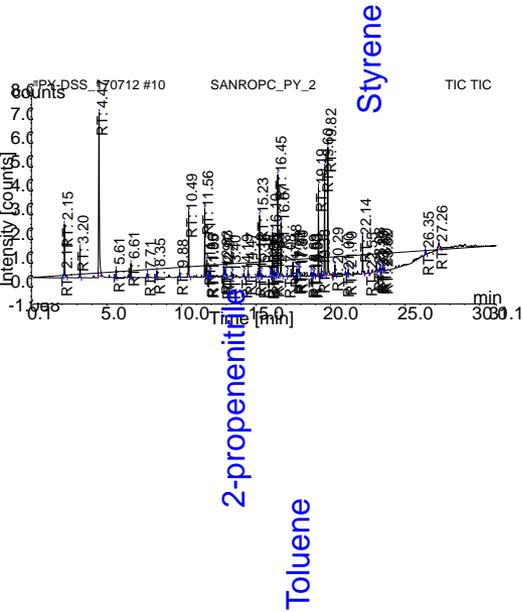
(2,3-diphenylcyclopropyl) methyl phenyl sulfoxide , trans

ผ่านซอฟต์แวร์ F-Search

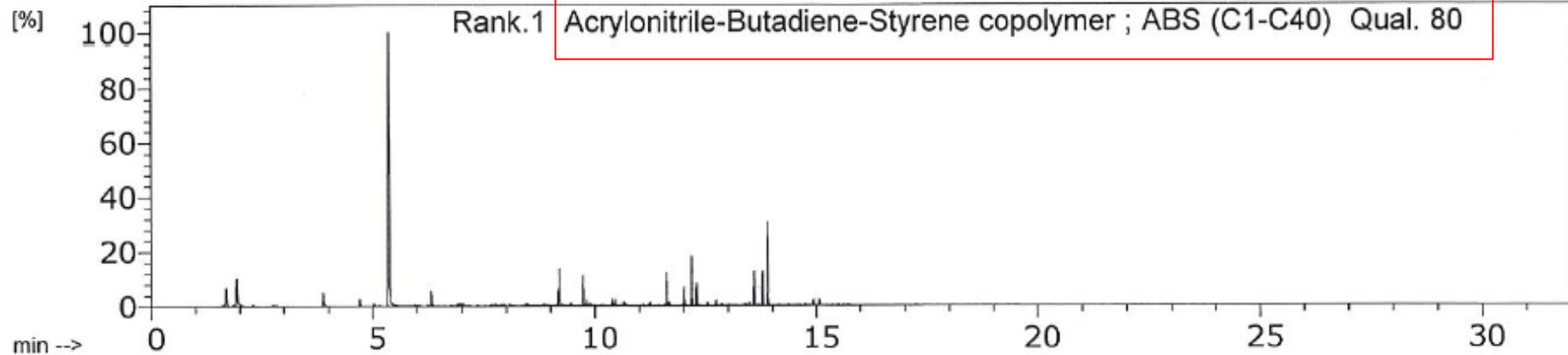
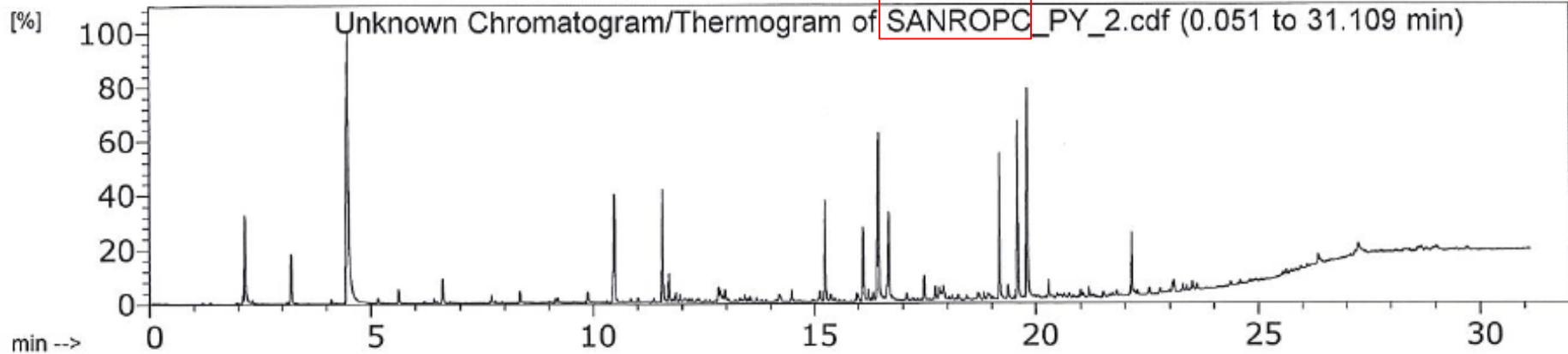


Rank.2 : Acrylonitrile-Butadiene-Styrene copolymer ; ABS (C1-C40) Qual.81

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



ผ่านซอฟต์แวร์ F-Search



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

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

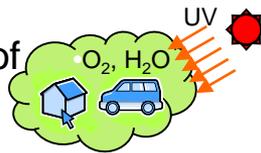
1: Characterization of polymers



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**



Your

Scientific
Specialist

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 polycyclic aromatic hydrocarbons in extender oils. ***listed in Table1***
- Sample Preparation Method : BS EN 16143:2013

