ROYAL SOCIETY OF CHEMISTRY
Approved training

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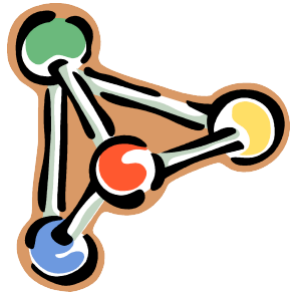
Bridging the Gap

Current Detector Options in GC – making the right choice!

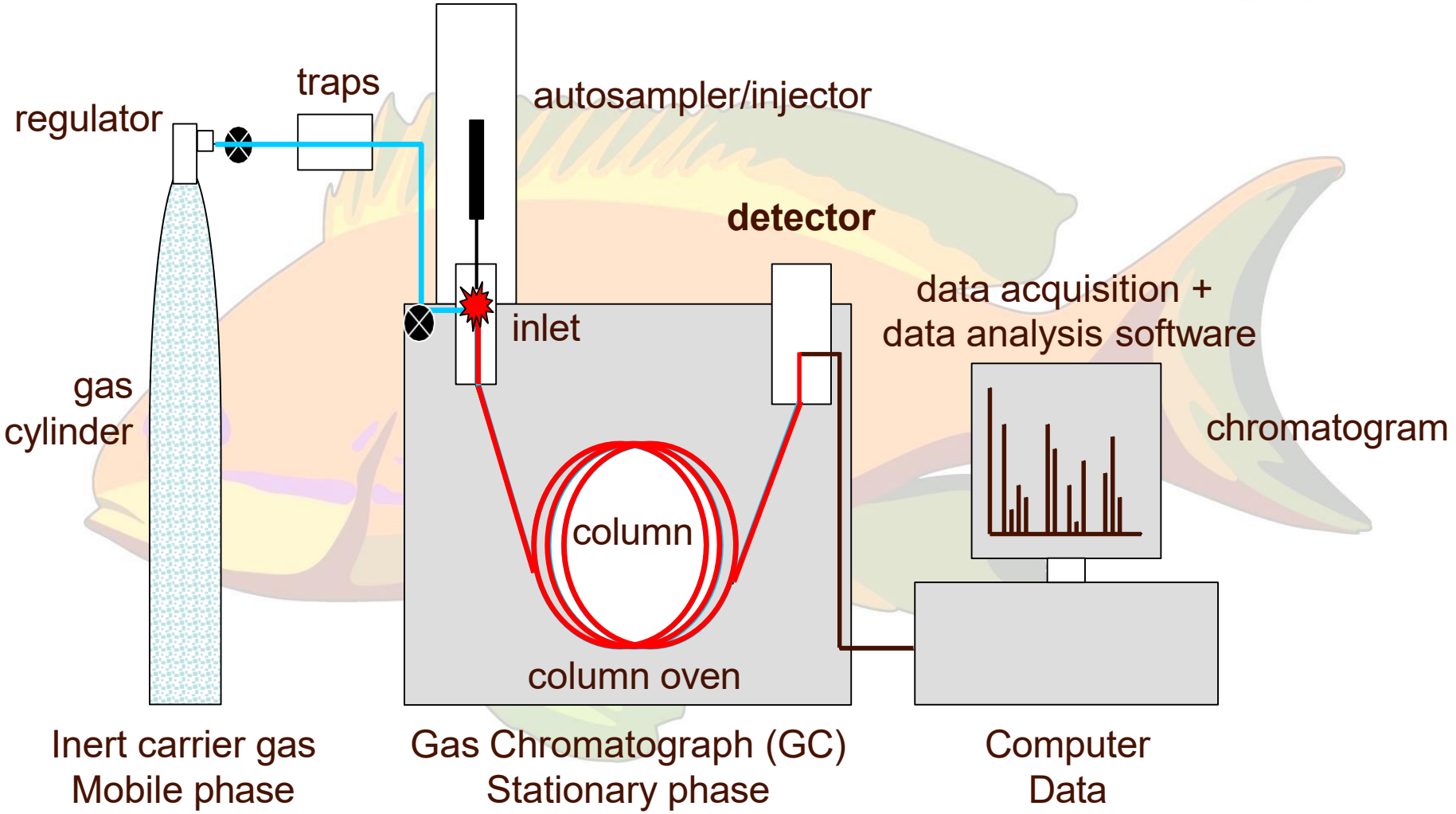
Diane Turner, Anthias Consulting

Selecting the right detector

- Why are you performing your analysis?
  - Qualitative analysis
  - Quantitative analysis
  - Identify unknowns
- What is the nature of the sample?
  - Analytes: Many/few
    - Volatile/semi-volatile/involatile
    - High/low concentration
    - Chemistry: elemental composition, functional groups, bonds, polarity
  - Matrix: Little/high loading
- How to handle matrix interferences?
  - Sample preparation, offline/online
  - Positive discrimination using the inlet
  - Selectivity of column, even using GC+GC or GCxGC
  - Selectivity of the detector



GC Instrumentation



Detector qualities

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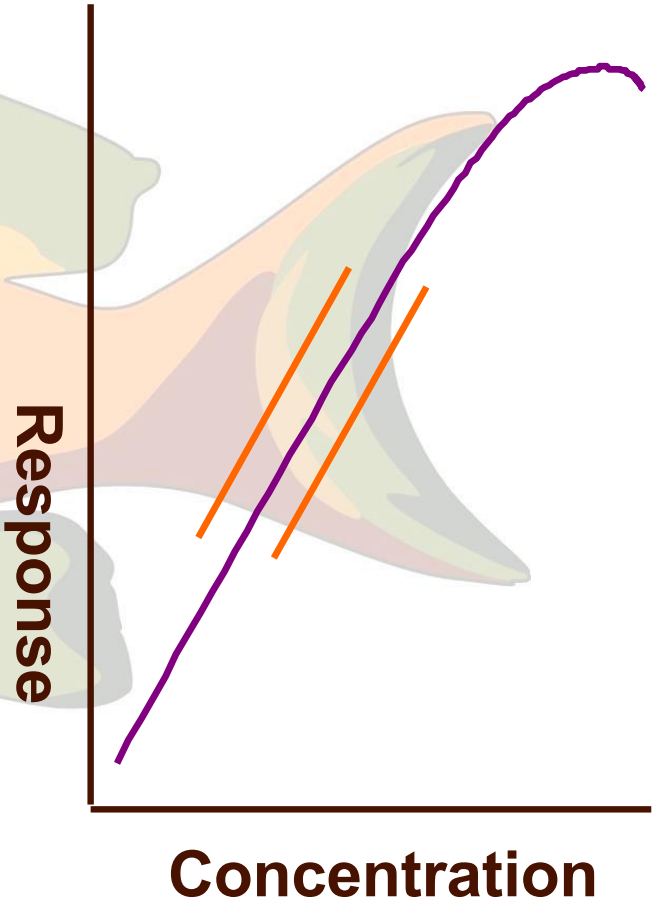
- Selecting your ideal detector, it will:
  1) Have adequate sensitivity for target analytes
  2) Give similar response to all analytes, or selective to one or more classes of analytes
  3) Be non-destructive of sample
  4) Have a dynamic range, preferably with linear response to target analytes over several orders magnitude – enough for application
  5) Have a quick response time, independent of flow rate (particularly important for narrow peaks)
  6) Give good stability & reproducibility in location
  7) Be easy to use, set-up & maintain
- No detector exhibits all of these qualities – choose one that is best for the application

Detector response

- Dynamic range = measure of increase in response with increasing amount of an analyte, without saturating the detector
- Linear dynamic range = response increases proportionally with increased concentration
- Non-linear = still usable so long as response is reproducible



Detector Characteristics

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Concentration Sensitive

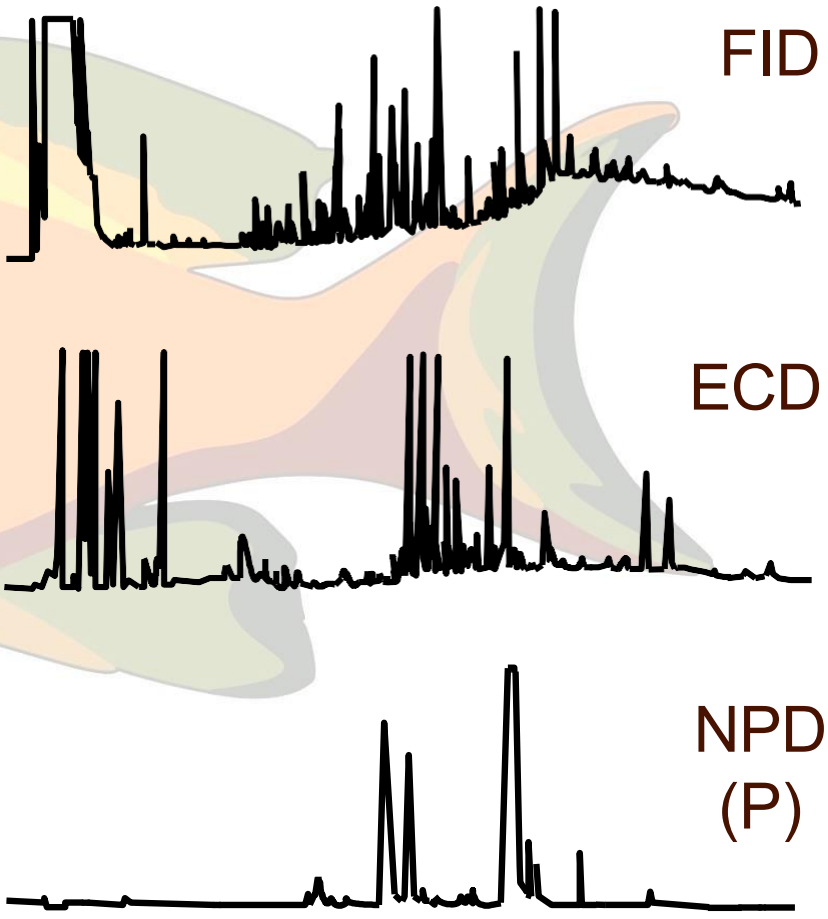
- Usually non-destructive
- Responds to concentration of analyte within detector, mass per unit volume, e.g. g/mL
- e.g TCD, ECD, PID

Mass Flow Sensitive

- Usually destructive
- Responds to amount of analyte within detector, mass per unit time (g/s) irrespective of carrier gas volume, e.g. number of functional groups or carbons within molecule
- e.g. FID, PFPD, NPD, ELCD, AED, MSD

Detector types

- Universal:
  - See most organic compounds
  - E.g. FID, TCD, HID
  - E.g. MS in scan mode
- Selective:
  - Reduced matrix interferences
  - Easier quantitation
  - Can get better MDLs
  - E.g. ECD, PFPD, NPD, SCD, ELCD, NCD, PID, IRD
  - E.g. MSD in SIM or MS/MS mode