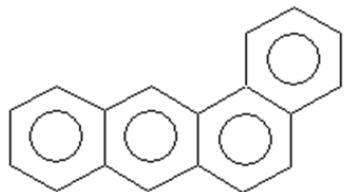
Name of PAH	Abbreviation	CAS Registry number
Benzo(a)pyrene	BaP	50-32-8
Benzo(e)pyrene	BeP	192-97-2
Benzo(a)anthracene	BaA	56-55-3
Chrysene	CHR	218-01-9
Benzo(b)fluoranthene	BbFA	205-99-2
Benzo(j)fluoranthene	BjFA	205-82-3
Benzo(k)fluoranthene	BkFA	207-08-9
Dibenzo(a,h)anthracene	DBahA	53-70-3

Table 1- List of individual PAHs in extender oils

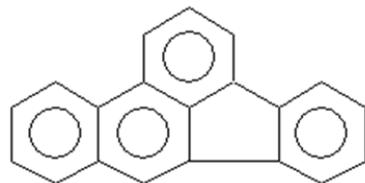
PAHs...

Consists of 8 natives of PAHs

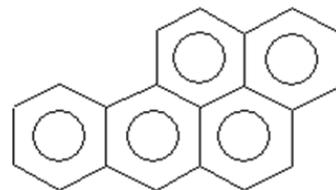
MW range 228-278 amu (16PAHs could be up to 300+)



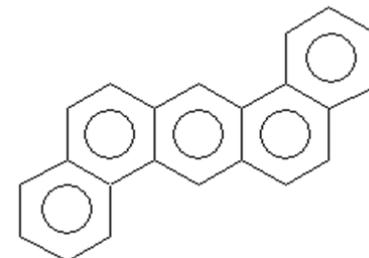
Benzo(a)anthracene



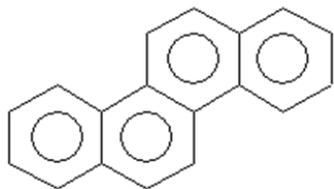
Benzo(b)fluoranthene



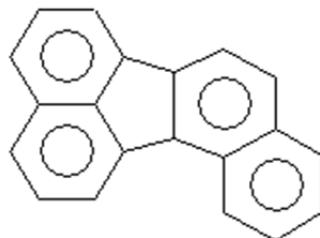
Benzo(a)pyrene



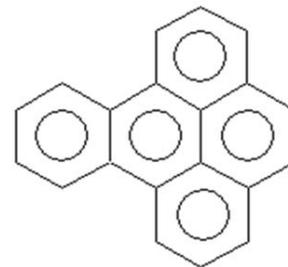
Dibenzo(a,h)anthracene



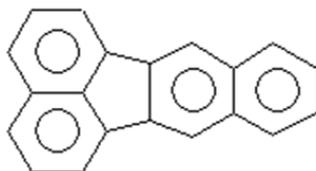
Chrysene



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).

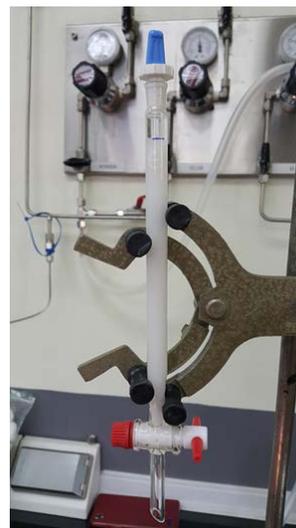
3.5 Rinse sample container with 2 ml *n*-Pentane. (not critical) and pour into column.

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.

*extended length of column to 25 cm. convenient for sample loading

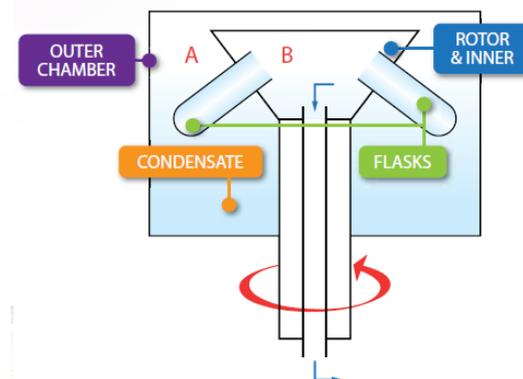
** pressurized with N₂ (1 bar est.) for faster elution



Pack column



Extracting



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.

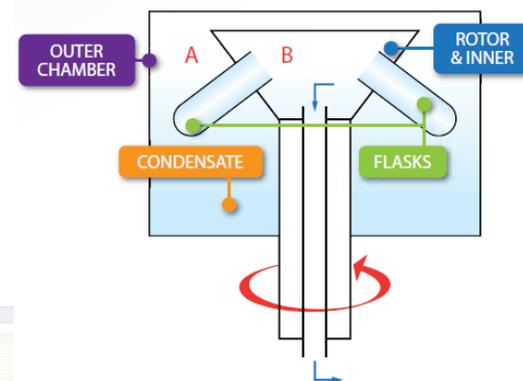
*DE = Decafluorodiphenyl



Fraction
collecting



Dissolved
Solution



Instrument Method

GC parameters

Parameter	Value
GC-column	60 m x 0.25 mm ID x 0.25 μ m
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 μ L
Carrier gas	He UHP grade 1.2 ml/min

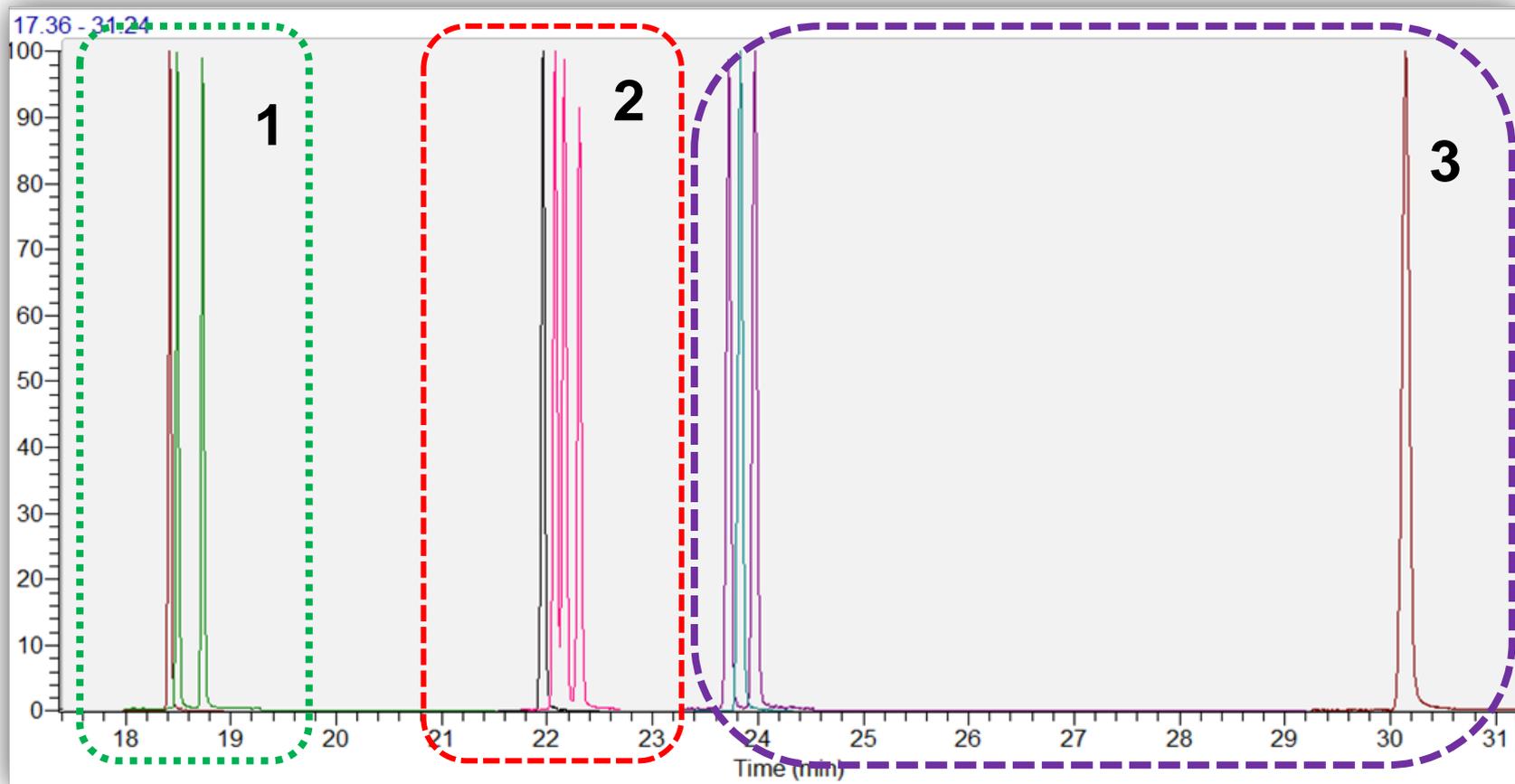
Instrument Method

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

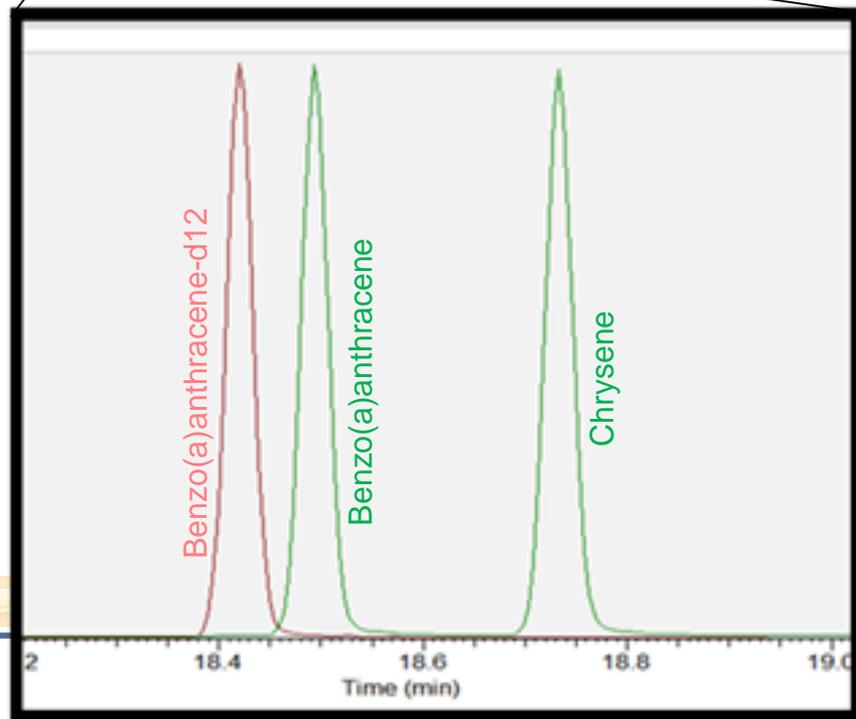
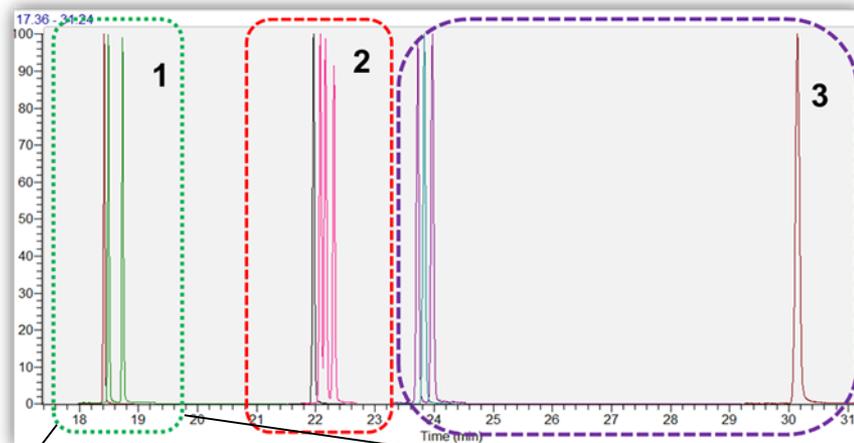
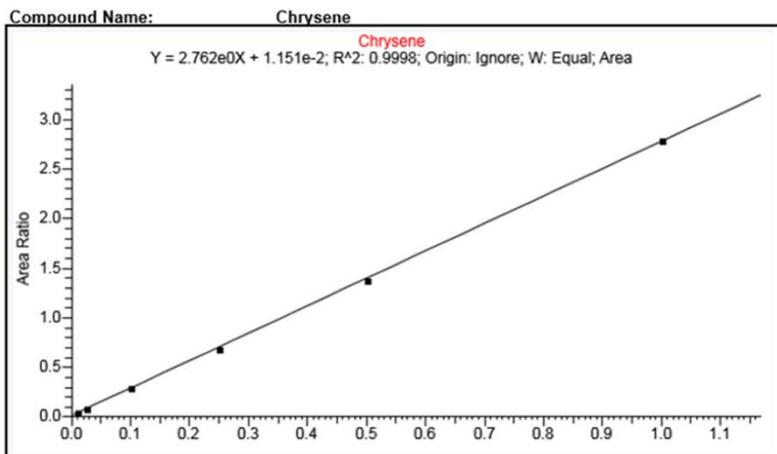
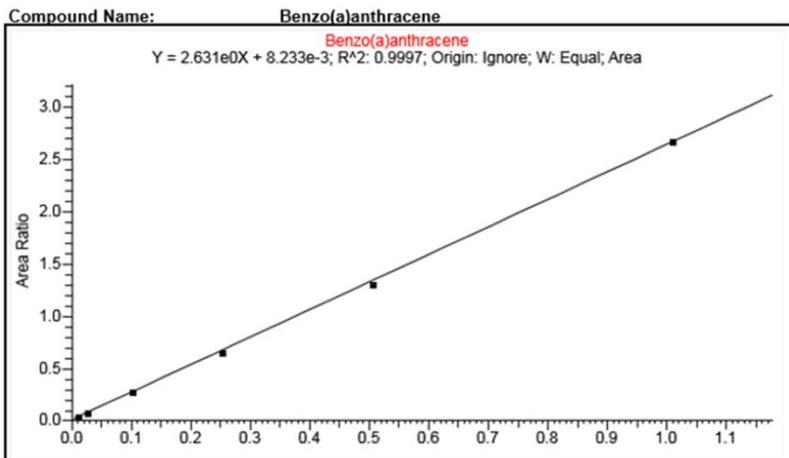
Component	RT	mass	product mass	Collision energy
Decfluorodiphenly	5.84	333.9	233.9	35
		333.9	264.9	25
Benzo(a)anthracene-D12	18.46	240.1	212.1	25
		240.1	236	30
Benzo(a)anthracene	18.53	228.1	202	25
		228.1	226	30
Chrysene	18.77	228.1	202	25
		228.1	226	30
Benzo(b)Fluoranthene-D12	22.02	264.1	236	30
		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