Matrix & analyte dependent

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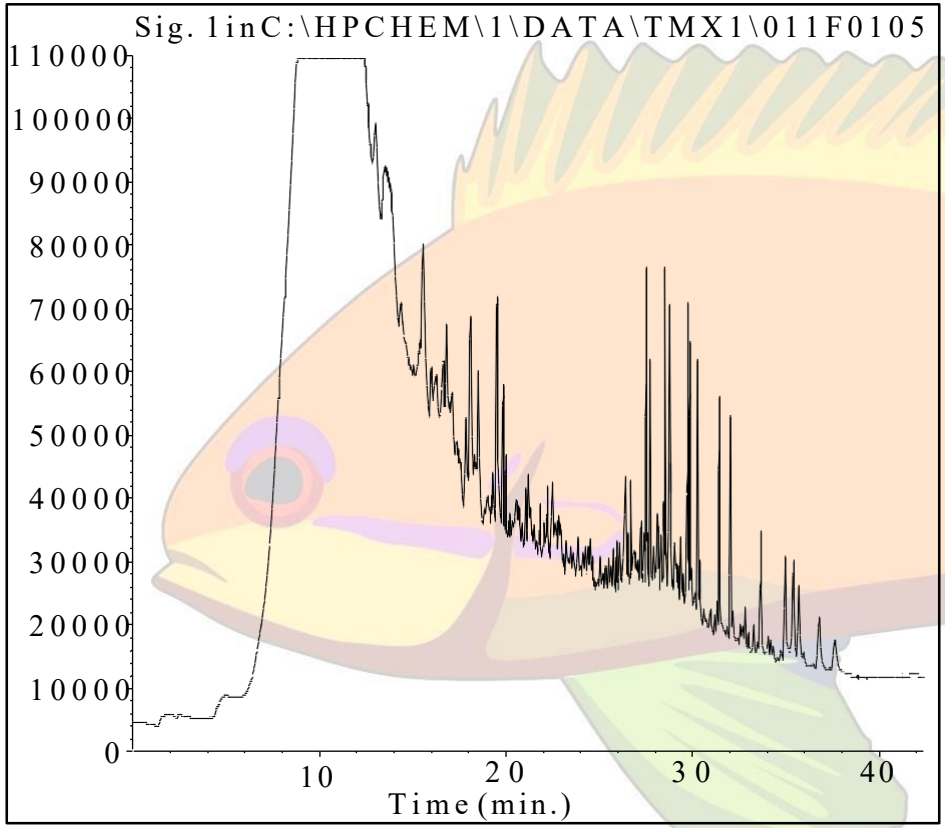
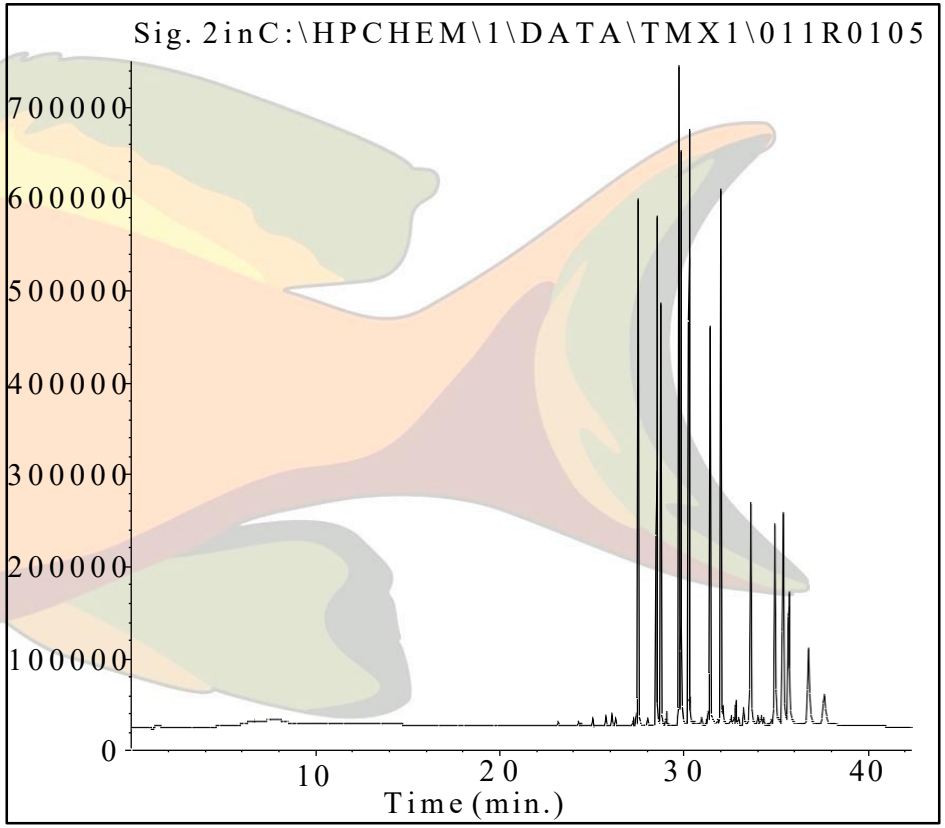
PID



- Selective for aromatics
- Still sees matrix interferences
- Difficult to ID target PCBs

ELCD



- Selective for halogens: PCBs
- Can't see matrix for this application

Detector types

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- Flame Ionisation Detector (FID)
- Electron Capture Detector (ECD)
- Thermal Conductivity Detector (TCD)
- **Pulsed Flame Photometric Detector (PFPD)**
- Nitrogen Phosphorus Detector (NPD)
- Barrier Discharge Ionisation Detector (BDID)
- **Photo Ionisation Detector (PID)**
- Helium Ionisation Detector (HID) & Discharge Ionisation Detector (DID)
- **Atomic Emission Detector (AED)**
- **Sulphur Chemiluminescence Detector (SCD)**
- **Nitrogen Chemiluminescence Detector (NCD)**
- Electrolytic Conductivity Detector (ELCD)
- **Thermal Energy Analyser (TEA)**
- **Vacuum UltraViolet (VUV)**
- **Infra-Red Detector (IRD)**
- Mass Selective Detector (MSD)

IYL 2015

International Year of Light & Light-Based Technologies

- Global initiative adopted by UN
- Raise awareness of how optical technologies promote sustainable development & provide solutions to worldwide challenges
- www.light2015.org

Focus on light-based GC detectors:

- PFPD
- PID
- VUV
- IRD
- SCD & NCD
- TEA
- AED

The PFPD

- Developed & patented by Dr Aviv Amirav at University of Tel Aviv
- Selective to S & P, minor applications in C & N, plus 24 other elements
- Sensitivity: <1pg S/s, <100fg P/s
- Range: S 10^6 (linear 10^3), P 10^5 (linear 10^3), equimolar
- Principles:
  - Combustible mixture of H_2 & air fills detector from bottom to top
  - Gas mixture is ignited in the cap
  - Propagation flame travels from cap towards head of GC column
  - As compounds elute from column inside quartz combustor they are combusted in flame
  - Excited species are formed, e.g. HPO*, S_2* and fluoresce
  - Flame is extinguished when reaches bottom of detector
  - Excited species continue to fluoresce for up to 25 ms
  - Cycle is repeated 3-4 times/sec

5 Phases of PFPD cycle

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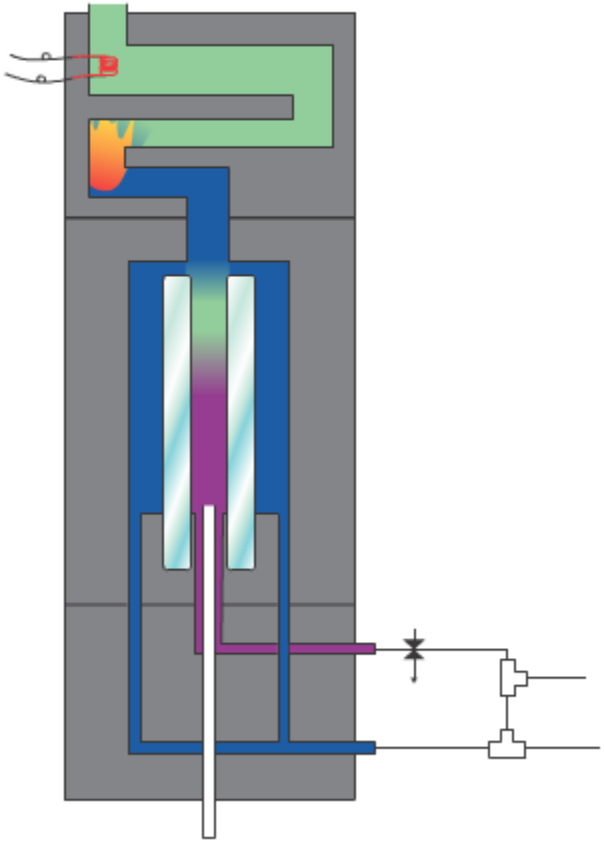
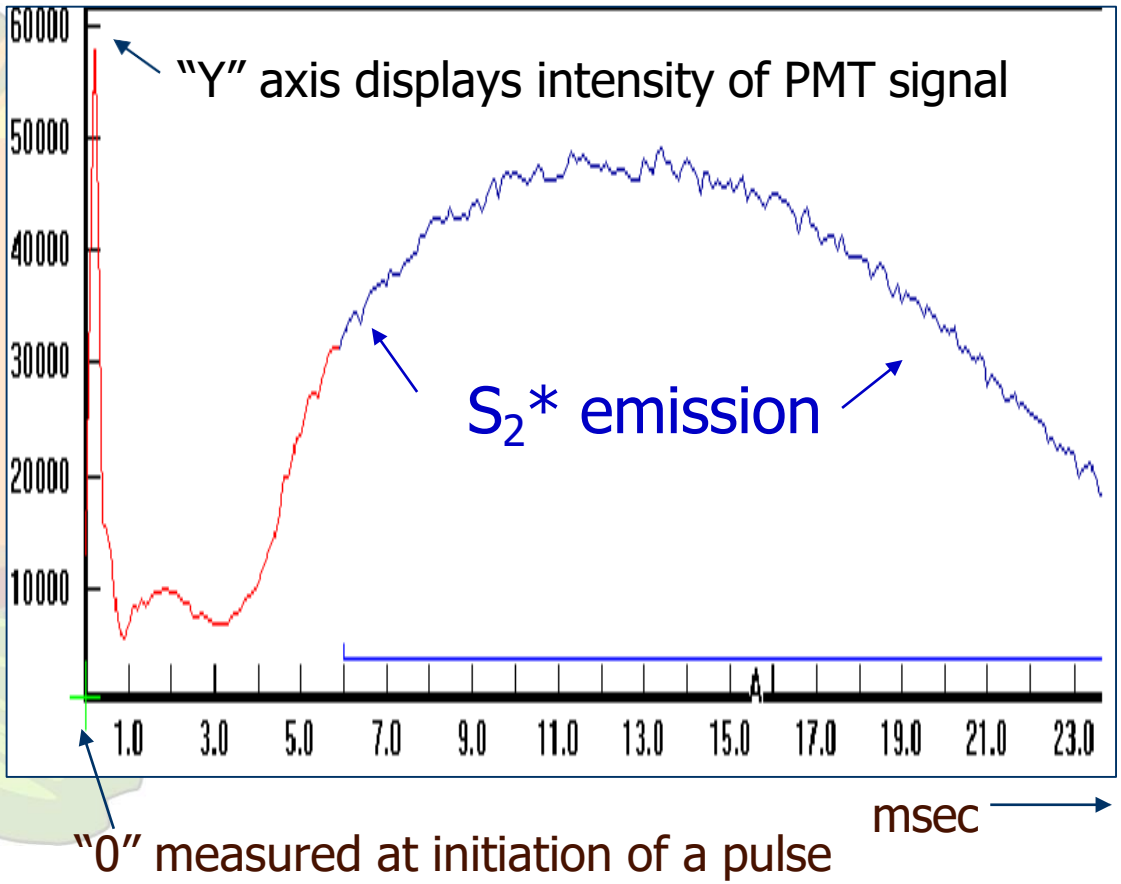
1) Filling
2) Ignition
3) Propagation
4) Combusion
5) Extinction



Courtesy of OI Analytical

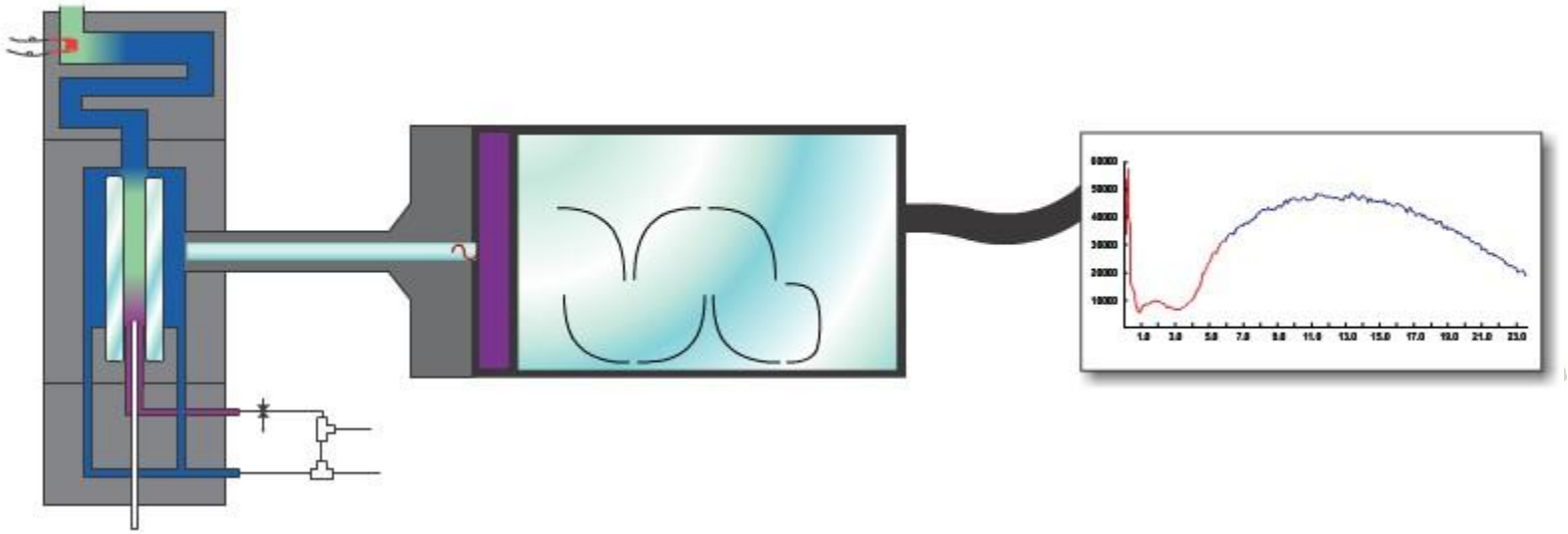
The PFPD

- Each fluorescing species has a different lifetime within the flame
  - Hydrocarbon: 1-3ms
  - Phosphorus: 4-15ms
  - Sulfur: 6-25 ms
- Individual HPO*, S_2*, HNO* heteroatom flame emissions are separated in time & have different luminescence spectra