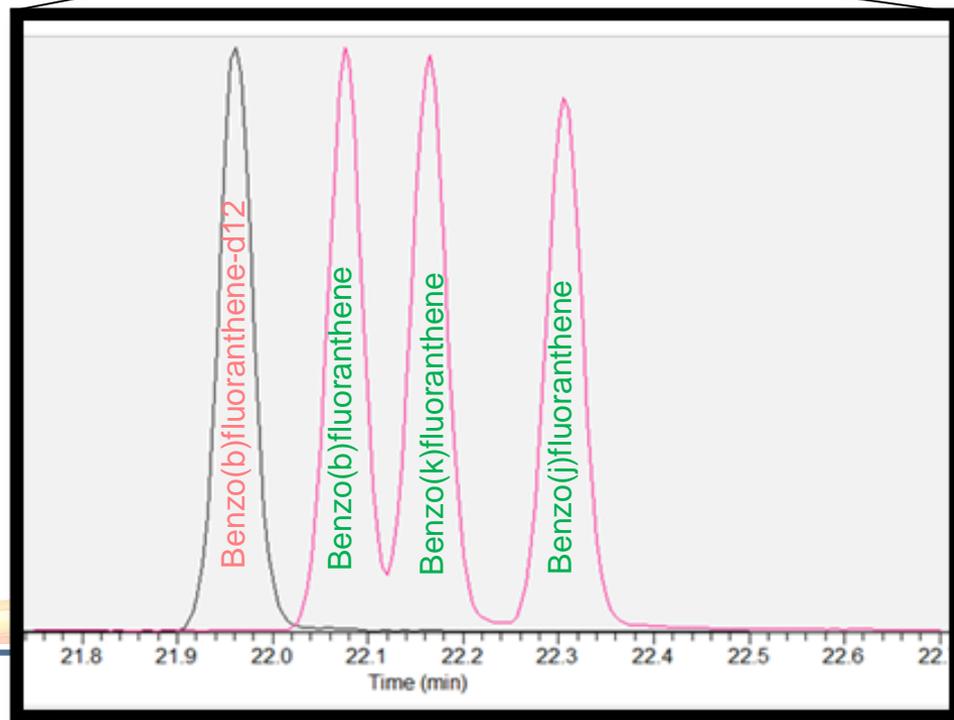
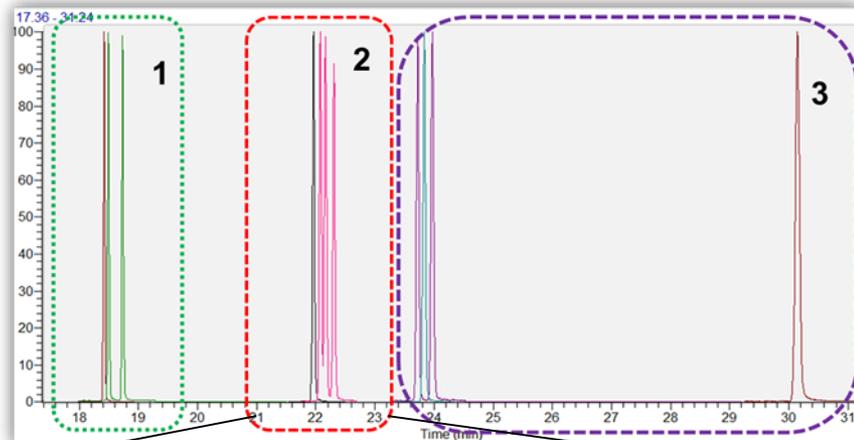
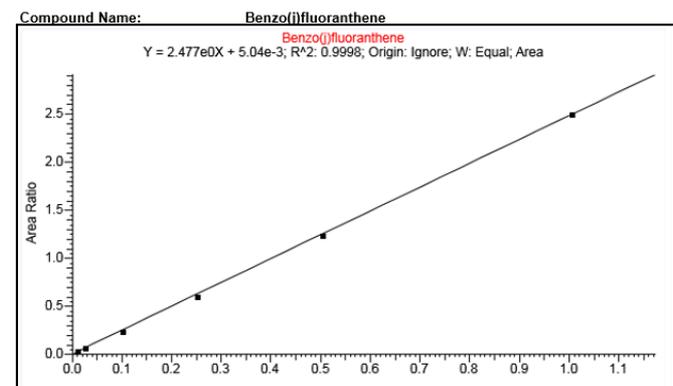
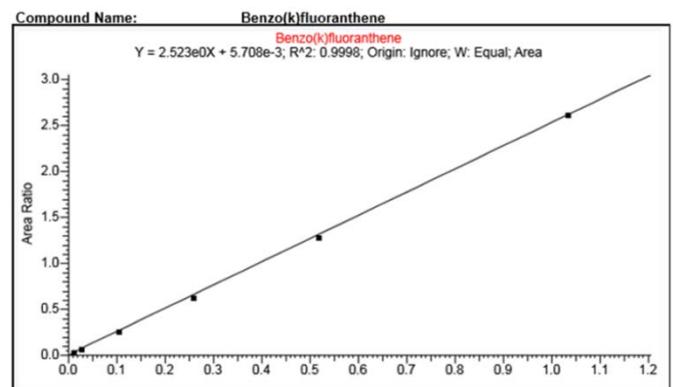
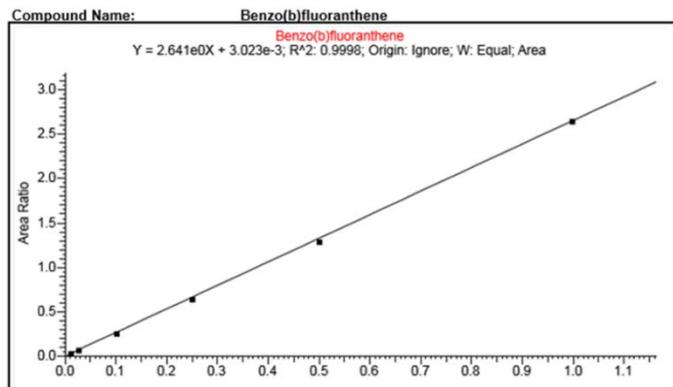
TIC



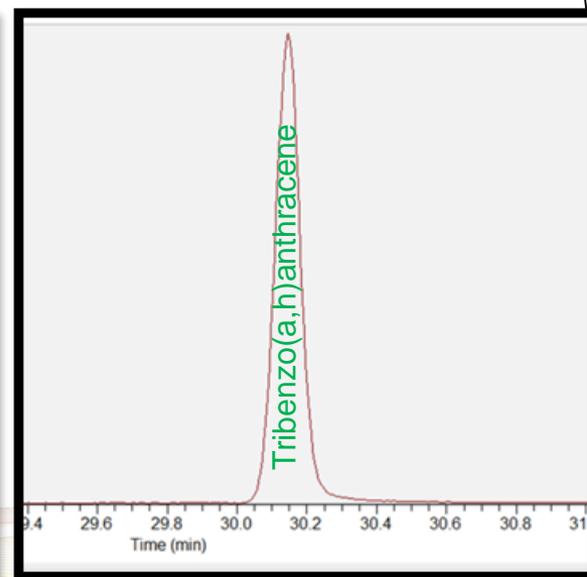
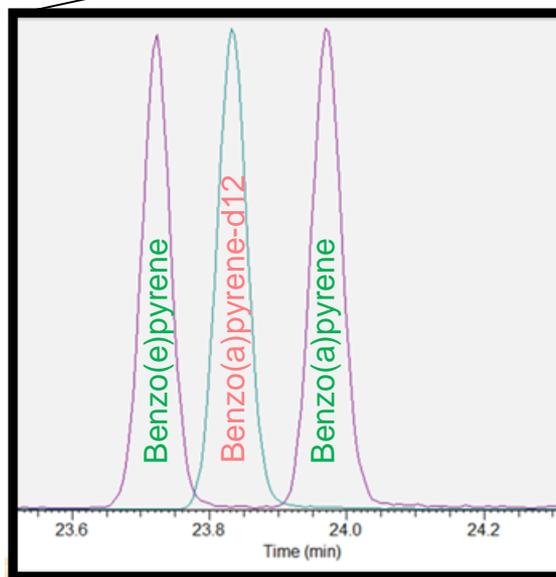
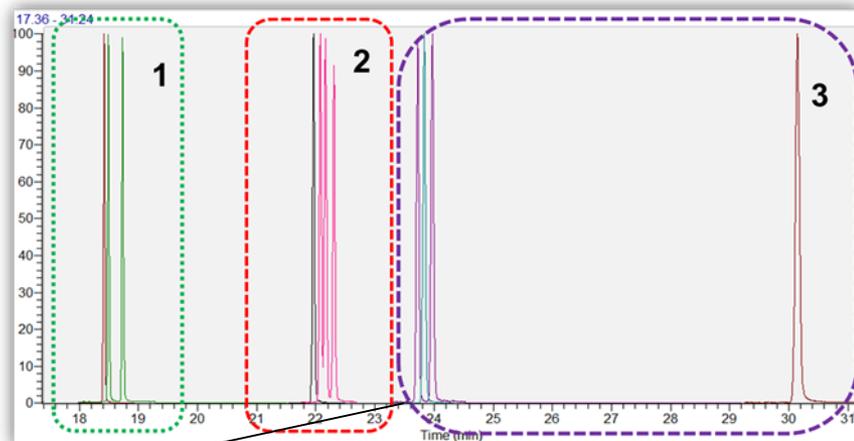
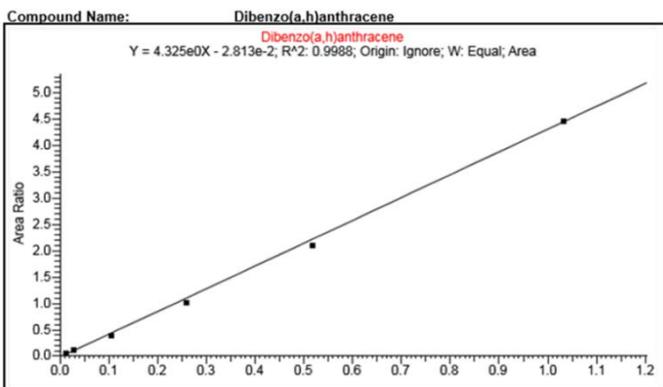
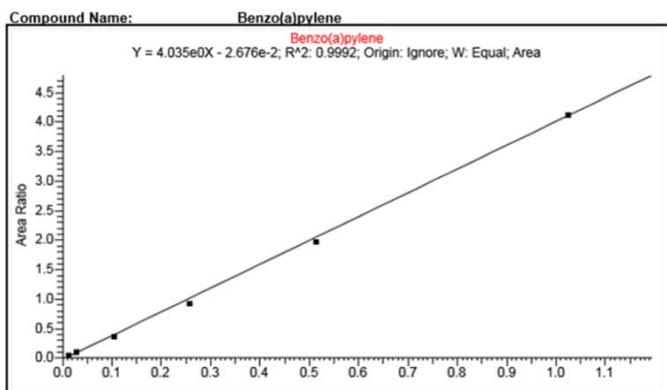
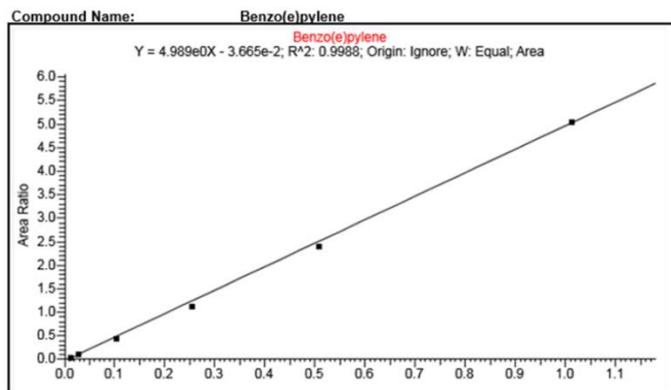
Chromatogram (1) – Standard 8 PAHs with 3 IS(d12)



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)