- Using both time & wave-length improves selectivity

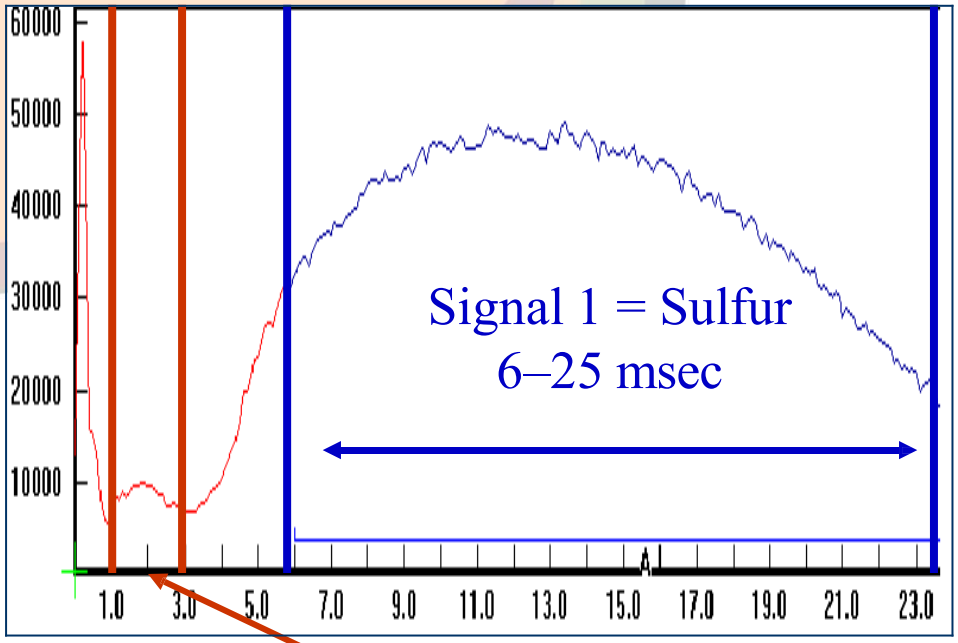
PFPD Operation principles



PFPD | Filter | Photo Multiplier Tube (PMT) | WinPulse software

The PFPD

- Light from species pass through the filter & into PMT
- Light strikes a photosensitive surface knocking loose an electron → amplified
- Signal converted to digital by ADC
- Time filter is applied, only desired portion of emission is integrated e.g. for S from 6-25 ms,
- Can produce 2 time filters
- Measured values converted to analog
- Two simultaneous chromatograms produced



Petrochemical application

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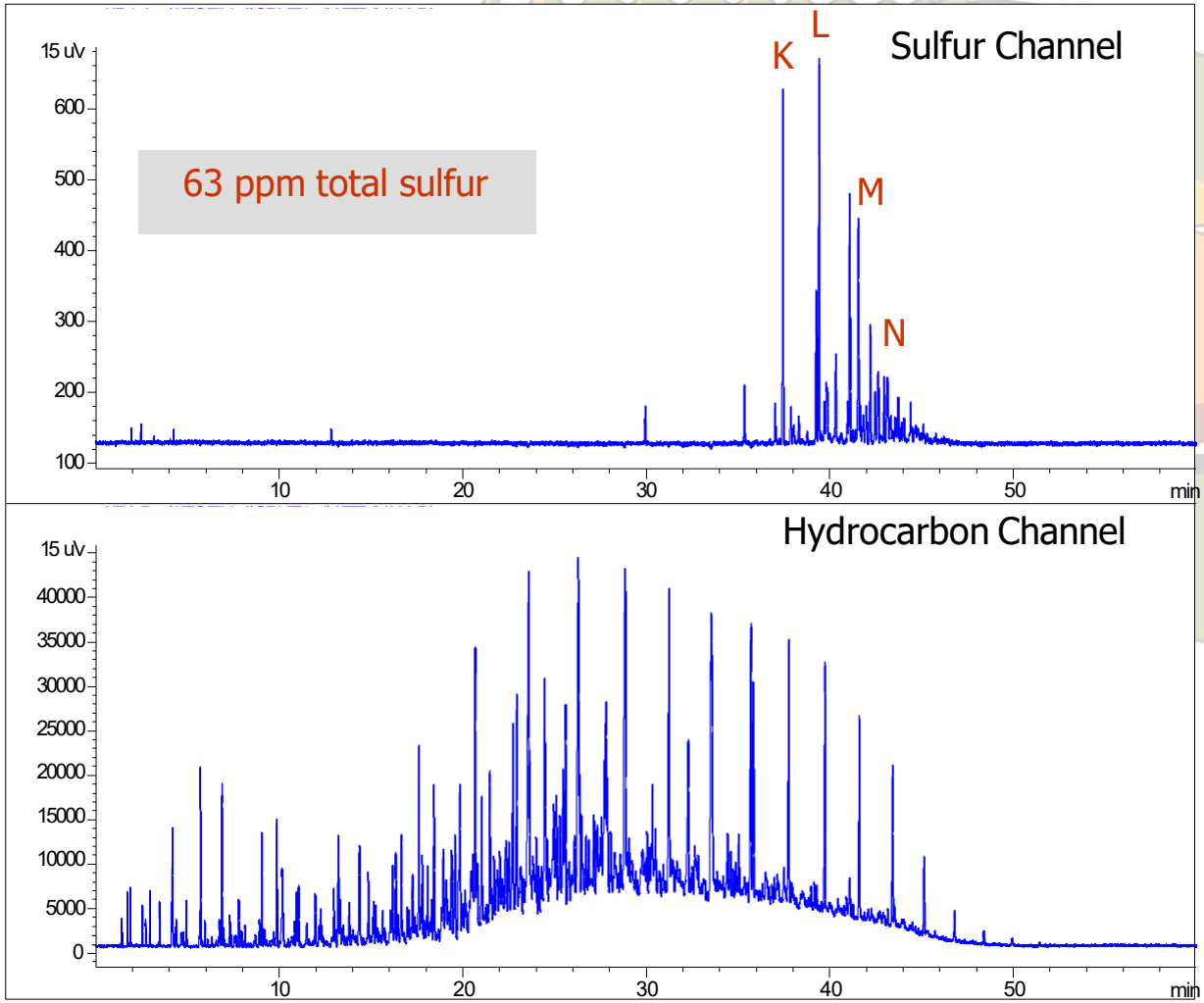
Simultaneous S & HC: 302 ppm total sulfur in diesel fuel



A. Methyl mercaptan
B. Thiophene
C. C1-Thiophenes
D. Tetrahydrothiophene
E. C2-Thiophenes
F. C3-Thiophenes
G. Benzothiophene
H. C1-Benzothiophenes
I C2-Benzothiophenes
J. C3-Benzothiophenes
K. Dibenzothiophene
L. C1-Dibenzothiophenes
M. C2-Dibenzothiophenes
N. C3-Dibenzothiophenes
O. Alkyl sulfides & substituted thiophenes

1 μL injection, split 100:1, Quantified by ASTM RR gasoline #10 as an external calibration standard

Courtesy of OI Analytical
www.anthias.co.uk

Environmental application

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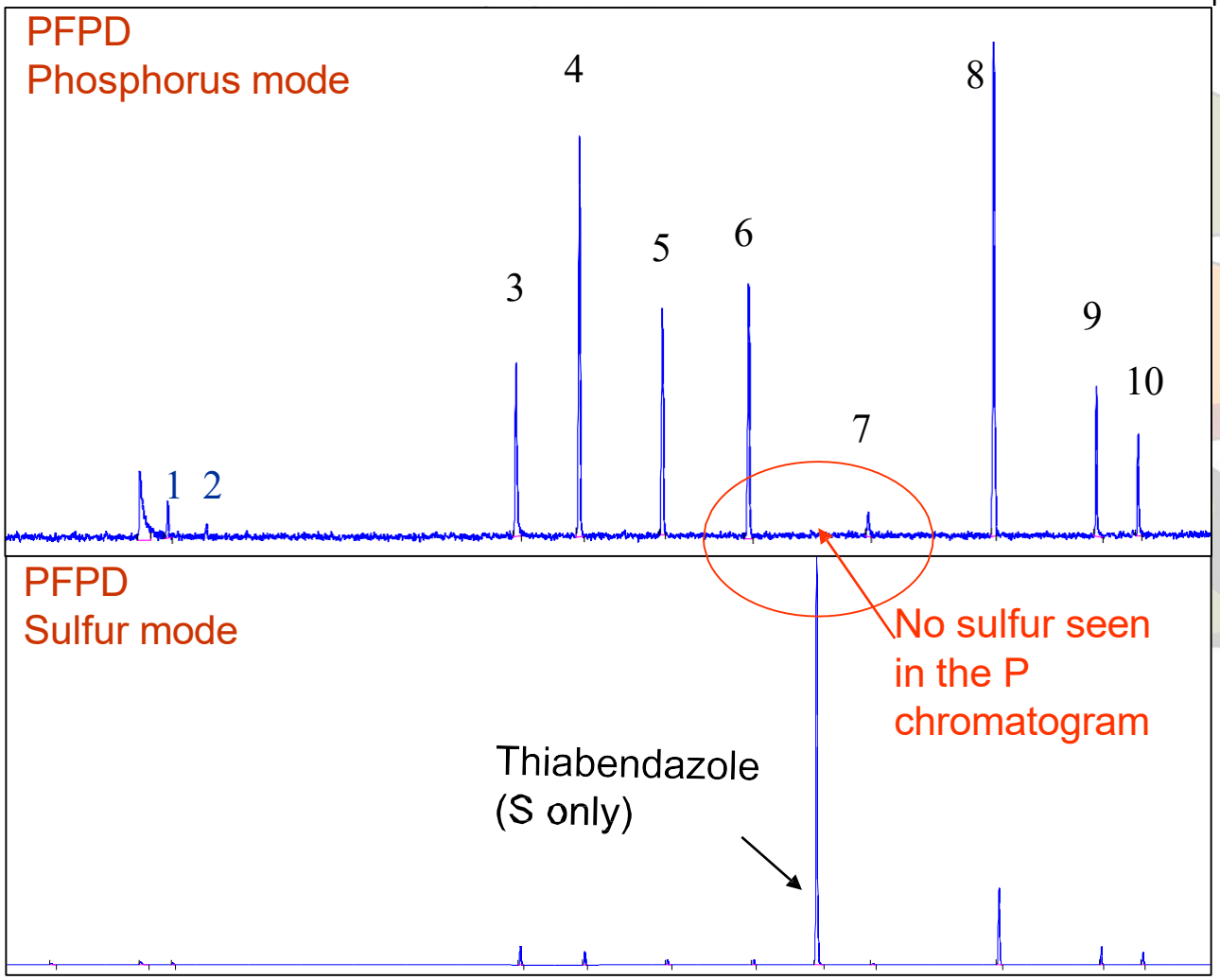
Simultaneous P & S



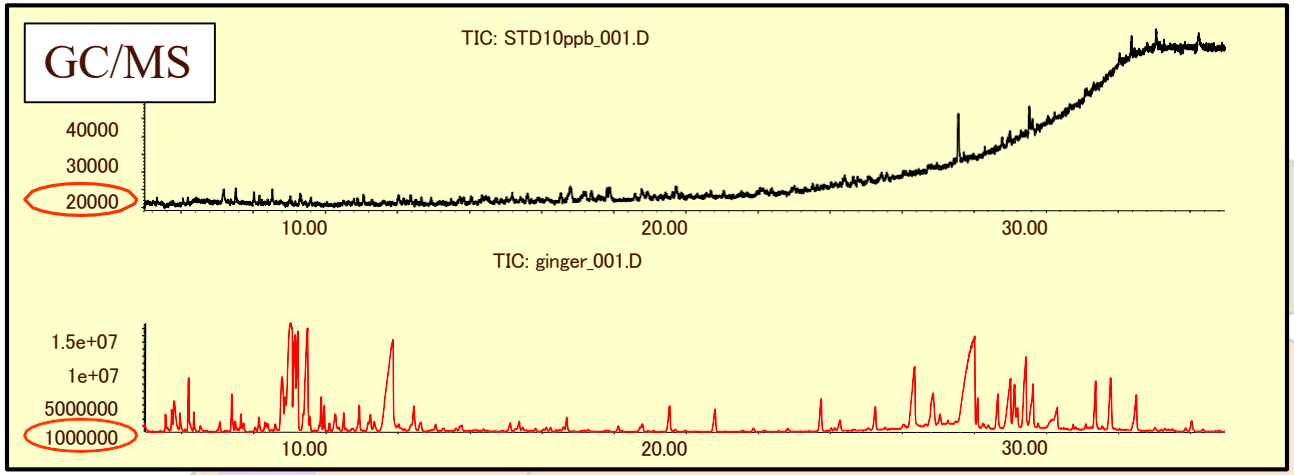
	Compound	ppb
1	Methamidophos	100
2	Acephate	60
3	Dimethoate	60
4	Diazinon	60
5	Chlorpyrifos-Me	50
6	Chlorpyrifos	50
7	Disulfoton sulfone	50
8	Ethion	60
9	Phosmet	100
10	Azinphos-Me	150
Thiabendazole		~ 1 ppm

- Compounds 1-10 contain both P & S
- Thiabendazole contains only S

www.anthias.co.uk

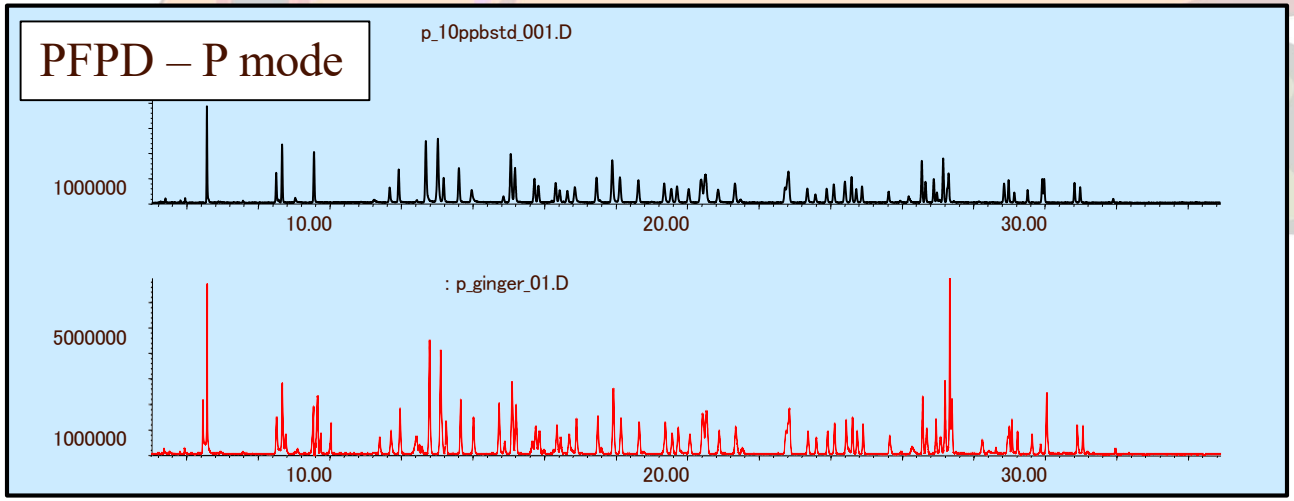
Courtesy of OI Analytical

Food analysis application



Standard Mix
307 compounds
10 ppb

Ginger extract +
307 compounds
10 ppb



Standard Mix
307 compounds
10 ppb

Ginger extract +
307 compounds
10 ppb

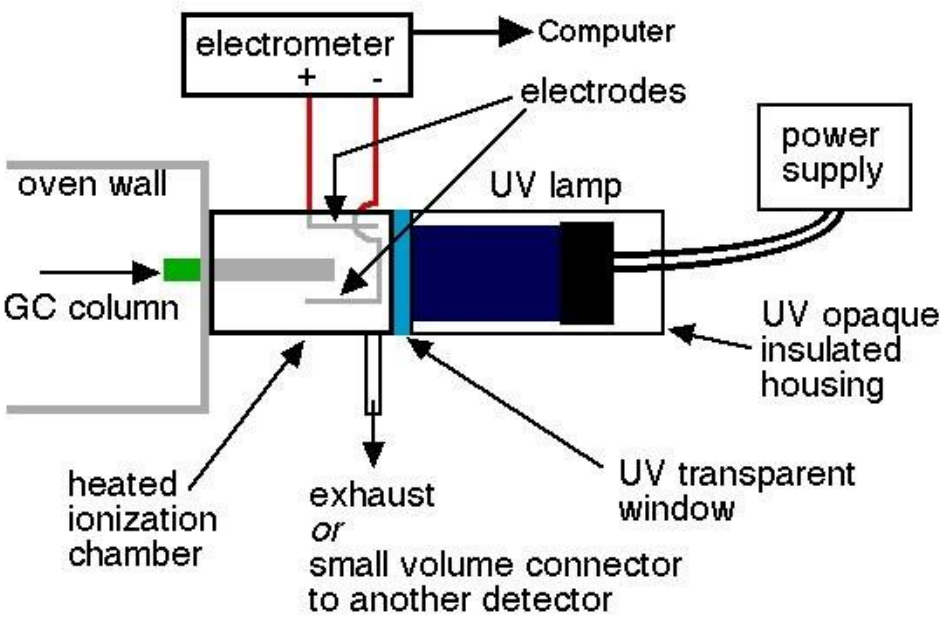
Courtesy of Kinryo Electric, Japan

The PID

- Non-destructive: use in tandem with FID/ELCD/XSD
- Selectively detects aromatic & olefinic HCs
- Sensitivity: 25pg aromatics, 50pg olefins
- Range: Linear 10^{5-7}
- Principles:
  - Sample stream flows through detector's reaction chamber & is continuously irradiated with high energy UV light
  - Compounds having a lower ionisation potential (<10 eV) are ionised: $R + photon \rightarrow R^{+} + e^{-}$
  - Ions formed are collected in electrical field, producing current proportional to compound concentration
  - Ion current is simplified & output by GC electrometer

The PID

- Solvent venting sweeps away undesirable sample solvent, controlled through GC



- Sensitivity: Robust, fast response, high accuracy & sensitivity
- Max. temp. 250°C (volatiles only)

- Non-destructive: sample streams flows from side port into jet reactor of 2nd universal or detector of different selectivity
- 2 simultaneous chromatograms produced

Courtesy of tissuegroup.chem.vt.edu

The PID

- Selectivity: wavelength of UV light depends on lamp gas type & is chosen for target analytes

Lamp energy	8.3 eV	9.5 eV	10.0 eV	11.7 eV
Lamp type		Xenon	Krypton	Argon
Analytes	PAH & Mercaptans	Benzene & aromatics >C6	HCs, ammonia, ethanol, acetone, amines >C4	Alkanes >C2, acetylene, formaldehyde, methanol
Selectivity	Highest selectivity	→	→	Lowest selectivity
Relative sensitivity	0.1	1	10-20	1.0

- Components detected are those with ionisation potential below emitted energy level
- E.g. with 10.0 eV lamp, compounds with IE <10.0 eV = large response, compounds with IE > 10 .0eV = little/no response

Tandem PID/ELCD

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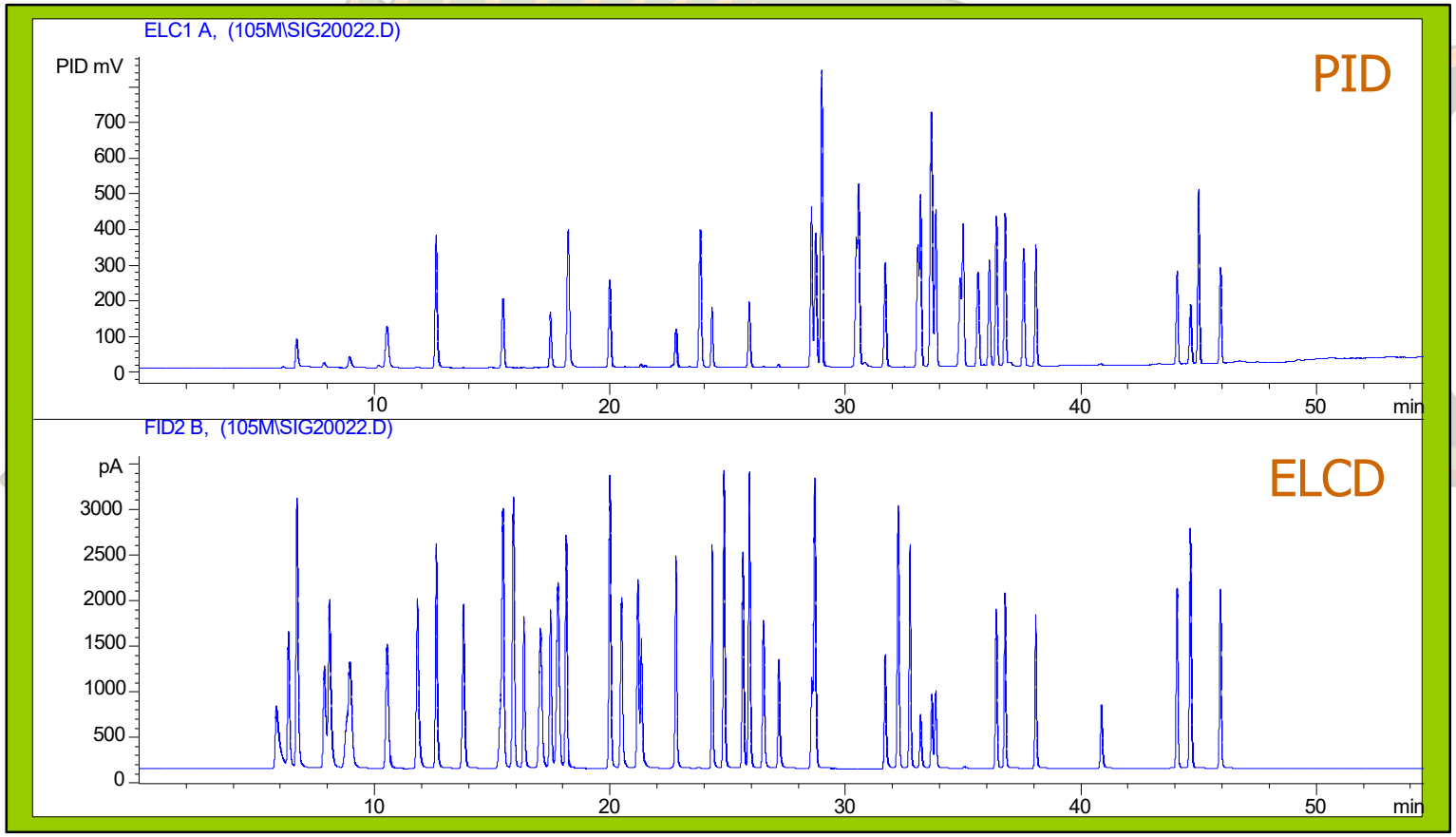
USEPA 502.2 VOC method on 105m column