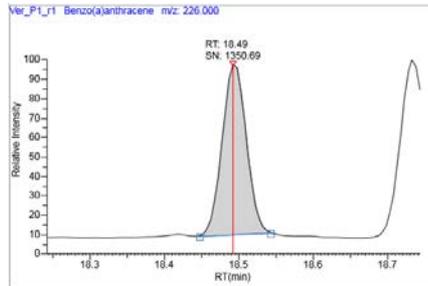
No.	PAHs (mg/kg)							
	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(j)fluoranthene	Benzo(e)pylene	Benzo(a)pylene	Dibenzo(a,h)anthracene
1	0.226	0.370	0.198	0.186	0.103	-0.507	0.144	0.125
2	0.220	0.367	0.177	0.165	0.117	-0.510	0.130	0.148
3	0.222	0.361	0.184	0.182	0.127	-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

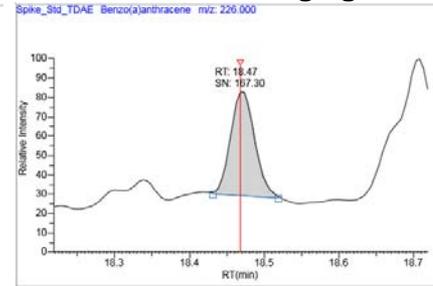
Peak Confirmation

Benzo(a)anthracene

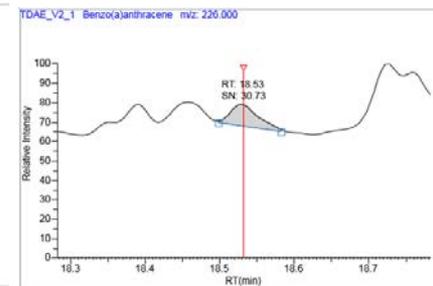
QC Check



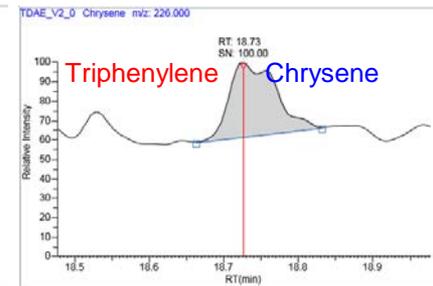
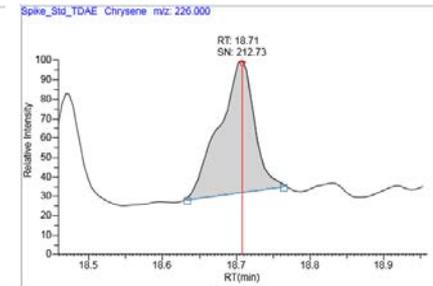
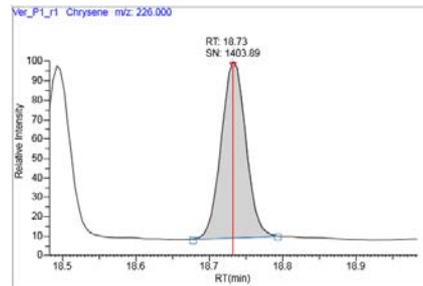
Sample spiked
3 ul of 0.5 mg/kg



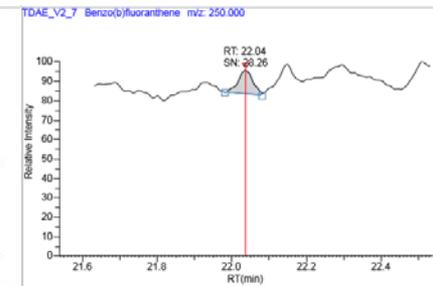
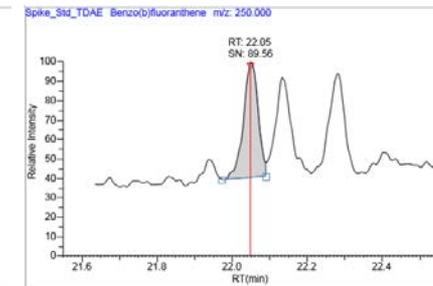
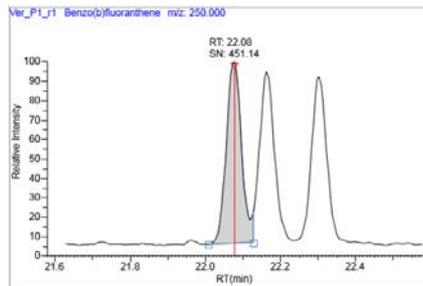
Sample(TDAE)



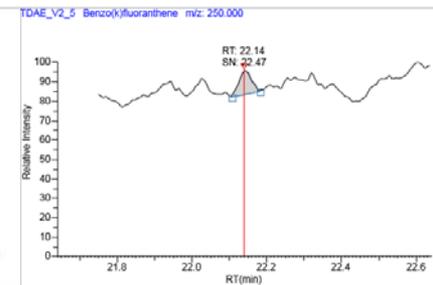
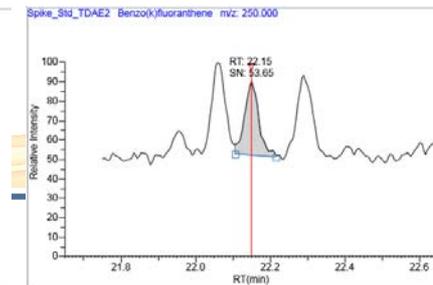
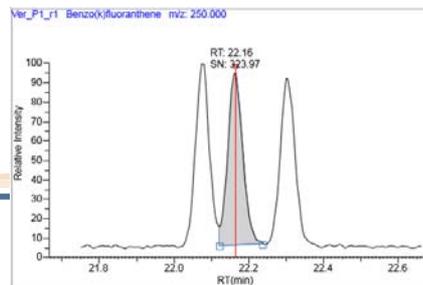
Chrysene