VPH application

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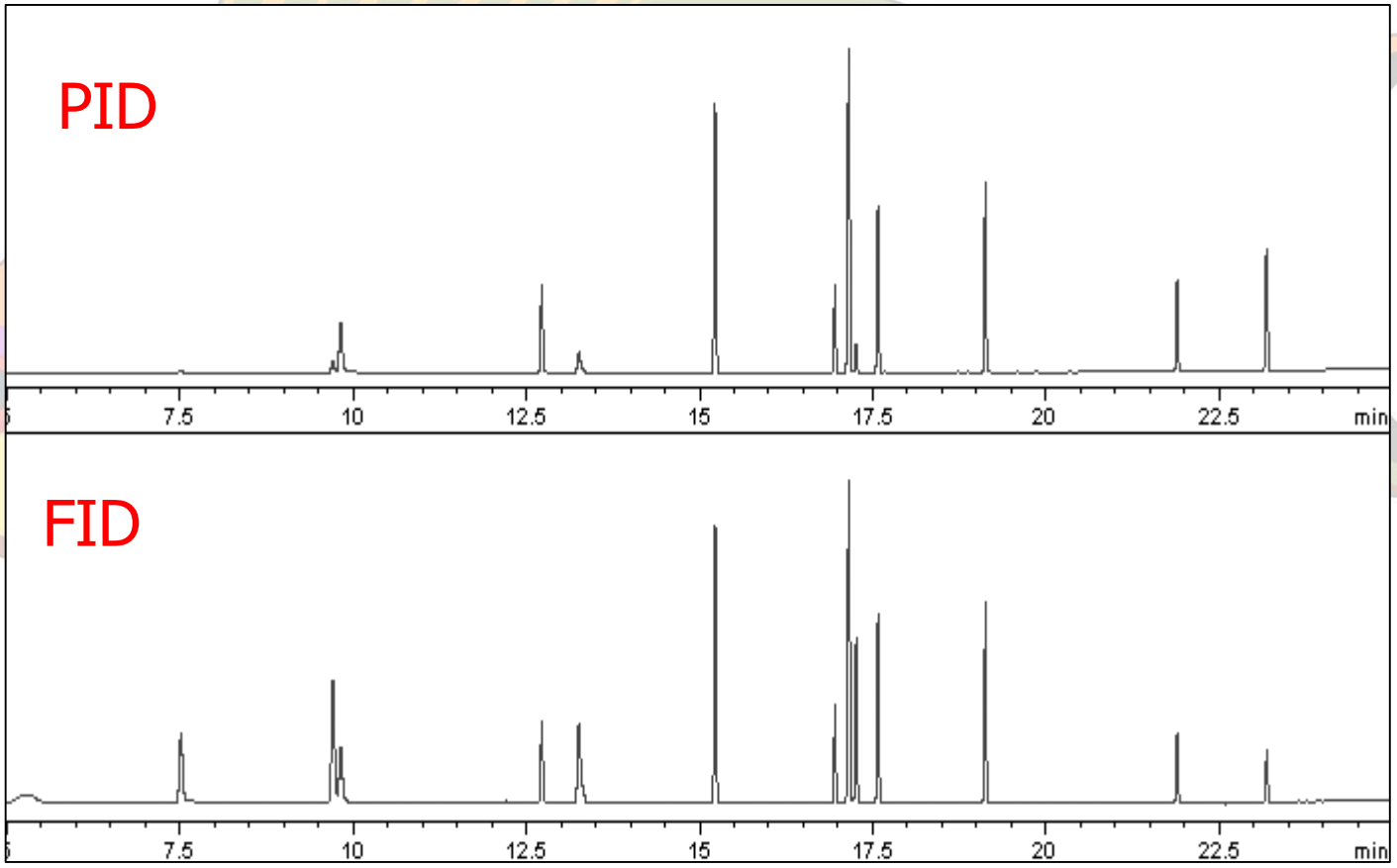
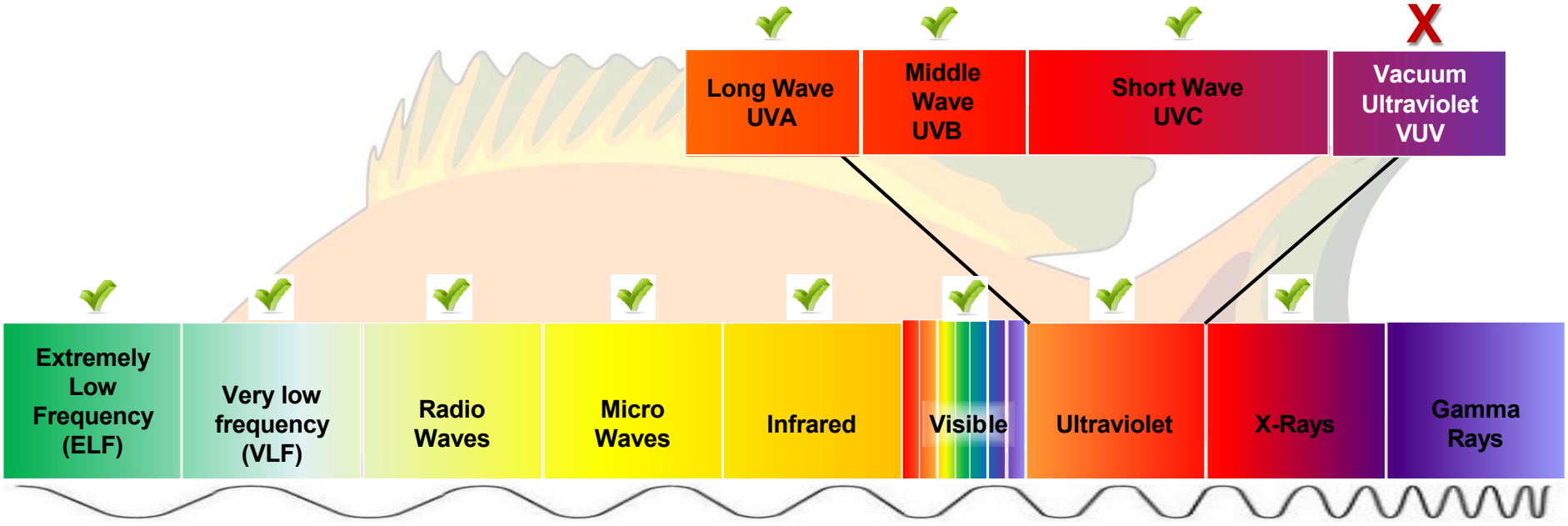
VOC by P&T



The VUV

- Non-destructive
- Universal: detects gaseous molecules except N_2, H_2, He
- Spectra enable ability to:
  - Perform deconvolution of co-eluting analytes
  - Get reduced matrix interferences
  - Differentiate isomers
- Sensitivity: mass on column, 15 pg benzene to 246 pg water
- Spectral resolution: <1 nm
- Range: 10^4 (linear)
- If absorption cross section known for analyte, number molecules present in flow cell can be determined without calibration (in absence of chemical interferents)
- No vacuum needed
- Vacuum UltraViolet absorption region 120-240 nm

What is VUV?



"The excitation energies associated with electrons forming most single bonds are sufficiently high that absorption by them is restricted to the so-called vacuum ultraviolet region (λ<185nm), where components in the atmosphere also absorb strongly."

Principals of Instrumental Analysis, by Douglass Skoog, Sixth Edition, 2006

VUV region

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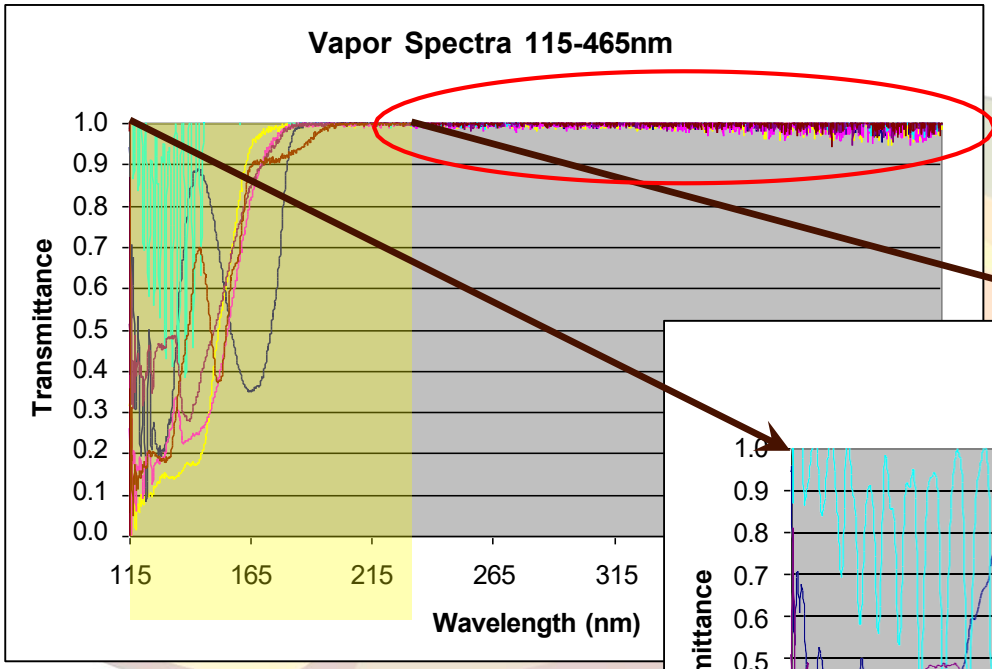
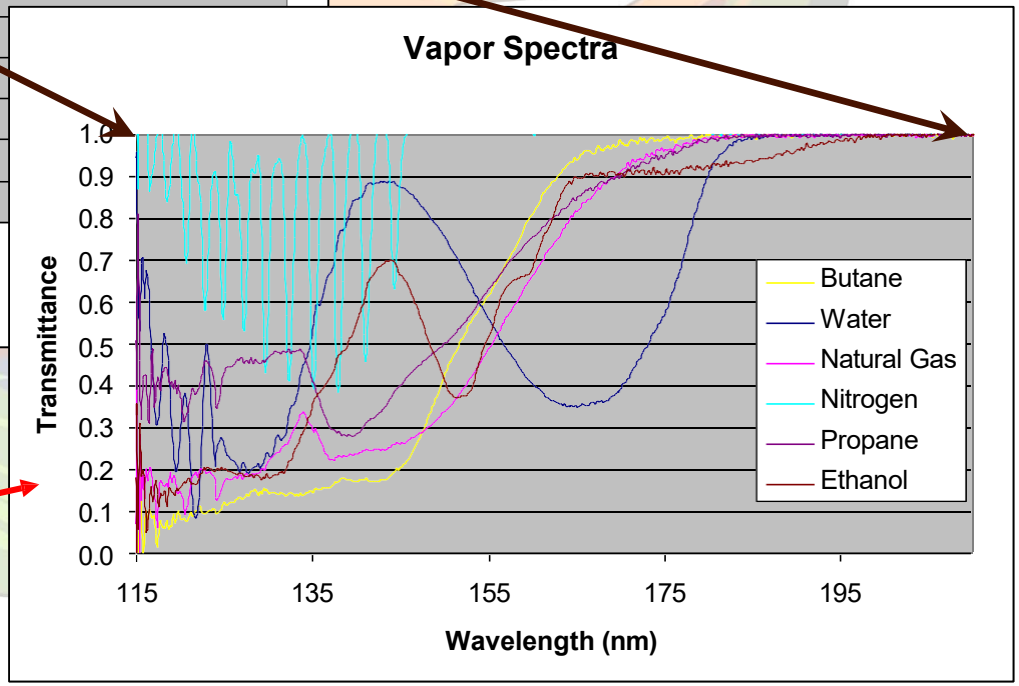


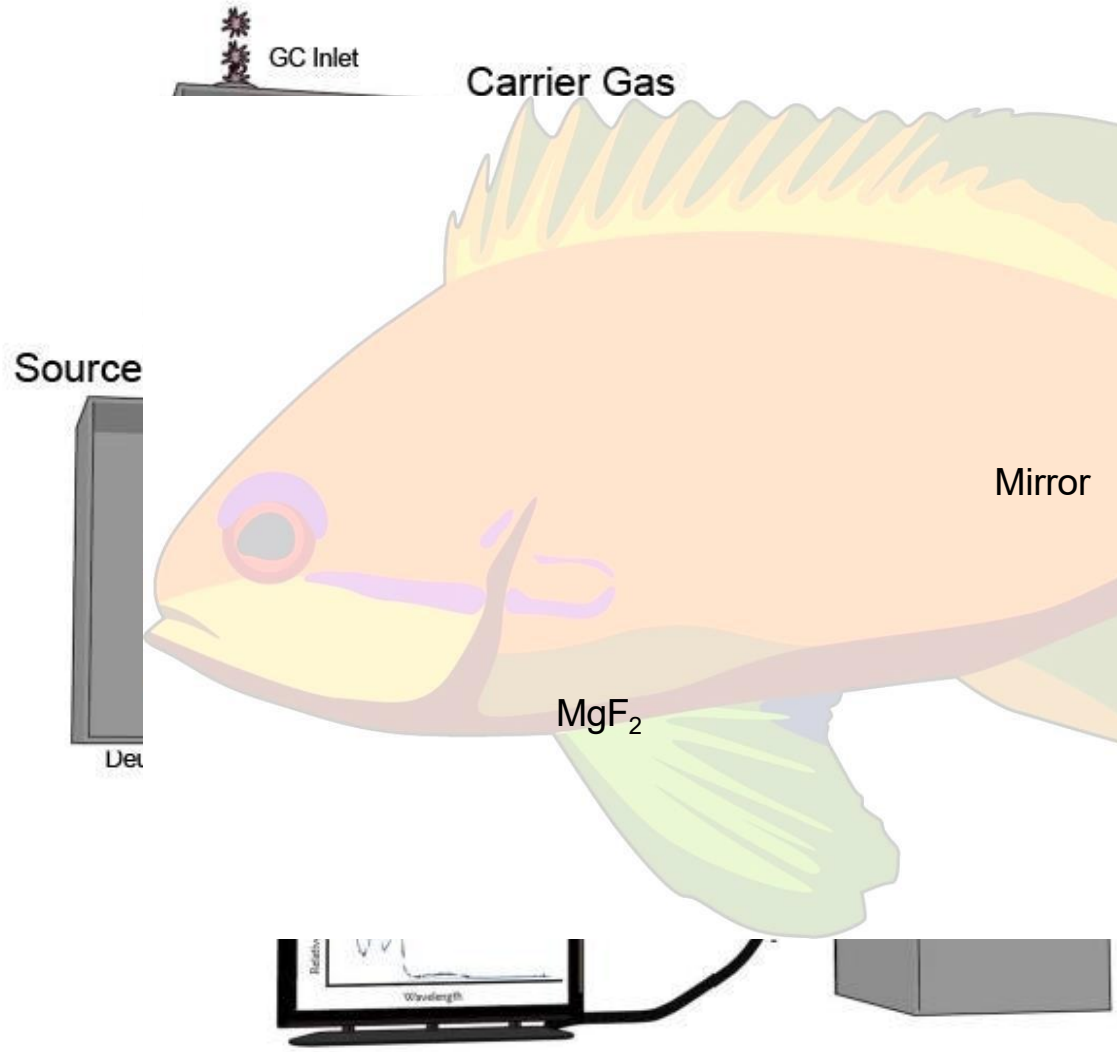
Most gas phase compounds have little or no absorption in visible or UV region



Most compounds absorb in Vacuum Ultraviolet region

Often hundreds of times stronger than in IR absorption

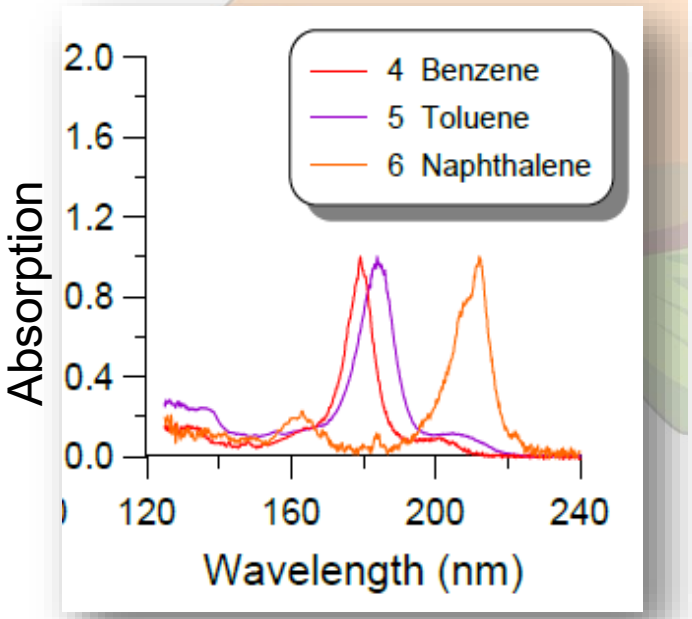
VUV Principles

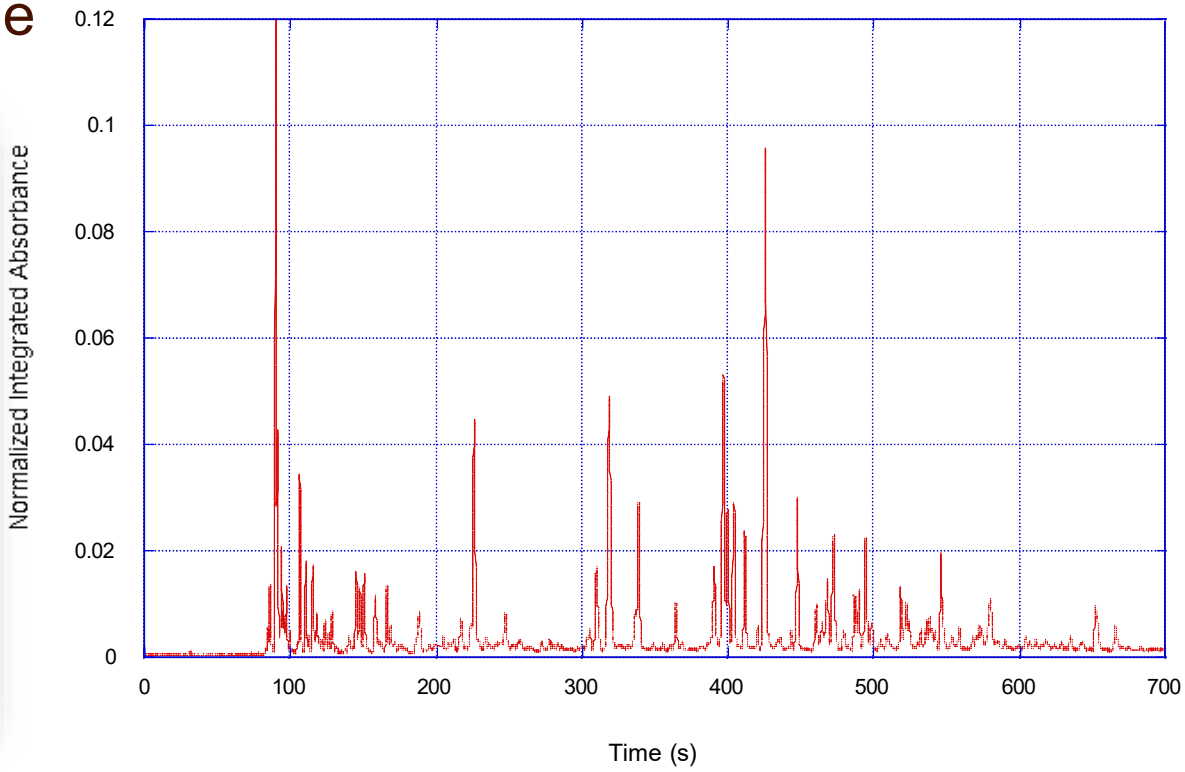


- Flow cell is make-up gas controlled ~80 µL
- Multi-λ acquisition
  - 120-240nm
  - Up to 100 Hz

VUV Data

- Data produced:
  - Total absorbance chromatogram
  - Extracted absorbance chromatograms (spectral filters)
- Absorption spectra:
  - Can be deconvoluted
  - Are library searchable





VUV Isomer identification

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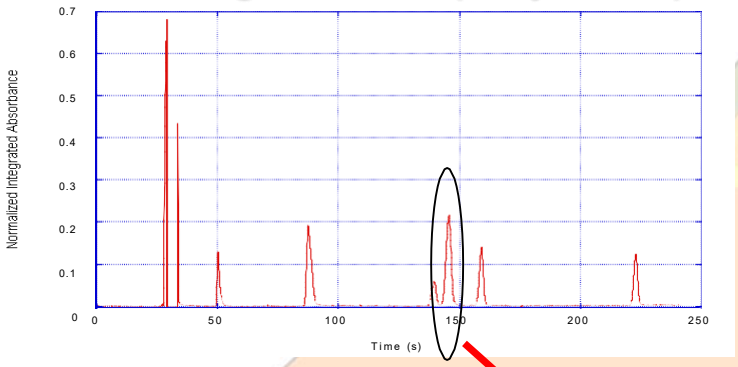
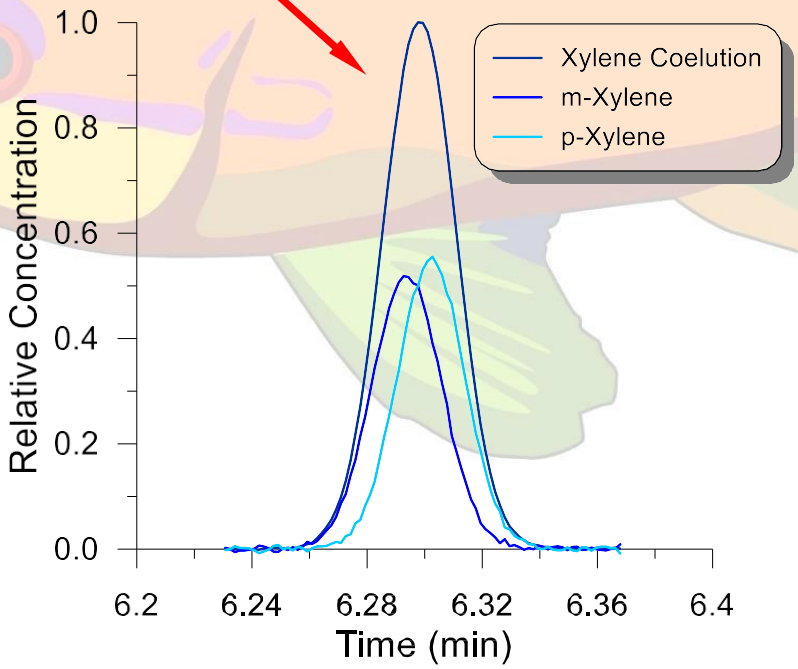
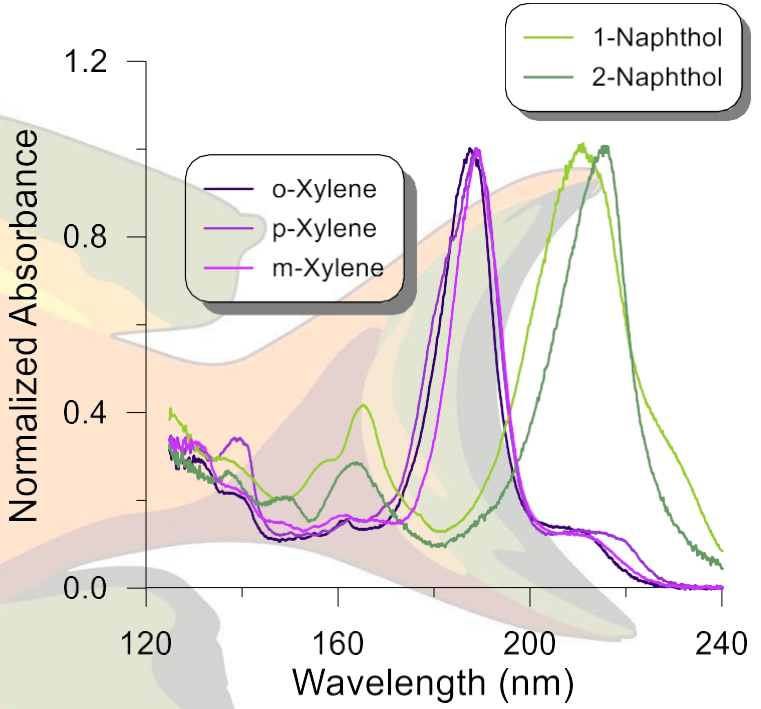
Co-eluting m- and p-xylene peak







Many isomers have unique absorption spectra

GC-VUV of FAMEs

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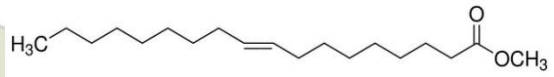
SLB-IL111 (60 m x 0.25 mm id x 0.25 µm d_f)
0.5 µL injection; 1 mL/min flow; 5:1 split
100 ms scan time; 130 – 160 nm