Benzo(b)fluoranthene



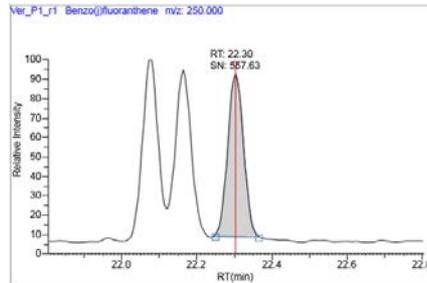
Benzo(k)fluoranthene



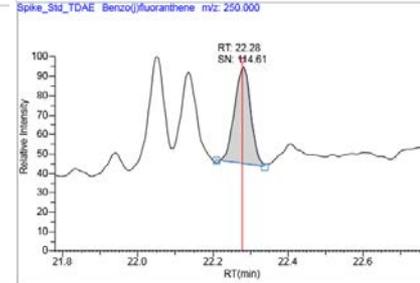
Peak Confirmation

Benzo(j)fluoranthene

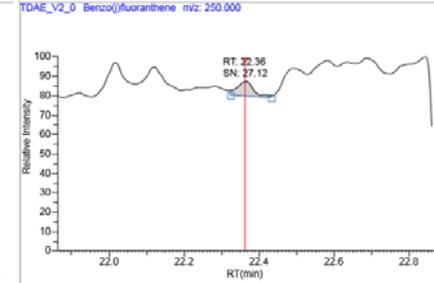
QC Check



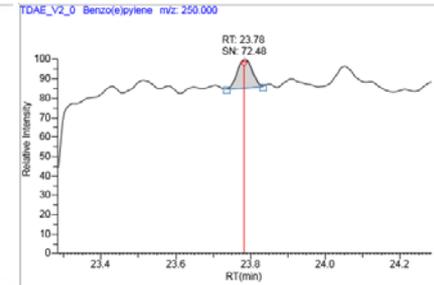
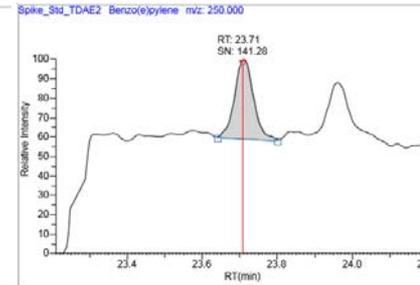
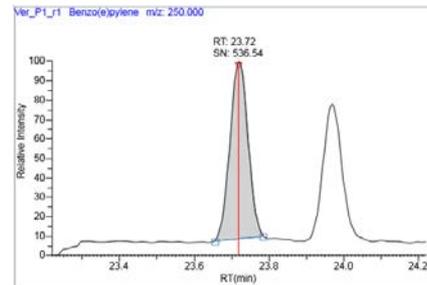
Sample spiked
3 ul of 0.5 mg/kg



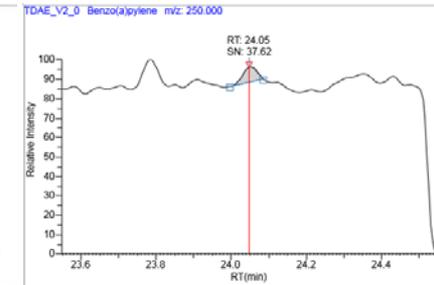
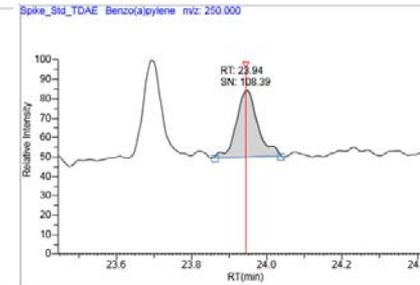
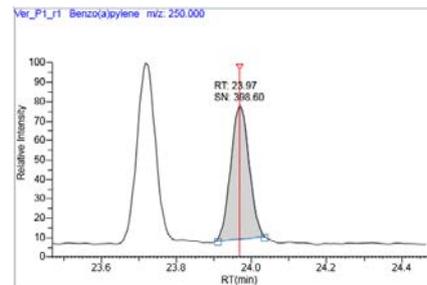
Sample-TDAE



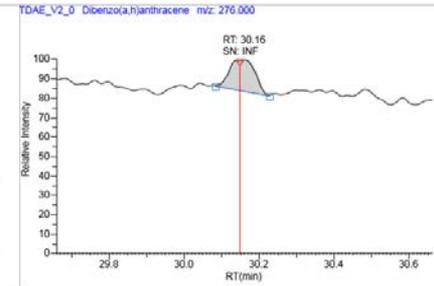
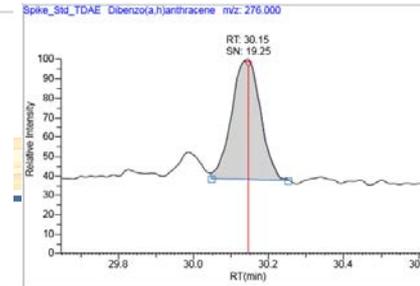
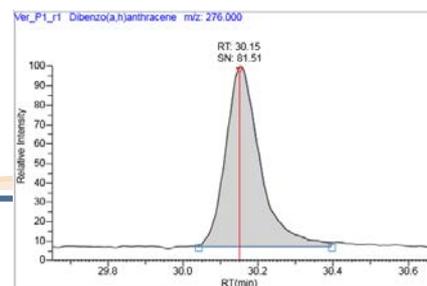
Benzo(e)pyrene



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.