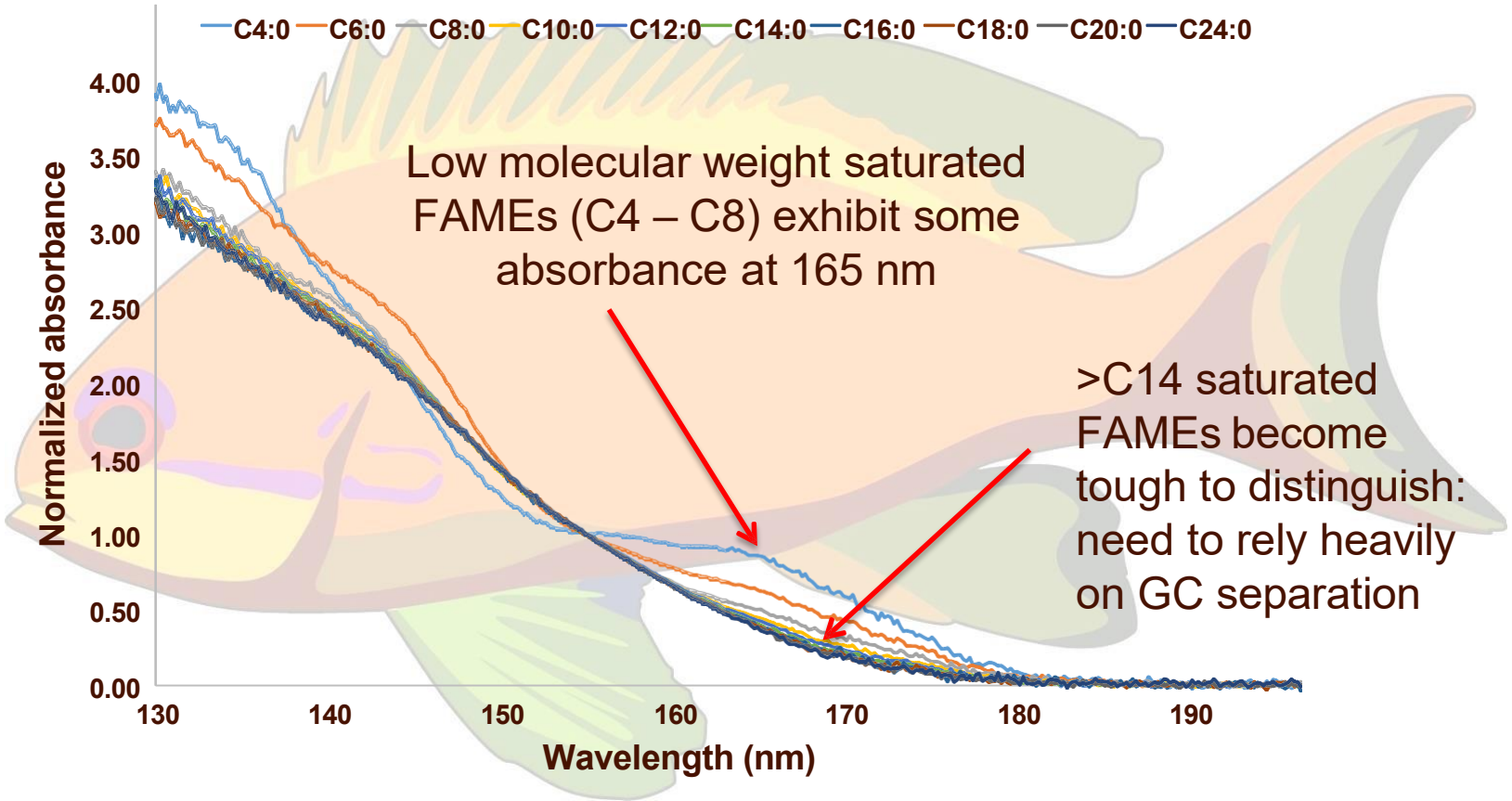


Elaidic acid methyl ester

www.anthias.co.uk

Courtesy of VUV Analytics

Saturated FAMEs



VUV spectra of saturated FAMEs normalized to their absorbance at 155nm

Comparison C18 FAMEs

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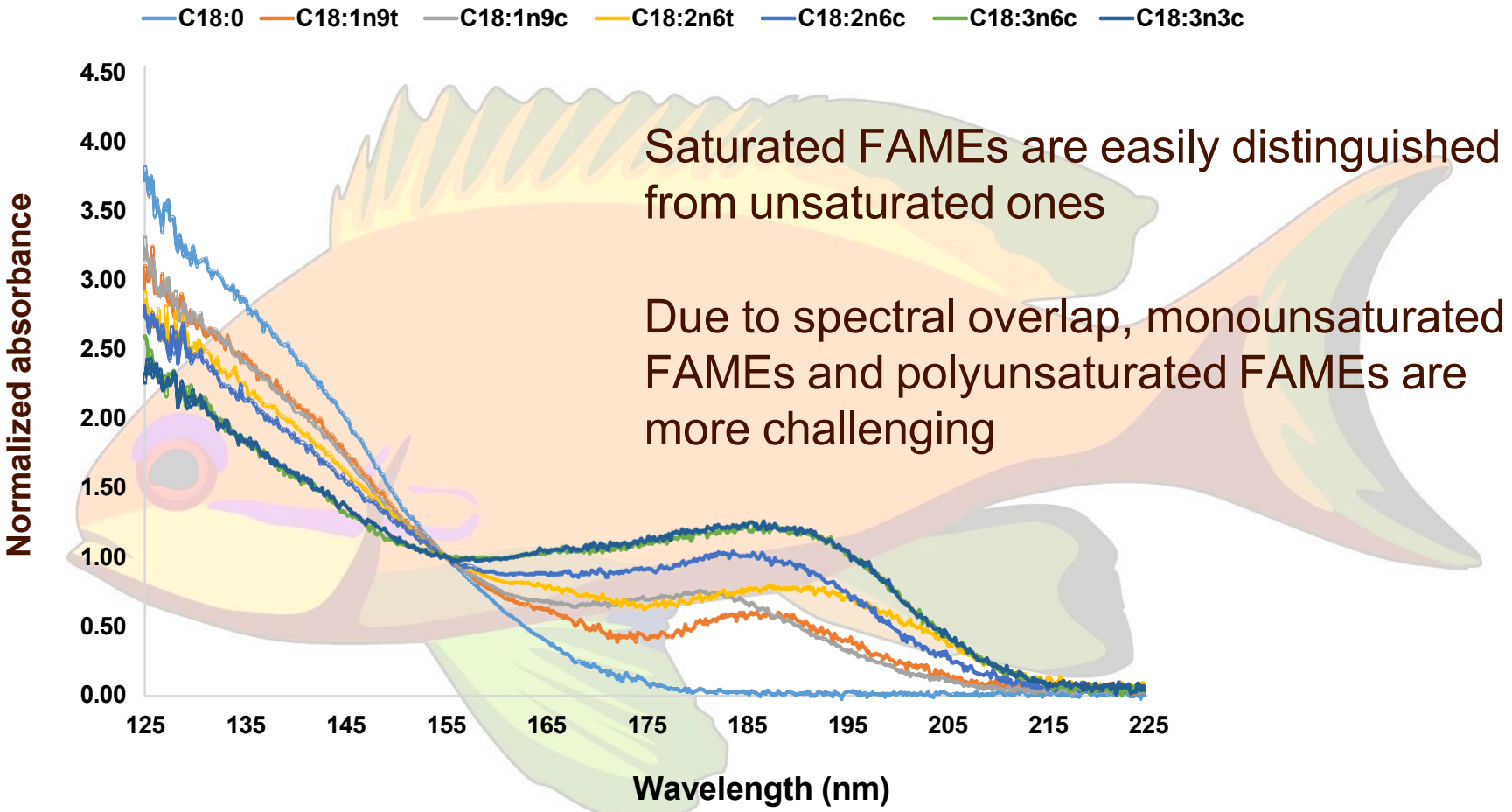
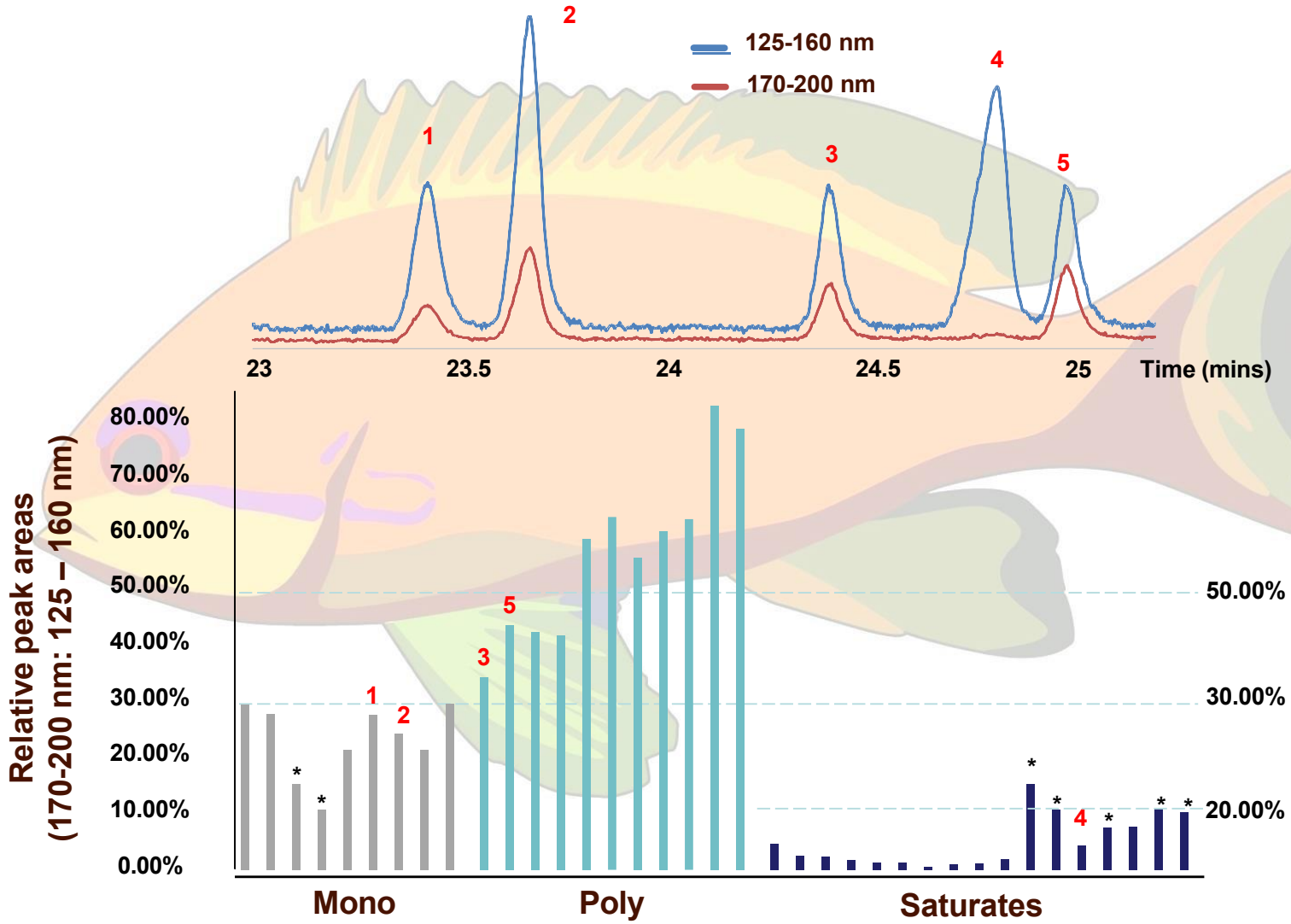


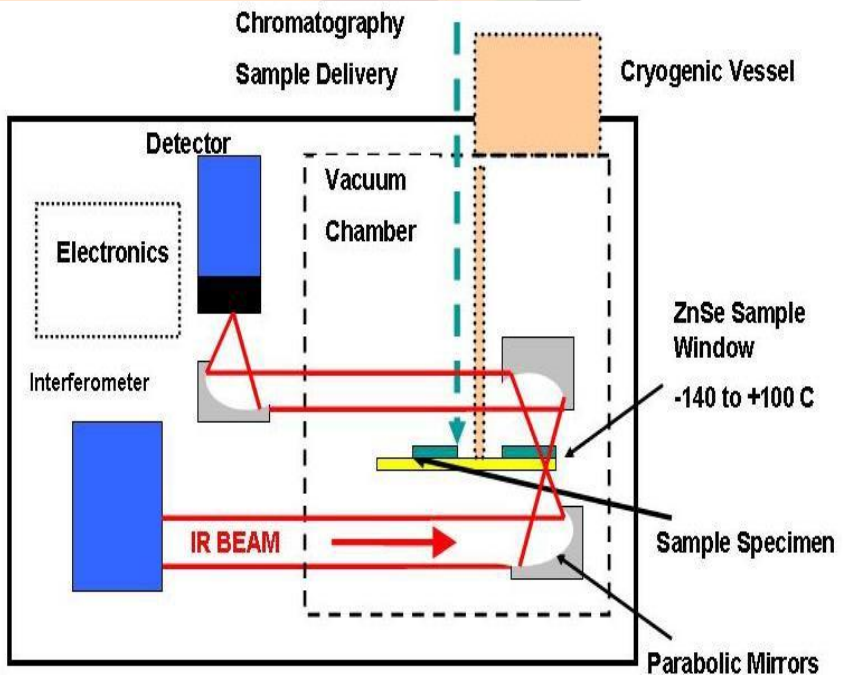
VUV spectra of saturated FAMEs normalized to their absorbance at 155nm

Classifying FAMEs using Relative Peak Areas

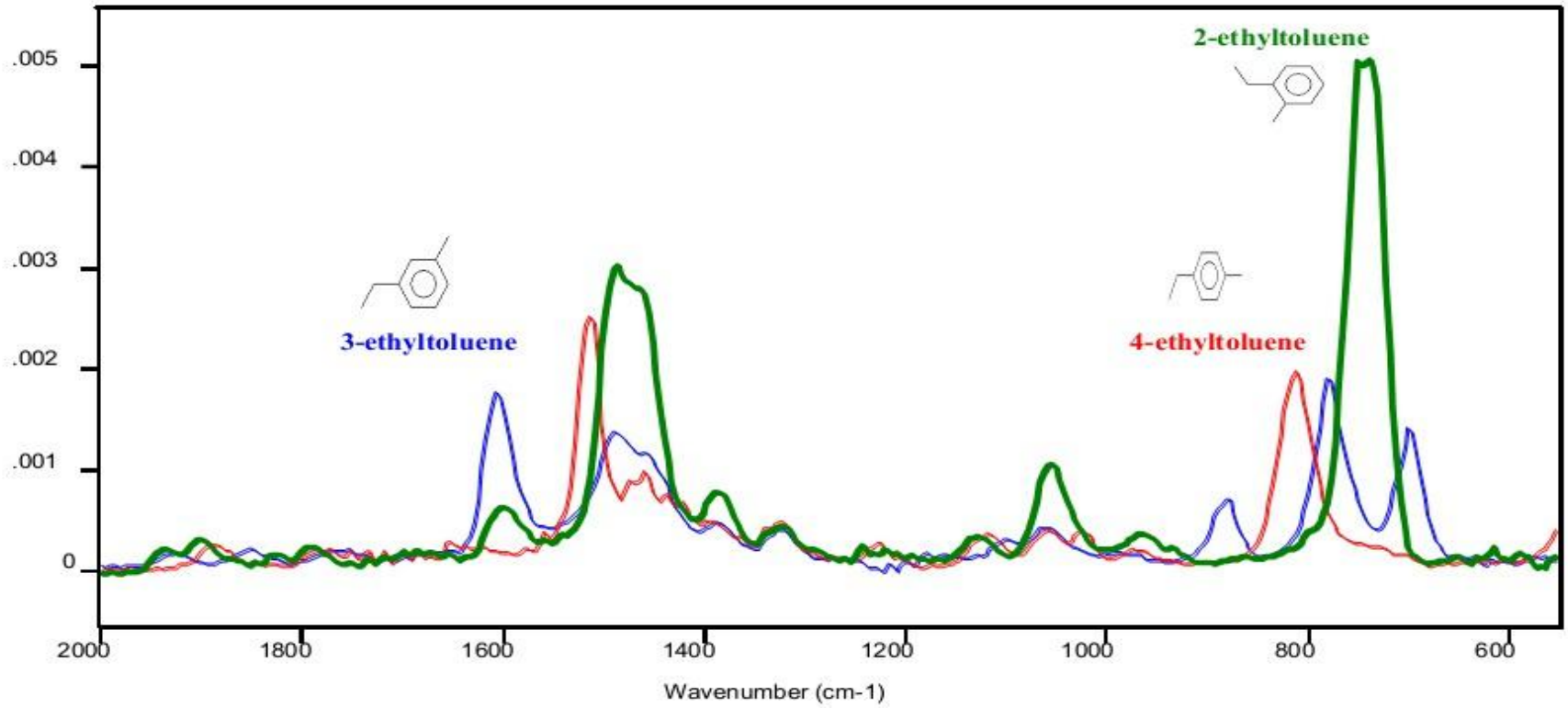


The IRD

- A tandem technique GC-IRD
- Vapour phase infrared spectrophotometric detection
- Molecules absorb infrared energy, frequencies are characteristic of bonds within that molecule
- Good for determining structural information like regio-isomeric relationships: differentiate isomers
- 4000-650 cm^{-1} range, $4cm^{-1}$ resolution
- Extensive searchable IR transmission libraries
- Sensitivity down to 1 ng
- Limited dynamic range 10^3



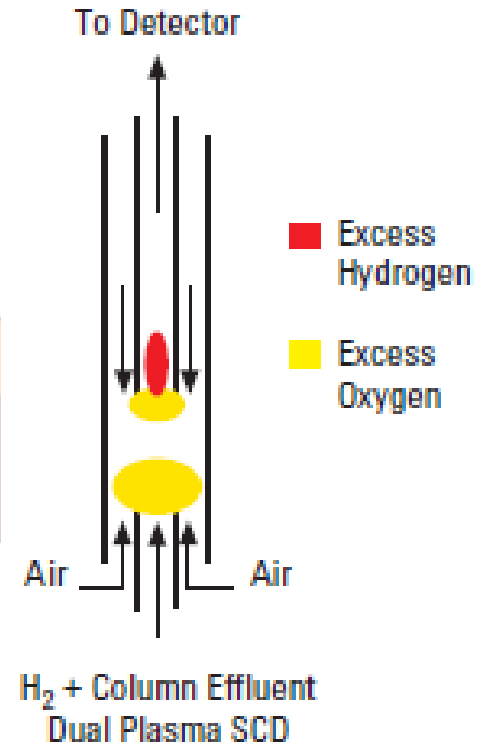
IR Spectra – Isomers of Ethyltoluene

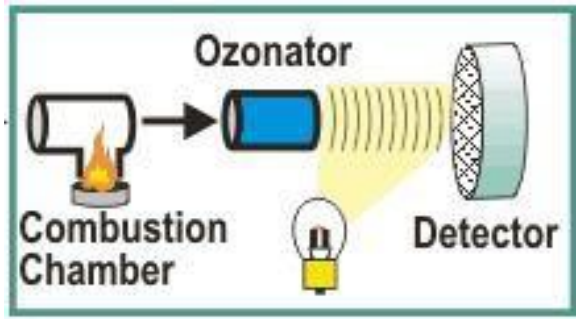


- Detects analytes with: aromatic substitution, cis-trans isomers, ring junctions & isomers, aliphatic chains, functional group selectivity
- Useful in forensic drug analysis clinical assays, food/flavour/fragrance

The SCD

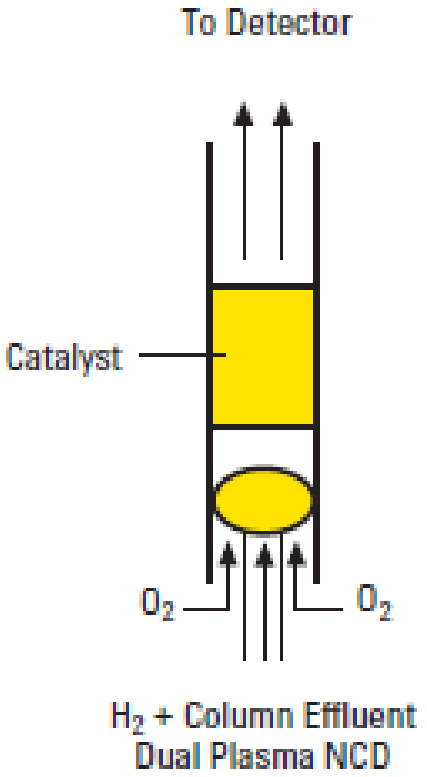
- Sulfur compounds quantitatively converted to SO_2 in combustion chamber at temperatures >1800°C
- RS + O → SO + Other Products
- Vacuum pulls combustion products into reaction cell where excess ozone added
- SO + O_3 → SO_2 + O_2 + light (300-400 nm)
- Light passes through optical filter & detected by photomultiplier tube
- Sensitivity: picogram levels
- Linear >10^4 with equimolar response
- Very sensitive & highly selective, no quenching





The NCD

- Nitrogen compounds converted to nitric oxide in H_2 and O_2 plasma in combustion tube
- Catalyst used to prevent 2nd N species being destroy potential interferences
- $RN + O_2 \rightarrow NO + CO_2 + H_2O$
- Nitric oxide reacts with ozone
- $NO + O_3 \rightarrow NO_2 + O_2$ + light (600-3200 nm)
- Light passes through optical filter & detected by photomultiplier tube
- NCD also responds to ammonia, hydrazine, cyanide & NO_X
- Sensitivity: picogram levels



- Linear >10^4 with equimolar response except N_2 and N-N_2 bonds
- Very sensitive & highly selective, no hydrocarbon quenching

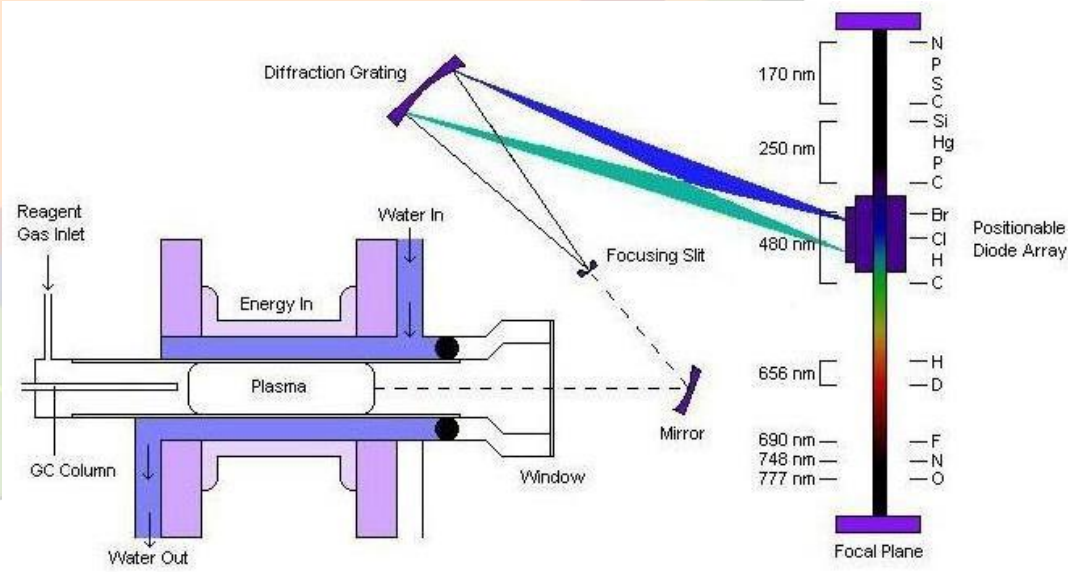
The TEA

- Nitrogen compounds converted to NO in H_2 & O_2 plasma
- R-NH + O_2 $\rightarrow$ NO* + CO_2 + H_2O
  NO* + O_3 $\rightarrow$ NO_2* + O_2
  NO_2* $\rightarrow$ light (600 nm) in reaction chamber
- Pyrolysis at 350-500°C for Nitroso (R-NO) & 600-900°C for Nitro (R-NO_2) & 700-825°C for Nitrogen (NH)
- Light passes optical filter & detected by photomultiplier
- Available in nitrogen & nitro/nitroso modes
- Sensitivity: picogram levels
- Linearity 10^4
- Very sensitive & highly selective

Courtesy of Ellutia

The AED

- Theory: column effluent heated in He-rich plasma chamber, analytes reduced to elemental state & excited
  → Excited analytes decay & emit light
  → Light strikes a photosensitive surface knocking loose an electron → Amplified & recorded
- Plasma: microwave-induced (MIP), inductively coupled (ICP) or direct current (DCP)
- Reagent gas: H_2, O_2, N_2 (analyte dependent)
- Sensitivity: low pg/sec
- Applications: VOCs, oil, water, diesel
- Simple, robust, fast response
- Can measure ~ 25 elements



Courtesy of chemwiki.ucdavis.edu

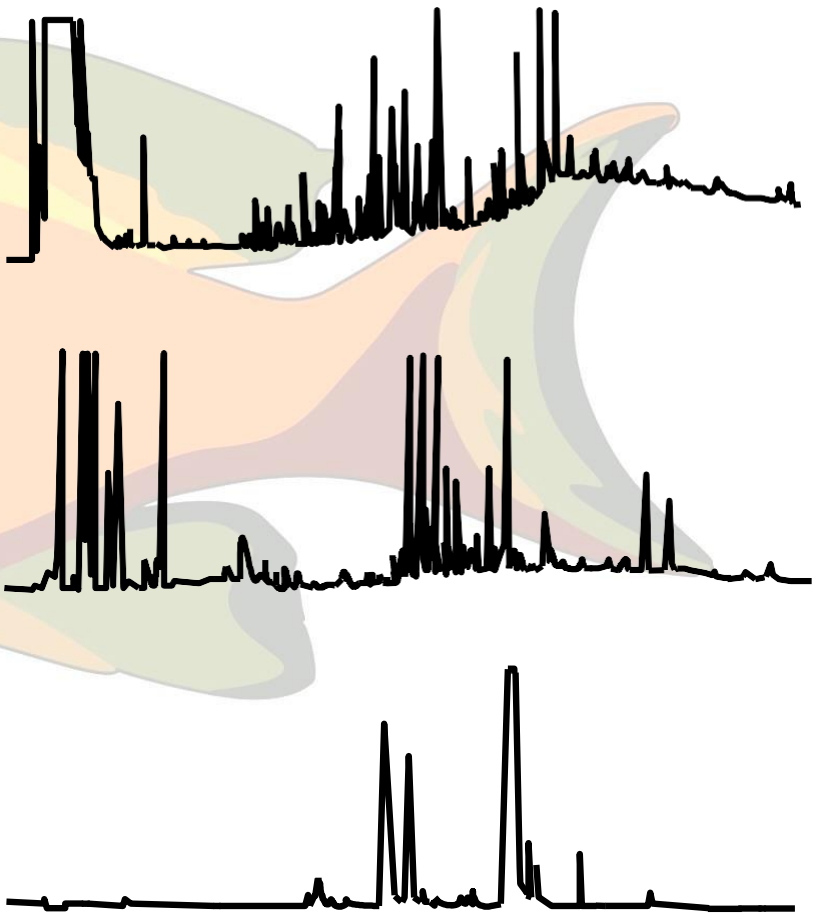
GC Detector summary

Anthias Consulting Ltd
Bridging the Gap

Detector	Analytes/atoms/bonds	Sensitivity	Linear range
FID	C-H bonds	100 pg C	10^7
PFPD	Sulphur/Phosphorus/other elements	S:pg P:fg	S:10^3 P:10^3
PID	VOCs	25-50 pg	10^{5-7}
VUV	Functional groups, isomers	pg	10^4
IRD	Functional groups, isomers	ng	10^3
SCD/NCD	Sulphur/Nitrogen	pg	10^4
TEA	Nitrogen groups	pg	10^4
AED	Heteroatoms & other elements	<pg	10^4
TCD	Organic & inorganic	<ng	10^5
NPD	Nitrogen/Phosphorus	50-500 fg	10^5
BID	Organic	low pg	10^5
HID/DID	Gases	0.1 ppm	10^2
ECD	Electron capturing, halides..	<50 fg	10^4
ELCD	Halogens, sulphur, nitrogen	5 ppb	10^3

Summary

- Many GC detectors available
- Consider chemistry of matrix as well as analytes when choosing selective detector
- Consider sensitivity & linear range of detector
- Some GC detectors like VUV & IRD offer another dimension of information for identification



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